Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Catalyst-Free Transfer Hydrogenation of Activated Alkenes Exploiting Isopropanol as the Sole and Traceless Reductant

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Contents

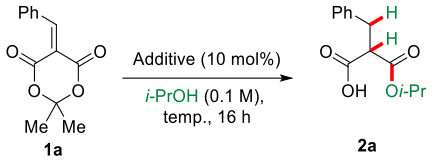
1. General Information

All reactions were carried out in oven-dried glassware unless otherwise noted. When needed, nonaqueous reagents were transferred under argon *via* syringe or cannula and dried prior to use. Dry solvents were obtained by passing deoxygenated solvents through activated alumina columns (MBraun SPS-800 series Solvent Purification System). Other solvents and reagents were used as obtained from the supplier unless otherwise noted. Isopropanol (>99.5%) was purchased from Sigma-Aldrich. Analytical TLC was performed using Merck silica gel F254 (230–400 mesh) plates and analyzed by UV light or by staining upon heating with $KMnO_4$ solution (1 g of $KMnO_4$, 6.7 g of K_2CO_3, 1.7 mL of 1 M NaOH, 100 mL of H_2O). Flash column chromatography was performed using Biotage Isolera One automated chromatograph with pre-packed KP-Sil cartridges using p.a. grade solvents unless otherwise noted. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-*d*6 on a Bruker Avance DRX-600 spectrometer. The chemical shifts are reported in ppm relative to residual $CHCl_3$ (δ 7.26) or DMSO (2.54 ppm) for ^1H NMR and $CDCl_3$ (δ 77.16) DMSO-*d*6 (39.52) for ^{13}C NMR. The diastereomeric ratios were determined by ^1H NMR analysis of crude reaction mixtures. Melting points (MP) were determined in open capillaries using a Mettler Toledo MP50 melting point system and are uncorrected. High-resolution mass spectrometric data were measured using Agilent 1290/6230 LCMS-TOF system with electrospray ionization (ESI) in negative/positive mode.

2. Optimization of the reaction condition

To an oven-dried 10 mL round bottom flask equipped with a magnetic stir bar was added the alkylidene Meldrum's acid (0.5 mmol) and additive (0.05 mmol). The resulting mixture was suspended on isopropanol (5 mL, 0.1 M) and heated to the given temperature for 16 hrs. Finally, excess solvent was evaporated under vacuum and the crude product was analyzed by ^{1}H NMR analysis using 1,3,5-trimethoxybenene as an internal standard.

Table S1: Reaction optimization



entry[a]	additive	temp	Yield (%) of **2a**
1	none	reflux	66[b]
2	none	60°C	32
3	none	25 °C	<5
4	HCl (2.0 M in ether)	reflux	82
5	HBr (aq. 33 wt%)	reflux	40
6	AcOH	reflux	60
7	Amberlyst	reflux	70
8	Camphor Sulfonic Acid (CSA)	reflux	64
9	$Sc(OTf)_3$	reflux	41
10	Boric Acid	reflux	70
11	Ph-$B(OH)_2$	reflux	58
12	4-MeO-Ph-$B(OH)_2$	reflux	67
13	4-NMe_2-Ph-$B(OH)_2$	reflux	59
14	4-NO_2-Ph-$B(OH)_2$	reflux	83
15	3,5-*di*-F-Ph-$B(OH)_2$	reflux	73
16	3,5-*bis*-CF_3-Ph-$B(OH)_2$	reflux	83[b]
17	3,5-*bis*-CF_3-Ph-$B(OH)_2$	25 °C	<5
18	3,5-*bis*-CF_3-Ph-$B(OH)_2$	40 °C	10
19	3,5-*bis*-CF_3-Ph-$B(OH)_2$	60 °C	32
20	3,5-*bis*-CF_3-Ph-$B(OH)_2$	reflux	60[c]
21	3,5-*bis*-CF_3-Ph-$B(OH)_2$	reflux	16[d]

3. General Procedure for the synthesis of alkylidene Meldrum's Acid

3.1. General procedure 1 (Ref[1]): Meldrum's acid (1.2 equiv.) was suspended on water (2.0 M) followed by the addition of aldehyde (1.0 equiv.). The resulting reaction mixture was heated at 75 °C for 4 h. Finally, the reaction was allowed to cool down to the room temperature and the resulting precipitate was filtered under vacuum and recrystallized from EtOH to obtain pure alkylidene Meldrum's acid **1**.

Compounds **1b**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1u**, **1v**, **1w**, **1x**, **1y**, **1aa**, **1ab**, **1ac**were prepared following this procedure.

3.2. General procedure 2 (Ref[2]): Following the modified literature procedure,Meldrum's acid (1.0 equiv.) and aldehyde (1.0 equiv.) were dissolved in ethanol (3.0 M) in a round-bottom flask. The reaction mixture was then heated to reflux for 2 h. The excess solvent was removed under vacuum and the resulting crude reaction mixture was crystallized from Ether to obtain the pure alkylidene Meldrum's acid **1.**

Alkylidene Meldrum's acids **1a** and **1c** was prepared following this procedure.

3.3. General procedure 3 (Ref[3]):

Meldrum's acid (1.0 equiv.) and triethyl chloroformate (3.0 equiv.) were heated to reflux for 3 hours. The reaction mixture was cooled down to room temperature and diluted with hexanes. The reaction mixture was cooled down to 0 °C using a water-ice bath and stirred for 30 min. The yellow precipitate was collected by vacuum filtration. This yellow precipitate was then dissolved in dry THF (0.2 M) and cooled down to –78 °C using an acetone-dry ice bath. Then Grignard reagent (1.05 equiv.) was added dropwise, and the reaction mixture was left stirring for 30 min. The reaction was quenched with methanol and the crude reaction mixture was purified through flash column chromatography.

Compound **1z**were prepared following this procedure.

3.4. General procedure 4 (Ref[4]): Meldrum's acid (1.0 equiv.) and aldehyde (1.0 equiv.) were heated to 100 °C for 5 min in a round-bottom flask. Then alumina (2.3 g/g of Meldrum's acid) was added, and the reaction was allowed to cool to room temperature. The crude was resuspended in DCM and the solids were filtered off. The reaction was concentrated in vacuo to give the desired product without further purification.

Compound **1k**were prepared following this procedure.

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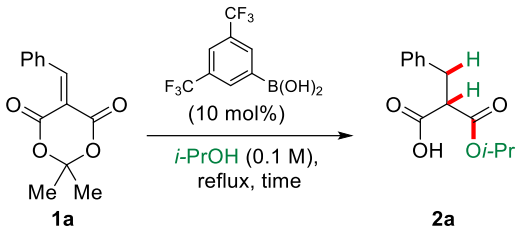
[1]T.Drennhaus,L. Öhler, S.Djalali, S.Höfmann, C. Müller, J. Pietruszka and D.Worgull, *Adv. Synth. Catal.* 2020, **362**, 2385; M. Jardim, L. L. Baldassari, M. E. Contreira, A. V. Moro andD. S. Lüdtke, Tetrahedron, 2020, **76**; DOI: 10.1016/j.tet.2020.130967.

[2] H. Liu, Z. Ren, W. Wang, J. Gong, M. Chu, Q. Ma, J. Wang and X. Lv, *Eur. J. Org. Chem.* 2018, **157**, 81.

[3] L. Zhang, C. Cheng, J. Li, L. Wang, A. Chumanevich, D. Porter, A. Mindich, S. Gorbunova, I. Roninson, M. Chen and C. McInnes, *J. Med. Chem.* 2022, **65**, 3420.

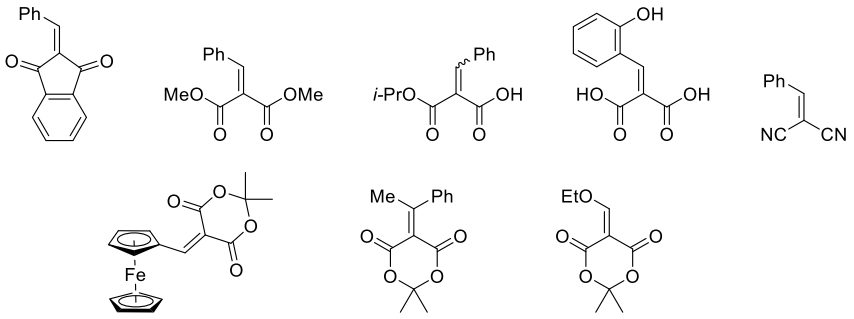
[4] X. Yang, T. Fox and H. Berke, *Chem. Commun.*2011, **47**, 2053.

4. General procedure for the transfer hydrogenation (TH) reaction:



To an oven-dried 10 mL round bottom flask equipped with a magnetic stir bar was added the alkylidene Meldrum's acid (0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl) boronic acid (0.05 mmol, 0.1 equiv.). The resulting mixture was suspended on isopropanol (>95.5%) (5 mL, 0.1 M) and refluxed for 16–40 hrs. Finally, the excess solvent was evaporated under vacuum and the resulting crude product was purified by flash column chromatography to obtain the pure substituted malonic acid half oxyesters **2**.

5. Unsuccessful Substrates:



6. X-Ray Data:

Single crystal X-ray diffraction data for 1A and 2I were collected using a Bruker Smart APEX II diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The cell parameters were obtained from the least squares refinement of the spots (from 36 collected frames) and data collection and data processing were performed using Apex 2.[5] Intrinsic phasing was used for structure solutions. The structures were corrected for absorption effects using SADABS and refined by least squares methods using SHELXL2018.[6] Calculated hydrogen atom positions were input and refined in a riding manner along with attached carbons. The crystallographic details are summarized in Table S2 (for **2I**) and S3 (for **1a**).

[5]Bruker-AXS, 2006

[6]"Crystal Structure Refinement with SHELXL" by G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3.

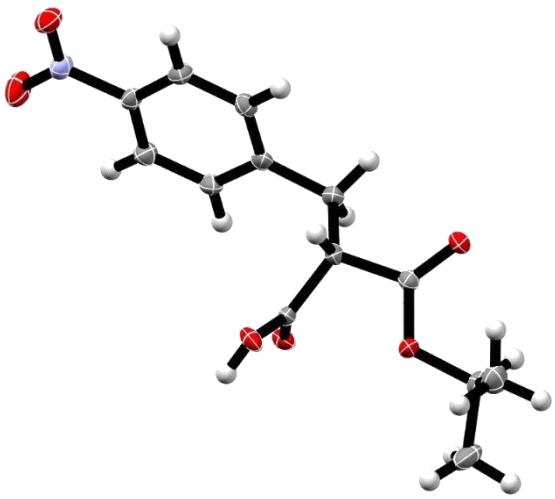


Table S2. Crystal data and structure refinement for C13 H15 N O6 (**2l**)

Identification code	**2l, CCDC: 2144478**	
Empirical formula	C13 H15 N O6	
Formula weight	281.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.911(4) Å	α= 90°.
	b = 4.6748(7) Å	β= 104.436(2)°.
	c = 23.299(4) Å	γ = 90°.
Volume	2733.1(7) $Å^3$	
Z	8	
Density (calculated)	1.367 Mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	1184	
Crystal size	0.150 x 0.050 x 0.020 mm^3	
Theta range for data collection	2.105 to 28.315°.	
Index ranges	-34<=h<=34, -6<=k<=6, -30<=l<=31	
Reflections collected	13697	
Independent reflections	3406 [R(int) = 0.0729]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.553	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3406 / 0 / 184	
Goodness-of-fit on F^2	1.035	

Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1097
R indices (all data)	R1 = 0.0746, wR2 = 0.1221
Extinction coefficient	n/a
Largest diff. peak and hole	0.493 and -0.370 e.Å^{-3}

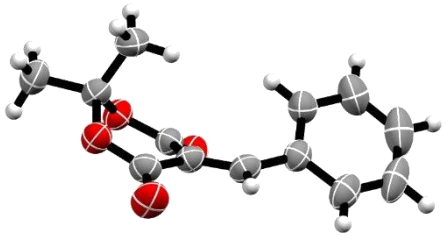


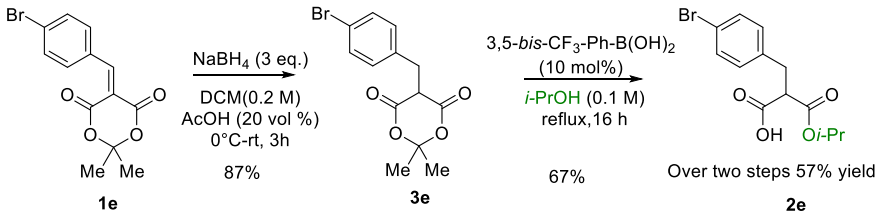
Table S3. Crystal data and structure refinement for C13 H12 O4 (**1a**).

Identification code	**1a , CCDC: 2173993**	
Empirical formula	C13 H12 O4	
Formula weight	232.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.5868(15) Å	α= 106.015(3)°.
	b = 8.2313(18) Å	β= 97.159(3)°.
	c = 11.126(3) Å	γ = 95.387(3)°.
Volume	570.1(2) Å^3	
Z	2	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	244	
Crystal size	0.180 x 0.110 x 0.050 mm^3	
Theta range for data collection	1.928 to 28.325°.	
Index ranges	-8<=h<=8, -10<=k<=10, -14<=l<=14	
Reflections collected	6051	
Independent reflections	2827 [R(int) = 0.0372]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.650	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	2827 / 0 / 156
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1116
R indices (all data)	R1 = 0.0703, wR2 = 0.1289
Extinction coefficient	n/a
Largest diff. peak and hole	0.167 and -0.198 e.$Å^{-3}$

7. Mechanistic Studies:

7.1. Synthesis of 5-(4-bromobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3e) and 2-(4-bromobenzyl)-3-isopropoxy-3-oxopropanoic acid (2e):

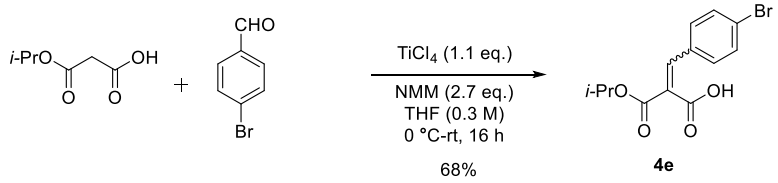


In a round-bottom flask, compound **1e** (1.0 g, 3.2 mmol, 1.0 equiv.) was dissolved in DCM (16 mL, 0.2 M) under N_2 followed by addition of glacial acetic acid (3.2 mL, 20% v/v). The reaction mixture was cooled down to 0 °C with an ice-water bath. $NaBH_4$ (364 mg, 9.6 mmol, 3.0 equiv.) was then added portion wise. The reaction was left to warm-up to room temperature slowly and it was allowed to stir for 3 hours, until TLC indicated full consumption of starting material. The reaction was quenched with distilled water (10 mL) and extracted with DCM (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Compound **3e** was obtained as a white solid in 87% yield (871 mg) without further purification. NMR data matches the ones reported in the literature[7]. **^{1}H NMR (600 MHz, CDCl3**) δ 7.41 (d, 2H, *J* = 8.4 Hz), 7.22 (d, 2H, *J* = 8.4 Hz), 3.73 (t, 1H, *J* = 4.9 Hz), 3.44 (d, 2H, *J* = 4.9 Hz), 1.75 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 165.1, 136.2, 131.8, 121.4, 48.1, 31.5, 28.6, 27.3.

5-(4-bromobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **3e** (157 mg, 0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (13 mg, 0.05 mmol, 0.1 equiv.) was suspended on isopropanol (>95.5%) (5 mL, 0.1 M) and refluxed for 16 h. Finally, the excess solvent was evaporated under vacuum and the resulting crude product was purified by flash column chromatography (5 to 20% EtOAc/Hex) to obtain the pure 2-(4-bromobenzyl)-3-isopropoxy-3-oxopropanoic acid **2e** as a colorless oil(0.211 g, 67% yield).

[7] C. Frost and B. Hartley, *J. Org. Chem.* 2009, **74**, 3599.

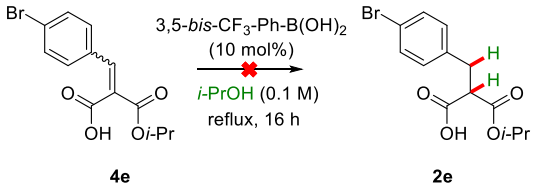
7.2. Synthesis of 3-(4-bromophenyl)-2-(isopropoxycarbonyl)acrylic acid (4e)



In a flame-dried round-bottom flask, 4-bromobenzaldehyde (3.5 g, 18.9 mmol, 1.5 equiv.) was dissolved in dry THF (63 mL, 0.3 M) under Ar. Isopropyl malonic half ester (2.0 g, 13.7 mmol, 1.0 equiv.) was then added and the mixture was cooled down to 0 °C with an ice-water bath. $TiCl_4$ solution in toluene (1.1 equiv., 20.8 mmol, 15 mL, 1 M solution) was then added, followed by *N*-methyl morpholine (4.1 mL, 51.0 mmol, 2.7 equiv.). The bath was then removed, and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with distilled water (20 mL) and extracted with ethyl acetate (3 × 60 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified with flash column chromatography (5 to 20% EtOAc/Hex) to give the product as yellow solid (2.895 g, 68%) as an inseparable mixture of *E:Z* isomers in a 3.3:1 ratio.

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.80 (s, 1H, *Z*), 7.77 (s, 1H, *E*), 7.54 – 7.52 (m, 2H, *Z*), 7.54 – 7.52 (m, 2H, *E*), 7.43 (d, 2H, *J* = 8.1 Hz, *E*), 7.36 (d, 2H, *J* = 7.5 Hz, *Z*), 5.27 – 5.17 (m, 1H, *E*), 5.27 – 5.17 (m, **1H**, *Z*), 1.35 (d, 6H, *J* = 6.3 Hz, *E*), 1.28 (d, 6H, *J* = 6.3 Hz, *Z*). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 170.1 (*E*), 169.2 (*Z*), 165.8 (*Z*), 164.4 (*E*), 143.9 (*E*), 143.7 (*Z*), 132.2 (*E*), 132.2 (*Z*), 131.7 (*Z*), 131.6 (*E*), 131.4 (*E*), 131.3 (Z), 125.9 (*Z*), 125.7 (*Z*), 125.6 (*E*), 70.5 (*E*), 70.3 (*Z*), 21.9 (*E*), 21.6 (*Z*).

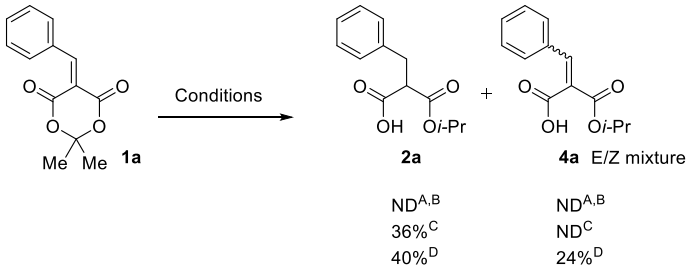
7.3. Attempt to reduce 3-(4-bromophenyl)-2-(isopropoxycarbonyl)acrylic acid (4e):



3-(4-bromophenyl)-2-(isopropoxycarbonyl)acrylic acid **4e** (Z&E mixture as obtained in the previous step) (156.6 mg, 0.5 mmol, 1 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (12.9 mg, 0.05 mmol, 0.1 equiv.) was suspended on isopropanol (>95.5%) (5 mL, 0.1 M) and heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture was purified by flash column chromatography (5% to 20% EtOAc/Hex).

*The reaction did not afford **2e**. Only starting material **4e** was recovered.*

6.4. Transfer hydrogenation reaction in the presence of isopropanol as co-solvent



Condition A: **1a** (0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.05 mmol, 10 mol%) were suspended on toluene (0.1 M) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture purified by column chromatography (5% to 20% EtOAc/Hex).

*Only unreacted substrate **1a** was recovered.*

Condition B: **1a** (0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.05 mmol, 10 mol%) ware suspended on toluene (0.1M) and *i*-PrOHl (190 µL, 5 equiv.) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture purified by column chromatography (5% to 20% EtOAc/Hex).

*Only unreacted substrate **1a** was recovered.*

Condition C:1a (0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.05 mmol, 10 mol%) were suspended on toluene/*i*-PrOH (1:1) (0.1 M) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture purified by column chromatography (5% to 20% EtOAc/Hex).

*Product **2a** was obtained in 36% yield (42 mg).*

Condition D:1a (0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.05 mmol, 10 mol%) was suspended on HFIP/*i*-PrOH (1:1) (5 mL, 0.1M) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture purified by column chromatography (5% to 20% EtOAc/Hex). Compound **2a** and **4a** was obtained as mixture and yields were estimated from ^{1}H NMR integral ratios.

*Compound **2a** (40%) and **4a** (24%) was obtained as a mixture.*

*7.5.*Mechanistic studies for the identification of reaction intermediates

To an oven-dried 10 mL round bottom flask equipped with a magnetic stir bar was added the alkylidene Meldrum's acid (0.5 mmol, 1.0 equiv.) and 3,5-*bis*(trifluoromethyl)phenyl) boronic acid (0.05 mmol, 0.1 equiv.). The resulting mixture was suspended on isopropanol (>95.5%) (5 mL, 0.1 M) and refluxed for 1 hr. Excess solvent was removed under vacuum and the resulting crude reaction mixture was analyzed by ^{1}H NMR spectroscopy comparing with the ^{1}H NMR spectrum of **1e**, **2e**, **3e** and **4e**.

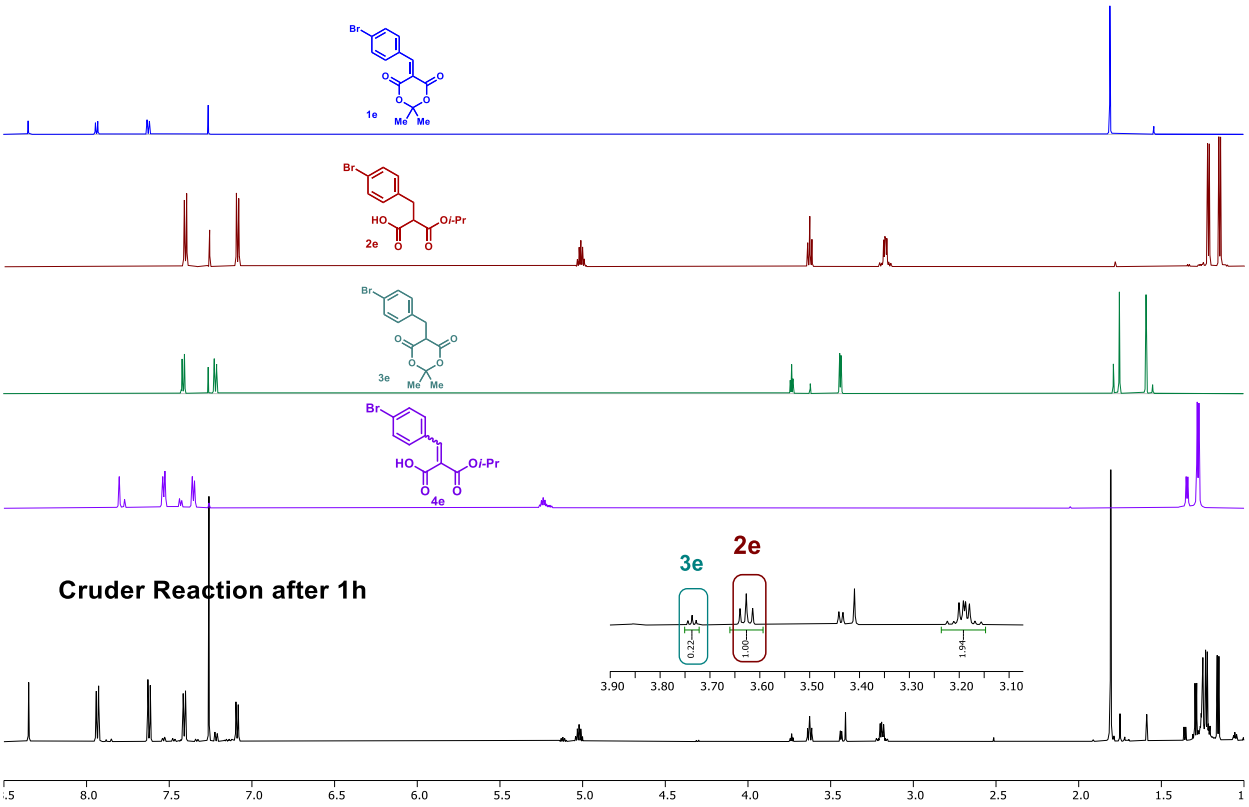
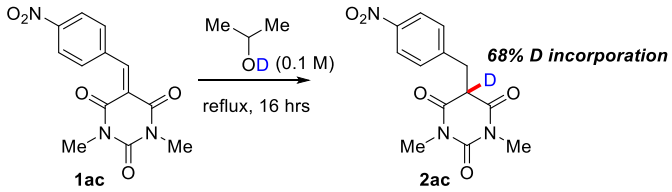


Figure S1: Mechanistic studies for the identification of reaction intermediates

7.6. Deuterium labelling experiments:

Experiment 1:



In a 10 mL round bottom flask equipped with a stir bar, compound **1ac** (0.1 mmol, 29 mg) was suspended on *i*-PrOD(0.1 M) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy (using $CDCl_3$ as solvent).

*Product **2ac** was detected with 68% D-incorporation at the α position.*

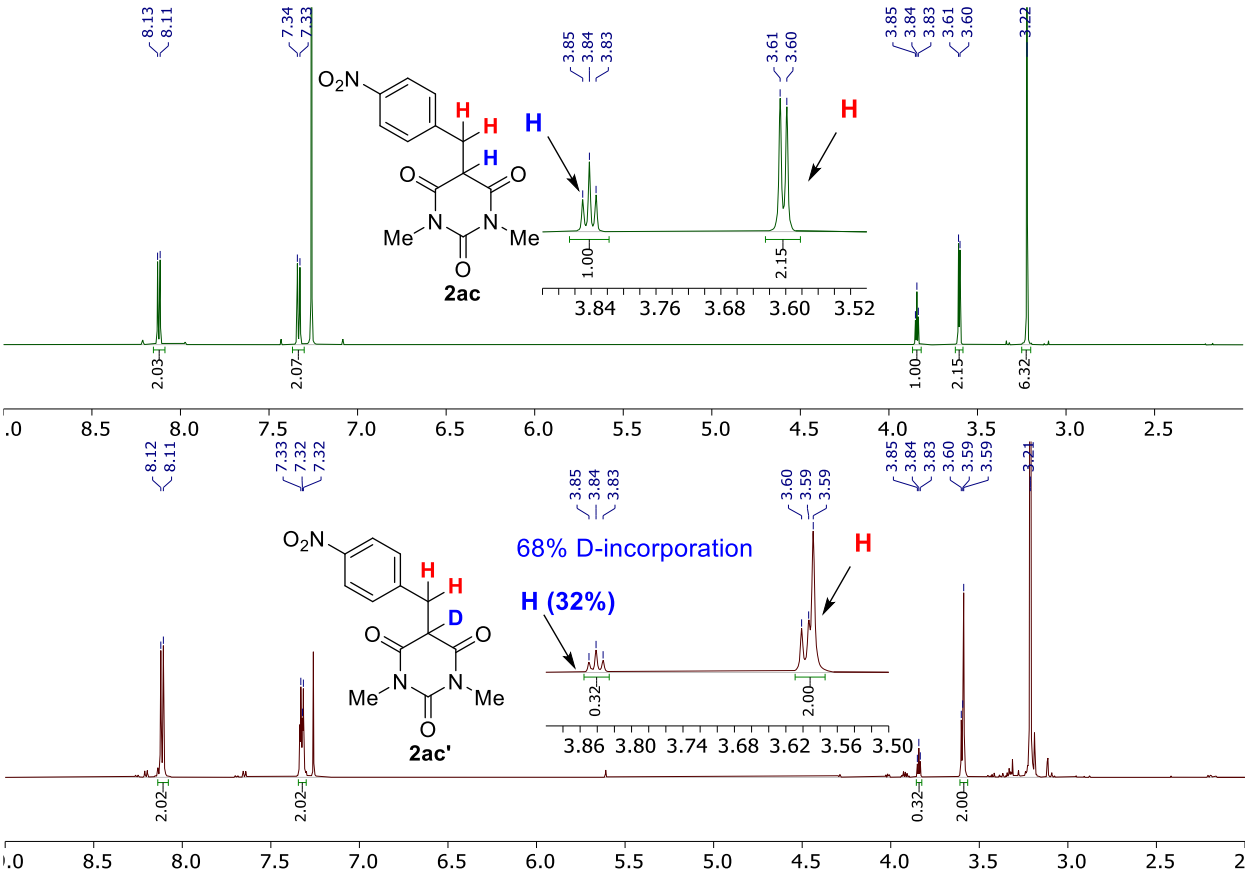
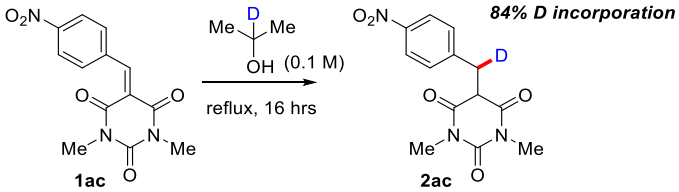


Figure S2: Deuterium labelling experiments with *i*-PrOD and barbituric acid.

Experiment 2:



In a 10 mL round bottom flask equipped with a stir bar, compound **1ac** (0.1 mmol, 29 mg) was suspended on *i*-PrOH-2-D(0.1 M) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy (using $CDCl_3$ as solvent).

*Product **2ac** was detected with 84% D-incorporation at benzylic position.*

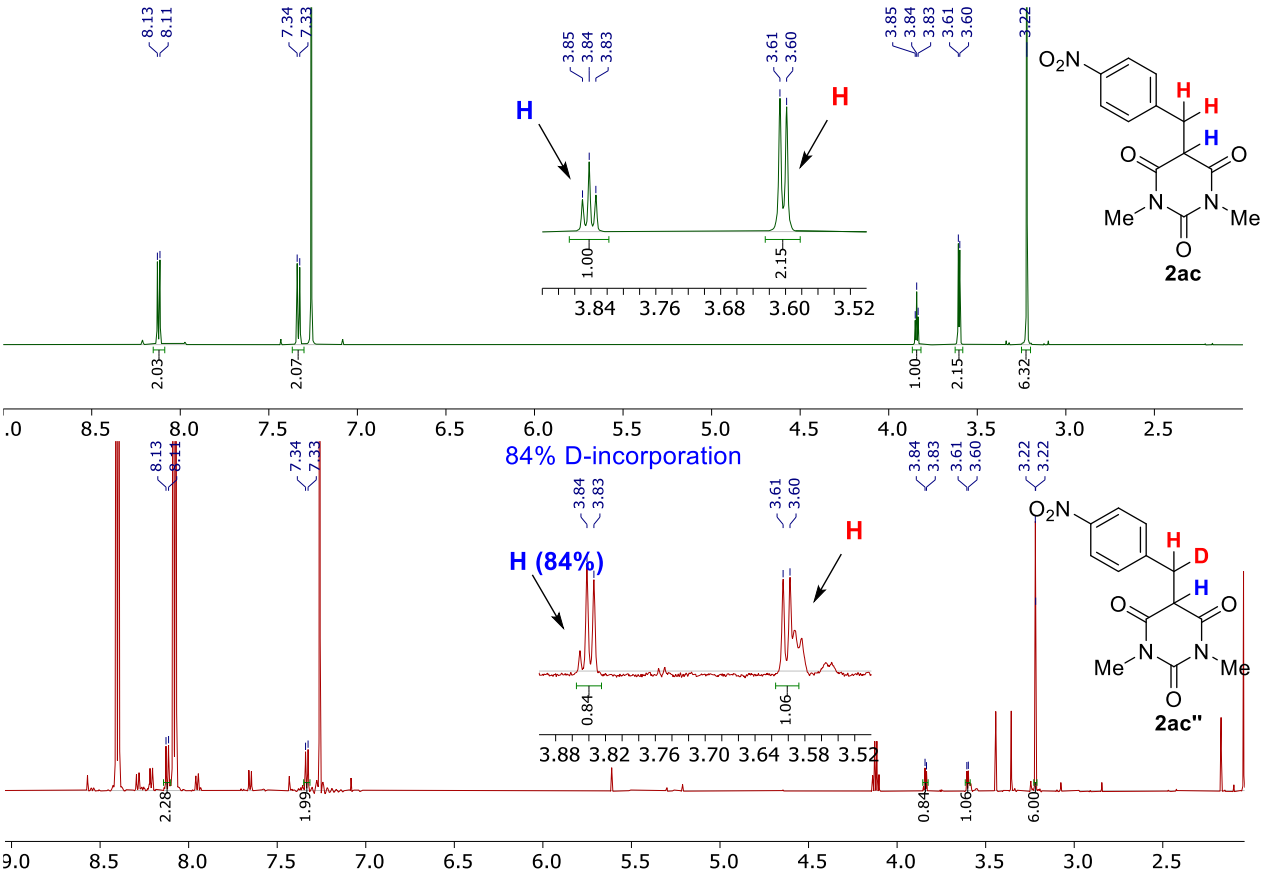
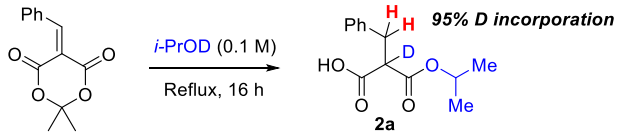


Figure S3: Deuterium labelling experiments with *i*-PrOH-2-D and barbituric acid.

Experiment 3:



In a 10 mL round bottom flask equipped with a stir bar, compound **1a** (26 mg, 0.1 mmol) was suspended on *i*-PrOD(0.1 M) and the resulting reaction mixture was heated to reflux for 16 hrs. Excess solvent was removed under vacuum and the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy (using $CDCl_3$ as solvent).

*Product **2a** was formed with 95% D-incorporation at the C2 position.*

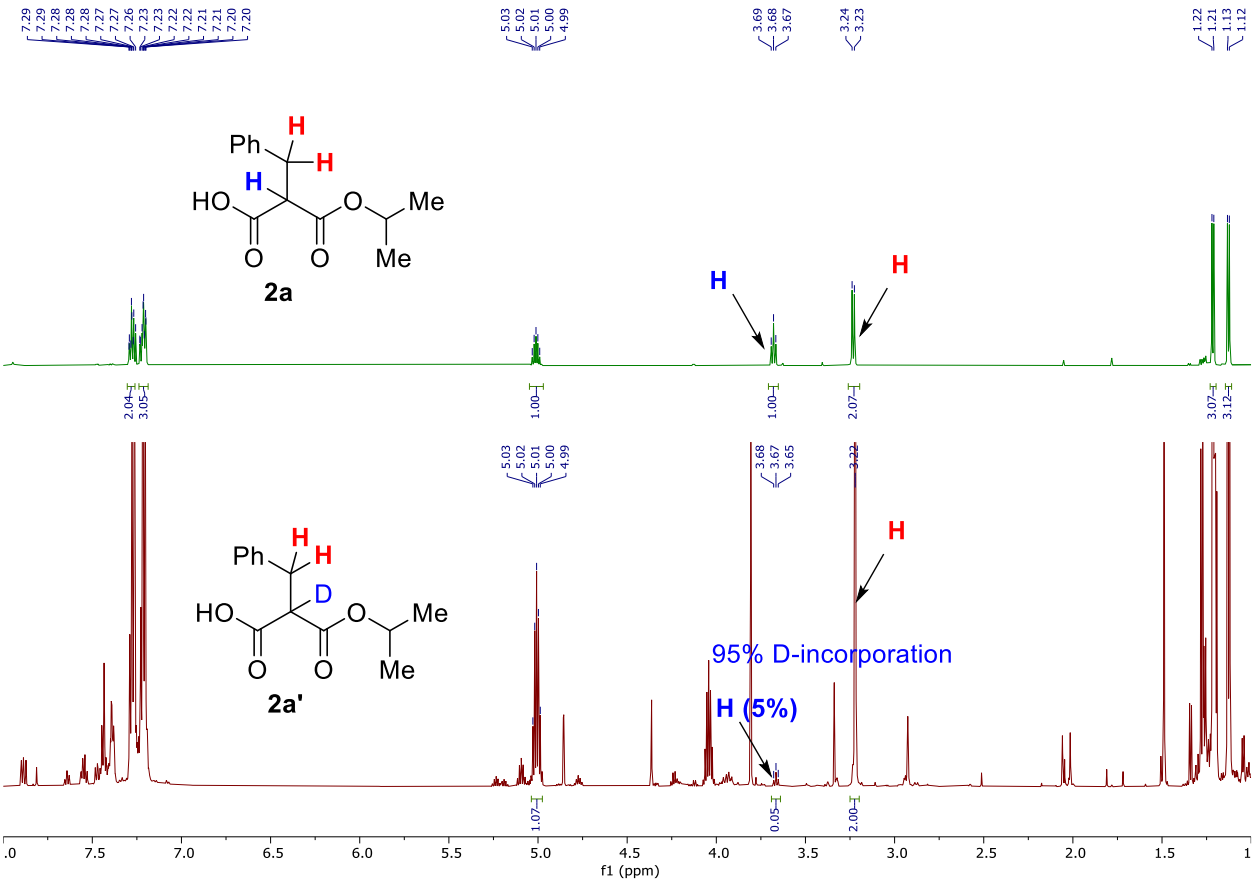


Figure S4: Deuterium labelling experiments with *i*-PrOD and Meldrum's acid.

8. Computational Details

Full conformational space of all stationary points were first studied using metadynamics (GFN2) with crest 2.11.2/xtb 6.4.1 and the resulting non-degenerate conformers (<10 kcal/mol, 298 K) were further DFT (B97-D3/def2-SVP) optimized using orca 5.0.2.[8,9,10] Final DFT geometry optimization and energy calculations were carried out using B97-D3/def2-TZVP level using Weigend J auxiliary basis set with defgrid2 (for gas phase T = 298.15 K, for solution 355.0 K) and TightSCF keyword using Orca 5.0.2. Implicit CPCM model was used for solvation (isopropanol, ε = 17.9). Relevant transition states were identified using scan method (B97-D3/def2-SVP) and further optimized with higher level DFT (B97-D3/def2-TZVP) in both gas phase and using CPCM solvent model. Avogadro 1.2.0 was used to visualize the structures.[11,12,13]

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[8]F. Neese, The ORCA Program System. *Wiley Interdiscip. Rev. Comput. Mol. Sci.*2012, **2**, 73.

[9]F. Neese, Software Update: The ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.*2018, **8**.

[10]P. Pracht, F. Bohle andS. Grimme, *Phys. Chem. Chem. Phys.*2020, **22**, 7169.

[11]S. Grimme, *J. Chem. Theory Comput.*2019, **15**, 2847.

[12]Avogadro: an open-source molecular builder and visualization tool. Version 1.2.0. http://avogadro.cc/

[13]M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *Journal of Cheminformatics*2012, **4**,17.DOI: 10.1186/1758-2946-4-17

8.1. Compiled Energetics

Table S4: Energetics of all stationary points and transition states (B97D3/def2-TZVP).

Structure	**Electronic energy** (Hartree)	**Enthalpy** (Hartree)	**Gibbs** (Hartree)	**Imaginary Vibrational freq**
$SM1_H$ (gas)	–803.33172730	–803.09526431	–803.15215907	N/A
$SM1_H$ (IPA, 355K))	–803.34907962	–803.10702952	–803.18039457	N/A
SM2 (gas)	–194.32224076	–194.21021281	–194.24419426	N/A
SM2 (IPA, 355K)	–194.32921110	–194.21540761	–194.25814406	N/A
$INT1_H$ (gas)	–997.66872408	–997.31739501	–997.38863858	N/A
$INT1_H$ (IPA, 355K)	–997.68723916	–997.32871400	–997.42229828	N/A
$TS1_H$ (gas)	–997.63131793	–997.28648117	–997.35560778	–251.31 cm^{-1}
$TS1_H$ (IPA, 355K)	–997.65548849	–997.30356609	–997.39408346	–863.27 cm^{-1}
$INT2_H$ (gas)	–997.67863287	–997.32861476	–997.39970887	N/A
$INT2_H$ (IPA, 355K)	–997.70002615	–997.34290170	–997.43593798	N/A
$PROD1_H$ (gas)	–804.55627646	–804.29634491	–804.35327576	N/A
$PROD1_H$ (IPA, 355K)	–804.57194744	–804.30625666	–804.38039800	N/A
PROD2 (gas)	–193.11743664	–193.02940701	–193.06403385	N/A
PROD2 (IPA, 355K)	–193.12553491	–193.03588702	–193.07849065	N/A
$INT3_H$ (gas)	–997.63832290	–997.28755131	–997.35734770	N/A
$INT3_H$ (IPA, 355K)	–997.65890371	–997.30057984	–997.39049418	N/A
$TS2_H$ (gas)	–997.60088572	–997.25537269	–997.32349704	–353.89 cm^{-1}
$TS2_H$ (IPA, 355K)	–997.62052119	–997.26736385	–997.35667694	–335.33 cm^{-1}
$SM3_{w/o\ C=O}$ (IPA, 355K))	–729.31838883	–729.05837444	–729.13011557	N/A
$INT4_{w/o\ C=O}$ (IPA, 355K)	–923.65717107	–923.28042326	–923.37181441	N/A
$TS3_{w/o\ C=O}$ (IPA, 355K)	–923.61074548	–923.24112634	–923.32864448	–355.42 cm^{-1}
$INT5_{w/o\ C=O}$ (IPA, 355K)	–923.64789619	–923.27280227	–923.36408960	N/A
$PROD3_{w/o\ C=O}$ (IPA, 355K)	–730.54242714	–730.25851574	–730.33098296	N/A

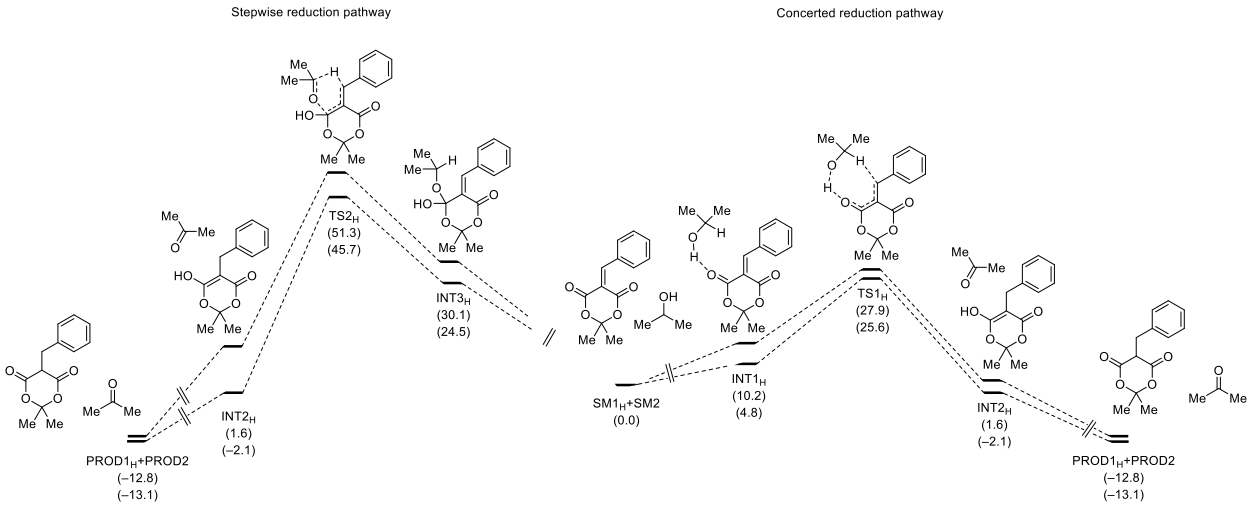


Figure S5: Reaction pathways with energies for concerted and stepwise reduction. All energies are reported in kcal/mol (top value for 355 K in isopropanol, lower value for gas phase).

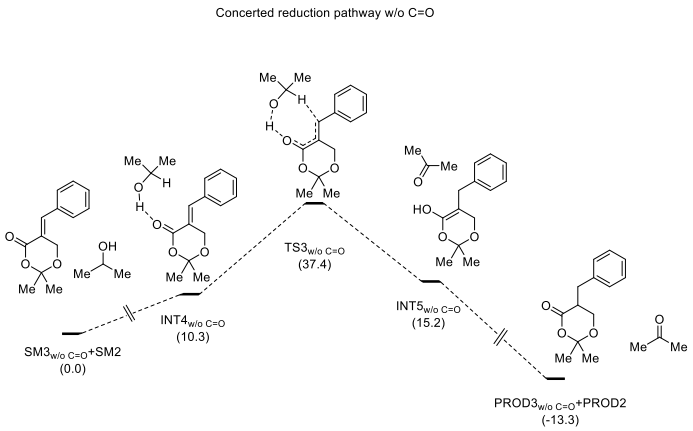
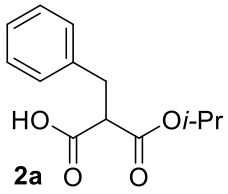


Figure S6: Reaction pathway without C=O with energies for concerted reduction. All energies are reported in kcal/mol (at 355 K in isopropanol).

9. Synthesis and characterization of SMAHOs:

2-benzyl-3-isopropoxy-3-oxopropanoic acid (2a)



2a

Following the general procedure for TH reaction, 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione **1a** (0.116 g, 0.5 mmol) and 3,5-bis(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 85/15) to afford 2-benzyl-3-isopropoxy-3-oxopropanoic acid **2a**as yellow oil (0.098 g, 83%).

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.30 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 5.01 (p, *J* = 6.3 Hz, 1H), 3.68 (t, *J* = 7.7 Hz, 1H), 3.23 (d, *J* = 7.8 Hz, 2H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H).

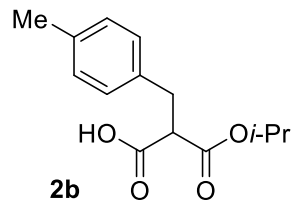
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 168.7, 137.5, 129.0, 128.7, 127.0, 69.9, 53.7, 34.9, 21.6, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{15}O_4^-$: 235.0976, found: 235.0983.

FTIR (cm^{-1}): 3185, 3032, 2983, 2937, 1731, 1713, 1455, 1375, 1279, 1185, 1103, 748, 699, 681.

3-isopropoxy-2-(4-methylbenzyl)-3-oxopropanoic acid (2b)

Following the general procedure for TH reaction, 2,2-dimethyl-5-(4-methylbenzylidene)-1,3-dioxane-4,6-dione **1b** (0.128 g, 0.5 mmol) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 85/15) to afford 3-isopropoxy-2-(4-methylbenzyl)-3-oxopropanoic acid **2b**as colorless solid (0.045 g, 36%).



2b

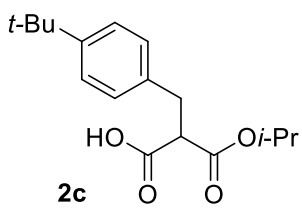
^{1}H NMR(600 MHz, $CDCl_3$)δ 7.11 – 7.08 (m, 4H), 5.02 (hept, *J* = 6.3 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 1H), 3.22 – 3.16 (m, 2H), 2.31 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 168.5, 136.5, 134.4, 129.3, 128.8, 77.4, 77.2, 76.9, 69.7, 53.9, 34.4, 21.6, 21.6, 21.1.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_4^-$: 249.1132, found: 249.1137.

FTIR (cm^{-1}): 3091, 3050, 3023, 2982, 2937, 2925, 2872, 1728, 1712, 1516, 1446, 1375, 1279, 1167, 1104, 1057, 908, 807.

2-(4-(*tert*-butyl)benzyl)-3-isopropoxy-3-oxopropanoic acid (2c)



2c

Following the general procedure for TH reaction, 5-(4-(*tert*-butyl)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1c** (0.144 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column

chromatography (Hexane/EtOAc = 80/20) to afford 2-(4-(*tert*-butyl)benzyl)-3-isopropoxy-3-oxopropanoic acid **2c**as purple oil (0.063 g, 43%).

^{1}H NMR(600 MHz, $CDCl_3$)δ7.30 (d, 2H, *J* = 8.3 Hz), 7.13 (d, 2H, *J* = 8.3 Hz), 5.01 (hept, 1H, *J* = 6.3), 3.66 (t, 1H, *J* = 7.5 Hz), 3.23 – 3.22 (m, 2H), 1.29 (s, 9H), 1.23 (d, 3H, *J* = 6.3 Hz), 1.11 (d, 3H, *J* = 6.3 Hz).

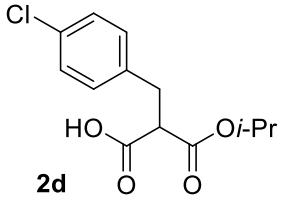
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 167.4, 150.0, 134.1, 128.7, 125.6, 70.1, 52.9, 35.0, 34.6, 31.5, 21.7, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{17}H_{23}O_4^-$: 291.1602, found: 291.1605.

FTIR (cm^{-1}): 3097, 3029, 2965, 2910, 2870, 1733, 1712, 1615, 1513, 1466, 1375, 1278, 1134, 1103, 815, 681.

2-(4-chlorobenzyl)-3-isopropoxy-3-oxopropanoic acid (2d)

Following the general procedure for TH reaction, 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1d** (0.133 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(4-chlorobenzyl)-3-isopropoxy-3-oxopropanoic acid **2d**as brown oil (0.072 g, 53%).



2d

Reaction carried out in 8.5 mmol scale (**1d**) afforded the product **2d** in 48% yield (1.1 grams).

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.25 (d, 2H, J = 8.4 Hz), 7.15 (d, 2H, J = 8.4 Hz), 5.01 (hept, 1H, J = 6.3 Hz), 3.66 (t, 1H, J = 7.8 Hz), 3.252– 3.16 (m, 2H), 1.22 (d, 3H, J = 6.3 Hz), 1.15 (d, 3H, J = 6.3 Hz).

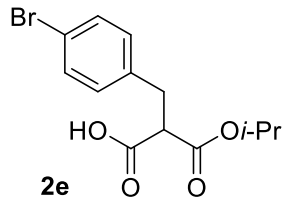
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 168.4, 135.9, 132.9, 130.4, 128.8, 70.1, 53.6, 34.1, 21.6, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}ClO_4^-$: 269.0586, found: 269.0594.

FTIR (cm^{-1}): 3035, 2983, 2938, 1733, 1712, 1483, 1374, 1319, 1278, 1134, 1102, 1015, 909, 908, 681.

2-(4-bromobenzyl)-3-isopropoxy-3-oxopropanoic acid (2e)

Following the general procedure for TH reaction, 5-(4-bromobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1e** (0.156 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(4-bromobenzyl)-3-isopropoxy-3-oxopropanoic acid **2e**as colorless solid (0.099 g, 63%).



2e

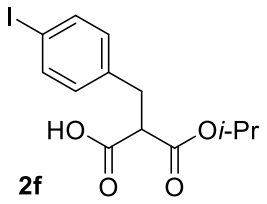
^{1}H NMR(600 MHz, $CDCl_3$)δ7.41 (d, 2H, *J* = 8.4 Hz), 7.09 (d, 2H, *J* = 8.4 Hz), 5.02 (hept, 1H, *J* = 6.3 Hz), 3.63 (t, 1H, *J* = 7.6 Hz), 3.22 – 3.16 (m, 2H), 1.23 (d, 3H, *J* = 6.3 Hz), 1.16 (d, 3H, *J* = 6.3 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 169.1, 134.9, 133.6, 132.6, 128.4, 127.8, 127.7, 127.6, 127.1, 126.3, 125.9, 70.0, 53.3, 35.3, 21.7, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}BrO_4^-$: 313.0081, found: 313.0095.

FTIR (cm^{-1}): 3204, 2982, 2934, 1733, 1722, 1389, 1375m 1195, 1104, 1055, 1033, 1012, 811, 715.

2-(4-iodobenzyl)-3-isopropoxy-3-oxopropanoic acid (2f)



2f

Following the general procedure for TH reaction, 5-(4-iodobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1f** (0.179 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(4-iodobenzyl)-3-isopropoxy-3-oxopropanoic acid **2f**as purple oil (0.125 g, 69%).

^{1}H NMR(600 MHz, $CDCl_3$)δ7.60 (d, 2H, *J* = 8.3 Hz), 6.97 (d, 2H, *J* = 8.3 Hz), 5.01 (hept, 1H, *J* = 6.3 Hz), 3.63 (t, 1H, *J* = 7.7 Hz), 3.19 – 3.13 (m, 2H), 1.22 (d, 3H, *J* = 6.3 Hz), 1.16 (d, 3H, *J* = 6.3 Hz).

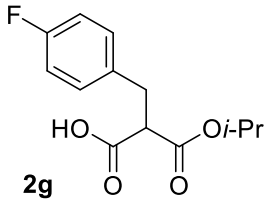
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.3, 168.2, 137.8, 137.2, 131.0, 92.4, 70.0, 53.5, 34.2, 21.6, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}O_4I^-$: 360.9942, found: 360.9954.

FTIR (cm^{-1}): 3074, 3023, 2981, 2929, 1731, 1696, 1452, 1374, 1302, 1277, 1246, 1212, 1105, 1007, 830, 808, 692.

2-(4-fluorobenzyl)-3-isopropoxy-3-oxopropanoic acid (2g)

Following the general procedure for TH reaction, 5-(4-fluorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1g** (0.125 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(4-fluorobenzyl)-3-isopropoxy-3-oxopropanoic acid **2g**as colorless oil (0.062 g, 49%).



2g

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.18 – 7.16 (m, 2H), 6.98 – 6.95 (m, 2H), 5.01 (hept, 1H, *J* = 6.3 Hz), 3.63 (t, 1H, *J* = 7.8 Hz), 3.22 – 3.16 (m, 2H), 1.22 (d, 3H, *J* = 6.3 Hz), 1.14 (d, 3H, *J* = 6.3 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.4, 168.5, 162.5 (d, *J* = 245 Hz), 133.1 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 21.4 Hz), 70.0, 53.8, 34.0, 21.7, 21.6.

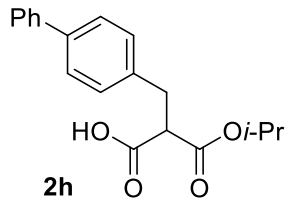
HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}O_4F^-$: 253.0882, found: 253.0886.

FTIR (cm^{-1}): 3082, 3051, 2983, 2937, 1728, 1698, 1604, 1507, 1253, 1209, 1105, 1093, 903, 820.

2-([1,1'-biphenyl]-4-ylmethyl)-3-isopropoxy-3-oxopropanoic acid (2h)

Following the general procedure for TH reaction, 5-([1,1'-biphenyl]-4-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1h** (0.154 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash

column chromatography (Hexane/EtOAc = 80/20) to afford 2-([1,1'-biphenyl]-4-ylmethyl)-3-isopropoxy-3-oxopropanoic acid **2h**as white crystalline solid (0.089 g, 57%).



2h

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.57 – 7.56 (m, 2H), 7.52 (d, 2H, *J* = 8.2 Hz), 7.44 – 7.41 (m, 2H), 7.35 – 7.32 (m, 1H), 7.29 (d, 2H, *J* = 8.2 Hz), 5.04 (hept, 1H, *J* = 6.3 Hz), 3.71 (t, 1H, *J* = 7.6 Hz), 3.30 – 3.29 (m, 2H), 1.24 (d, 3H, *J* = 6.3 Hz), 1.15 (d, 3H, *J* = 6.3 Hz).

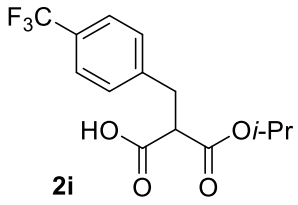
^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 169.1, 140.9, 140.0, 136.5, 130.9, 129.8, 129.4, 128.9, 127.4, 127.4, 127.2, 70.0, 53.2, 34.8, 21.7, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{19}H_{19}O_4^-$: 311.1289, found: 311.1294.

FTIR (cm^{-1}): 3086, 3059, 3030, 2981, 2936, 1741, 1701, 1412, 1284, 1248, 1173, 1101, 1002, 756, 699.

3-isopropoxy-3-oxo-2-(4-(trifluoromethyl)benzyl)propanoic acid (2i)

Following the general procedure for TH reaction, 2,2-dimethyl-5-(4-(trifluoromethyl)benzylidene)-1,3-dioxane-4,6-dione **1i** (0.151 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-3-oxo-2-(4-(trifluoromethyl)benzyl)propanoic acid **2i**as colorless oil (0.097 g, 64%).



2i

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.55 (d, 2H, *J* = 7.9 Hz), 7.34 (d, 2H, *J* = 7.9 Hz), 5.02 (hept, 1H, *J* = 6.3 Hz), 3.68 (t, 1H, *J* = 7.7 Hz), 3.30 – 3.28 (m, 2H), 1.23 (d, 3H, *J* = 6.3 Hz), 1.14 (d, 3H, *J* = 6.3 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 168.4, 141.6, 129.4, 129.0 (q, *J* = 25 Hz), 125.7 (q, *J* = 3.8 Hz), 125.2 (q, *J* = 271 Hz) 70.2, 53.0, 34.6, 21.6, 21.6.

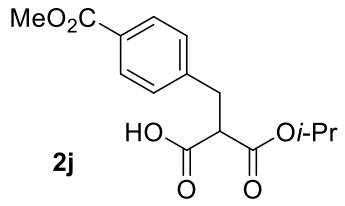
^{19}F NMR (562 MHz, $CDCl_3$) δ -62.52.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{14}O_4F_3^-$: 303.0850, found: 303.0857

FTIR (cm^{-1}): 3110, 3056, 2987, 2938, 1735, 1698, 1620, 1420, 1325, 1104, 1066, 1020, 906, 825, 691.

3-isopropoxy-2-(4-(methoxycarbonyl)benzyl)-3-oxopropanoic acid (2j)

Procedure A: Methyl 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)benzoate **1j** (145 mg, 0.5 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and heated at 60 °C for 24 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(4-(methoxycarbonyl)benzyl)-3-oxopropanoic acid**2j** as colorless solid (0.110 g, 75%).



2j

Procedure B: Methyl 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)benzoate **1j** (145 mg, 0.5 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(4-(methoxycarbonyl)benzyl)-3-oxopropanoic acid **2j**as colorless solid (0.118 g, 80%).

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.97 – 7.93 (m, 2H), 7.31 – 7.26 (m, 2H), 5.00 (p, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.68 (t, *J* = 7.8 Hz, 1H), 3.31 – 3.23 (m, 2H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ173.8, 168.1, 167.1, 143.0, 130.0, 129.0, 128.9, 69.9, 53.3, 52.3, 34.6, 21.6, 21.6.

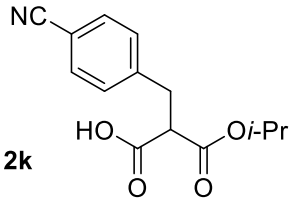
HRMS: Calculated $[M-H]^-$ for $C_{15}H_{17}O_6^-$: 293.1031, found: 293.1041.

FTIR (cm^{-1}): 3148, 3094, 2990, 2936, 1744, 1720, 1684, 1435, 1377, 1313, 1279, 1239, 1196, 1155, 1123, 1104, 1059, 999, 829, 766, 703.

2-(4-cyanobenzyl)-3-isopropoxy-3-oxopropanoic acid (2k)

Following the general procedure for TH reaction, 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)benzonitrile **1k** (0.129 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(4-cyanobenzyl)-3-isopropoxy-3-oxopropanoic acid **2k**as white crystalline solid (0.114 g, 87%).

Reaction carried out in 15.6 mmol scale (**1k**) afforded product **2k** in 57% yield (2.32 g).



2k

^{1}H NMR(600 MHz, $CDCl_3$)δ7.58 (d, 2H, *J* = 8.3 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 5.01 (hept, 1H, *J* = 6.2 Hz), 3.67 (t, 1H, *J* = 7.7 Hz), 3.28 – 3.26 (m, 2H), 1.21 (d, 3H, *J* = 6.3 Hz), 1.14 (d, 3H, *J* = 6.3 Hz).

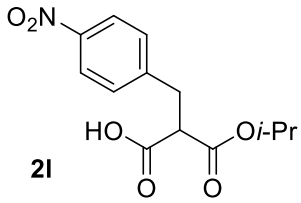
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 167.8, 143.2, 132.5, 129.9, 118.8, 111.0, 70.1, 53.0, 34.6, 21.6, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{14}O_4N^-$: 260.0928, found: 260.0935.

FTIR (cm^{-1}): 3071, 3056, 2984, 2939, 2229, 1737, 1701, 1420, 1313, 1259, 1238, 1163, 1103, 816.

3-isopropoxy-2-(4-nitrobenzyl)-3-oxopropanoic acid (2l)

2,2-dimethyl-5-(4-nitrobenzylidene)-1,3-dioxane-4,6-dione **1l**(0.277 g, 1.0 mmol) was dissolved in *i*-PrOH (10.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 70/30) to afford 3-isopropoxy-2-(4-nitrobenzyl)-3-oxopropanoic acid **2l** as colorless solid (0.173 g, 62%).



2l

^{1}H NMR(600 MHz, $CDCl_3$)δ 8.18 – 8.10 (m, 2H), 7.43 – 7.34 (m, 2H), 5.06 – 5.00 (m, 1H), 3.70 (td, *J* = 7.8, 1.6 Hz, 1H), 3.36 – 3.29 (m, 2H), 1.22 (dd, *J* = 6.3, 3.5 Hz, 3H), 1.15 (dd, *J* = 6.3, 3.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.81, 167.68, 147.22, 147.20, 145.21, 145.18, 129.98, 124.02, 123.99, 123.96, 70.32, 70.30, 53.05, 34.40, 34.34, 21.82, 21.66, 21.61, 21.59.

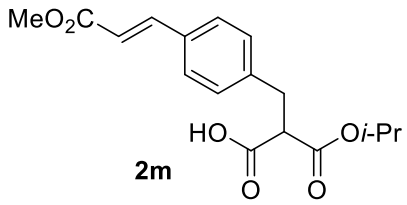
^{13}C DEPT135 (150 MHz, $CDCl_3$) δ129.98, 123.97, 123.96, 70.32, 70.30, 53.05, 52.93, 34.34, 21.67, 21.66, 21.61, 21.60.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}O_6N^-$: 280.0827, found: 280.0838.

FTIR (cm^{-1}): 3111, 3082, 2981, 2937, 1724, 1697, 1603, 1518, 1452, 1430, 1346, 1271, 1250, 1213, 1101, 870, 822, 690.

(*E*)-3-isopropoxy-2-(4-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-oxopropanoic acid (2m)

Following the general procedure for TH reaction, methyl (*E*)-3-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl)phenyl)acrylate**1m**(0.158 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford (*E*)-3-isopropoxy-2-(4-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-oxopropanoic acid **2m**as brown solid (0.106 g, 66%).



2m

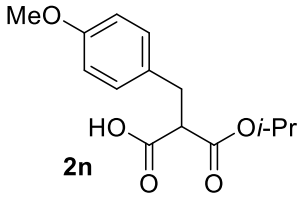
^{1}H NMR(600 MHz, $CDCl_3$)δ7.65 (d, 1H, *J* = 16.0 Hz), 7.44 (d, 2H, *J* = 8.0 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 6.40 (d, 1H, *J* = 16.0 Hz), 5.00 (hept, 1H, *J* = 6.3 Hz), 3.79 (s, 3H), 3.67 (t, 1H, *J* = 7.7 Hz), 3.24 – 3.23 (m, 2H), 1.21 (d, 3H, *J* = 6.3 Hz), 1.13 (d, 3H, *J* = 6.3 Hz).**^{13}C NMR (150 MHz, $CDCl_3$) δ** 173.8, 168.2, 167.8, 144.7, 140.1, 133.1, 129.6, 128.4, 117.6, 69.8, 53.4, 51.9, 34.5, 21.6, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{17}H_{19}O_6^-$: 319.1187, found: 319.1200.

FTIR (cm^{-1}): 3068, 3041, 2986, 2947, 1743, 1701, 1636, 1609, 1435, 1420, 1317, 1207, 1174, 1105, 987, 823, 675.

3-isopropoxy-2-(4-methoxybenzyl)-3-oxopropanoic acid (2n)

Following the general procedure for TH reaction, 5-(4-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1n** (0.131 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.113 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 40 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(4-methoxybenzyl)-3-oxopropanoic acid **2n**as yellow oil (0.083 g, 62%).



2n

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.13 (d, 2H, *J* = 8.6 Hz), 6.82 (d, 2H, *J* = 8.6 Hz), 5.01 (hept, 1H, *J* = 6.3 Hz), 3.77 (s, 3H), 3.63 (t, 1H, *J* = 7.7 Hz), 3.17 – 3.16 (m, 2H), 1.22 (d, 3H, *J* = 6.3 Hz), 1.15 (d, 3H, *J* = 6.3 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.3, 168.7, 158.6, 130.0, 129.5, 114.1, 69.7 55.3, 54.0, 34.1, 21.6.

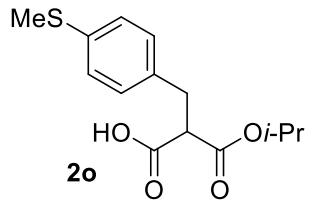
HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_5^-$: 265.1081, found: 265.1086.

FTIR (cm^{-1}): 3038, 2983, 2938, 1712, 1612, 1513, 1279, 1246, 1176, 1102, 1032, 813.

3-isopropoxy-2-(4-(methylthio)benzyl)-3-oxopropanoic acid (2o)

Following the general procedure for TH reaction, 2,2-dimethyl-5-(4-(methylthio)benzylidene)-1,3-dioxane-4,6-dione **1o**(0.139 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 40 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 75/25) to afford 3-isopropoxy-2-(4-(methylthio)benzyl)-3-oxopropanoic acid **2o**as yellow solid (0.097 g, 69%).

^{1}H NMR(600 MHz, $CDCl_3$) δ7.18 (d, 2H, *J* = 8.3 Hz), 7.13 (d, 2H, *J* = 8.3 Hz), 5.02 (hept, 1H, *J* = 6.2 Hz), 3.63 (t, 1H, *J* = 7.5 Hz), 3.21 – 3.19 (m, 2H), 2.46 (s, 3H), 1.23 (d, 3H, *J* = 6.2 Hz), 1.15 (d, 3H, *J* = 6.2 Hz).



2o

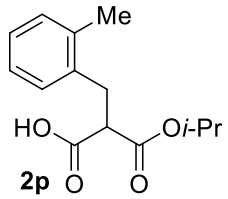
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 169.3, 137.1, 134.5, 129.5, 127.0, 70.0, 53.2, 34.7, 21.7, 21.7, 16.1.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_4^-$: 281.0853, found: 281.0866.

FTIR (cm^{-1}): 3077, 3020, 2984, 2922, 1724, 1698, 1494, 1374, 1302, 1276, 1269, 1249, 1214, 1162, 1102, 1093, 905, 831, 807, 694.

3-isopropoxy-2-(2-methylbenzyl)-3-oxopropanoic acid (2p)

Following the general procedure for TH reaction, 2,2-dimethyl-5-(2-methylbenzylidene)-1,3-dioxane-4,6-dione **1p** (0.123 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 40 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(2-methylbenzyl)-3-oxopropanoic acid **2p**as colorless oil (0.058 g, 46%).



2p

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.15 – 7.10 (m, 4H), 5.01 (hept, 1H, *J* = 6.3 Hz), 3.68 (t, 1H, *J* = 7.8 Hz), 3.25 – 3.24 (m, 2H), 2.35 (s, 3H), 1.23 (d, 3H, *J* = 6.3 Hz), 1.13 (d, 3H, *J* = 6.3 Hz).

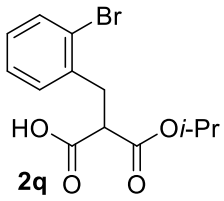
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 168.7, 136.4, 135.7, 130.6, 129.4, 127.2, 126.2, 69.8, 52.3, 32.2, 21.6, 21.6, 19.4.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_4^-$: 249.1132, found: 249.1138.

FTIR (cm^{-1}): 3080, 3050, 3022, 2984, 2939, 1737, 1697, 1305, 1256, 1195, 1168, 1105, 909, 747.

2-(2-bromobenzyl)-3-isopropoxy-3-oxopropanoic acid (2q)

Following the general procedure for TH reaction, 5-(2-bromobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1q** (155.5 mg, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(2-bromobenzyl)-3-isopropoxy-3-oxopropanoic acid **2q** as colorless solid (0.108 g, 69%).



2q

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.21 (td, *J* = 7.4, 1.3 Hz, 1H), 7.10 (td, *J* = 7.6, 1.8 Hz, 1H), 5.01 (p, *J* = 6.3 Hz, 1H), 3.89 (dd, *J* = 8.5, 7.1 Hz, 1H), 3.39 – 3.29 (m, 2H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ174.3, 174.2, 168.3, 136.8, 133.1, 131.6, 128.9, 127.6, 124.7, 69.9, 51.6, 35.2, 21.61.

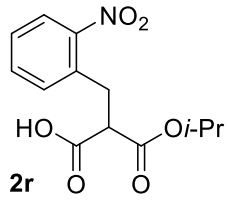
^{13}C DEPT 135 (150 MHz, $CDCl_3$) δ 133.5, 132.0, 129.3, 128.1, 70.3, 52.0, 35.6, 22.0, 22.0.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}O_2Br^-$: 313.0081, found: 313.0087.

FTIR (cm^{-1}): 3062, 2982, 2938, 1733, 1712, 1471, 1443, 1375, 1279, 1181, 1134, 1102, 1026, 907, 751.

3-isopropoxy-2-(2-nitrobenzyl)-3-oxopropanoic acid (2r)

Following the general procedure for TH reaction, 2,2-dimethyl-5-(2-nitrobenzylidene)-1,3-dioxane-4,6-dione **1r** (0.139 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 70/30) to afford 3-3-isopropoxy-2-(2-nitrobenzyl)-3-oxopropanoic acid **2r**as colorless solid (0.045 g, 36%).



2r

^{1}H NMR(600 MHz, $CDCl_3$)δ 8.02 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 5.00 (p, *J* = 6.3 Hz, 1H), 3.90 (dd, *J* = 8.3, 6.9 Hz, 1H), 3.58 – 3.44 (m, 2H), 1.81 (s, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H).

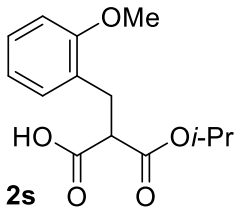
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 168.0, 149.2, 133.5, 133.2, 132.9, 128.5, 125.4,70.0, 52.3, 32.3, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{14}O_6N^-$: 280.0827, found: 280.0829.

FTIR (cm^{-1}): 3077, 3038, 2983, 2939, 1726, 1703, 1525, 1342, 1319, 1301, 1275, 1244, 1184, 1099, 791, 744, 694.

3-Isopropoxy-2-(2-methoxybenzyl)-3-oxopropanoic acid (2s)

Following the general procedure for TH reaction 5-(2-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1s** (0.131 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 40 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(2-methoxybenzyl)-3-oxopropanoic acid **2s**as colorless solid (0.112 g, 84%).



2s

NMR yield 98%.

^{1}H NMR(600 MHz, $CDCl_3$) δ 7.21 (td, *J* = 7.8, 1.8 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.87 – 6.81 (m, 2H), 4.98 (hept, *J* = 6.3 Hz, 1H), 3.85 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.82 (s, 3H), 3.29 – 3.14 (m, 2H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H).

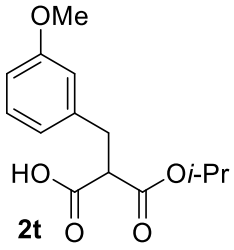
^{13}C NMR (150 MHz, $CDCl_3$) δ169.1, 157.7, 131.1, 128.5, 125.6, 120.5, 110.3, 69.5, 55.3, 51.4, 30.7, 21.7, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_5^-$: 265.1081, found: 265.1091.

FTIR (cm^{-1}): 3032, 2980, 2935, 2843, 1728, 1706, 1496, 1365, 1314, 1300, 1281, 1246, 1161, 1116, 1100, 1040, 1032, 913, 754, 680.

3-isopropoxy-2-(3-methoxybenzyl)-3-oxopropanoic acid (2t)

Following the general procedure for TH reaction, 5-(3-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1t**(0.131 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(3-methoxybenzyl)-3-oxopropanoic acid **2t**as yellow oil (0.080 g, 60%).



2t

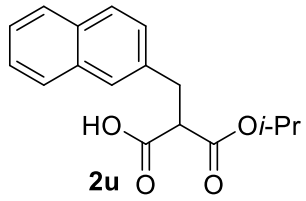
^{1}H NMR(600 MHz, $CDCl_3$)δ 7.11 – 7.08 (m, 4H), 5.02 (hept, *J* = 6.3 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 1H), 3.22 – 3.16 (m, 2H), 2.31 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 168.5, 134.4, 129.4, 128.8, 69.7, 53.9, 34.4, 21.6, 21.2.

HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_5^-$: 265.1081, found: 265.1092.

FTIR (cm^{-1}): 3175, 3056, 2983, 2939, 2838, 1728, 1712, 1602, 1586, 1375, 1279, 1258, 1153, 1102, 1041, 779, 695.

3-isopropoxy-2-(naphthalen-2-ylmethyl)-3-oxopropanoic acid (2u)



2u

Following the general procedure for TH recation, 2,2-dimethyl-5-(naphthalen-2-ylmethylene)-1,3-dioxane-4,6-dione **1u** (0.141 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 40 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 3-isopropoxy-2-(naphthalen-2-ylmethyl)-3-oxopropanoic acid**2u** as yellow oil (0.105 g, 73%).

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.81 – 7.76 (m, 3H), 7.66 (s, 1H), 7.47 – 7.43 (m, 2H), 7.34 (dd, 1H, *J* = 8.4 Hz, 1.8 Hz), 5.01 (hept, 1H, *J* = 6.3 Hz), 3.78 (t, 1H, *J* = 7.6 Hz), 3.44 – 3.38 (m, 2H), 1.22 (d, 3H, *J* = 6.3 Hz), 1.10 (d, 3H, *J* = 6.3 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 169.1, 134.9, 133.6, 132.6, 128.4, 127.8, 127.7, 127.6, 127.1, 126.3, 125.9, 70.0, 53.3, 35.3, 21.7, 21.6.

HRMS: Calculated $[M-H]^-$ for $C_{17}H_{17}O_4^-$: 285.1132, found: 285.1138.

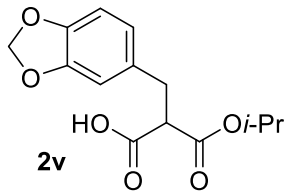
FTIR (cm^{-1}): 3089, 3054, 3021, 2982, 2937, 1730, 1709, 1374, 1322, 1235, 1163, 1146, 1101, 1005, 894, 860, 812, 744.

2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-3-isopropoxy-3-oxopropanoic acid (2v)

Following the general procedure for TH reaction, 5-(benzo[*d*][1,3]dioxol-5-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1v** (0.138 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH 5.0 mL, 0.1 M) and refluxed for 48 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-3-isopropoxy-3-oxopropanoic acid **2v**as yellow sticky solid (0.070 g, 50%).

^{1}H NMR(600 MHz, $CDCl_3$)δ 6.72 – 6.67 (m, 2H), 6.65 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.91 (s, 2H), 5.02 (p, *J* = 6.3 Hz, 1H), 3.61 (t, *J* = 7.7 Hz, 1H), 3.40 (s, 1H), 3.18 – 3.09 (m, 2H), 1.27 (d, *J* = 6.3 Hz, 2H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ174.3, 168.6, 147.8, 146.6, 131.1, 122.1, 109.4, 108.4, 101.1, 70.1, 69.9, 54.0, 34.6, 21.7, 21.6, 21.6.



2v

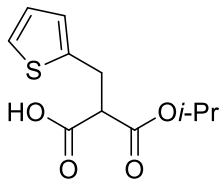
^{13}C DEPT135 (150 MHz, $CDCl_3$) δ122.0, 109.3, 108.4, 101.1, 69.9, 54.0, 34.6, 21.7, 21.6, 21.6.

HRMS: Calculated [M-H]$^-$ for $C_{14}H_{215}O_6^-$: 279.0874, found: 279.0882.

FTIR (cm^{-1}): 3083, 3011, 2975, 2937, 2920, 2901, 2845, 1733, 1696, 1500, 1487, 1441, 1270, 1245, 1206, 1101, 1036, 937, 925, 800.

3-isopropoxy-3-oxo-2-(thiophen-2-ylmethyl)propanoic acid (2w)

Following the general procedure for TH reaction, 2,2-dimethyl-5-(thiophen-2-ylmethylene)-1,3-dioxane-4,6-dione **1w** (0.238 g, 1.0 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.026 g, 0.01 mmol) was dissolved in *i*-PrOH (10.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 75/25) to afford 3-isopropoxy-3-oxo-2-(thiophen-2-ylmethyl)propanoic acid **2w**as colorless solid (0.080 g, 33%).



2w

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.15 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (dd, *J* = 3.5, 1.1 Hz, 1H), 5.06 (p, *J* = 6.3 Hz, 1H), 3.69 (t, *J* = 7.4 Hz, 1H), 3.46 (qdd, *J* = 15.1, 7.4, 0.9 Hz, 2H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.21 (d, *J* = 6.3 Hz, 3H).

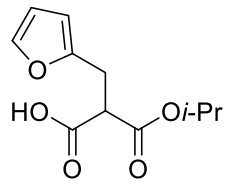
^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 168.4, 139.5, 127.1, 126.4, 124.6, 70.1, 53.7, 29.2, 21.7, 21.7.

HRMS: Calculated [M-H]$^-$ for $C_{11}H_{13}O_4S^-$: 241.0540, found: 241.0556.

FTIR (cm^{-1}):2986, 2939, 1712, 1616, 1571, 1438, 1376, 1278, 1200, 1179, 1131, 1102, 906, 851.

2-(furan-2-ylmethyl)-3-isopropoxy-3-oxopropanoic acid (2x)

Following the general procedure for TH reaction, 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1x** (0.111 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 40 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 75/25) to afford 2-(furan-2-ylmethyl)-3-isopropoxy-3-oxopropanoic acid**2x** as black oil (0.021 g, 19%).



2x

^{1}H NMR(600 MHz, $CDCl_3$) δ 7.30 (dd, 1H, J = 1.9, 0.8 Hz), 6.27 (dd, 1H, J = 3.2,1.9 Hz), 6.09 (dd, 1H, J = 3.2, 0.9 Hz), 5.05 (hept, 1H, *J* = 6.3 Hz), 3.75 (m, 1H), 3.29 – 3.26 (m, 2H), 1.25 (d, 3H, *J* = 6.3 Hz), 1.22 (d, 3H, *J* = 6.3 Hz).

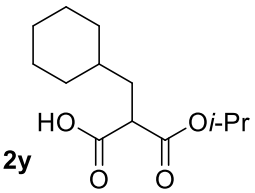
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 168.7, 151.2, 142.0, 110.5, 107.1, 70.2, 50.8, 27.6, 21.6.

HRMS: Calculated [M-H]$^-$ for $C_{11}H_{13}O_5^-$: 225.0768, found: 225.0774.

FTIR (cm^{-1}): 3443, 3253, 2986, 2939, 1713, 1617, 1376, 1277, 1168, 1127, 1100, 905, 708, 681.

2-(cyclohexylmethyl)-3-isopropoxy-3-oxopropanoic acid (2y)

Following the general procedure for TH reaction, 5-(cyclohexylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1y** (0.119 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(cyclohexylmethyl)-3-isopropoxy-3-oxopropanoic acid **2y** as colorless oil (0.079 g, 65%).



2y

^{1}H NMR(600 MHz, $CDCl_3$)δ 9.43 (brs, 1H), 5.06 (hept, 1H, *J* = 6.3 Hz), 3.45 (t, 1H, *J* = 7.7 Hz), 1.83 – 1.74 (m, 3H), 1.72 – 1.67 (m, 4H), 1.65 – 1.62 (m, 1H), 1.25 (d, 6H, *J* = 6.3 Hz), 1.21 – 1.11 (m, 3H), 0.94 – 0.87 (m, 2H).

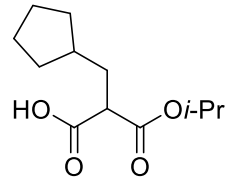
^{13}C NMR (150 MHz, $CDCl_3$) δ 175.4, 169.6, 69.4, 49.5, 36.5, 35.6, 33.1, 32.9, 26.5, 26.2, 26.2, 21.8, 21.7.

HRMS: Calculated $[M-H]^-$ for $C_{13}H_{21}O_4^-$: 241.1445, found: 241.1448.

FTIR (cm^{-1}): 3192, 2982, 2923, 2852, 1733, 1709, 1449, 1375, 1277, 1258, 1182, 1167, 1139, 1103.

2-(cyclopentylmethyl)-3-isopropoxy-3-oxopropanoic acid (2z)

Following the general procedure for TH reaction, 5-(cyclopentylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **1z** (0.112 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 2-(cyclopentylmethyl)-3-isopropoxy-3-oxopropanoic acid **2z**as yellow oil (0.063 g, 55%).



2z

^{1}H NMR(600 MHz, $CDCl_3$)δ 5.09 (hept, 1H, *J* = 6.3 Hz), 3.39 (t, 1H, *J* = 7.5 Hz), 1.99 – 1.91 (h, 2H, *J* = 6.7 Hz), 1.83 – 1.78 (m, 3H), 1.67 – 1.62 (m, 4H), 1.55 – 1.50 (m, 2H), 1.27 (d, 6H, *J* = 6.3 Hz).

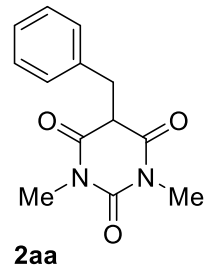
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 170.2, 69.7, 51.0, 38.1, 35.6, 32.6, 32.5, 25.2, 25.2, 21.8, 21.7.

HRMS: Calculated $[M-H]^-$ for $C_{12}H_{19}O_4^-$: 227.1289, found: 227.1292.

FTIR (cm^{-1}): 2982, 2949, 2869, 1731, 1712, 1375, 1278, 1170, 1132, 1102, 1054, 1033, 682.

5-benzyl-1,3-dimethylpyrimidine-2,4,6(*1H,3H,5H*)-trione (2aa)

Following the general procedure for TH reaction, 5-benzylidene-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **1aa** (0.122 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 5-benzyl-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **2aa**as white crystalline solid (0.083 g, 55%). NMR data matches the ones reported in the literature.[14]



2aa

^{1}H NMR(600 MHz, $CDCl_3$)δ 7.23 – 7.22 (m, 3H), 7.03 – 7.02 (m, 2H), 3.77 (t, *J* = 4.8

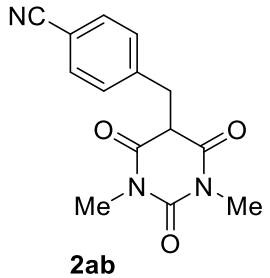
[14] A. Putra, Y. Oe and T. Ohta, *Eur. J. Org. Chem.* 2015, 7799.

Hz, 1H), 3.45 (d, *J* = 4.8 Hz, 2H), 3.12 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 151.1, 135.2, 129.0, 128.7, 128.0, 50.8, 38.0, 28.3.

4-((1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)methyl)benzonitrile (2ab)

Following the general procedure for TH reaction, 4-((1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene)methyl)benzonitrile **1ab** (0.135 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 4-((1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)methyl) **2ab**as yellow solid (0.031 g, 23%). NMR data matches the ones reported in the literature.[15]



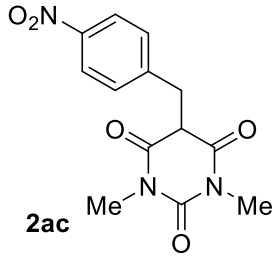
2ab

^{1}H NMR(600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.82 (t, *J* = 4.9 Hz, 1H), 3.55 (d, *J* = 4.9 Hz, 2H), 3.20 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 150.9, 141.8, 132.5, 130.3, 118.6, 111.8, 50.2, 35.4, 28.7.

1,3-dimethyl-5-(4-nitrobenzyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (2ac)

Following the general procedure for TH reaction, 1,3-dimethyl-5-(4-nitrobenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **1ac** (0.145 g, 0.5 mmol) and (3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *i*-PrOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 80/20) to afford 1,3-dimethyl-5-(4-nitrobenzyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **2ac**as pale yellow solid (0.138 g, 95%). NMR data matches the ones reported in the literature.[15]



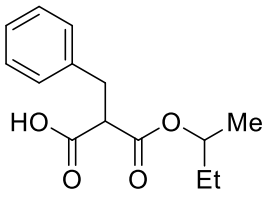
2ac

^{1}H NMR(600 MHz, $CDCl_3$)δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 3.84 (t, *J* = 4.9 Hz, 1H), 3.61 (d, *J* = 4.9 Hz, 2H), 3.22 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 150.9, 147.5, 143.9, 130.5, 123.9, 50.2, 34.9, 28.8.

2-benzyl-3-(sec-butoxy)-3-oxopropanoic acid (2ad)

Following the general procedure for TH reaction, 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione **1a** (0.116 g, 0.5 mmol) and 3,5-*bis*(trifluoromethyl)phenyl)boronic acid (0.013 g, 0.05 mmol) was dissolved in *sec*-BuOH (5.0 mL, 0.1 M) and refluxed for 16 hrs. After completion of the reaction, excess solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 85/15) to afford 2-benzyl-3-(sec-butoxy)-3-oxopropanoic acid **2ad**as a colorless oil (0.055 g, 44%) in a 1:1 inseparable mixture of diastereomers.



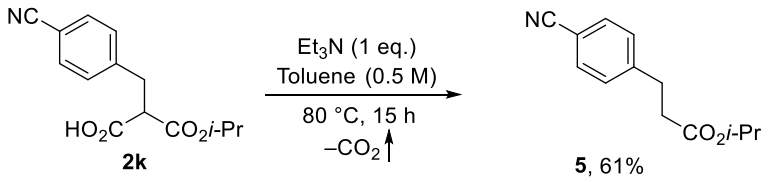
2ad

[15]E. Fillion, A. Kavoosi, K. Nguyen and C. Ieritano, *Chem. Commun.* 2016, **52**, 12813.

^{1}H NMR(600 MHz, $CDCl_3$)δ 9.15 (brs, 2H), 7.29 – 7.27 (m, 4H), 7.22 – 7.20 (m, 5H), 4.86 (hept, *J* = 6.3 Hz, 2H), 3.71 (t, *J* = 7.6 Hz, 2H), 3.25 (m, 4H), 1.60 – 1.45 (m, 4H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.75 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 168.8, 168.7, 137.5, 137.5, 128.9, 128.7, 128.7, 127.0, 74.4, 53.9, 53.8, 34.8, 34.8, 28.7, 28.6, 19.2, 9.6, 9.5.
HRMS: Calculated $[M-H]^-$ for $C_{14}H_{17}O_4^-$: 249.1132, found: 249.1135.
FTIR (cm^{-1}): 3087, 3067, 3031, 2975, 2938, 2881, 1734, 1711,1497, 1455, 1380, 1279, 1165, 1128, 1110, 1000, 863, 698.

10. Procedures for SMHO functionalization and characterization:

10.1: Synthesis of isopropyl 3-(4-cyanophenyl)propanoate (6)

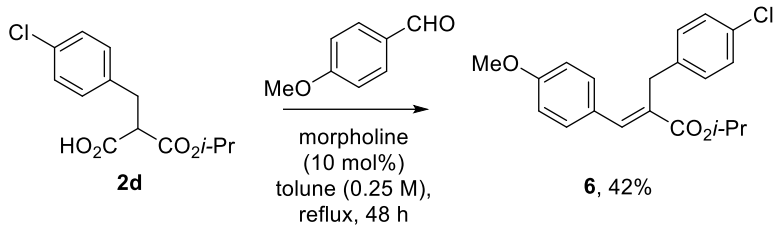


Following a modified literature procedure[16], a 25 ml round bottom flask equipped with a stir bar, under N_2 atmosphere, was charged with compound **2k** (271 mg, 1.1 mmol, 1 equiv.), triethylamine (0.150 ml, 1.1 mmol, 1 equiv.) in dry toluene (2.2 mL, 0.5 M). The reaction mixture was heated to 80 °C overnight. The excess solvent was removed under vacuum and the pure isopropyl 3-(4-cyanophenyl)propanoate (**5**) was obtained (141 mg, 61% yield) after flash column chromatography (10% to 20% EtOAc/Hex) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.62 – 7.55 (m, 1H), 7.35 – 7.28 (m, 1H), 3.00 (t, *J* = 7.6 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$)δ 171.9, 146.4, 132.4, 129.3, 119.1, 110.4, 68.2, 35.5, 31.1, 21.9.
HRMS: Calculated $[M+H]^+$ for $C_{13}H_{16}NO_2^+$: 218.1176, found: 218.1179.
FTIR (cm^{-1}): 3067, 3041, 2981, 2937, 2228, 1724, 1608, 1416, 1734, 1261, 1178, 1145, 1105, 925, 829.

[16]M. Rishel, K. Amarasinghe, S. Dinn and B.Johnson, *J. Org. Chem.* 2009, **74**, 4001.

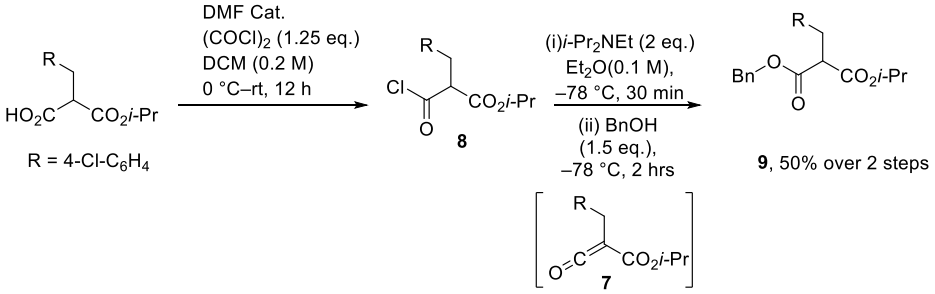
10.2. Galat Reaction:



Following the literature reported procedure[17], a 10 mL round bottom flask equipped with a stir bar and reflux condenser was charged with compound **2d** (135 mg, 0.5 mmol, 1 equiv.) and 4-methoxy benzaldehyde (136 mg, 0.5 mmol, 1 equiv.) dry toluene (2.0 mL, 0.25 M) and morpholine (5 µL, 0.05 mmol, 0.1 equiv.). The reaction mixture was heated to reflux for 48 hrs. The excess solvent was removed under vacuum and the pure isopropyl €-2-(4-chlorobenzyl)-3-(4-methoxyphenyl)acrylate **6** was obtained (72 mg, 42% yield) after flash column chromatography.

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.87 (s, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.10 – 5.03 (m, 1H), 3.92 (s, 2H), 3.81 (s, 3H), 1.21 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$)δ 167.8, 160.2, 140.6, 138.4, 131.8, 131.1, 129.4, 128.9, 128.7, 127.9, 114.2, 68.3, 55.4, 32.8, 21.9.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{22}ClO_3^+$: 345.1252, found: 345.1266.
FTIR (cm^{-1}): 2980, 2936, 2838, 1775,1697, 1604, 1510, 1490, 1253, 1218, 1204, 1173, 1106, 1091, 1032, 1014, 921, 826.

10.2. Synthesis of unsymmetrical substituted malonate via Ketene intermediate:



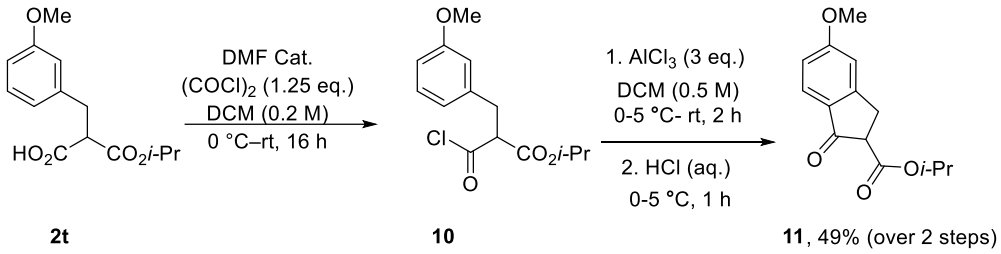
Following the modified literature procedure[18], to a stirred solution of compound **2d** (135 mg, 0.5 mmol, 1.0 equiv.) in DCM (2.5 mL, 0.2 M) added one drop of DMF followed by dropwise addition of oxalyl chloride (54 µL, 0.625 mmol, 1.25 equiv.). The resulting solution was stirred at 0 °C and then 12 h at room temperature. After removing the excess solvent and oxalyl chloride in vacuo, the crude acid chloride was dried by azeotropic distillation with toluene. The crude acid chloride was dissolved in dry ether (5 mL) and cooled to –78 °C. To this solution *i*-Pr_2NEt (166 µL, 1 mmol,2 equiv.) was added dropwise for the generation of the ketene intermediate. After 30 minutes freshly distilled benzyl alcohol (77 µL, 0.75 mmol, 1.5 equiv.) was added dropwise at –78 °C and the resulting reaction mixture was

[17] T. Xavier, S. Condon, C. Pichon, E. L. Gall and M. Presset, *Org. Lett.*2019, **21**, 6135.
[18]A. K. Basak, N. Shimada, W.F. Bow, D. A. Vicic, M. A. Tius, *J. Am. Chem. Soc.* 2010, **132**, 8266.

allowed to stir for 2 hours at the same temperature. Finally, the excess solvent was removed under vacuum and the crude reaction mixture was purified by flash column chromatography (Hexane:EtOAc = 85:15) to obtain compound **9** (90 mg, 50% yield).

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.34 – 7.31 (m, 3H), 7.26 – 7.19 (m, 5H), 7.10 (dd, *J* = 8.6, 2.2 Hz, 3H), 5.13 (q, *J* = 12.3 Hz, 2H), 4.98 (p, *J* = 6.3 Hz, 1H), 3.63 (t, *J* = 7.9 Hz, 1H), 3.18 (d, *J* = 7.9 Hz, 2H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$)δ 168.7, 168.0, 161.5, 136.3, 135.4, 132.7, 130.4, 129.9, 128.7, 128.6, 128.5, 128.4, 128.3, 69.4, 67.2, 53.9, 34.0, 21.8, 21.6, 21.5.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{22}ClO_4^+$: 361.1201, found: 361.1212.
FTIR (cm^{-1}): 3034, 2983, 2939, 1746, 1726, 1492, 1277, 1223, 1145, 1102, 1093, 1015, 808.

10.3. Synthesis of 2,3-dihydroindenone derivative using Friedel-Crafts acylation reaction:



2t **10** **11**, 49% (over 2 steps)

Following the modified literature procedure[19], to a stirred solution of compound **2t** (200 mg, 0.75 mmol, 1.0 equiv.) in DCM (4.0 mL, 0.2 M) added one drop of DMF followed by dropwise addition of oxalyl chloride (80 µL, 0.94 mmol, 1.25 equiv.). The resulting solution was stirred at 0 °C and then 16 h at room temperature. After removing the excess solvent and oxalyl chloride in vacuo, the crude acid chloride was dried by azeotropic distillation with toluene. The acid chloride **10**was dissolved in dry DCM (7.5 mL) and added dropwise to a suspension of $AlCl_3$ (300 mg, 2.25 mmol, 3.0 eq.) in DCM (7.5 mL) at 0-5 °C. The resulting solution was stirred for 2 hours at rt. The mixture was poured into ice-cold dilute HCl (aq.) (3 M) with vigorous stirring and the stirring was continued for 1 hour (at 0-5 °C). Finally, the organic and aqueous layers were separated, and the aqueous phase was extracted several times with DCM. The combined organic phase was dried over sodium sulfate and the resulting crude product was purified by flash column chromatography (Hexane:EtOAc = 85:15) to obtain compound **11** in 49% yield (92.0 mg).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.1 Hz, 1H), 6.93 – 6.89 (m, 2H), 5.08 (p, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.65 (dd, *J* = 8.2, 4.0 Hz, 1H), 3.48 (dd, *J* = 17.1, 3.9 Hz, 1H), 3.29 (dd, *J* = 17.2, 8.2 Hz, 1H), 1.28 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 169.1, 165.9, 156.9, 128.7, 126.4, 116.0, 109.7, 69.3, 55.9, 53.9, 30.4, 21.9, 21.9.
HRMS: Calculated $[M+H]^+$ for $C_{14}H_{17}O_4^+$: 249.1121, found: 249.1126.
FTIR (cm^{-1}): 2981, 2935,2843, 1728, 1700, 1596, 1490, 1305, 1254, 1101, 1087, 1020, 986.

[19] A. K. Basak, N. Shimada, W.F. Bow, D. A. Vicic, M. A. Tius, *J. Am. Chem. Soc.* 2010, **132**, 8266.

11.1. Coordinates

11.1.1. $SM1_H$ (gas)

C	-7.19413171295844	-0.24958137986022	-0.12704296670129
C	-6.25475275262030	-0.96233754381427	-1.02250824798167
O	-5.01596013567114	-1.21865604030033	-0.49758559189154
O	-6.50135338060906	-1.39419059393436	-2.12593652199275
C	-6.94475082601774	-0.34724684141801	1.34656670121218
C	-8.30687793630914	0.46255030397895	-0.47559136435872
O	-7.77705122418825	-0.17690373871243	2.20516269800757
O	-5.67231532135124	-0.69284220929953	1.71331503414436
C	-4.62164326240488	-0.58021950191738	0.73450626752741
C	-4.27768184868181	0.88581291594905	0.48703945892050
H	-5.13977622086192	1.43262475352937	0.09578710370477
H	-3.46150225454152	0.95237477765474	-0.23710511987133
H	-3.96389853853619	1.35064075141220	1.42538388009792
C	-3.45440935811740	-1.38575404959424	1.27060407639731
H	-3.76162135921317	-2.42261352151437	1.42487073549281
H	-3.12138600384533	-0.96356839767475	2.22210609053868
H	-2.62890119203669	-1.35748840949889	0.55499288343644
C	-8.92645343524443	0.90492822953004	-1.70924043389778
C	-10.04216047690591	1.76388368114986	-1.55487495089151
H	-10.37037313630754	2.02295933061199	-0.55114633922598
C	-10.71546869889150	2.28098814291240	-2.65380755343179
H	-11.56918490956929	2.93702245323833	-2.50805388509704
C	-10.29017581351701	1.95348772855729	-3.94303957228261
H	-10.81423454667671	2.35253240697205	-4.80772266962697
C	-9.19347271659871	1.10478506137110	-4.11740207703154
H	-8.86689422528148	0.84151606517994	-5.11994213381142
C	-8.51799560671329	0.58003097833815	-3.02180760571117
H	-7.68955781549433	-0.09916448217167	-3.16573823329456
H	-8.83408529083542	0.82925912932497	0.40561033761980

8.2.2. SM2 (gas)

C	-7.67876775098457	0.27294340640757	0.45441820800623
C	-6.50962796769189	1.25552993815105	0.40604124896979
H	-7.78596511916885	-0.24425459296574	-0.50887725711093
H	-8.61360421384617	0.79960720349872	0.66942434541152
H	-7.52102877207206	-0.49006056411703	1.22593523753342
C	-5.18174932542230	0.56603344167644	0.09544198865121
H	-4.94094143164645	-0.18579907024998	0.85628115068937
H	-4.36947475869561	1.29839412101791	0.05800763081294
H	-5.23232004645194	0.05447759742135	-0.87540828604600
O	-6.76845688527617	2.32565019942354	-0.52027273111458
H	-6.42985472893008	1.76478841588619	1.37512362210998
H	-6.85048899981389	1.93116990384997	-1.40031515791295

8.2.3. INT1$_H$ (gas)

C	-4.08976141900502	0.88272386627034	-1.17834066259187
O	-3.67106497058501	-0.37415926621286	-0.82135519336289
C	-3.21908196250798	1.99572390866355	-0.73996175155773
C	-1.79884244496498	1.67286231870704	-0.41803490247256
O	-1.52503863692397	0.36424754767700	-0.15622683386154
C	-3.56015656635587	3.31183941214981	-0.58664945812621
C	-4.77933529792217	4.09072300355614	-0.61656566104394
H	-2.71070196217404	3.91774643038453	-0.27769253940158
C	-4.65895968155174	5.39749847567922	-0.07978244879015
C	-5.75655848207366	6.24415931445843	-0.00046114581985
C	-7.00034494471199	5.81276666373815	-0.46755449636955
C	-7.13403470940785	4.53300155458334	-1.01426279139825
C	-6.04267272401661	3.67591270444242	-1.09301273389214
H	-3.68922430482895	5.72227818493446	0.28935384177307
H	-5.64415642416467	7.23929987697811	0.42108338669477
H	-7.86150961325108	6.47408780215647	-0.41370321485204
H	-8.09906041314368	4.20296496131002	-1.38965124593907
H	-6.14556249891129	2.69541572277232	-1.53715183946521
O	-5.07857269048400	0.97398813841550	-1.86902490239961
O	-0.88436268749184	2.47104941002208	-0.38876294385076
C	-2.62655094023260	-0.51654952204988	0.15774317289843
C	-2.09267091105535	-1.92743649345833	0.01163504146053
C	-3.15807069080638	-0.21301254931810	1.55576586124283
H	-1.72276332646875	-2.07910840791185	-1.00498980509338
H	-2.89188830429704	-2.64458655977032	0.21440953248229
H	-1.27618534828576	-2.08680854451955	0.72039868943375
H	-2.35280615739671	-0.32317177566283	2.28658813905818
H	-3.96334842223675	-0.91104753697499	1.79853231366972
H	-3.54801691264489	0.80650232563045	1.61491038917059
C	-2.58698119804279	4.92769961214623	3.52333556323005
C	-1.96923372915385	3.93917943231818	2.54437711568143
H	-3.11480964124437	4.39759037267256	4.32331805852178
H	-1.80656448434925	5.55235867082133	3.97199878173442
H	-3.30075709185561	5.58055831040795	3.01086024011500
C	-0.96989044912162	2.99577873522757	3.21212102526614
H	-2.78268984404861	3.33349234100912	2.10413955621564
O	-1.34516733458123	4.71318868741167	1.50853652499798
H	-0.15959691237497	3.57029040654115	3.67484514884788
H	-0.53112552969075	2.30974552117766	2.47901135446650
H	-1.46200310980147	2.39825063899331	3.98915136175625
H	-0.91313722783468	4.09314630462240	0.89692947157106

8.2.4. TS1$_H$ (gas)

C	-0.68388832179047	-1.34868047103873	-1.35373707229659
O	-0.35175491925350	-2.66492524021891	-1.67963919551196
C	0.39274500542902	-0.56122725962573	-0.77498525521563

C	1.70079710558687	-1.12786081153177	-0.62151817588461
O	1.89326837863315	-2.43221746030602	-0.95662250281480
C	0.28076380791860	0.87623368717929	-0.56373601962574
C	-0.98366306659282	1.64365180296607	-0.74336003229303
H	1.14692519793827	1.41672472627152	-0.96456479369792
C	-1.01015923848515	2.73705737923605	-1.61656446813020
C	-2.16561924562665	3.50698934789516	-1.75599295027097
C	-3.29635725452737	3.21028167557931	-0.99665072329083
C	-3.26917487173458	2.13650960247930	-0.10096586551005
C	-2.12355821375792	1.35991059589594	0.02203834485534
H	-0.12510989911271	2.97410503822736	-2.20253185049027
H	-2.17825291610173	4.34085184481590	-2.45291923835283
H	-4.19551652445844	3.81225260311237	-1.09849215495025
H	-4.14856941995724	1.90095978448310	0.49261270623611
H	-2.11003913718316	0.51334010379662	0.70254791544444
O	-1.79516008731226	-0.97375182188857	-1.66148024277589
O	2.72086980852224	-0.53282877075201	-0.21528558468025
C	0.72786518516708	-3.29309409622117	-1.00111740100963
C	1.12940777307716	-4.50060450653839	-1.82771482440469
C	0.32113612392712	-3.65730375078169	0.42775027115944
H	1.41525499752358	-4.17913988548547	-2.83201007847463
H	0.28564700722527	-5.19159269812742	-1.89870833887279
H	1.97471160042007	-5.00983540387085	-1.35726425416313
H	0.02067292776791	-2.76427082938598	0.98223561672762
H	1.15874887446859	-4.13346246728512	0.94465017391575
H	-0.52491597204531	-4.34908473327197	0.39888850561385
C	0.78628474275633	2.73335779022929	2.23962193751880
C	1.38416493247690	1.43711293450144	1.77983944845200
H	-0.29044152907980	2.63346795214098	2.39881257143511
H	1.25015921080754	3.02737901981994	3.19199653819682
H	0.97612263603052	3.52192014741503	1.50750728743920
C	1.04466677704611	0.17825452272192	2.53597205573368
H	0.54456941025670	1.11071298049205	0.61693593851863
O	2.58284273181968	1.55034705167488	1.22180433962240
H	1.65352384164679	0.14978001466816	3.45007251129958
H	1.27389372343831	-0.71607852222296	1.95241714840054
H	-0.01126682592462	0.16592400363770	2.81768006757305
H	2.76740564305995	0.69026411931341	0.68237764457431

8.2.5. INT2$_H$ (gas)

C	0.43339191605030	-0.92100283753160	-2.90677885878908
O	0.67875031873424	-2.27804167654653	-3.14493169774725
C	0.71903574977535	-0.44764927575452	-1.56618802380718
C	1.26471383485764	-1.32665569808134	-0.66549302503458
O	1.42467501601016	-2.63419254655255	-0.92290945937765
C	0.54171134147942	1.02102411082278	-1.28733363779422
C	-0.64692700108096	1.42814730527666	-0.43394190571050
H	0.43933425278700	1.51253447568469	-2.26200524811220

C	-0.73931344354243	2.75238814010781	0.02045303045304
C	-1.82074448519334	3.17741148783150	0.78926201854509
C	-2.83871317664859	2.28038365510129	1.12512447833551
C	-2.76022071985754	0.96173825989233	0.67679186926238
C	-1.67303298239070	0.54355621567640	-0.09386595709057
H	0.05143873539945	3.45529950444073	-0.23462725202799
H	-1.87270492782679	4.21041496982763	1.12565222212170
H	-3.68374820556199	2.60802067739712	1.72490411619884
H	-3.54649900824578	0.25396838914116	0.92787477811826
H	-1.61633335590713	-0.48496639345658	-0.43504219911959
O	0.07340805283761	-0.24312396384743	-3.84614660129955
O	1.72486814089947	-1.06291119271092	0.54712669923345
C	0.64817717045976	-3.16668920391020	-2.03912503717646
C	1.36150052261314	-4.43660938320816	-2.46249444325915
C	-0.78572870056957	-3.41355064953554	-1.57482066090437
H	2.37999067256867	-4.19844184424937	-2.77773157998123
H	0.82556926262766	-4.89406543856767	-3.29781738440217
H	1.39575745459380	-5.14094835773738	-1.62716397810291
H	-1.26065219469023	-2.48083255217847	-1.26411076801978
H	-0.79232604894119	-4.11517095591961	-0.73627502884673
H	-1.36151222329995	-3.83563043174943	-2.40271460364334
C	1.31045048489044	3.16263178641846	2.97531447654964
C	1.23422229971840	1.76147434512094	2.42406231004783
H	0.30833711262189	3.60080485177813	3.02848295679432
H	1.69981307774661	3.12210702756861	4.00121911870852
H	1.96750589566285	3.78239061958388	2.36332053274339
C	0.17974362820486	0.85918803123559	3.00446568062711
H	1.44771441053407	1.44382711441036	-0.83500969270991
O	2.00857673250574	1.39370360632119	1.54483815013870
H	0.13696569426065	0.96780425234547	4.09385887903821
H	0.35081851048898	-0.18253363347379	2.73048968000683
H	-0.79480865467313	1.17471425846194	2.61009704390435
H	1.77119484010117	-0.09127704943359	0.77825900212923

8.2.6. PROD1$_H$ (gas)

C	0.20266803883992	-0.91724353903160	-3.10838689899469
O	0.13096520285129	-2.21627323832422	-2.71518068459620
C	1.15561378025270	-0.00262098077286	-2.35308192251692
C	1.92130283024491	-0.61618988009439	-1.19057277510762
O	1.73408449705708	-1.93973428502412	-0.94288370255908
C	0.48766182019290	1.34643946418407	-1.96843163399149
C	-0.62342291757139	1.19065589111025	-0.96093290793669
H	0.10697700365791	1.79216918591400	-2.89068814586815
C	-0.35236709532799	1.22818946533656	0.41357030645814
C	-1.37051586166030	1.02299772793769	1.34486559661003
C	-2.67600931464726	0.77988443058936	0.91478628735780
C	-2.95828630036657	0.75161791197929	-0.45195491534541
C	-1.93952212124754	0.95693148297723	-1.38242167131326

H	0.66475017569748	1.40851367965881	0.75114624017181
H	-1.14359781709790	1.05443956482514	2.40745606532985
H	-3.46950912732527	0.62034265294691	1.64015527368303
H	-3.97360453953517	0.57045956440403	-0.79534968930201
H	-2.16066671459850	0.92615681091757	-2.44593024255791
O	-0.41095895240788	-0.55549136047838	-4.07998753330466
O	2.73880445757323	-0.00142032775123	-0.55414986092565
C	0.55340038917852	-2.63938079328834	-1.39813156309846
C	0.95783985000944	-4.09468428993456	-1.53687847666518
C	-0.57983790891020	-2.41106689859978	-0.40900044759431
H	1.77498987920265	-4.18741677944441	-2.25640402863434
H	0.10354870992464	-4.68050876486793	-1.88482965597329
H	1.28685108519613	-4.47751001806236	-0.56764448456934
H	-0.83174401002551	-1.35144999839377	-0.34270032177642
H	-0.27710130364842	-2.76331972201036	0.58054368058414
H	-1.46548115463579	-2.96336496465520	-0.73374379310091
H	1.27467704555977	1.99343574448584	-1.57295790832242
H	1.93617037356713	0.23767226346678	-3.09013018614037

8.2.7. PROD2 (gas)

C	-7.68580364838683	0.16522805273292	0.44890233603120
C	-6.52265239426338	1.11059701672818	0.19994193686915
H	-7.73751925107005	-0.59061136413678	-0.34469164211634
H	-8.62295115907115	0.72302479490411	0.49199312611951
H	-7.53391092767459	-0.37677764361600	1.39093185663719
C	-5.15302627368562	0.46478995132617	0.07507882963617
H	-4.92917658891797	-0.13050222048944	0.96900608341055
H	-4.38645187592304	1.22902440659247	-0.06468196803116
H	-5.14307751530129	-0.22853721899677	-0.77558546472575
O	-6.67881036570606	2.31193422495513	0.10470490616948

8.2.8. INT3$_H$ (gas)

C	1.03703727807799	1.94054070426286	-0.21326325290452
C	-0.25859210732349	2.42863177283098	-0.03538691914067
C	-1.33846342513762	1.55414774477446	-0.07884864048665
C	-1.15963287077426	0.16833612576136	-0.29244947235274
C	0.15568870797242	-0.30338199872550	-0.48210664875515
C	1.23335825165838	0.57595574048285	-0.43832679871955
H	-2.34602343302185	1.93812526872698	0.06466597205654
H	1.88588096294850	2.61899171369785	-0.18499172097391
H	-0.42655196202902	3.48883549573597	0.13487233906717
H	0.31861715905130	-1.35288807438691	-0.68451752457688
H	2.23871494592654	0.19125385851190	-0.59001837416302
C	-2.37935461209179	-0.63393858805277	-0.28588642181365
C	-2.66121833268083	-1.95844641162574	-0.25511855289485
H	-3.27129893892492	-0.01317001926020	-0.23341007674571
C	-4.10041970606901	-2.44079081788607	-0.12952393592591
C	-1.72122841818677	-3.10109589127871	-0.30217402339540

O	-0.66187890938860	-3.14040478929384	-0.89098796811859
O	-4.97497902336447	-1.36601245853669	0.01715632136380
O	-4.21256569016062	-3.22274661883947	1.04016560428724
O	-2.15159554182327	-4.24235338213966	0.30752951475816
C	-3.27503957863751	-4.29325067388173	1.22577527181390
C	-3.96196724073385	-5.62468668153218	0.95988423230837
C	-2.73021178259164	-4.15652331247845	2.64154242454710
H	-3.55465552883960	-4.20052867821361	3.35883710138897
H	-2.02496619857176	-4.96489711313313	2.85211921304763
H	-2.22100086770515	-3.19455627108035	2.74816474971366
H	-4.32719555913523	-5.64540639000475	-0.06821931095865
H	-4.80636312220554	-5.73708363183900	1.64583165422864
H	-3.25953985952683	-6.44809244573286	1.11703805969799
O	-4.48626497428185	-3.28159806434919	-1.20192690745746
H	-5.85999457904099	-1.75476764597890	0.08400133669698
C	-4.40528153663303	-2.71280772639288	-2.54192497499086
C	-5.81869307534511	-2.51435238882634	-3.07677172812791
H	-5.78727744102432	-2.12052990049462	-4.09897297659353
H	-6.37478526527056	-1.80652878797913	-2.45483656564788
H	-6.35698430240648	-3.46859524786083	-3.09120043798498
C	-3.57321645315318	-3.65879046352708	-3.39787716035865
H	-3.90154097396474	-1.74105926766838	-2.47716046234576
H	-2.55987668209386	-3.75679781517669	-3.00009832538223
H	-3.50799002806612	-3.28181159698561	-4.42468249764049
H	-4.03587928543126	-4.65174527162396	-3.42396211652059

8.2.9. $TS2_H$ (gas)

C	0.56953712913374	1.38901002717526	-1.64685489319561
C	-0.57903552562377	2.05433391869535	-1.21796598045287
C	-1.66700542028776	1.32532571710828	-0.74422663855973
C	-1.61716662955869	-0.07773428187857	-0.66002416358399
C	-0.45774632402326	-0.73400329197667	-1.10714971212090
C	0.62059686119420	-0.00719931326117	-1.59679940662650
H	-2.56694125051457	1.84430545702357	-0.42149475134209
H	1.41828478796814	1.95276638989447	-2.02517407791945
H	-0.63128146991624	3.13907456002347	-1.25954840158039
H	-0.40601193352807	-1.81491774258472	-1.07196999287077
H	1.50872017086284	-0.53092997388252	-1.94028712841542
C	-2.81878798366509	-0.78517049818373	-0.19854057759047
C	-2.92061131696936	-1.93173205782866	0.62043280477856
H	-3.71153806176800	-0.16167152580263	-0.20648514337284
C	-4.21043206897829	-2.50650542710778	0.76025392755053
C	-1.80202886216525	-2.60211691257777	1.29195691442811
O	-0.66842611327640	-2.19668232342899	1.38845021456935
O	-5.29734666206637	-1.72045580828077	0.70096898978891
O	-4.42569761523389	-3.64093675191210	1.41745258202521
O	-2.14045827951351	-3.73632500265964	2.02199907062163
C	-3.26887511863294	-4.52066348813767	1.65406320539474

C	-2.97439436868166	-5.35561197659546	0.41848612365001
C	-3.64661182726850	-5.34647266436005	2.86867773162321
H	-4.54409024066794	-5.93235114712886	2.65404989003052
H	-2.82582548528758	-6.02598456286178	3.11090389367177
H	-3.83410781340534	-4.69177782340354	3.72301144371514
H	-2.78992812409706	-4.71666087037963	-0.44479778361644
H	-3.83266241395508	-5.99190216546432	0.18753981702517
H	-2.10290442224711	-5.98275702113416	0.62641771718985
O	-4.33400694485834	-3.21426650798766	-1.22264637457231
H	-6.05036531307904	-2.28509379727164	0.46146385323539
C	-3.97016732192389	-2.31661490207108	-2.12163884352898
C	-5.10105912175620	-1.48661127805278	-2.75283797368697
H	-4.70578007637295	-0.65950552659853	-3.35342535978583
H	-5.75102104620299	-1.07683296121666	-1.97474040145187
H	-5.70409992689263	-2.13066905177324	-3.40504872000216
C	-2.92228931156720	-2.81012651081804	-3.13241020159290
H	-3.33918756342059	-1.47017651253734	-1.51052430480073
H	-2.08724985180416	-3.28037743930421	-2.60447964632454
H	-2.53601017977849	-1.99241172144381	-3.75015098942784
H	-3.37843696017066	-3.56100723001422	-3.78926671287650

8.2.10. SM1$_H$ (IPA, 355K)

C	-7.27186258822674	-0.11026166210264	0.03439525324073
C	-6.51255210334728	-1.00602134440912	-0.86802880275928
O	-5.25921485232545	-1.34153201012648	-0.45397203202940
O	-6.94767201283272	-1.53537063980243	-1.87065976500472
C	-6.89297122309564	-0.13133385354505	1.47280008314687
C	-8.35052504667934	0.65135202204974	-0.30369144645341
O	-7.62502836370283	0.15412541197324	2.39934269208179
O	-5.62360647403647	-0.53952712984606	1.74414548804483
C	-4.66525578933823	-0.62149330240097	0.65707621310081
C	-4.23084840276413	0.76961386344566	0.22024864453927
H	-5.07726163248012	1.35591119314718	-0.14736566038341
H	-3.48949449387463	0.67923277661003	-0.57793527293972
H	-3.77957806979235	1.28889062486998	1.06948756054126
C	-3.52822321985380	-1.48344233738928	1.16092335529619
H	-3.90687900891416	-2.46361420122817	1.46151261305887
H	-3.05493180065427	-0.99683981540355	2.01739066440801
H	-2.78640973898844	-1.60704001531497	0.36801160608958
C	-8.91973052115942	1.02156048030822	-1.58368757737567
C	-10.26048127333087	1.46697713189450	-1.58465665962458
H	-10.80765494182625	1.49507035151068	-0.64553819591935
C	-10.88491418495230	1.84807972563587	-2.76787637829293
H	-11.92268294357484	2.16953663026149	-2.75431800842370
C	-10.16762680040204	1.83538527275722	-3.96673235220950
H	-10.64672727759569	2.14737502689441	-4.89109231844267
C	-8.82439301654640	1.44035131764268	-3.97414797481654
H	-8.25913745974568	1.45682261887088	-4.90205878573828

C	-8.20560263442556	1.03019787021923	-2.79975209224000
H	-7.16241266492289	0.74112828130513	-2.81803008772369
H	-8.86442146061131	1.08971571217257	0.55159923682866

8.2.11. SM2 (IPA, 355K)

C	-7.67760190819323	0.27345626919299	0.45424754283183
C	-6.50919503543459	1.25542693378643	0.40890358870460
H	-7.78559069682775	-0.23420185890658	-0.51322954195394
H	-8.61315753390566	0.79569720382990	0.68067496006929
H	-7.51093005695454	-0.49115146201533	1.22196960116782
C	-5.18293001167418	0.56630386666689	0.09589649177849
H	-4.95068116521657	-0.18814212576560	0.85647387935636
H	-4.36596588173991	1.29503791128506	0.06759493295095
H	-5.23656807853953	0.06257452143967	-0.87809999668428
O	-6.77003616115322	2.32617616914747	-0.52930746468365
H	-6.42983733676770	1.76660289738430	1.37674716528100
H	-6.84978613359310	1.92069967395482	-1.40608115881846

8.2.12. $INT1_H$ (IPA, 355K)

C	-4.00008771949163	1.05725058430469	-1.24440594812292
O	-3.63808739307912	-0.21505290172729	-0.91607674186444
C	-3.10874028371259	2.13026416129279	-0.75140570313416
C	-1.70159998080722	1.75468268460679	-0.46619692253234
O	-1.47544610579690	0.44194827156595	-0.21390351853118
C	-3.42955090052075	3.44910109887536	-0.60414806985895
C	-4.68819776910923	4.16063540219185	-0.58766807717872
H	-2.57236198580299	4.08950113908581	-0.40232650904499
C	-4.62021221086136	5.56871618565515	-0.69738444874907
C	-5.77332949710135	6.34505221561249	-0.66593886587205
C	-7.01590842620609	5.73358236286399	-0.48184786714515
C	-7.09638137530700	4.34391888548786	-0.32808952445609
C	-5.95015273958706	3.56178181938797	-0.38590998708333
H	-3.64811997120176	6.04107692231207	-0.81410467514248
H	-5.70408199681767	7.42443239403910	-0.76808637158387
H	-7.91898436032446	6.33705945075998	-0.44237157208161
H	-8.06057277202076	3.87233616532756	-0.15871923195309
H	-6.02809001913200	2.49069336572089	-0.25238250287653
O	-4.94683106717633	1.21106728418160	-1.98923665490978
O	-0.75203152437426	2.51995293647690	-0.45647463428701
C	-2.61107779664765	-0.41630843437206	0.08631365990876
C	-2.12091822243715	-1.83765958981766	-0.08202623783163
C	-3.15085343553971	-0.11659160241338	1.47686164487434
H	-1.74283070969661	-1.98686186307405	-1.09651307091553
H	-2.94618927962825	-2.52896670307977	0.10533311274767
H	-1.32279266975489	-2.03298943450562	0.63837685339168
H	-2.36047614508658	-0.27989862798534	2.21323020649212
H	-3.98276479215651	-0.79331609519330	1.68783460124647
H	-3.50286531794081	0.91477644429190	1.55800558573135

C	-2.67220998934182	4.82309281500714	3.53184771305148
C	-1.99417838171100	3.81992673196353	2.61142548299106
H	-3.34690178709981	4.30531558118292	4.22163680693542
H	-1.92415495575397	5.36673758105261	4.12140387704117
H	-3.25587364995851	5.54639404240248	2.95220412111671
C	-1.18789389173027	2.77025217993885	3.37254951979110
H	-2.76980858704843	3.30691747699074	2.02131694396421
O	-1.14963044238603	4.57397301396154	1.71257689302551
H	-0.42254590468420	3.25272268779965	3.99198475669105
H	-0.69359945174125	2.08224278876768	2.67765483193841
H	-1.84529204656036	2.18143181395683	4.02268100648943
H	-0.79162444466541	3.95100876510363	1.05785951772697

8.2.13. $TS1_H$ (IPA, 355K)

C	-0.61355897743162	-1.30047010103083	-1.49745627380926
O	-0.33603651467574	-2.64224076292320	-1.71796965746888
C	0.44536328292506	-0.52368301055443	-0.89154385979035
C	1.74496152220241	-1.10710141179499	-0.71849850176090
O	1.90256667735020	-2.43524540809358	-0.99294040583077
C	0.33885758861691	0.90459533256752	-0.64934794668955
C	-0.93525575022087	1.65938451374860	-0.76073473973051
H	1.19921828048939	1.47002729443737	-1.02300384921024
C	-1.00386784705217	2.78231274120110	-1.59550615783207
C	-2.18267422403593	3.52532941962192	-1.68456741531563
C	-3.28988064309184	3.17371422997018	-0.91077653647763
C	-3.21564895838989	2.07370855261659	-0.04778883602826
C	-2.04827736710959	1.32150369157613	0.02426966718511
H	-0.13513411465108	3.06368426702467	-2.18588541675831
H	-2.23109120351241	4.38388793484685	-2.34938972651842
H	-4.20445812960462	3.75816215474567	-0.97019009397776
H	-4.07107827775240	1.80560728882898	0.56693404795171
H	-1.98807787295160	0.46778855384723	0.69376296120458
O	-1.68597269424679	-0.89987946053066	-1.92846541534205
O	2.77505504576094	-0.50954354043587	-0.35735034741628
C	0.71486615140718	-3.26822010200413	-0.96840052011779
C	1.07596568487456	-4.54596600264307	-1.69845236395202
C	0.27726663396611	-3.50276894104963	0.47373836807242
H	1.38145179457378	-4.31710849990749	-2.72283190237176
H	0.20912438748450	-5.21156882416255	-1.71835498411233
H	1.89597184896688	-5.04791342123653	-1.17815444222720
H	0.01787535821748	-2.56134841549819	0.96346989082135
H	1.08772579173772	-3.98327016769559	1.02827962192052
H	-0.59735254271100	-4.15881712994190	0.48181340483031
C	0.67648517336949	2.63941589527276	2.20726098934491
C	1.34327497123662	1.38456752152257	1.73105559444440
H	-0.38413314830899	2.46245707257175	2.39884605270867
H	1.15059275708769	2.95384733962065	3.14708990066137
H	0.79097894917814	3.44160670007649	1.47332520750160

C	1.04851440759984	0.10267890784488	2.46529619586629
H	0.62653367110765	1.09683304831833	0.57121259936459
O	2.59228501804105	1.58442574092449	1.26645563002422
H	1.40281001701538	0.22246690172625	3.49851755783043
H	1.56201871603935	-0.75154238085310	2.02187233596549
H	-0.02736093880147	-0.08796211169818	2.49097818356286
H	2.85909547529974	0.76807458914294	0.75333118347713

8.2.14. INT2$_H$ (IPA, 355K)

C	0.22970991005715	-0.93679621857449	-2.82361985694710
O	0.42931855316926	-2.28829595101270	-3.06295328621033
C	0.71997964674361	-0.40563361271392	-1.57659811171035
C	1.43122705479642	-1.24482056369469	-0.75139279975429
O	1.62051045993796	-2.54679767795470	-1.03173630003179
C	0.56366520815941	1.06992231954905	-1.31897950978630
C	-0.64650973266713	1.50304657771446	-0.50922072057712
H	0.51154276161142	1.56678601489865	-2.29527775210752
C	-0.68298820944617	2.80148506949582	0.02047188990968
C	-1.77632191171230	3.24379992916688	0.76415231816534
C	-2.86063800872656	2.39117290251530	0.99190588918506
C	-2.83889641395908	1.09982027239612	0.46193073230708
C	-1.73980076307029	0.66239659246900	-0.28193662195282
H	0.16400465664489	3.46519456656093	-0.14095234193594
H	-1.77782055276793	4.24998716168226	1.17622893425834
H	-3.71049654224933	2.72963118374812	1.57904478261337
H	-3.67587935368747	0.42677177719892	0.63220398697650
H	-1.73035521159206	-0.34653491936747	-0.68191892788788
O	-0.29274243620224	-0.29138736880268	-3.72442617329418
O	2.06392161875704	-0.94432025288485	0.36425980016068
C	0.66178088018492	-3.15662731816138	-1.94475082677348
C	1.32862471253736	-4.40537013629500	-2.48258311334149
C	-0.63558002948648	-3.43905816611437	-1.19836033516035
H	2.25137384387572	-4.14132062711990	-3.00568843860701
H	0.64894054195710	-4.90654231533231	-3.17624569146018
H	1.55826310180494	-5.08524854222413	-1.65807815830599
H	-1.06774233116946	-2.52183292579338	-0.79348495395052
H	-0.43937094392427	-4.13331593926685	-0.37696010324300
H	-1.35175875197423	-3.89506504490165	-1.88695918543905
C	1.22489736984887	2.99834107971097	3.08037163831425
C	1.19064170572277	1.66140935347447	2.39811350565136
H	0.21277341923561	3.40435795679917	3.17219308780662
H	1.60557160146148	2.85391723717557	4.10070187174281
H	1.87372408727669	3.69405229340149	2.54572411611366
C	0.13219024273712	0.69547668332213	2.84071583448205
H	1.46177144332406	1.46923900065628	-0.83624459151759
O	2.02009904177209	1.38398874099934	1.52646380200845
H	0.13172673181657	0.62522059401099	3.93458639168516
H	0.26917044052087	-0.28999375201551	2.39453413400344

H -0.84639801742255 1.09624129367240 2.54905643922778
H 1.95226017610422 0.00596273161166 0.70074864538269

8.2.15. PROD1$_H$ (IPA, 355K)

C 0.56972045107886 -1.04041085969400 -3.13367444090708
O 0.92229077400519 -2.38347084252951 -3.12921047781907
C 0.53357768719191 -0.37609433593898 -1.85467801695928
C 0.96877347830700 -1.07798148655681 -0.76156172889224
O 1.29746574280014 -2.37141005363286 -0.79025985368752
C 0.15965652757978 1.08851557321740 -1.78773475581740
C -0.76998514812492 1.43528118371220 -0.64164196730088
H -0.32179400068984 1.34198103929157 -2.73790278334243
C -0.42379453087398 2.41991606248368 0.29251546129064
C -1.27660821857162 2.72690450386344 1.35878909014607
C -2.48864045796315 2.05241930587622 1.49946981171022
C -2.84436747983162 1.06803649692682 0.56996140364553
C -1.99103778853322 0.76072908125095 -0.48726959224183
H 0.52025005210625 2.95043884214229 0.18337735487624
H -0.98992002160669 3.49191013712074 2.07601001549469
H -3.15300064174983 2.28695903218217 2.32715760079364
H -3.78834596513035 0.53851737413182 0.67357440067153
H -2.26468445263851 -0.01259352777006 -1.20134433894870
O 0.38561181150470 -0.51798720838308 -4.22415546871724
O 1.15821082001512 -0.59295337647164 0.46644180040223
C 0.74064494062383 -3.12818074416343 -1.91795932102121
C 1.57917285679836 -4.38240198383242 -2.03007588320239
C -0.73489052946304 -3.40037373636427 -1.65903634333454
H 2.62494154118120 -4.11940851892394 -2.20814319157228
H 1.21034740520119 -4.98908145416661 -2.86086116915692
H 1.49906078626418 -4.96025782479705 -1.10594869288252
H -1.29942886043267 -2.47094440504172 -1.55285940433510
H -0.84094031833316 -3.99256461133951 -0.74646205216521
H -1.14077843443719 -3.96756916140421 -2.50081345682210
H 1.06003530005909 1.71360840062360 -1.72226050790323
H 0.87426667366304 0.34125709818718 0.50369650799841

8.2.16. PROD2 (IPA, 355K)

C -7.68080541849801 0.16703861618527 0.44836237847686
C -6.52173542993667 1.10566569447616 0.20187812653562
H -7.80881005608629 -0.48270730072446 -0.42712134704740
H -8.60152621176175 0.72517428288840 0.62984711357762
H -7.46051232758661 -0.49056910834549 1.29763681861467
C -5.15870891773747 0.46468761782501 0.07303263164280
H -4.88551468308819 0.00711793678115 1.03278220405107
H -4.40608361712160 1.20392625250951 -0.20850056991210
H -5.18968699112262 -0.34648484095136 -0.66402351926327
O -6.67800634706076 2.31630084935581 0.11181616332412

8.2.17. INT3$_H$ (IPA, 355K)

C	1.07676735537222	1.36000752904732	-0.26830685849105
C	-0.05022240317614	1.81532166137106	-0.95699677436285
C	-1.22165877339636	1.06075122032742	-0.95188793501961
C	-1.27618839793772	-0.17989132811504	-0.28901165976183
C	-0.14163768932521	-0.61573441593223	0.41815152692521
C	1.02167361062847	0.14851510033753	0.42856068002551
H	-2.10388176009360	1.42073549048808	-1.47629355773430
H	1.98781430135457	1.95271572803501	-0.25951979345677
H	-0.01990319655787	2.76326575629485	-1.48791851764390
H	-0.17956941985986	-1.54202315045509	0.98221358912739
H	1.88716470842934	-0.19689319707305	0.98819465406984
C	-2.53491418622428	-0.92493021285614	-0.31433633418348
C	-2.73568439159341	-2.25702121979974	-0.30837861005453
H	-3.42796114771274	-0.30373019048683	-0.31472355972905
C	-4.13558798783818	-2.85384078591557	-0.26672071709360
C	-1.65791044359009	-3.27516305980724	-0.42521732746368
O	-0.69941251506806	-3.21035990609533	-1.17103134981601
O	-5.01320258681892	-1.94154934385193	0.32962811016843
O	-4.15091037781307	-4.09330183789260	0.43343388192223
O	-1.82110767573616	-4.37913959613504	0.34224824247222
C	-3.01583266128385	-4.44001186367027	1.20968363997433
C	-3.17324777066572	-5.90485198669659	1.56961007306730
C	-2.81478127204018	-3.55738277337679	2.43763243601148
H	-3.68772906278183	-3.65721742725958	3.08855595219798
H	-1.92702225715645	-3.89180959451022	2.98117595656795
H	-2.69267082341929	-2.50648099188186	2.17247093022827
H	-3.28740992565765	-6.50266155280321	0.66189961619795
H	-4.05834508583147	-6.02832302922228	2.19917823383370
H	-2.29443104439039	-6.24485218907228	2.12317255270306
O	-4.58225384683335	-3.25263870818295	-1.54708875848759
H	-5.90796380195959	-2.30602041803323	0.22830094669365
C	-4.75044393873527	-2.19873106936855	-2.54826844550727
C	-6.16162177440490	-2.32284236559939	-3.10564448512771
H	-6.32981067775099	-1.55745943239881	-3.87122281782990
H	-6.90387737025400	-2.19215900427262	-2.31158626709324
H	-6.30617719665354	-3.30758653664123	-3.56456592831443
C	-3.67174294894699	-2.35522491703809	-3.61191630834384
H	-4.64552859627296	-1.22851970131933	-2.05341825532536
H	-2.67427153163819	-2.26543497809997	-3.17282377191294
H	-3.78541778252411	-1.57845610524914	-4.37649860021013
H	-3.75631765384182	-3.33389959678874	-4.09779438922336

8.2.18. TS2$_H$ (IPA, 355K)

C	0.60783002797109	1.29856052501311	-1.63311308250288
C	-0.51107680151752	2.00816584120989	-1.19239410694130
C	-1.63163875718496	1.32179978074971	-0.72604750698686

C	-1.63887864985135	-0.08316243901356	-0.66219182609537
C	-0.51145107041618	-0.78585599708426	-1.12304205760071
C	0.59848024028376	-0.10112196680557	-1.60519091169269
H	-2.50989240980705	1.87283817976535	-0.39752898774552
H	1.47856223861533	1.83022254864253	-2.00817497822024
H	-0.51602790076514	3.09468947300228	-1.22140312878326
H	-0.51896976154222	-1.87005006909412	-1.11669321897096
H	1.45980807987788	-0.65740467553501	-1.96608209462405
C	-2.85770867756045	-0.75894464445919	-0.20254482175580
C	-2.95590074476120	-1.90727543170673	0.60978206528248
H	-3.74539063528490	-0.12892856364741	-0.22909586825088
C	-4.24249517976716	-2.51414754906738	0.73062948378347
C	-1.85583716266331	-2.51794934010337	1.34876164006075
O	-0.75269064262231	-2.03881737716874	1.53691292472835
O	-5.32821086734871	-1.73964746741033	0.68765128961808
O	-4.42785458101190	-3.65618903086650	1.38390015749105
O	-2.15880873633365	-3.66974643101879	2.04895504138927
C	-3.25207408634922	-4.50260911209652	1.64187734183767
C	-2.87686158917739	-5.31246805986428	0.41421385267667
C	-3.63144486355529	-5.35101125859268	2.83754229134301
H	-4.49027926699420	-5.97693709062555	2.58242157422474
H	-2.78961529185288	-5.99586132273699	3.10150291189111
H	-3.88276917396361	-4.71319902114369	3.68867437327907
H	-2.63537651169173	-4.65917382218165	-0.42356156591730
H	-3.71496963300921	-5.95321549518737	0.12874189227739
H	-2.01799971563473	-5.93950180272314	0.66946055305198
O	-4.30485920392120	-3.22573097197336	-1.23743344225358
H	-6.12080114894733	-2.30109884048768	0.62897238714241
C	-3.98020863271463	-2.30233841781417	-2.13583005639962
C	-5.14877901375963	-1.51962972022207	-2.75784468420814
H	-4.78898287442159	-0.65623400970343	-3.32866571203912
H	-5.82960452381063	-1.17078249527458	-1.97674970073218
H	-5.70395582895620	-2.17746932264177	-3.43912968291787
C	-2.92446912933077	-2.75537147827793	-3.15630484793737
H	-3.38564681712013	-1.44270330115080	-1.52879337664670
H	-2.06654648164065	-3.19229550823781	-2.63635497344472
H	-2.57932479504530	-1.91980421000294	-3.77471296514764
H	-3.35972942641347	-3.51904010446331	-3.81347618226271

8.2.19. SM3$_{w/o\ C=O}$ (IPA, 355K)

C	-7.19271058168400	0.14811609835327	-0.02905053000685
C	-6.23193623331027	-0.43725746135962	-1.03289586183093
O	-5.26596605751992	-1.28647036775645	-0.40560620912519
C	-6.86159109136288	0.02744734271794	1.41874324782247
C	-8.36368774701588	0.76134546081633	-0.33299429926999
O	-7.62638929642444	0.30739097498397	2.33089969753515
O	-5.63401596655101	-0.43918663367090	1.75238544845112
C	-4.62552594132378	-0.69082382487404	0.69456760995199

C	-3.93879041690074	0.63531549313818	0.37820627660740
H	-4.65446409356161	1.40896892243125	0.08973064767471
H	-3.22160601995231	0.48859263597482	-0.43476492485633
H	-3.40270241141231	0.98158929180374	1.26532808450248
C	-3.67724258212527	-1.72194261721834	1.27478357900565
H	-4.21487093979094	-2.65305245993790	1.47298412712829
H	-3.24439942443001	-1.34689600998680	2.20528628719365
H	-2.87179239821169	-1.91335313860066	0.56043856770945
C	-8.99362604699563	1.04377233086265	-1.61362063450372
C	-10.34553891811374	1.45698132270328	-1.58145755596868
H	-10.84229749885489	1.54826031399765	-0.61851077578057
C	-11.04532437338273	1.73617901012438	-2.75031580384559
H	-12.08616072132551	2.04457163817384	-2.69747876016729
C	-10.40664473244652	1.62711902296797	-3.98882984097840
H	-10.94763202432650	1.84937187360025	-4.90490363572650
C	-9.06454769920253	1.24143886309244	-4.04219979492716
H	-8.55761639615001	1.16980988702340	-5.00097375336251
C	-8.36374031136539	0.95124526371459	-2.87418431631961
H	-7.31889730685008	0.68153742932925	-2.95454842282812
H	-8.94849624400817	1.08133102769677	0.52757717028838
H	-6.76324750980458	-1.07901705817950	-1.74248500784373
H	-5.72351901559648	0.34977536807822	-1.60713061652954

8.2.20. INT4$_{w/o\ C=O}$ (IPA, 355K)

C	-4.19326555283975	1.04131391953570	-0.89686265801444
O	-3.56980576789926	-0.24683918447981	-0.89385827454608
C	-3.20064669400162	2.15692948266287	-0.68497181452795
C	-1.77961774867233	1.79854951663913	-0.44945607115653
O	-1.49880029202532	0.52247020867104	-0.11671163131195
C	-3.50648383261901	3.47753561702389	-0.61622670461915
C	-4.77842594561428	4.17652347383083	-0.68409290496822
H	-2.66122462318003	4.13429266874927	-0.42478336641263
C	-4.76586409521133	5.54537438176457	-0.32794340325506
C	-5.93054558209245	6.30484256161970	-0.33228241512585
C	-7.14358624310228	5.71915085895085	-0.70546487334528
C	-7.17632696799931	4.37124559811744	-1.07348185176121
C	-6.01366329931923	3.60525691178611	-1.06221464525933
H	-3.82283720314024	6.00251868572310	-0.03819076340202
H	-5.89413500528326	7.35322314159753	-0.04816861472695
H	-8.05613891432453	6.30940187251591	-0.71418560057766
H	-8.11515059853498	3.91296803014273	-1.37327916236828
H	-6.07653239351870	2.56938664764675	-1.36721917782657
O	-0.84051937163144	2.58678033757481	-0.52381858235981
C	-2.62314951423468	-0.42091462875263	0.12807742843922
C	-2.02800276310741	-1.80477962345246	-0.03472176813514
C	-3.16087709957578	-0.16377352590946	1.53287908282287
H	-1.66501866557606	-1.93718249502465	-1.05737243748258
H	-2.79500397703493	-2.55461639022098	0.17743249680221

H	-1.19974996663622	-1.93691657000223	0.66557951913680
H	-2.37634809080304	-0.37453406536387	2.26332710217968
H	-4.00858708144908	-0.82963745297296	1.71826185011985
H	-3.48263456341849	0.87140461962393	1.66829396738891
C	-2.32718066767053	4.88441290659885	3.64352908018289
C	-1.85019709765578	3.85031596631713	2.63443980204106
H	-2.98731038932296	4.41626572292411	4.38138662414645
H	-1.47312705757206	5.32369844411898	4.17314649523040
H	-2.87963020780796	5.68722964584075	3.14339542662155
C	-1.09826872607836	2.69310636491520	3.28954259272894
H	-2.72694759908935	3.44576136541080	2.10431514791743
O	-1.01189213458629	4.54073346780895	1.68093239911789
H	-0.22919897459969	3.06863659669285	3.84273361278526
H	-0.75177692773250	1.97915943783208	2.53476106359047
H	-1.75288500184647	2.15712010428416	3.98668231832765
H	-0.80133512271064	3.90820787893924	0.97063168830527
H	-4.99206859194626	1.08187814132411	-0.14198258142767
H	-4.65806964853587	1.12243935899551	-1.88432839527449

8.2.21. $TS3_{w/o\ C=O}$ (IPA, 355K)

C	-0.74553850279104	-1.25659120720890	-0.96329945424072
O	-0.34416157060537	-2.43294516217628	-1.68634427811833
C	0.45490504312982	-0.41513759148194	-0.61294979059441
C	1.73017771268630	-1.02250197912414	-0.55533991399573
O	1.87159984121405	-2.34478654765659	-0.88221136440960
C	0.35056723034937	1.01806361954214	-0.44392170578990
C	-0.94792768245947	1.68832046243304	-0.77460809329567
H	1.21505425234212	1.56175300150695	-0.84220392255684
C	-1.04502507594707	2.53067314524171	-1.88928167044833
C	-2.25689550979114	3.14642735248573	-2.20928642936362
C	-3.38269258902158	2.93682589552581	-1.40930593723439
C	-3.29047241891928	2.10888170551558	-0.28695231165533
C	-2.08076549730908	1.49012990636584	0.02717085175779
H	-0.16792150465413	2.69683087100545	-2.51049316078122
H	-2.31996532320824	3.79346861499499	-3.08070038492856
H	-4.32478009315146	3.42027389585573	-1.65505926222044
H	-4.16031600894798	1.94823553768531	0.34514173440796
H	-2.00615552410187	0.85258816772414	0.90493617933599
O	2.81893174098449	-0.45914575063012	-0.23957930584647
C	0.66443823526721	-3.17072454673768	-1.03661085061021
C	1.05660089752336	-4.30449429180326	-1.96695267074281
C	0.25576391259953	-3.66322498648720	0.35151879707670
H	1.32559208048391	-3.90293629863304	-2.94790406979442
H	0.21607762458452	-4.99543048101917	-2.07697037706194
H	1.90938544843038	-4.84720703916437	-1.55149006889764
H	0.08058714093417	-2.83211789966182	1.03823526940928
H	1.05282245919055	-4.28679813990187	0.76468448977888
H	-0.65745092318790	-4.26046373414965	0.27119160311553

C	0.98440134045401	2.70598282888510	2.57819939134364
C	1.46546455937145	1.44551482410982	1.92812977785218
H	-0.07773278926425	2.63182667626907	2.82451770230890
H	1.53957113494362	2.86129501377951	3.51550423149911
H	1.15645233398719	3.56884854087382	1.92917577619384
C	1.08587087265896	0.11823468822321	2.50188740397477
H	0.53278347087232	1.31626635255908	0.73248281907691
O	2.63673432170740	1.56111178530488	1.29713997016720
H	1.93885491344126	-0.30741002495083	3.04388661793331
H	0.82531750329224	-0.59800956199613	1.70235395135232
H	0.22827909990590	0.21720832452077	3.17012896448640
H	2.78926200174914	0.71882766309139	0.71627483683400
H	-1.34180676527705	-1.54763239054653	-0.08486255098437
H	-1.41322739346636	-0.71762124016957	-1.64154279433377

8.2.22. INT5$_{w/o\ C=O}$ (IPA, 355K)

C	0.21562374320621	-0.96206180226646	-2.83181939633196
O	0.71145614317489	-2.27503928793480	-3.14303690601232
C	0.76291451989323	-0.44129343221263	-1.53207438969296
C	1.37697570998628	-1.30922798436720	-0.70291438866317
O	1.51957908903661	-2.64046701681591	-0.96645244906299
C	0.61044532496638	1.02821839833417	-1.25304731012658
C	-0.61527246327639	1.46279526108766	-0.46041146947716
H	0.58975569334337	1.56098948750263	-2.21541951719092
C	-0.71289447118038	2.79256044603695	-0.02371560672531
C	-1.81264077715770	3.22851879889951	0.71428990452981
C	-2.84464987494994	2.33858878637094	1.02795959499613
C	-2.76061742785817	1.01415835138627	0.59479986904786
C	-1.65219084252525	0.58298065302593	-0.13913001143770
H	0.09289954185430	3.48766181762749	-0.25224542070607
H	-1.86057473636263	4.26023702870563	1.05460801547514
H	-3.70019304053836	2.67361134219637	1.60890537879972
H	-3.55320009893295	0.31014664071670	0.83755174201058
H	-1.58236667549612	-0.45415212536283	-0.45119461931842
O	1.97348836504470	-1.06213929619106	0.48257688472452
C	0.68110369958248	-3.16474897590743	-2.04493978433259
C	1.34990671721652	-4.45025038149096	-2.49774275338893
C	-0.72781973873204	-3.39857623692605	-1.50133274394369
H	2.34251751918154	-4.23086001071957	-2.90063842296535
H	0.74214853263450	-4.92536591374838	-3.27262536647206
H	1.44539134949737	-5.13667216752023	-1.65256928709361
H	-1.14688608391574	-2.48901568673371	-1.06772586723684
H	-0.69652533216007	-4.16775646983130	-0.72510764644082
H	-1.37831416326682	-3.73935288411452	-2.31232951043356
C	1.23884688531472	3.13423233983968	3.04963650298429
C	1.21903184712238	1.74765340634474	2.46606904459570
H	0.22525560851437	3.54639977537927	3.08496092875272
H	1.59374881184721	3.06880297721408	4.08702552475318

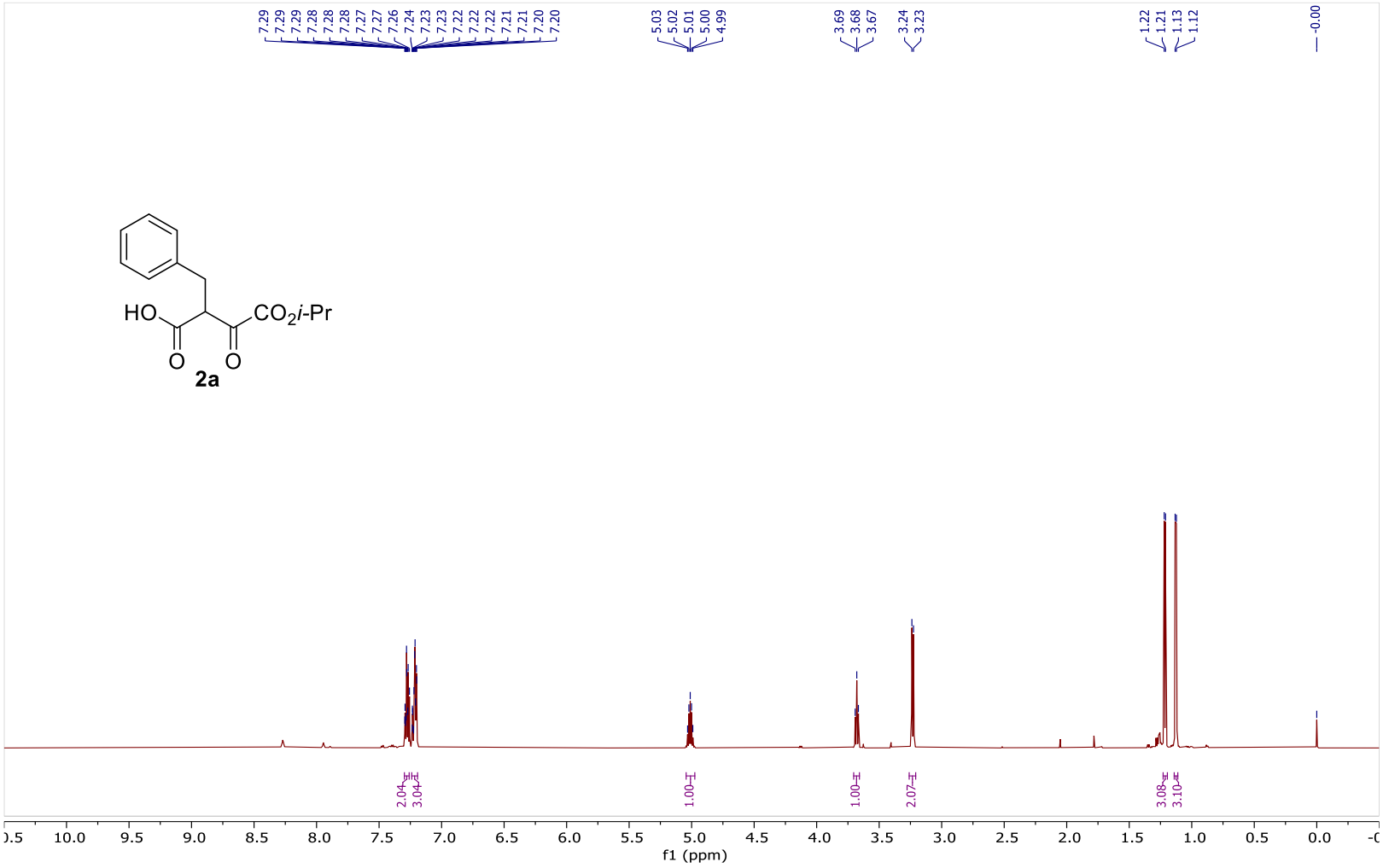
H	1.90037398946251	3.78897967640345	2.47959776951284
C	0.15738650640202	0.81356171381129	2.97239326779467
H	1.49537007116937	1.41890532364441	-0.73617078790900
O	2.05141282487767	1.40514511129270	1.62551651594324
H	0.13609058927312	0.83282246359294	4.06817039035266
H	0.31422474398778	-0.20307026143421	2.60961336657122
H	-0.81886004811244	1.17683220324055	2.62891060921937
H	1.91459564502277	-0.11265104454826	0.76666576527257
H	-0.88866244512849	-0.96521259602533	-2.84588076795129
H	0.54493474798117	-0.32970842850255	-3.66609665242291

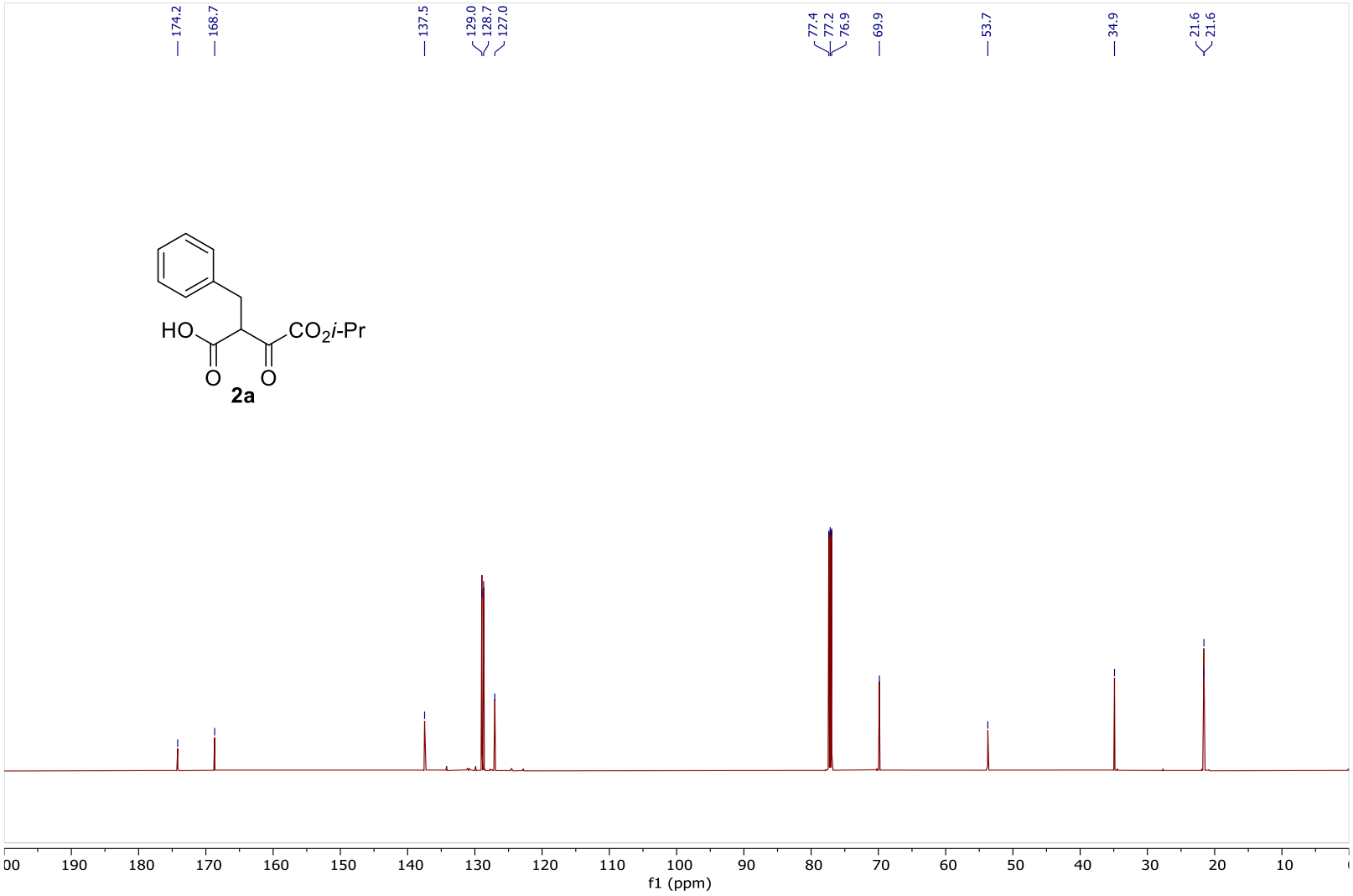
8.2.23. PROD3$_{w/o\ C=O}$ (IPA, 355K)

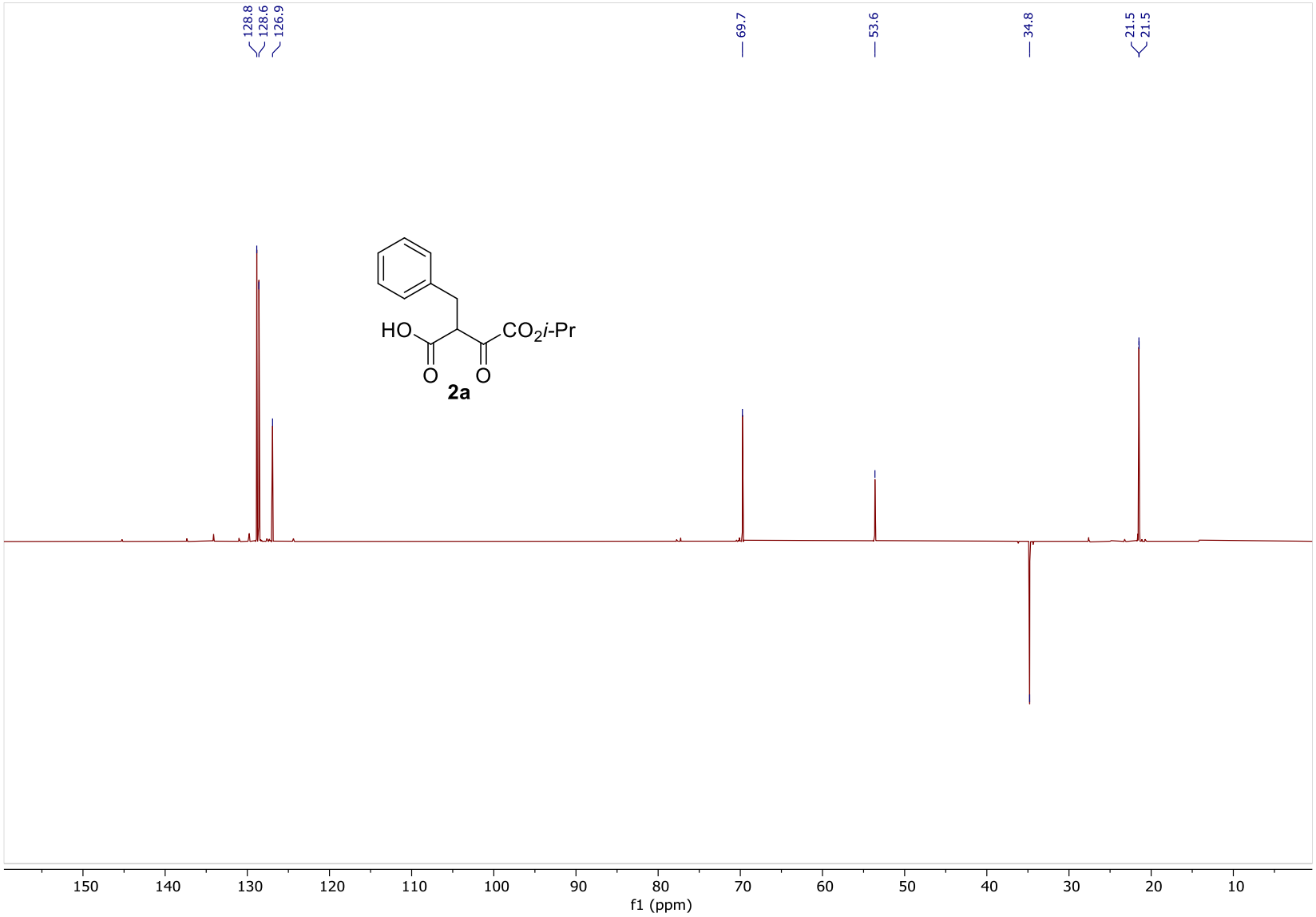
C	-0.09444152213062	-0.21939012395628	1.72402062757194
O	1.30605555240218	-0.40113226613544	1.97409210447287
C	-0.31803992582572	0.59588982958454	0.44599880898154
C	0.78410248089781	0.44482447620396	-0.59845980080986
O	1.86766371492933	-0.30231873241245	-0.32501883889210
C	-1.72113591635340	0.34916644650845	-0.17146388844459
C	-1.94965607534089	-1.07529591024418	-0.62005186469529
H	-1.84463310541054	1.03599630814557	-1.01316389236243
C	-2.59892028044946	-1.99537914535730	0.21519847075247
C	-2.76053894761037	-3.32761390586394	-0.17022083591595
C	-2.27852313425909	-3.76205724098909	-1.40689331824344
C	-1.64621593652201	-2.85156531481795	-2.25690398459641
C	-1.48624521428340	-1.52086000971657	-1.86703864283866
H	-2.98085378273870	-1.66328784739186	1.17821831881176
H	-3.26357487588672	-4.02506523763830	0.49516056404215
H	-2.40159724717391	-4.79903270002804	-1.70897980932586
H	-1.27787293344502	-3.17682506008001	-3.22686073884097
H	-0.99532266314581	-0.81936197837054	-2.53554790577896
O	0.74277735580855	1.03364543879248	-1.66477250416878
C	1.96859270497753	-1.08502676555926	0.94660743730205
C	1.41914748875911	-2.47890497799244	0.65385150832192
C	3.44570363557756	-1.09338893921600	1.29052850406029
H	0.40230749890291	-2.44703887214212	0.25814829775459
H	1.43019907995403	-3.07071984841686	1.57395719578347
H	2.05623512321608	-2.96642584692797	-0.08823065391088
H	4.01949683585269	-1.51255879088214	0.46060679513054
H	3.60448611379169	-1.71145884262433	2.17868823248085
H	3.78759968802848	-0.07476215584869	1.49239219852605
H	-2.46315279626620	0.62062133704430	0.58740216812376
H	-0.26874210779387	1.66158807548062	0.70623276133065
H	-0.59607504845289	-1.19002624578743	1.67149507219796
H	-0.48547576000933	0.31790484663930	2.5906576131

11. Spectroscopic Data:

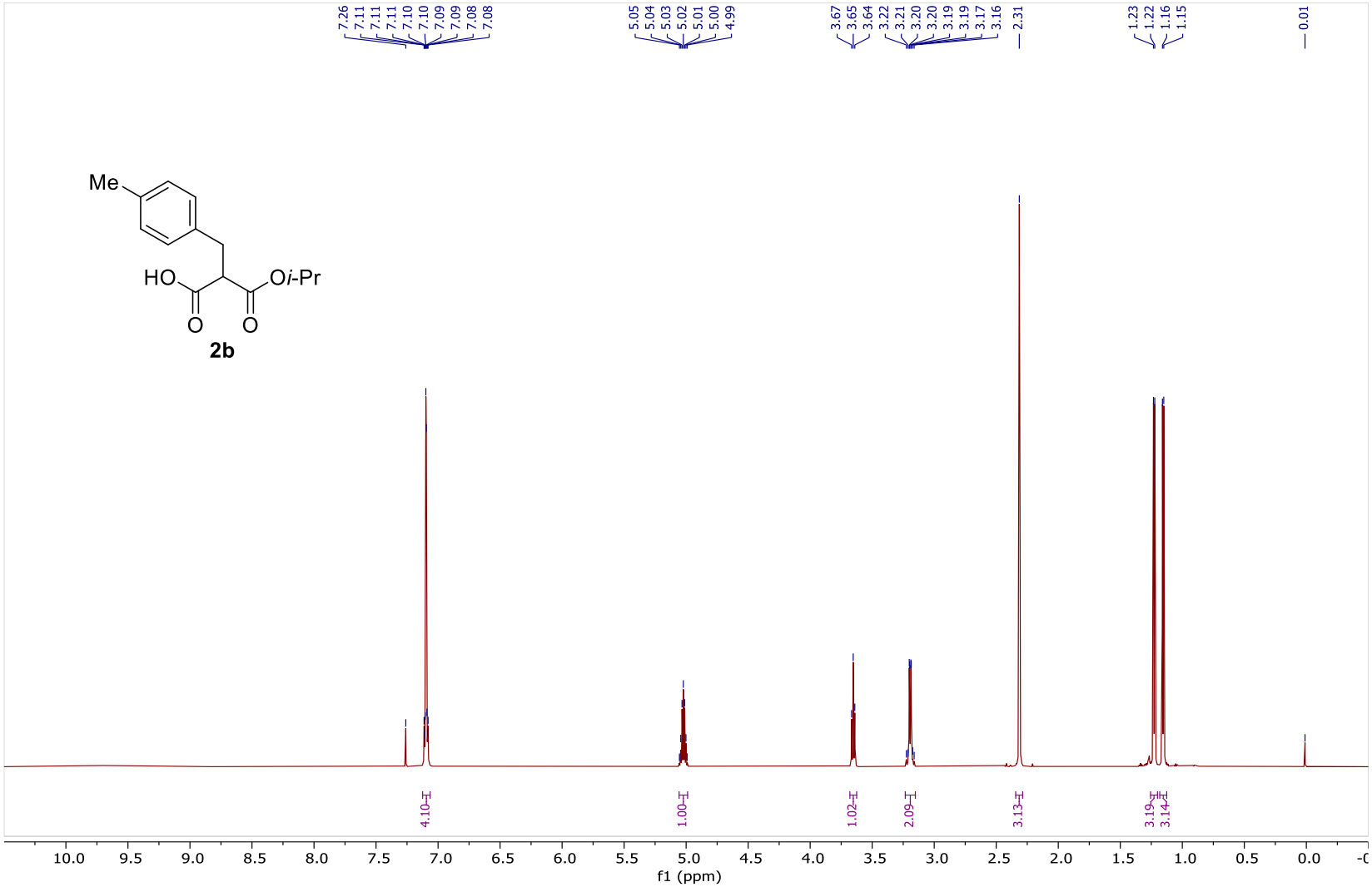
^{1}H &^{13}C NMR($CDCl_3$) of **2a**

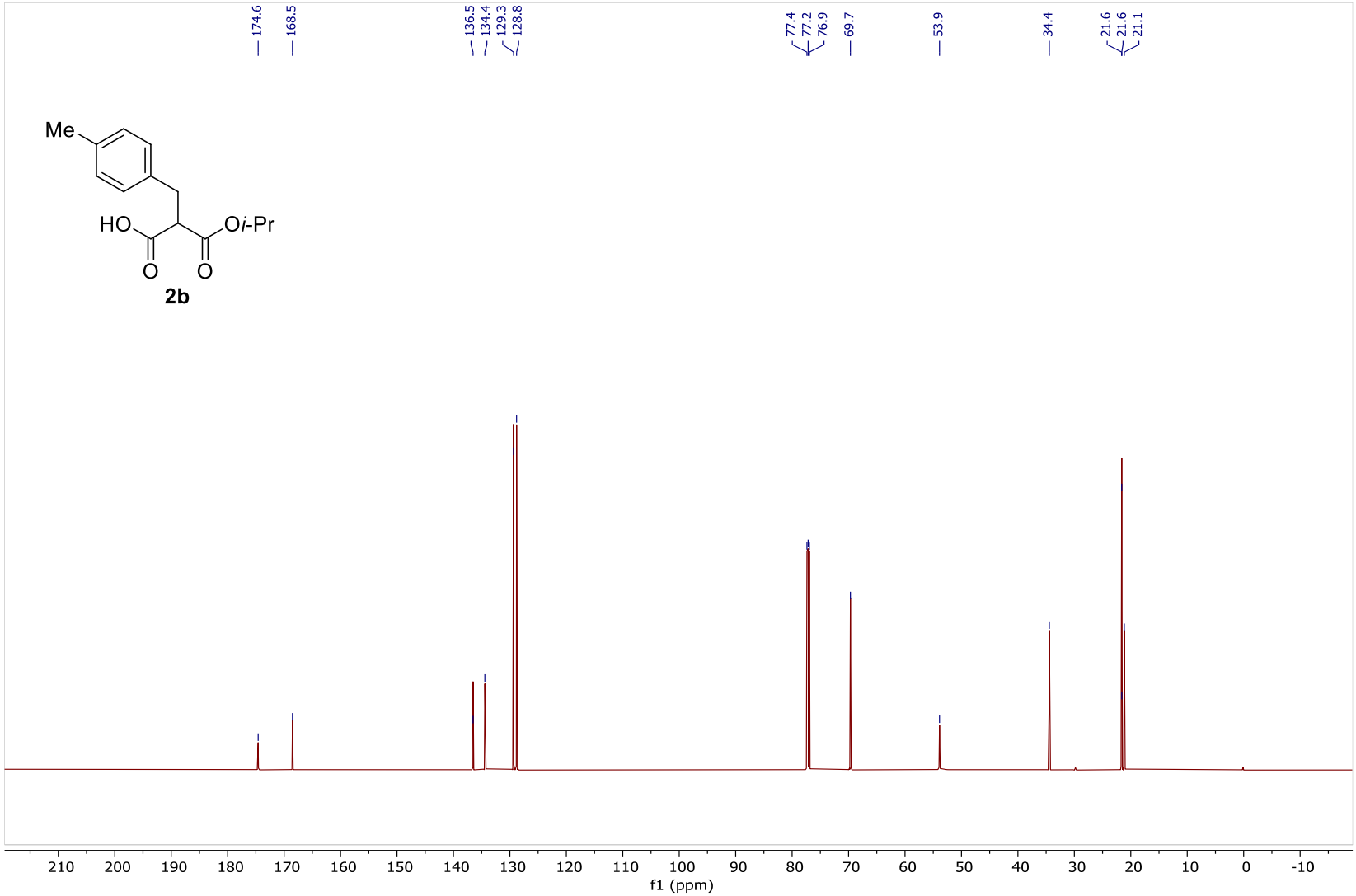


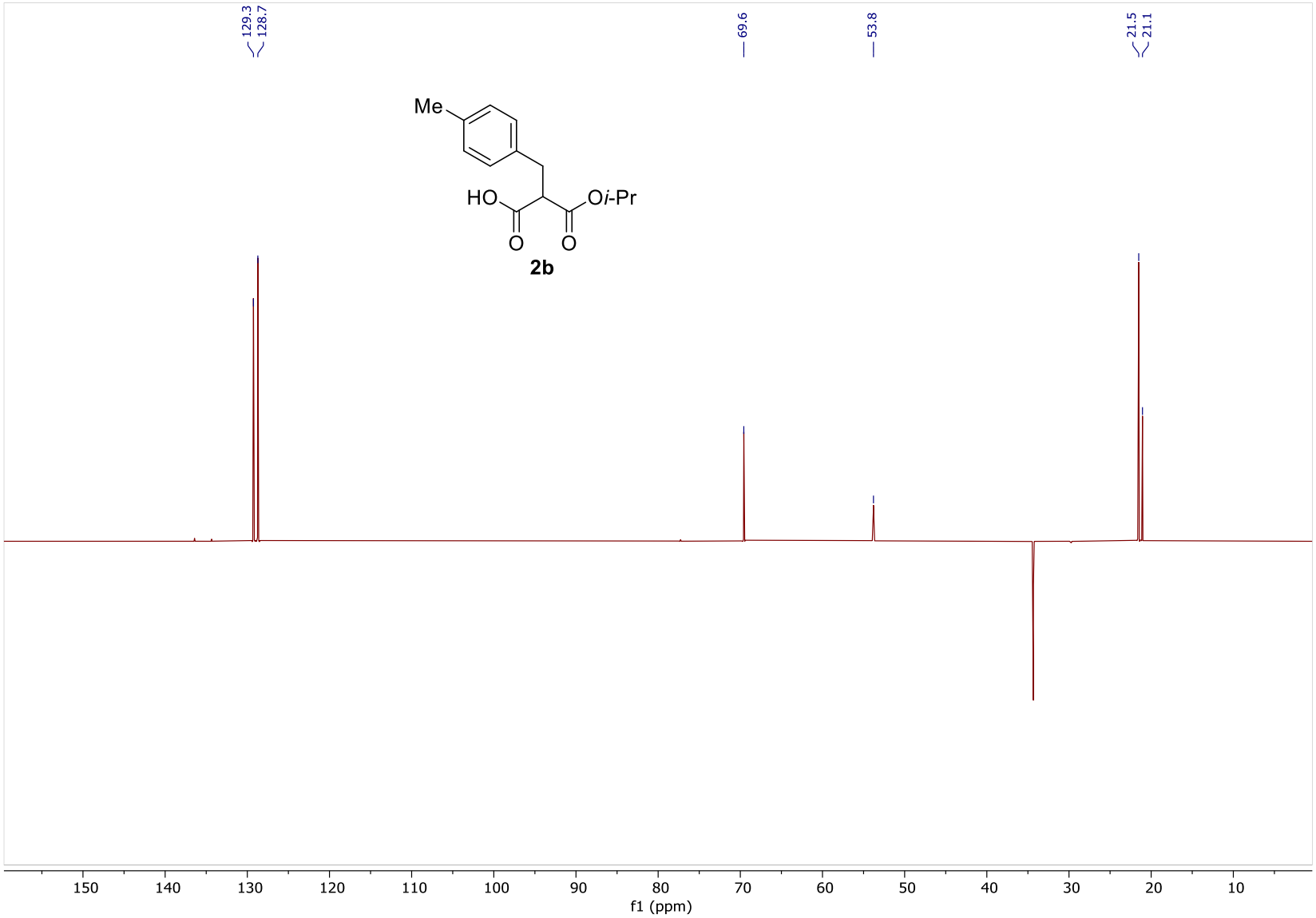

174.2
168.7
137.5
129.0
128.7
127.0
77.4
77.2
76.9
69.9
53.7
34.9
21.6
21.6
HO
CO2i-Pr
O
O
2a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


128.8
128.6
126.9
69.7
53.6
34.8
21.5
21.5
HO
O
O
CO2i-Pr
2a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

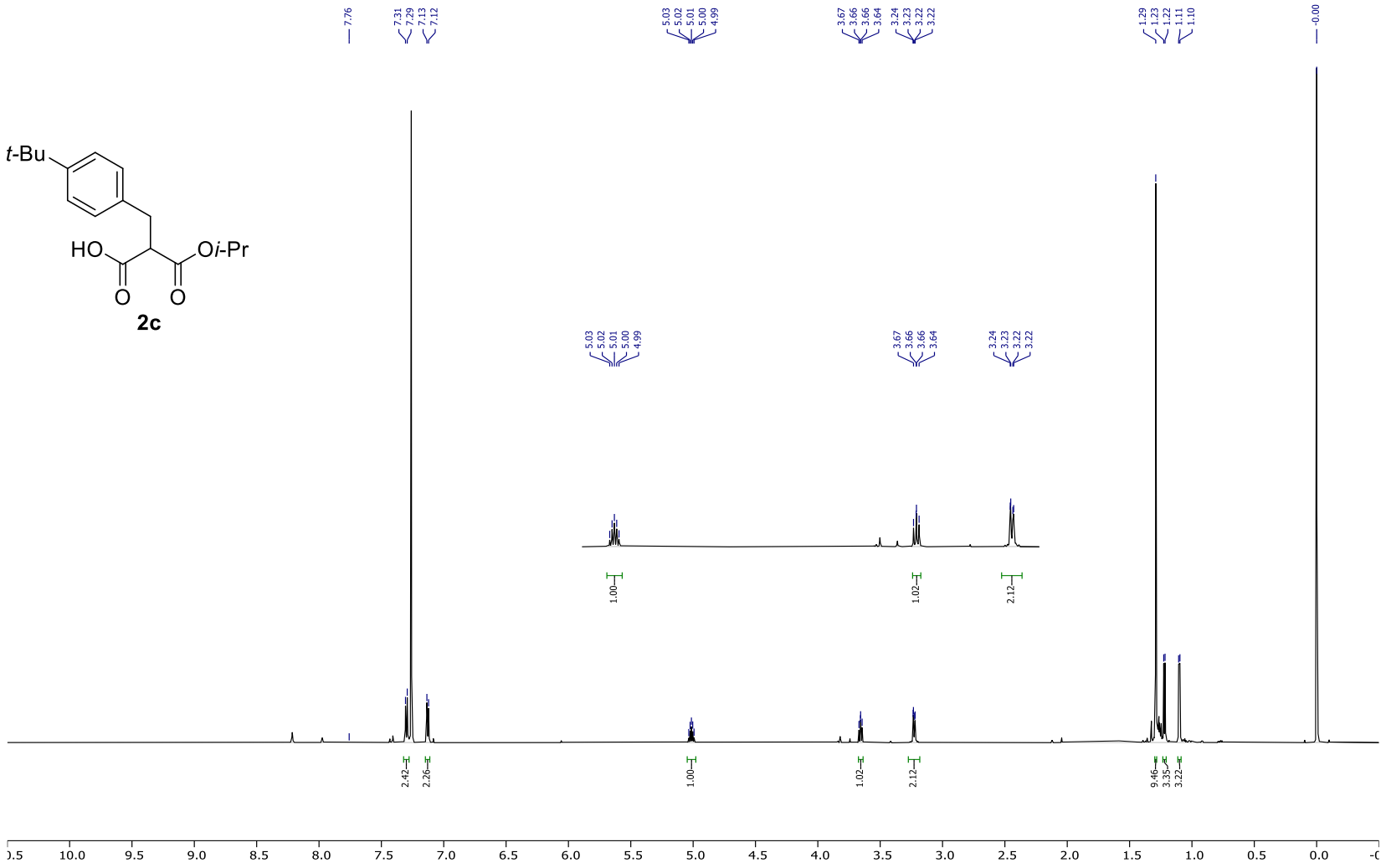
^{1}H,^{13}C and DEPT-135 NMR ($CDCl_3$) of **2b**

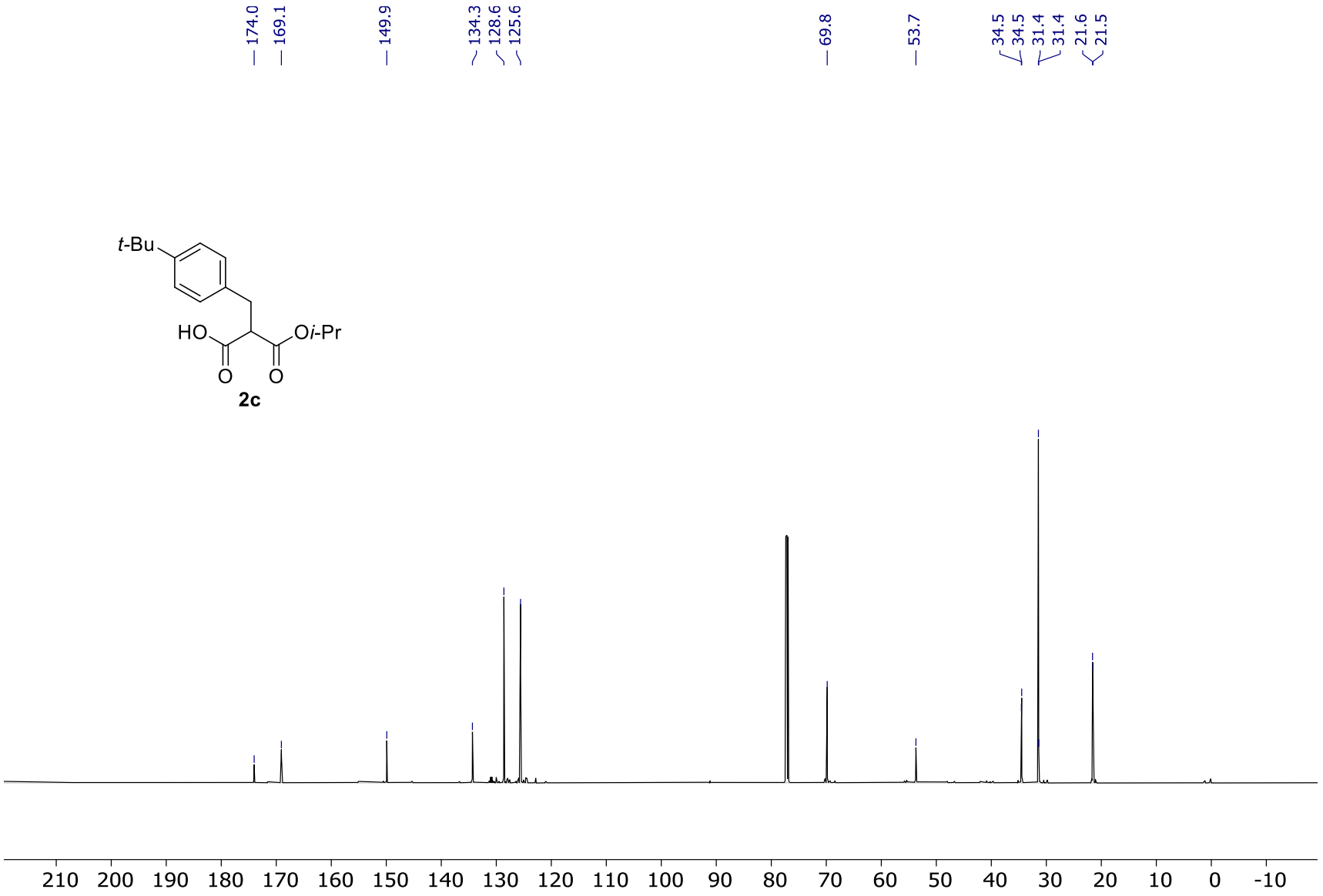



174.6
168.5
136.5
134.4
129.3
128.8
77.4
77.2
76.9
69.7
53.9
34.4
21.6
21.6
21.1
Me
HO
O
O
Oi-Pr
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

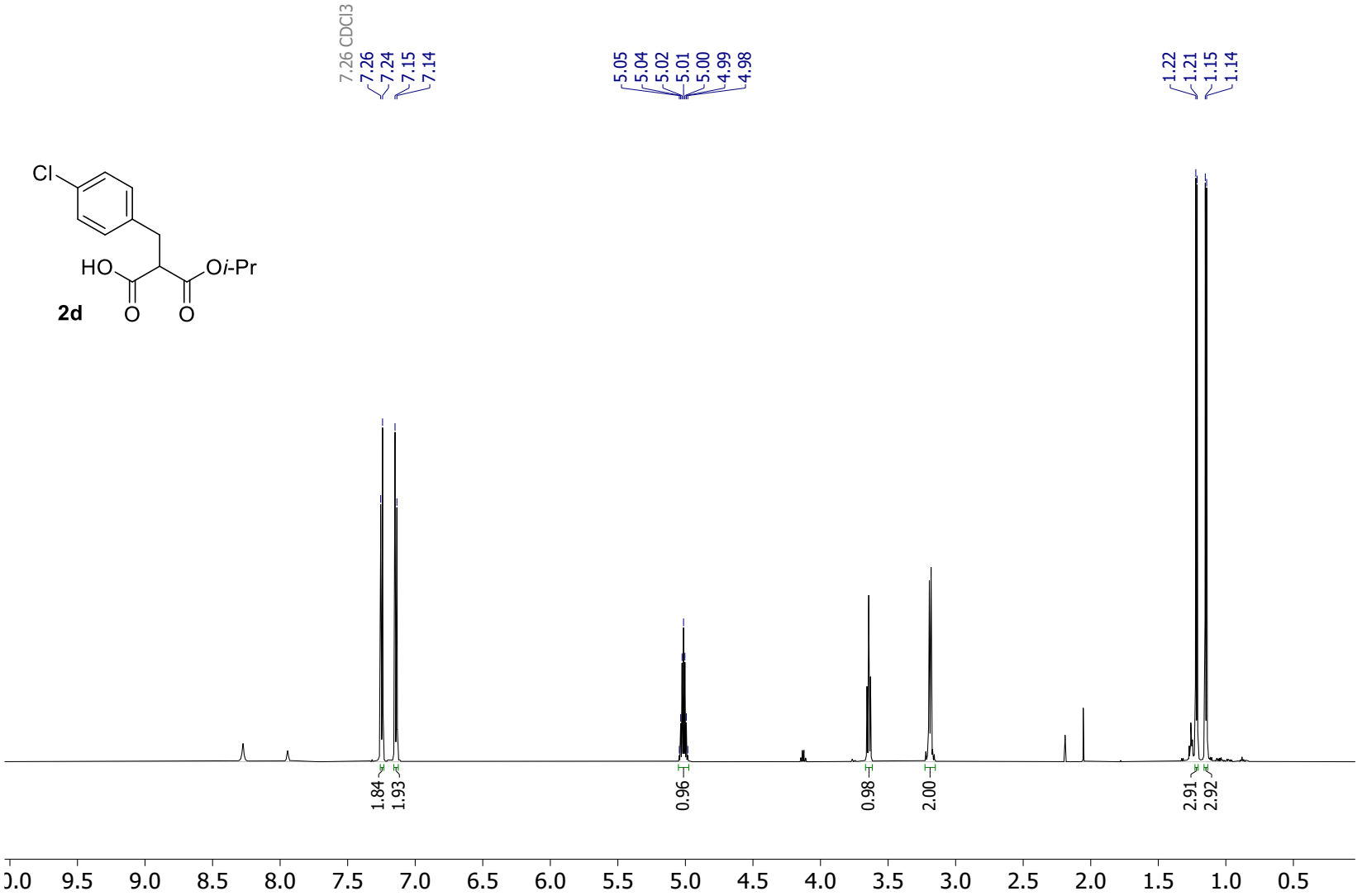

129.3
128.7
69.6
53.8
21.5
21.1
Me
HO
O
O
Oi-Pr
2b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

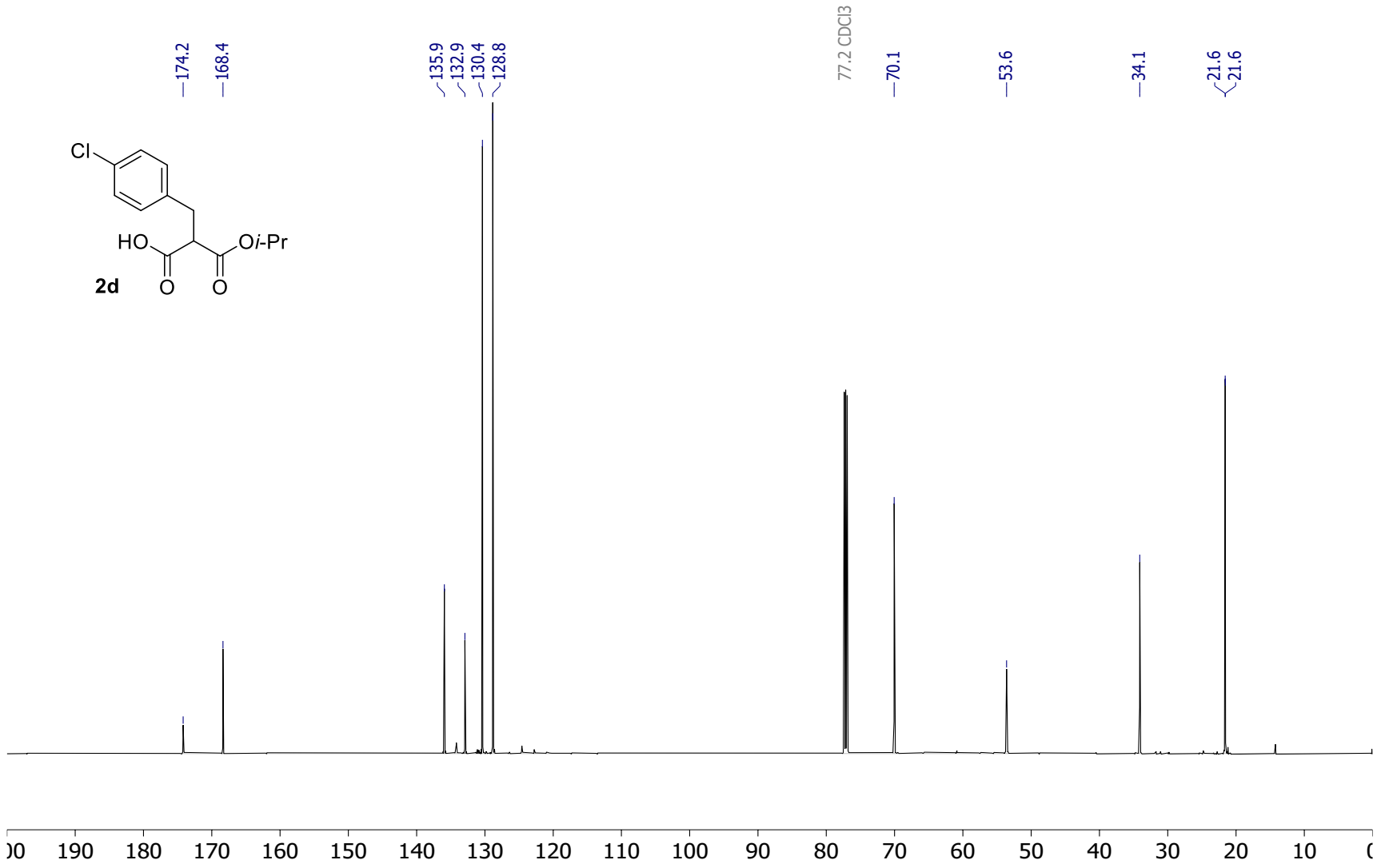
^{1}H &^{13}C NMR($CDCl_3$) of **2c**



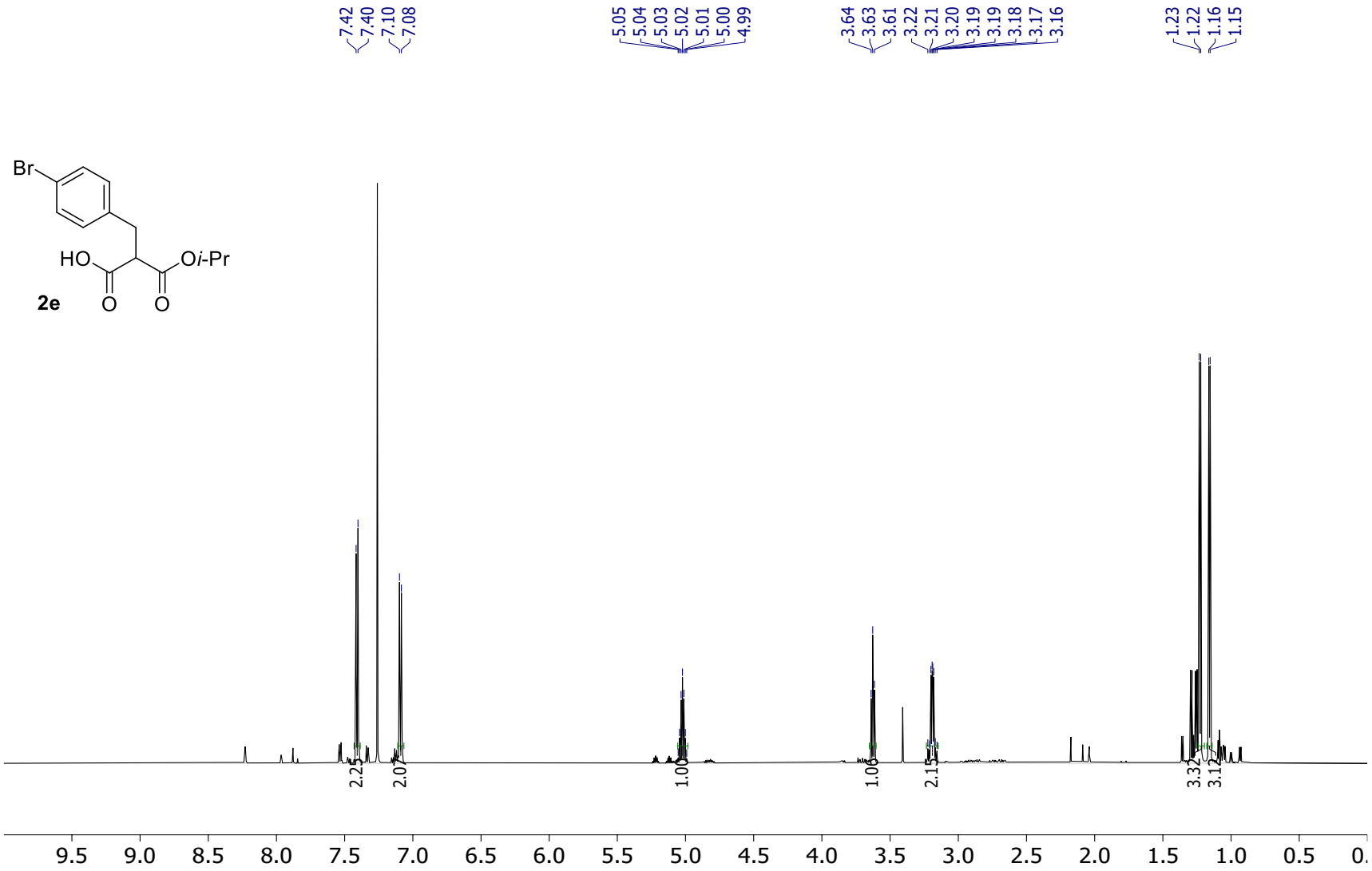

174.0
169.1
149.9
134.3
128.6
125.6
69.8
53.7
34.5
34.5
31.4
31.4
21.6
21.5
t-Bu
HO
O
O
Oi-Pr
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

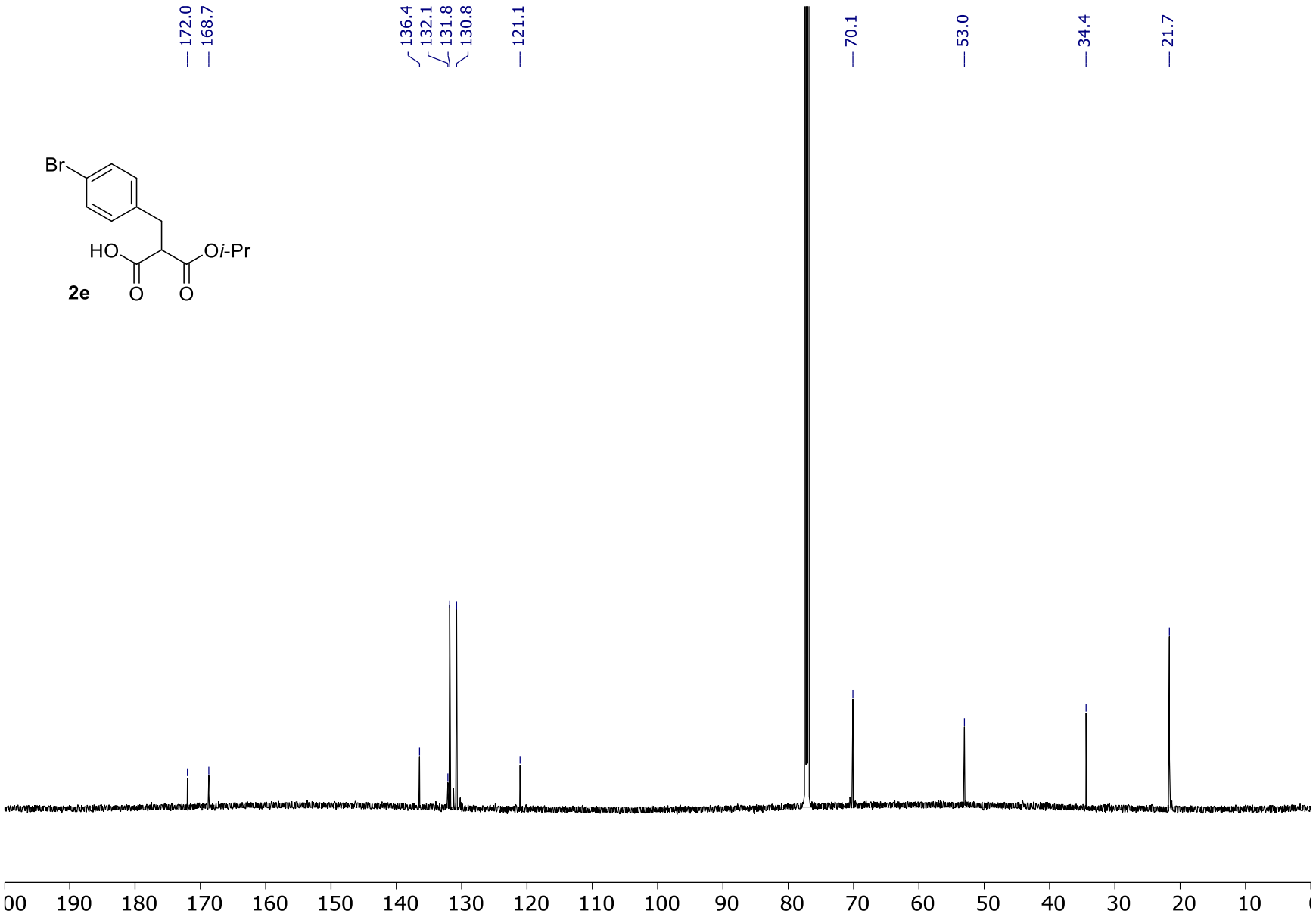
^{1}H &^{13}C NMR($CDCl_3$) of **2d**



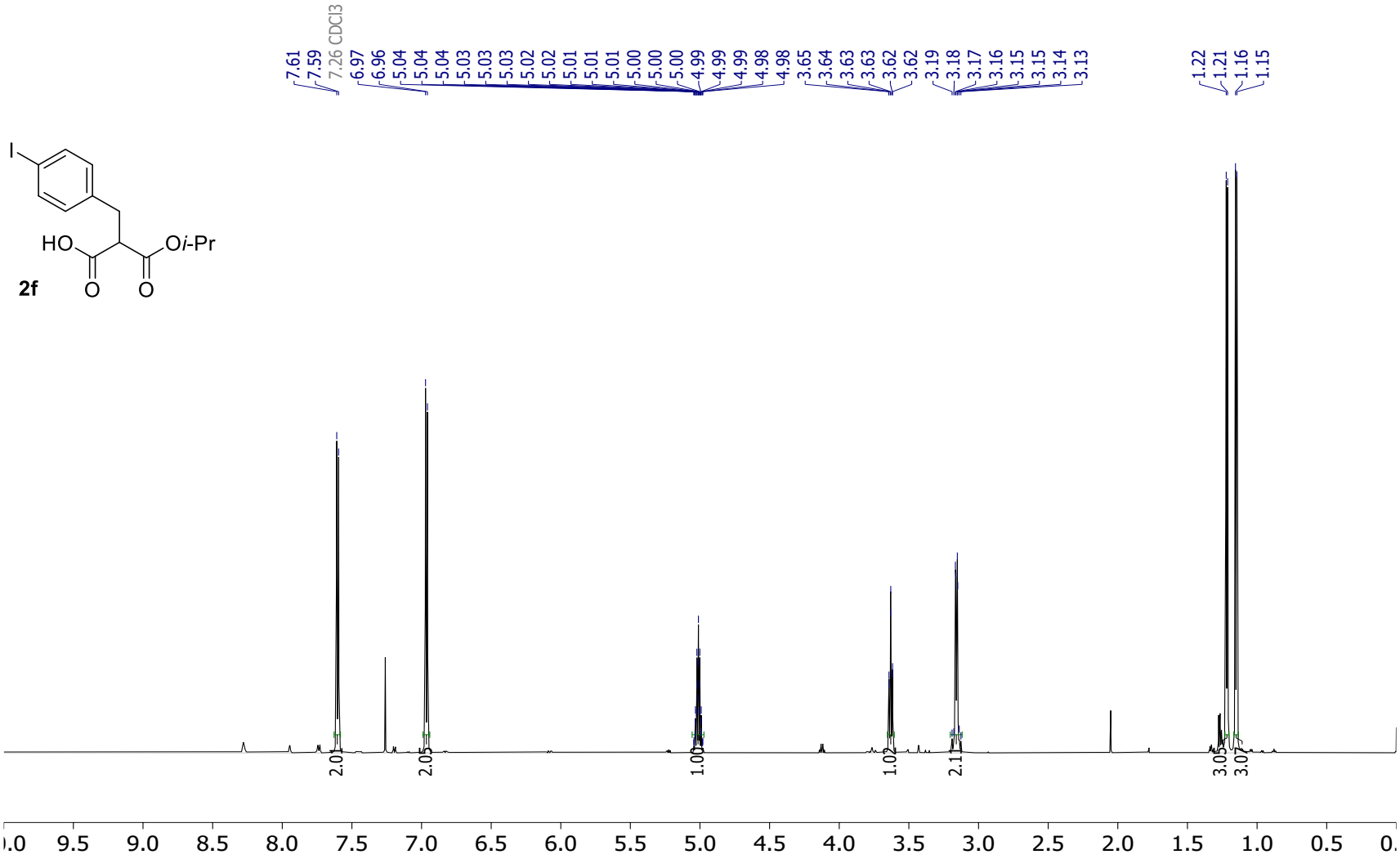

174.2
168.4
135.9
132.9
130.4
128.8
77.2 CDCl3
70.1
53.6
34.1
21.6
21.6
Cl
HO
O
O
O
O
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

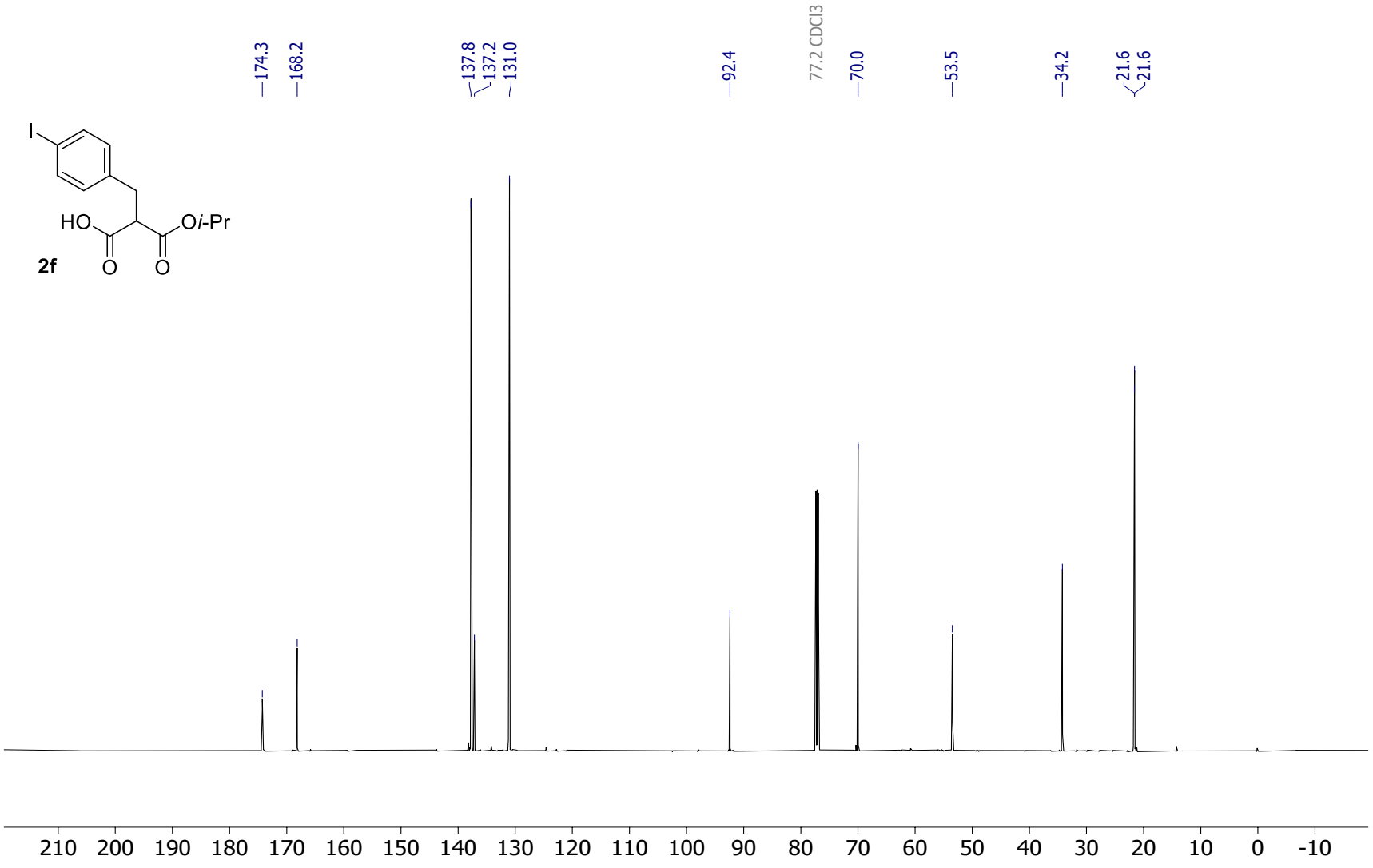
^{1}H &^{13}C NMR($CDCl_3$) of **2e**



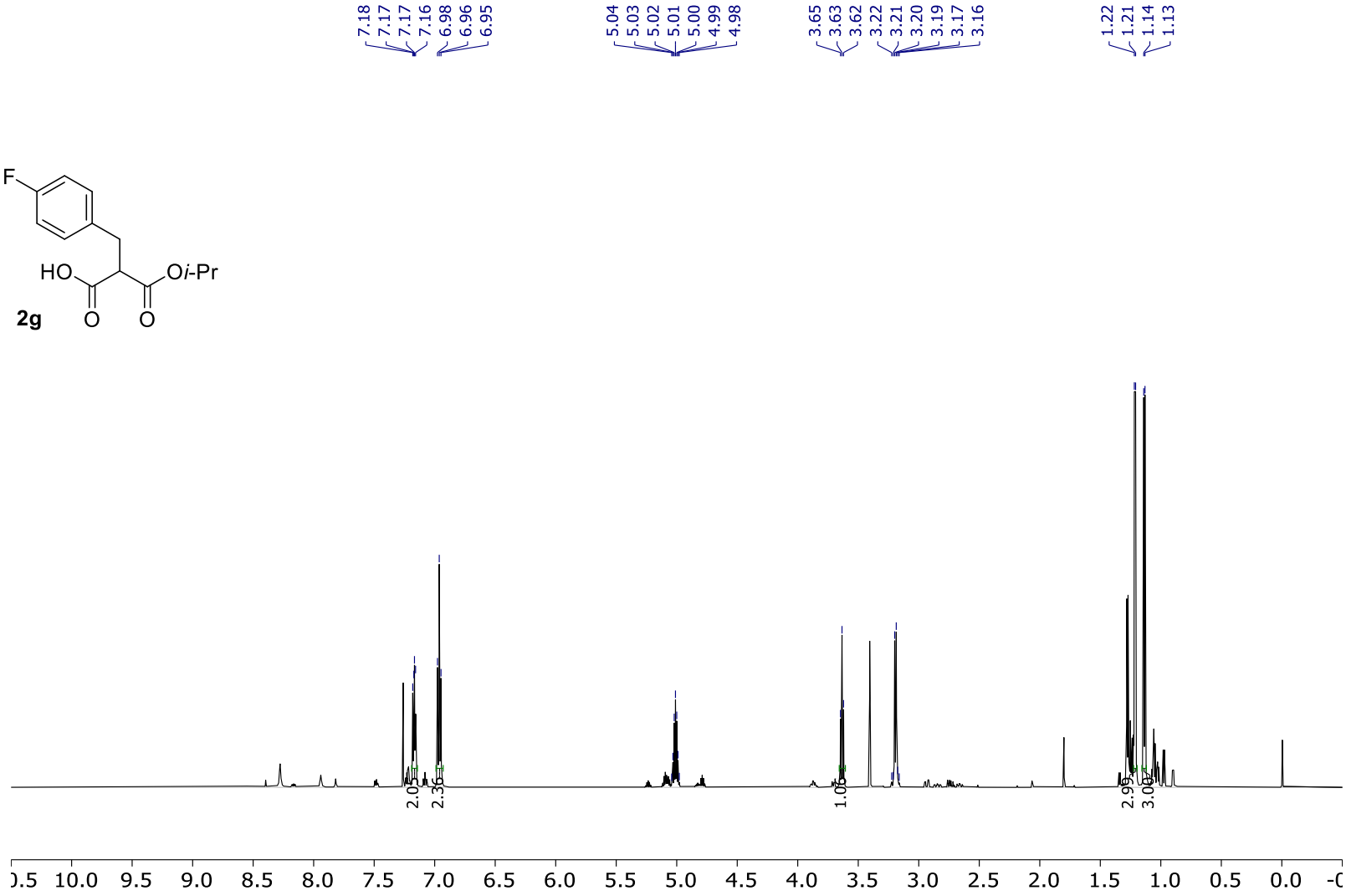

172.0
168.7
136.4
132.1
131.8
130.8
121.1
70.1
53.0
34.4
21.7
Br
HO
O
O
O
Oi-Pr
2e
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

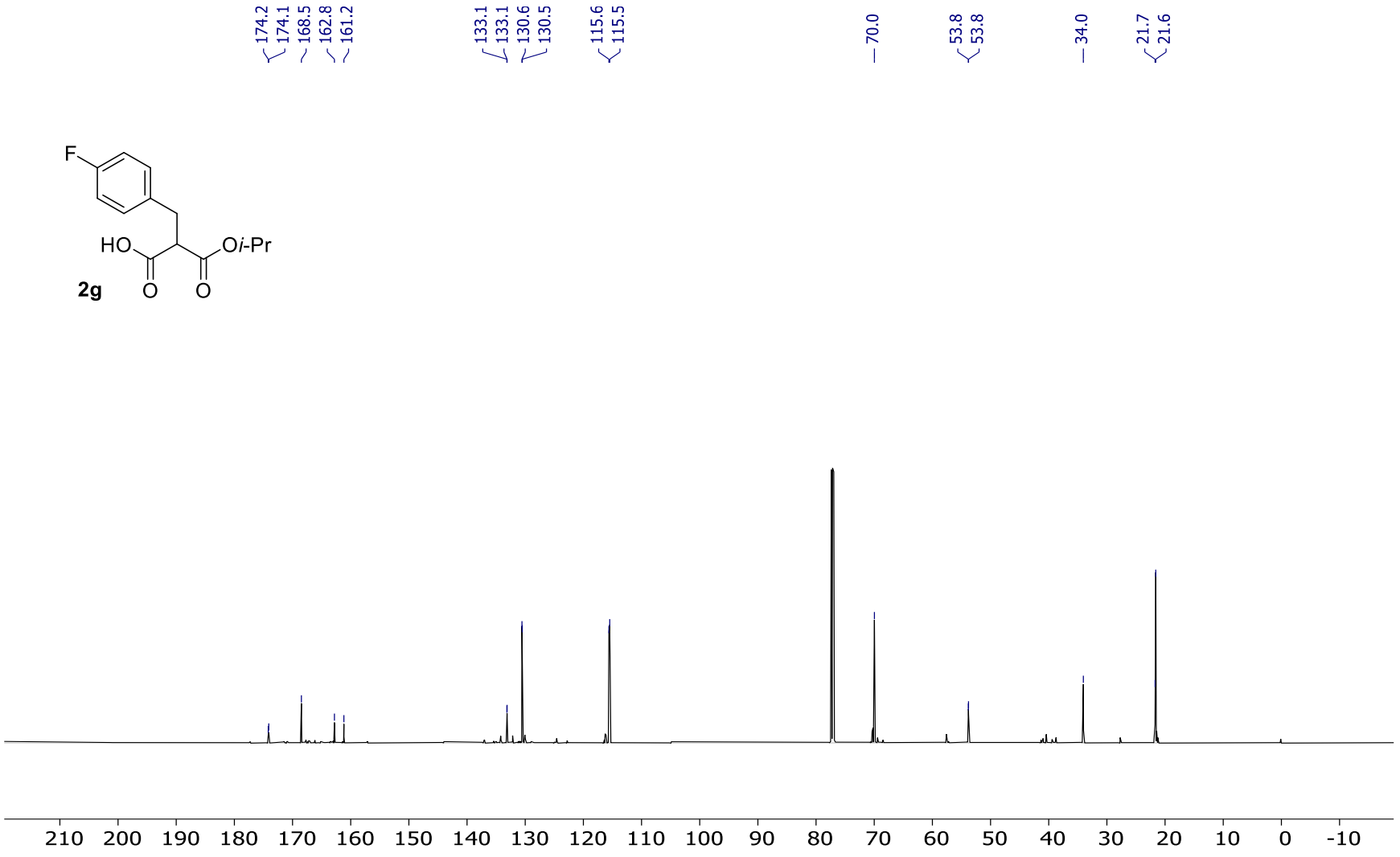
^{1}H &^{13}C NMR($CDCl_3$) of **2f**



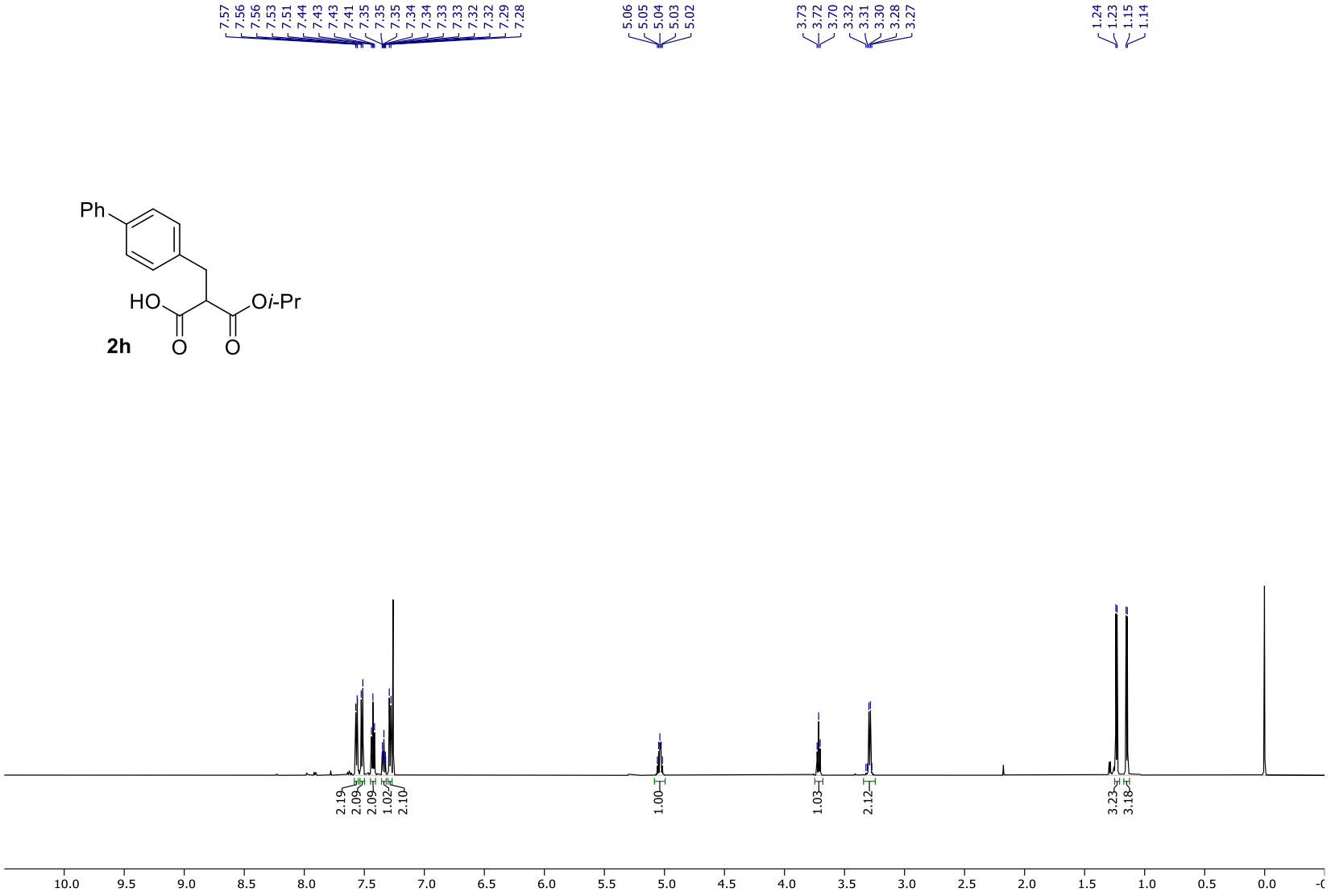

174.3
168.2
137.8
137.2
131.0
92.4
77.2 CDCl3
70.0
53.5
34.2
21.6
21.6
I
HO
O
O
O*i*-Pr
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

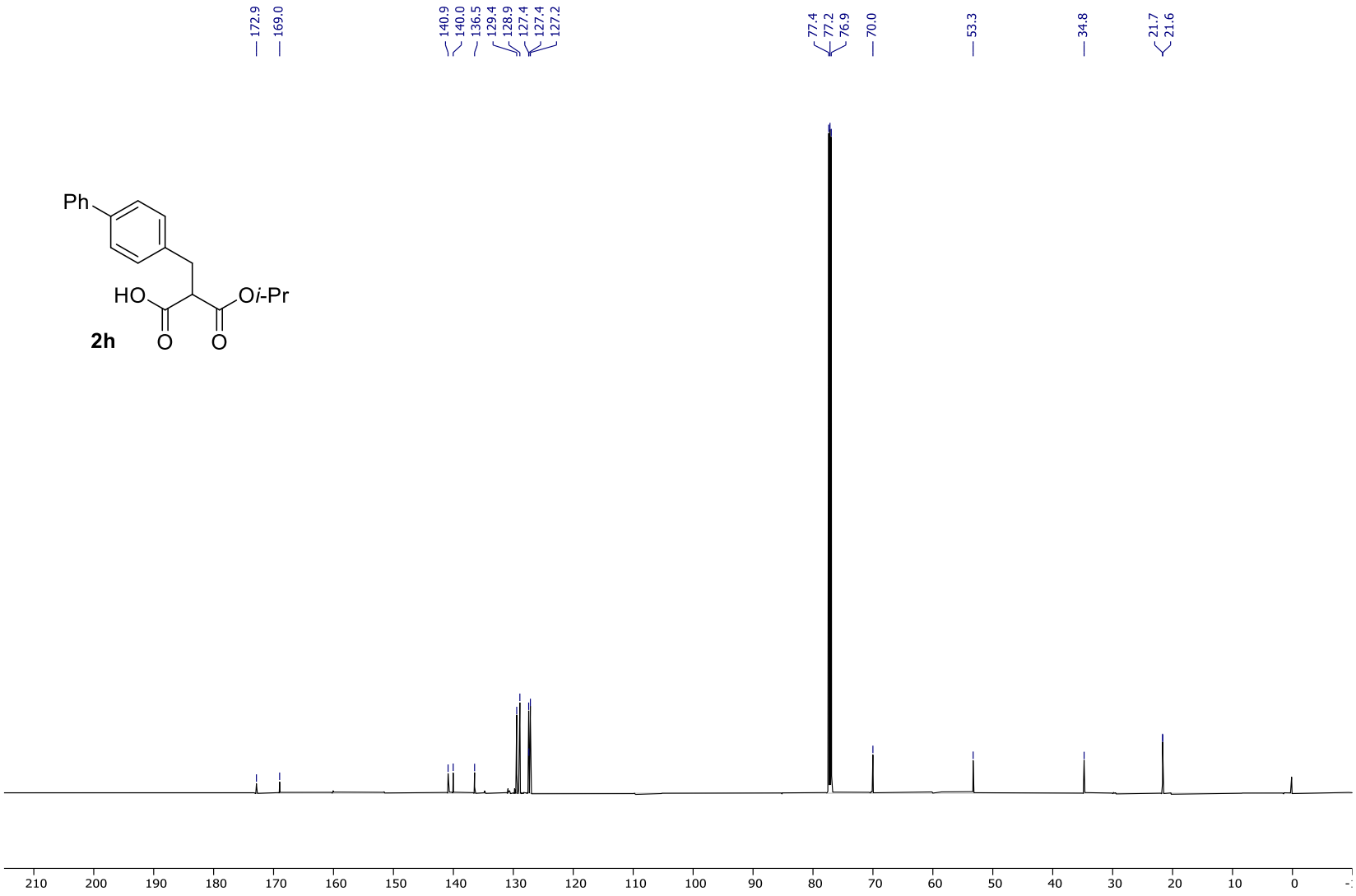
^{1}H &^{13}C NMR($CDCl_3$) of **2g**



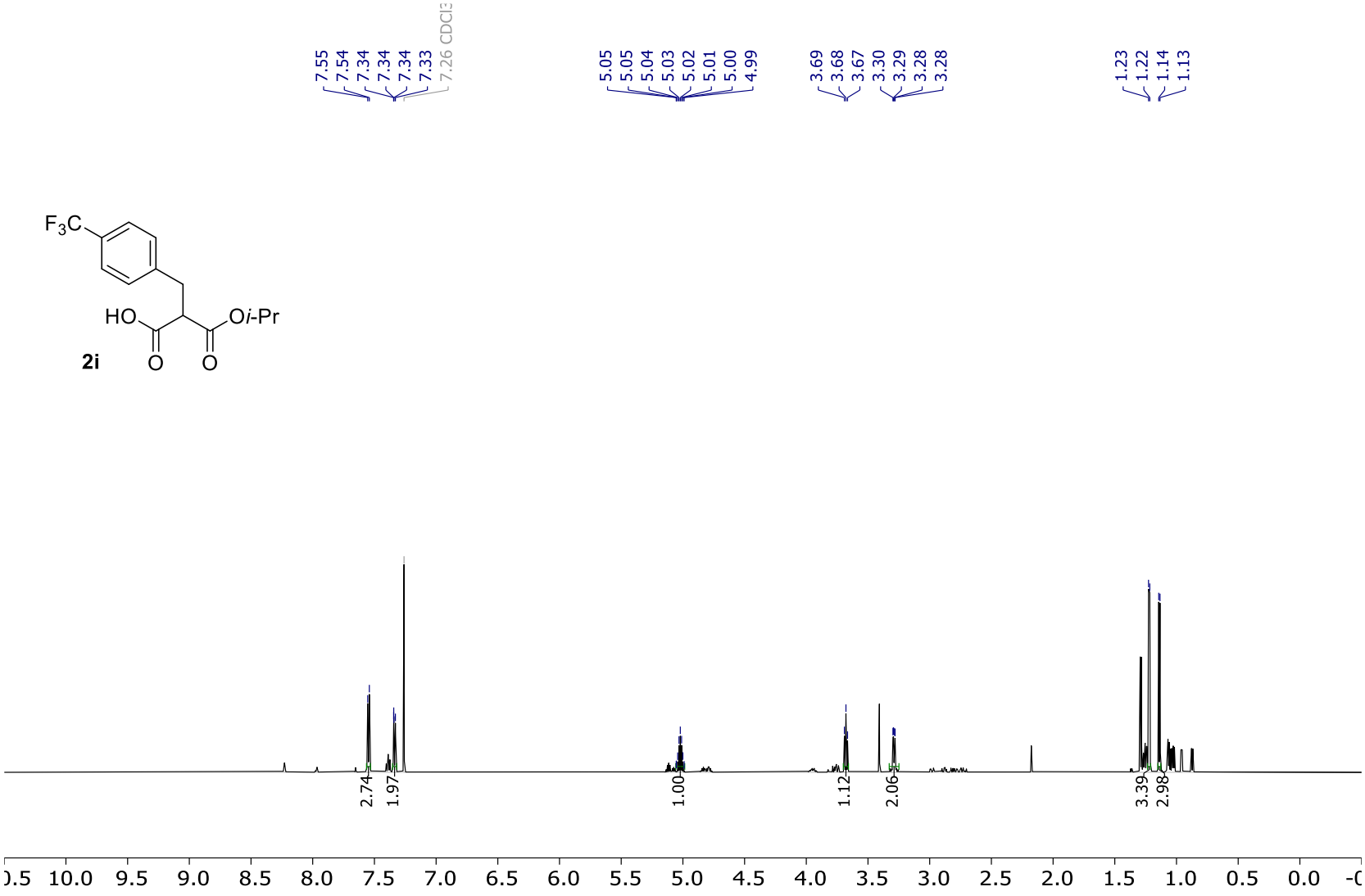

174.2
174.1
168.5
162.8
161.2
133.1
133.1
130.6
130.5
115.6
115.5
70.0
53.8
53.8
34.0
21.7
21.6
F
HO
O
O
Oi-Pr
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

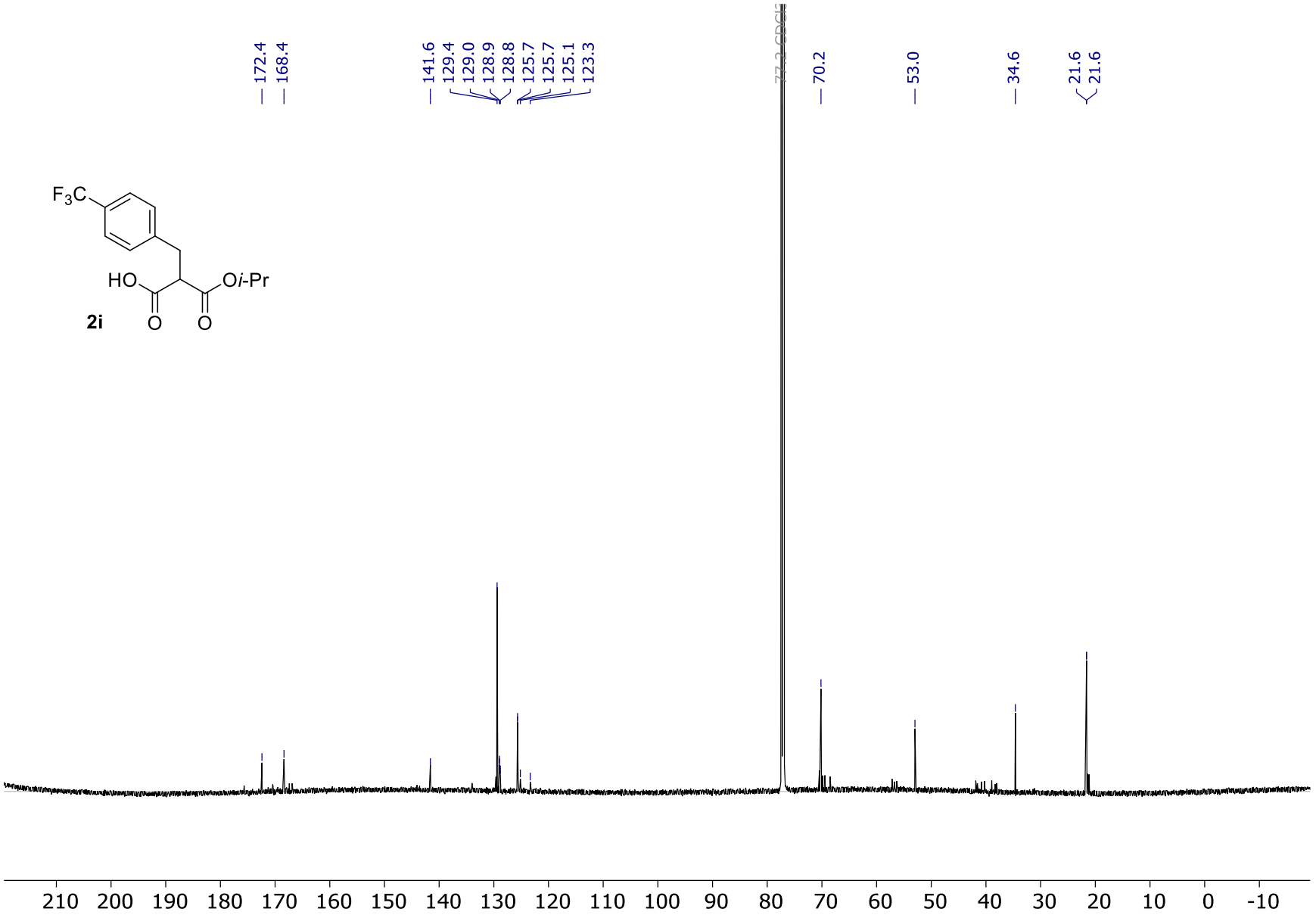
^{1}H &^{13}C NMR($CDCl_3$) of **2h**

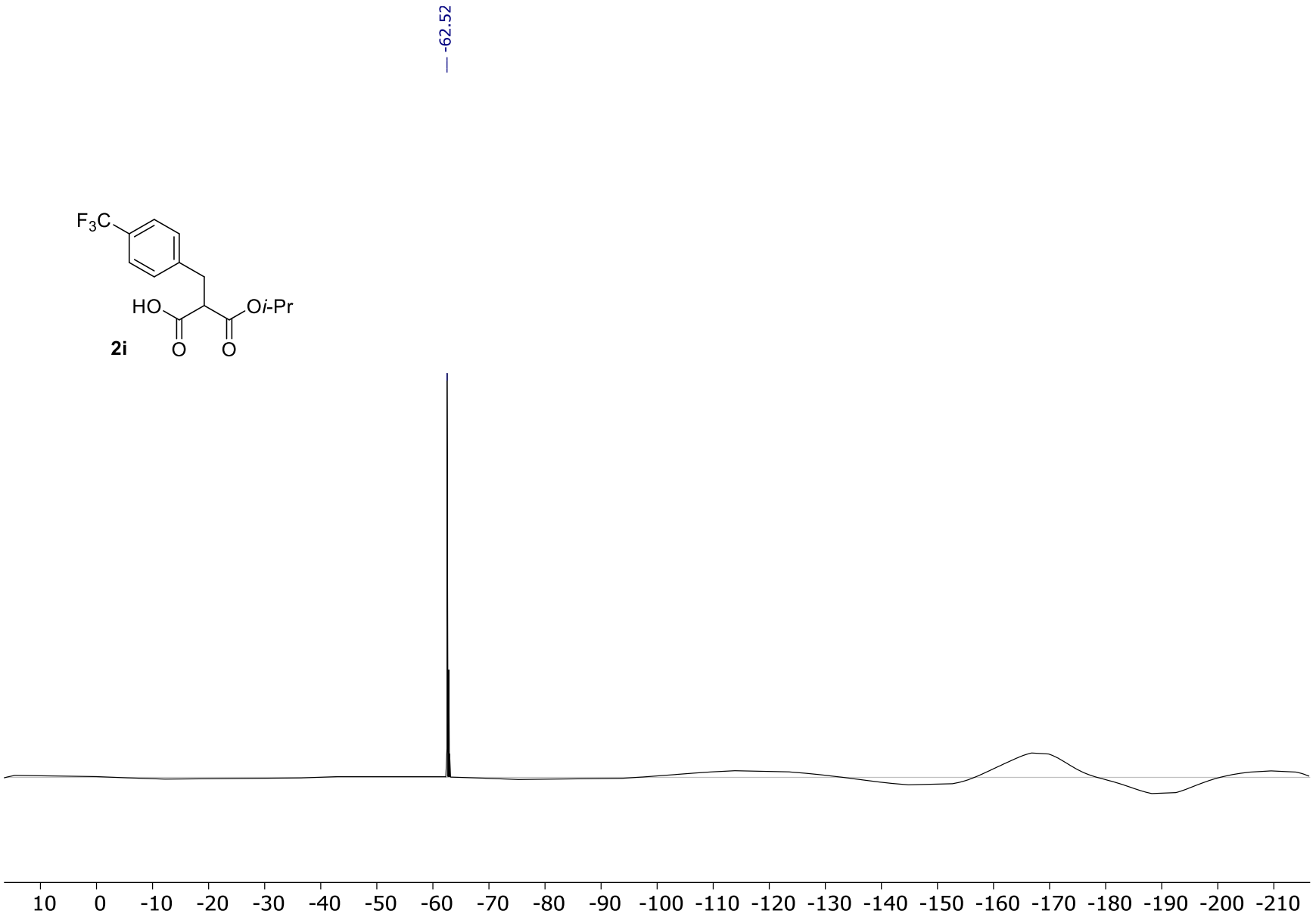



172.9
169.0
140.9
140.0
136.5
129.4
128.9
127.4
127.4
127.2
77.4
77.2
76.9
70.0
53.3
34.8
21.7
21.6
Ph
HO
O
O
O*i*-Pr
O
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

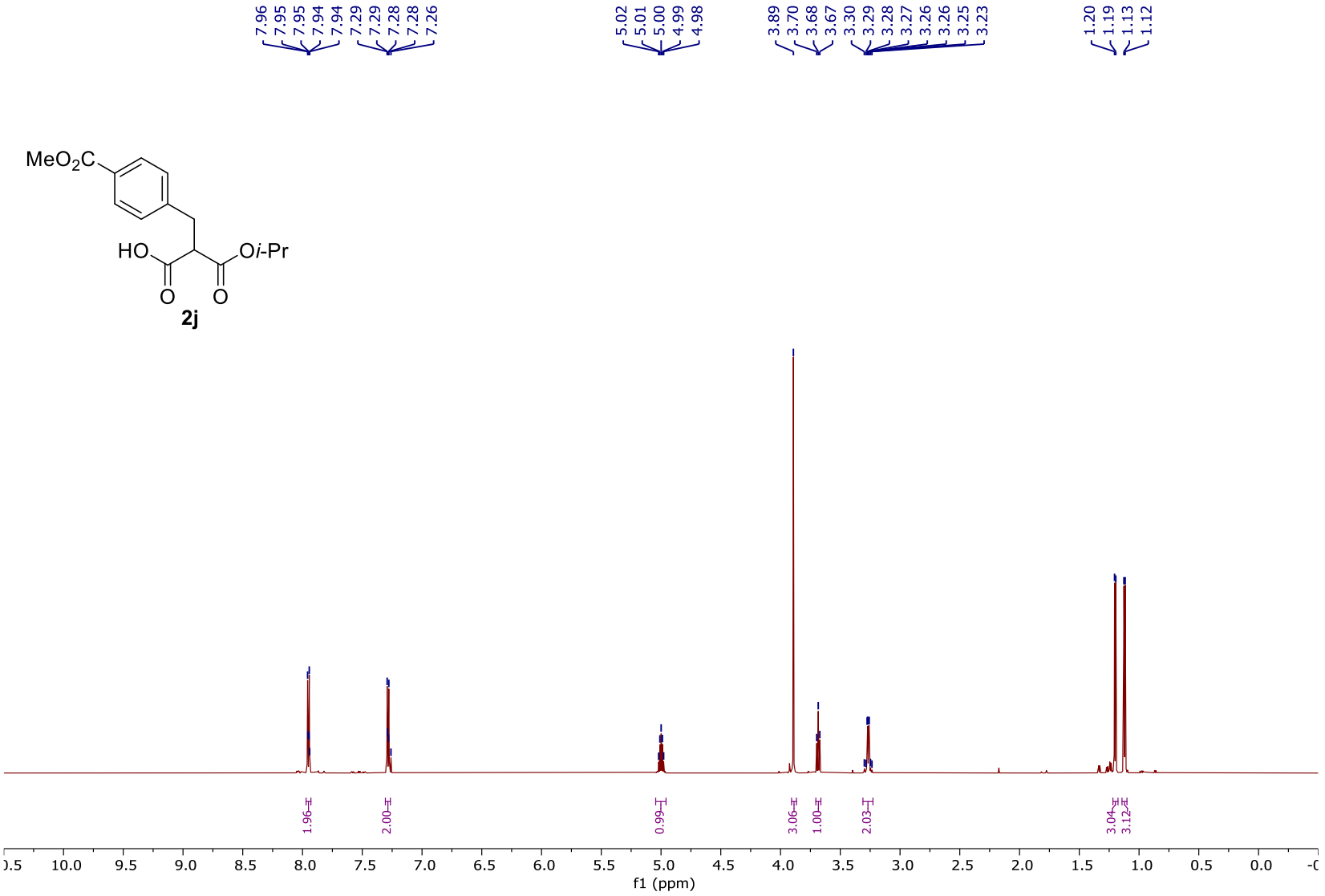
^{1}H,^{13}C and ^{19}F NMR($CDCl_3$) of **2i**

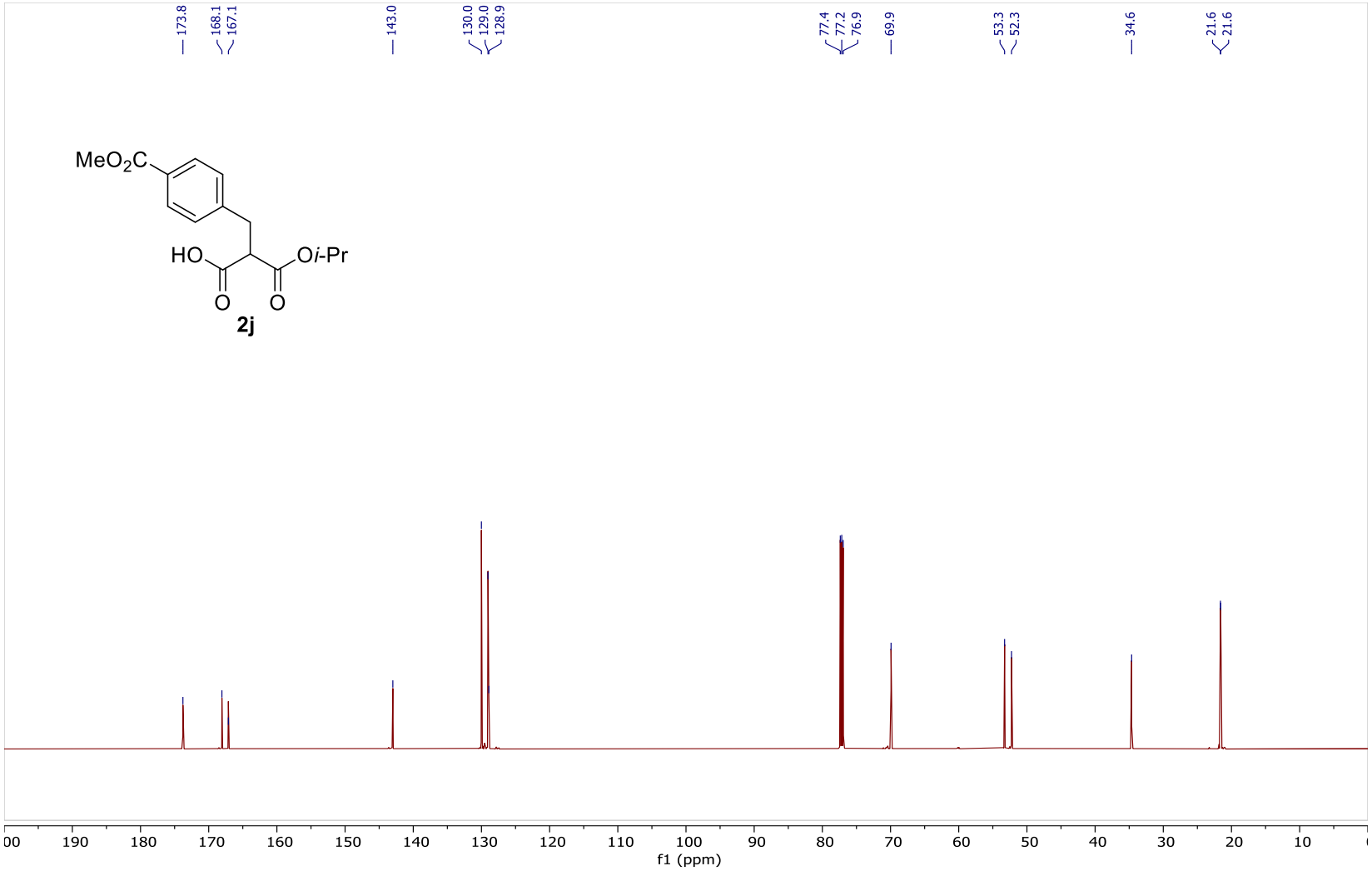



172.4
168.4
141.6
129.4
129.0
128.9
128.8
125.7
125.7
125.1
123.3
77.2 CDCl3
70.2
53.0
34.6
21.6
21.6
F3C
HO
O
O
O
O
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

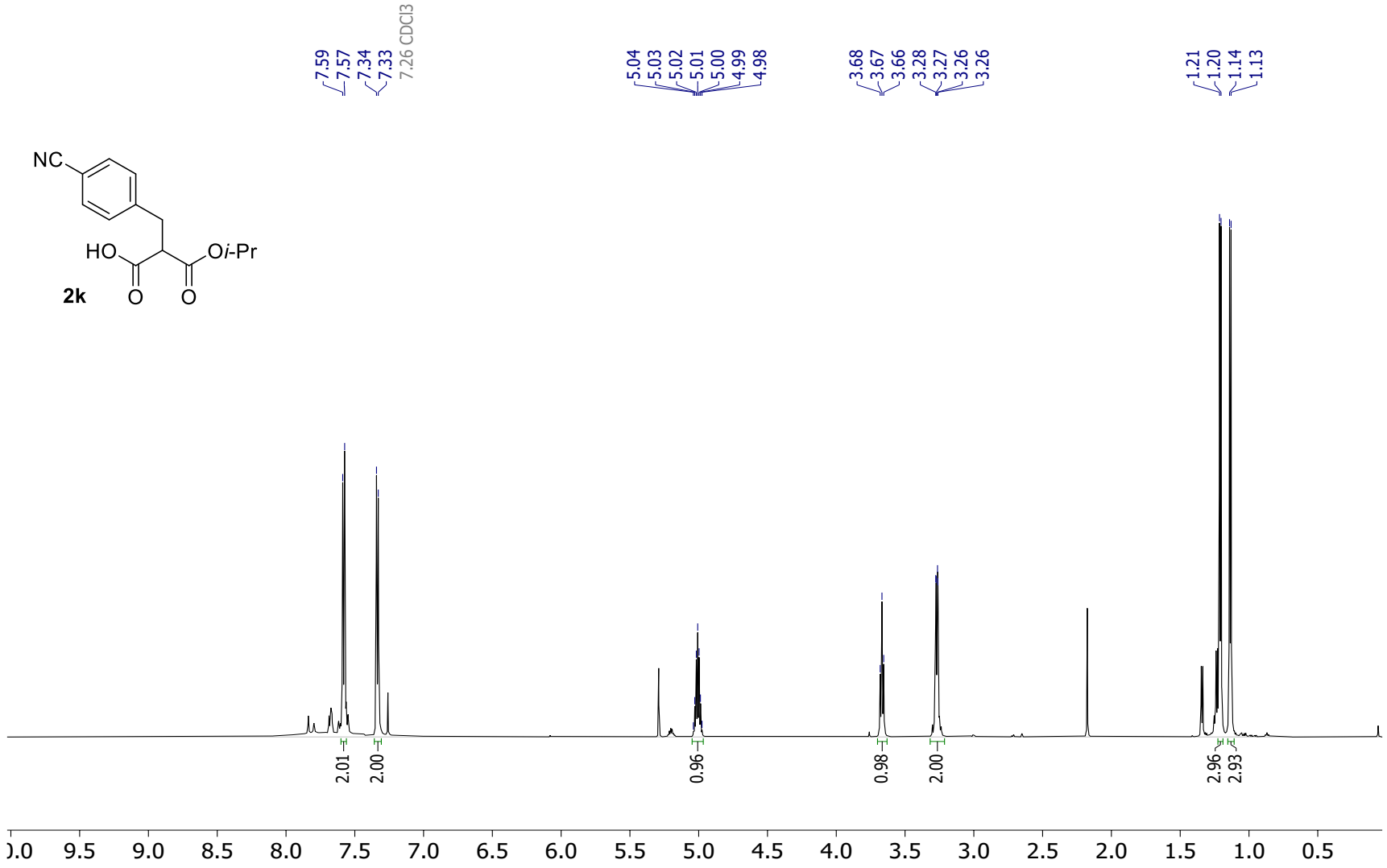

-62.52
F3C
HO
Oi-Pr
O
O
2i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

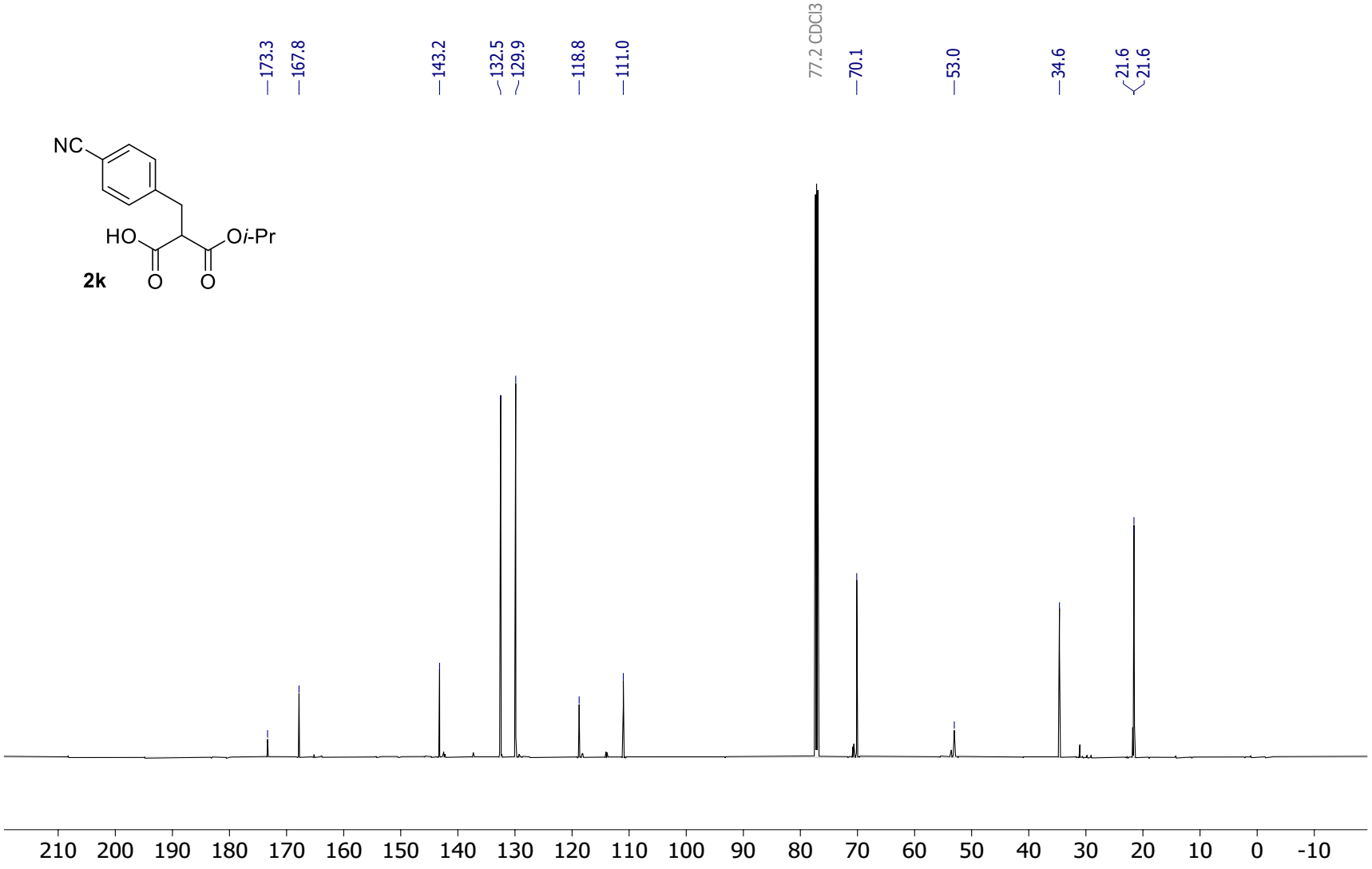
^{1}H &^{13}C NMR($CDCl_3$) of **2j**



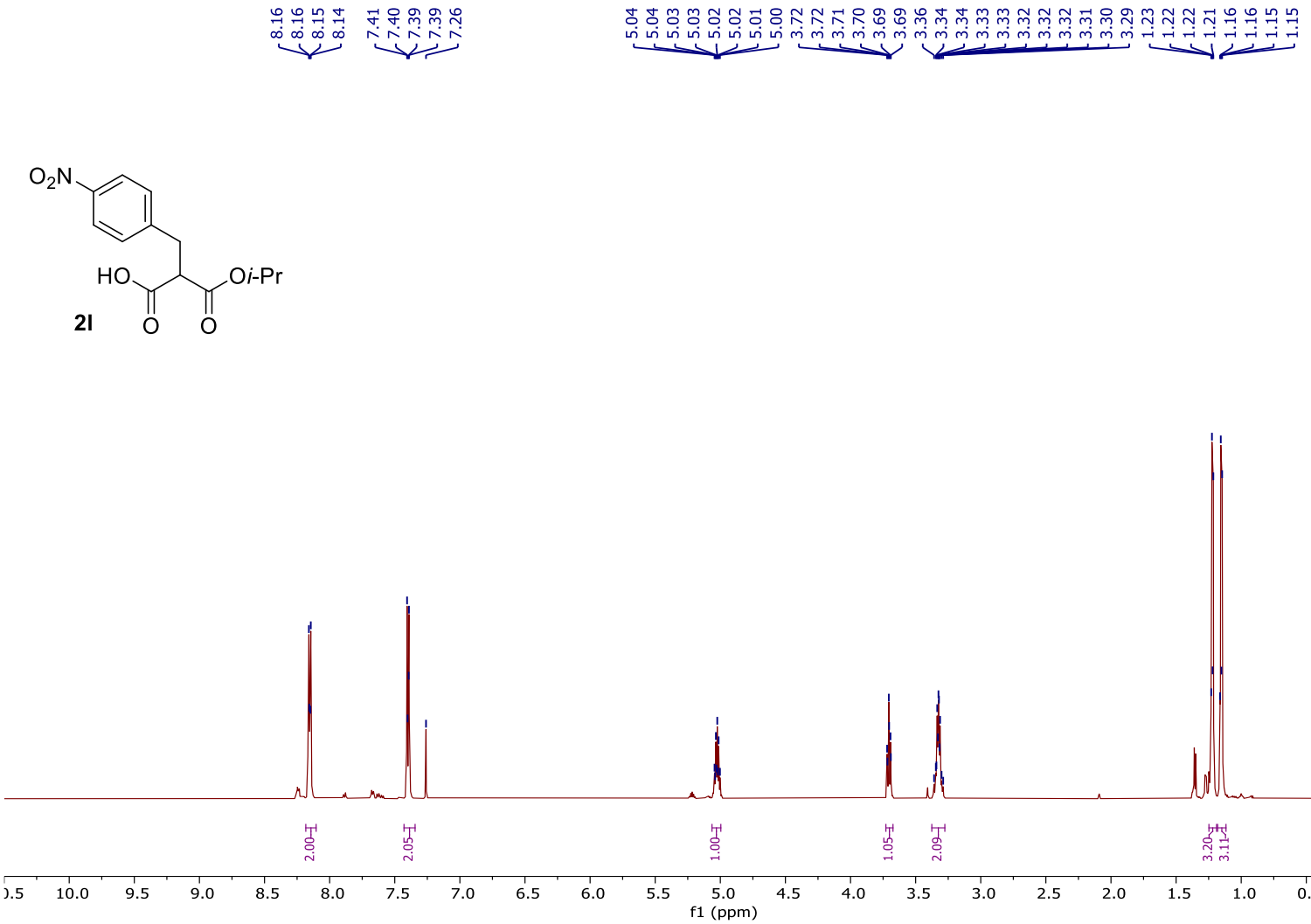

173.8
168.1
167.1
143.0
130.0
129.0
128.9
77.4
77.2
76.9
69.9
53.3
52.3
34.6
21.6
21.6
MeO2C
HO
Oi-Pr
O
O
2j
f1 (ppm)

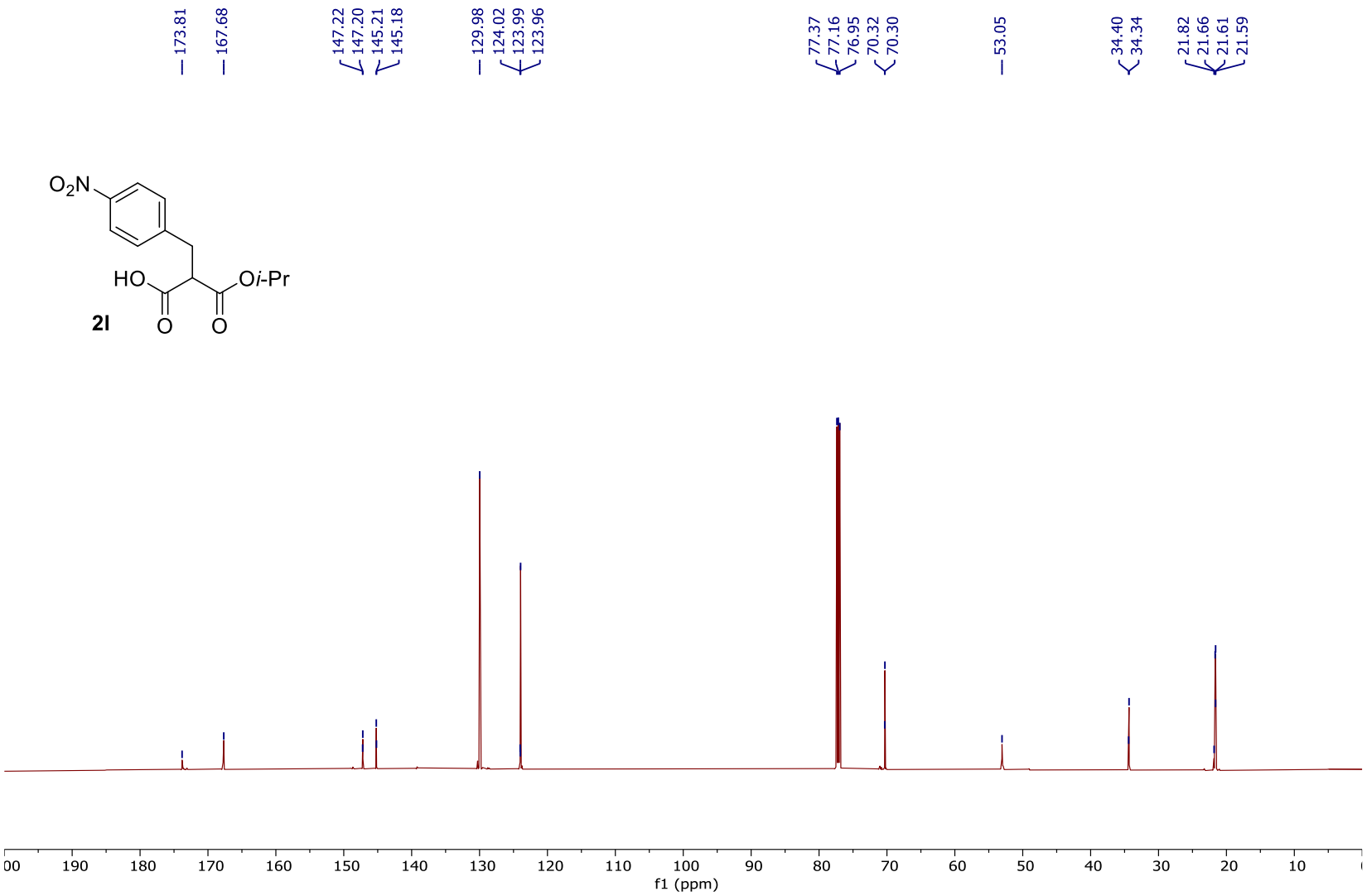
^{1}H &^{13}C NMR($CDCl_3$) of **2k**



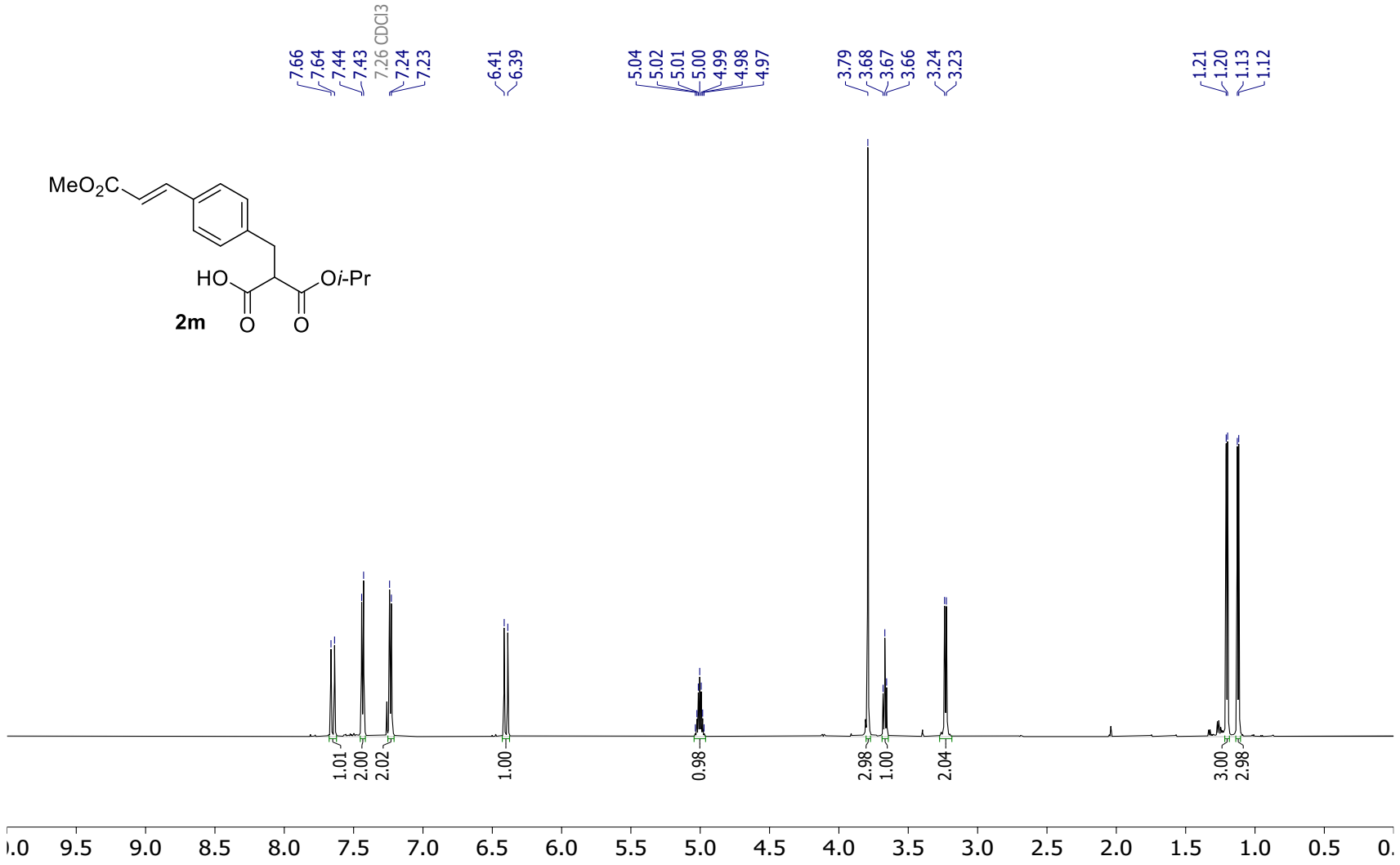

173.3
167.8
143.2
132.5
129.9
118.8
111.0
77.2 CDCl3
70.1
53.0
34.6
21.6
21.6
NC
HO
O
O
O
O
i-Pr
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

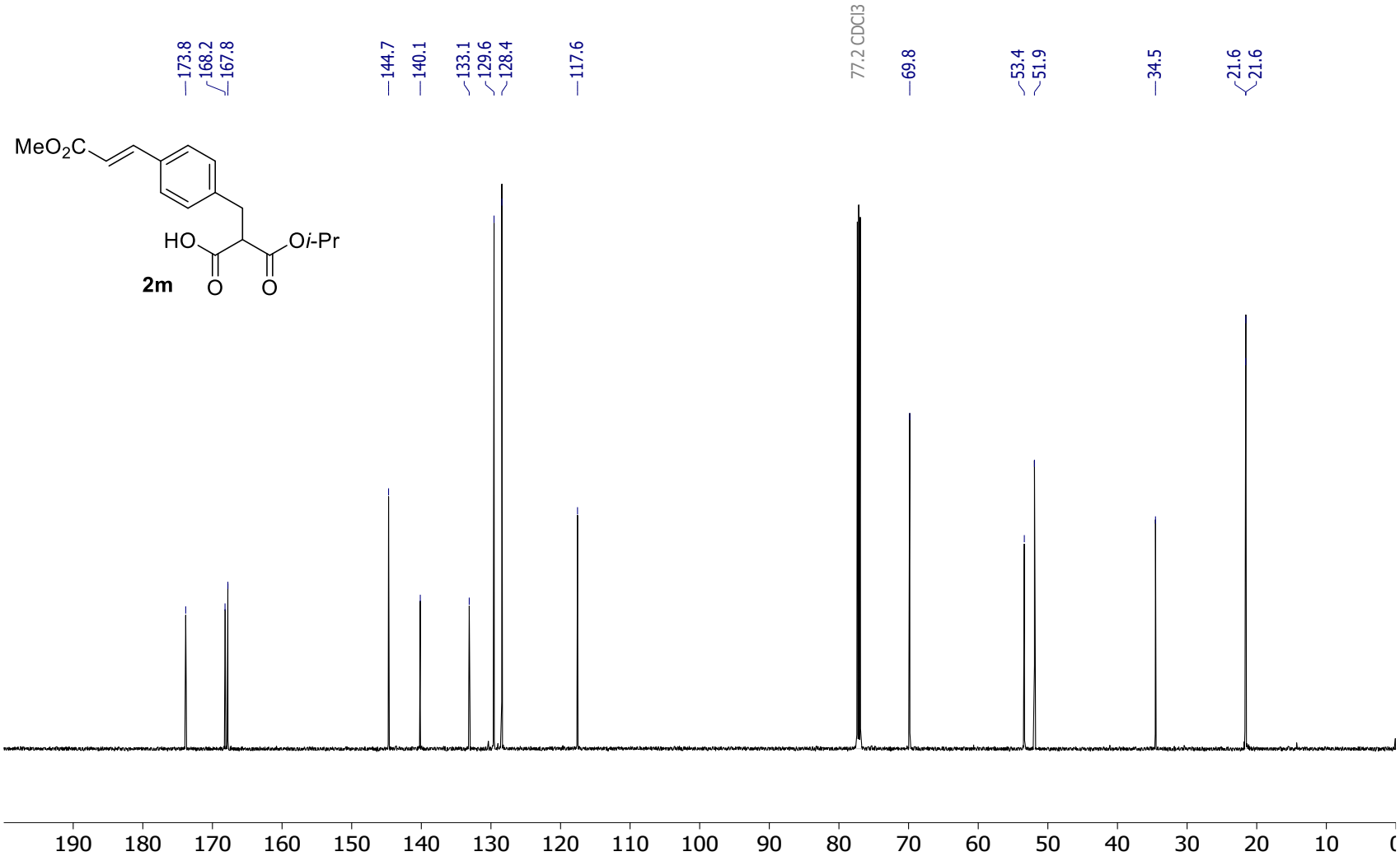
^{1}H &^{13}C NMR($CDCl_3$) of **2l**



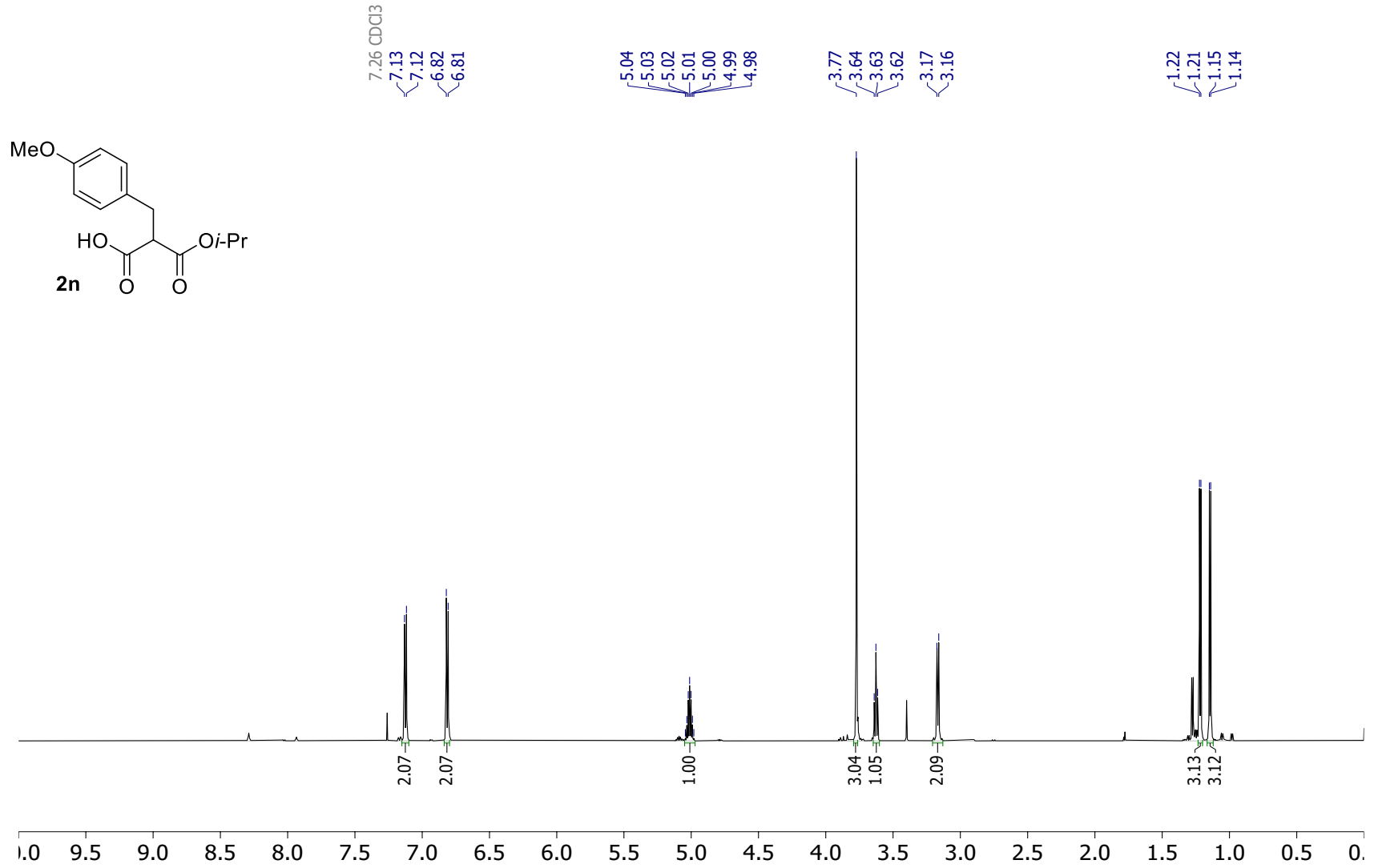

173.81
167.68
147.22
147.20
145.21
145.18
129.98
124.02
123.99
123.96
77.37
77.16
76.95
70.32
70.30
53.05
34.40
34.34
21.82
21.66
21.61
21.59
O2N
HO
Oi-Pr
O
O
2l
f1 (ppm)

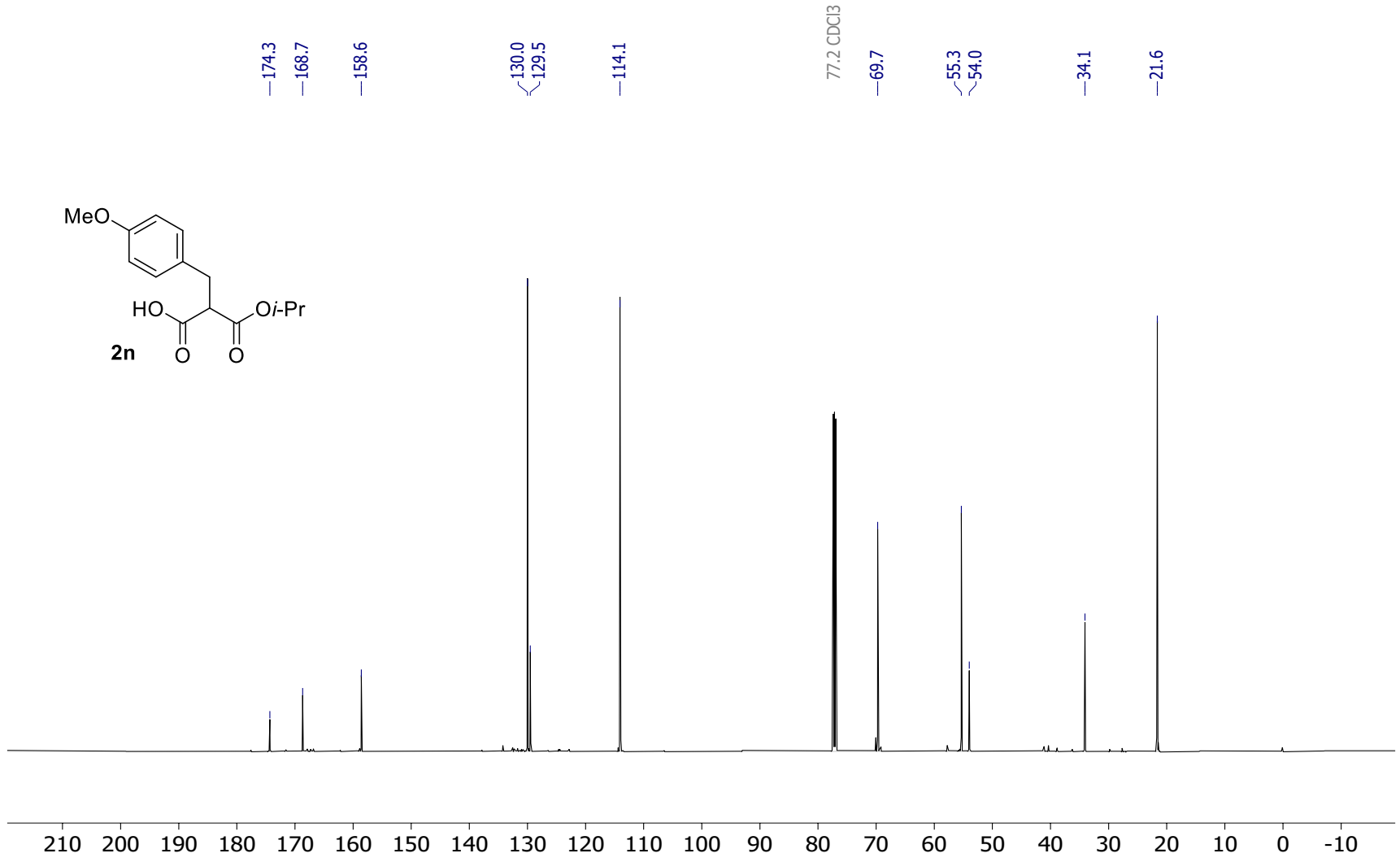
^{1}H &^{13}C NMR($CDCl_3$) of **2m**



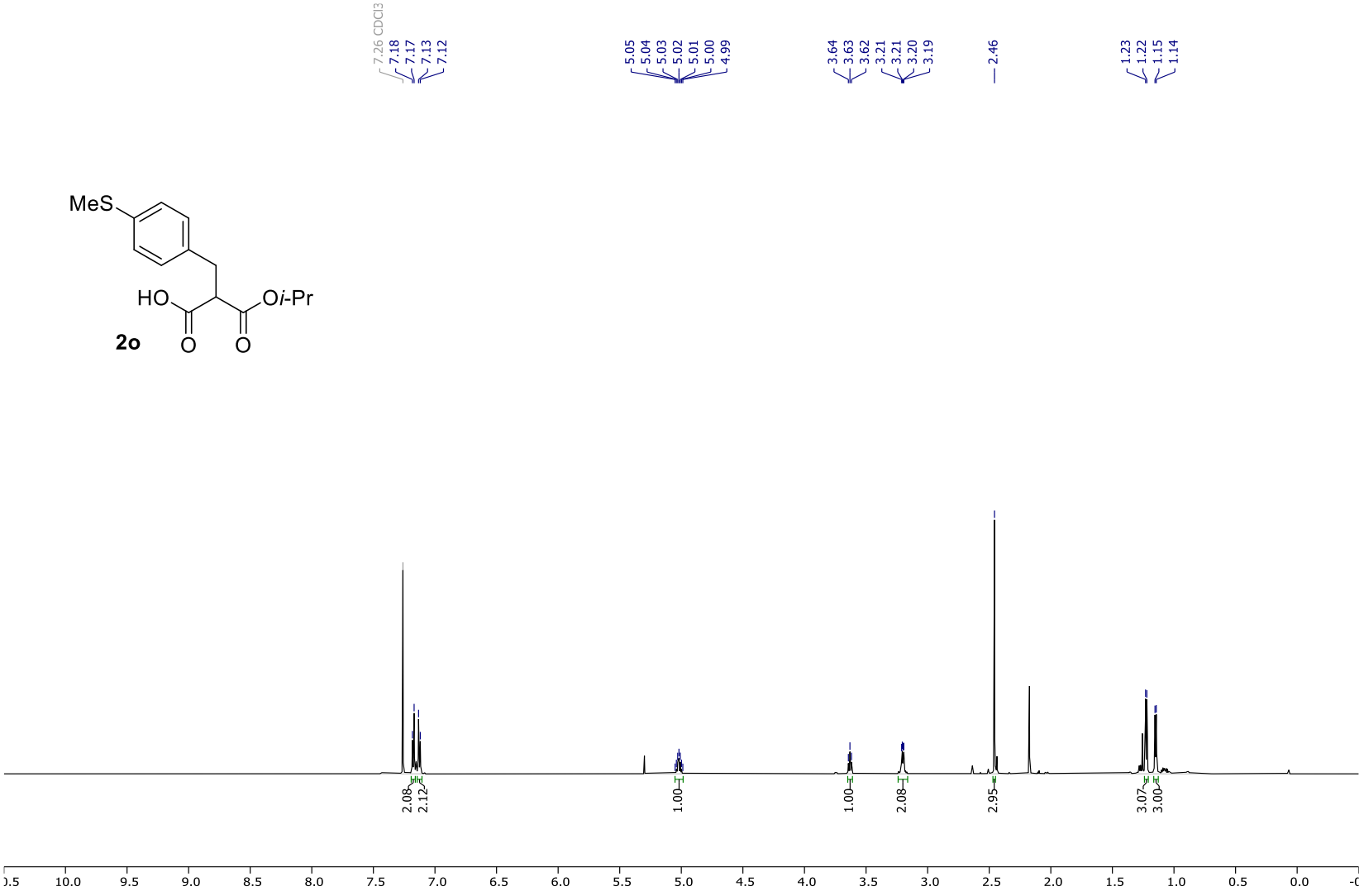

173.8
168.2
167.8
144.7
140.1
133.1
129.6
128.4
117.6
77.2 CDCl3
69.8
53.4
51.9
34.5
21.6
21.6
MeO2C
HO
Oi-Pr
O
O
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

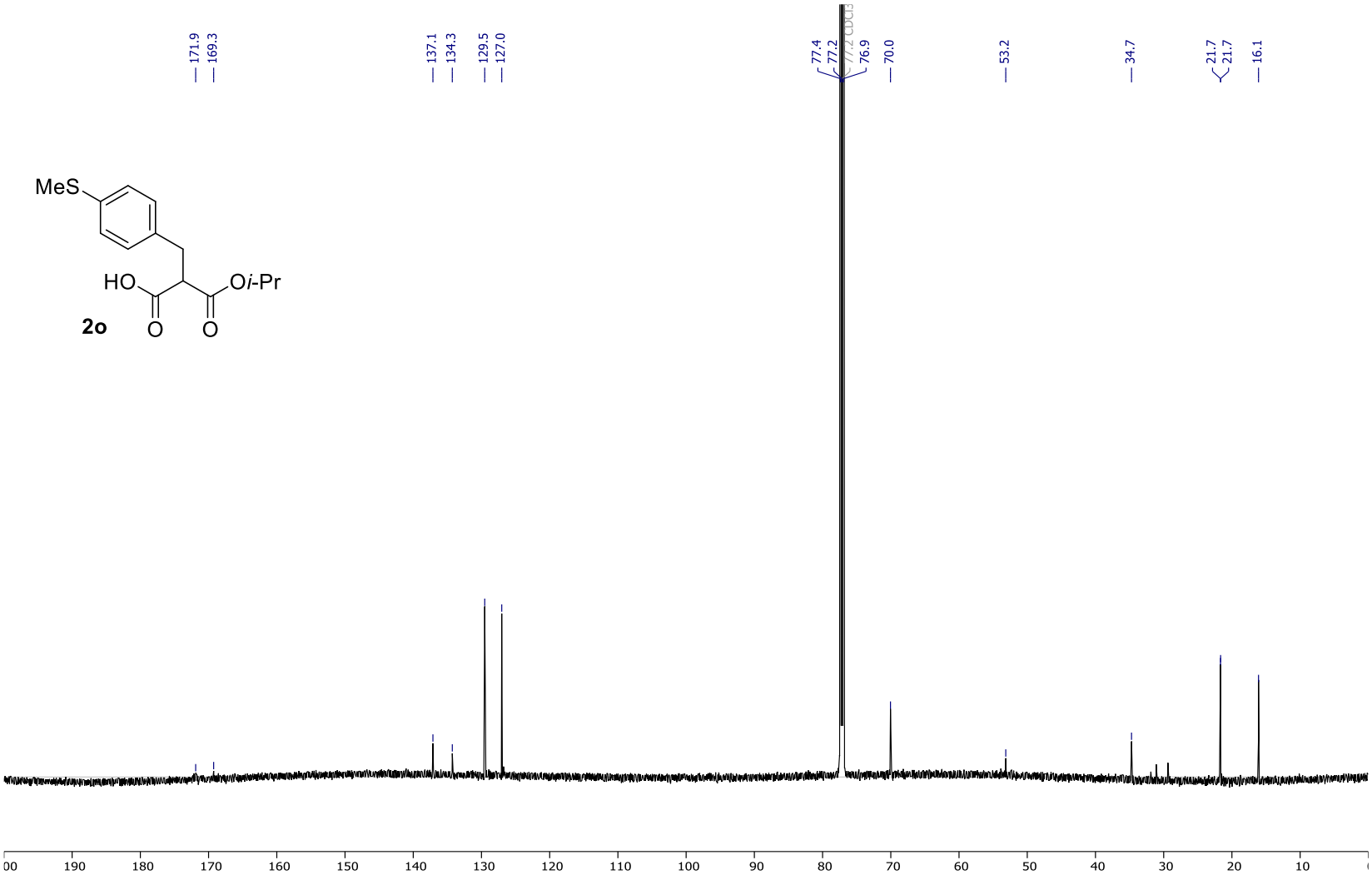
^{1}H &^{13}C NMR($CDCl_3$) of **2n**



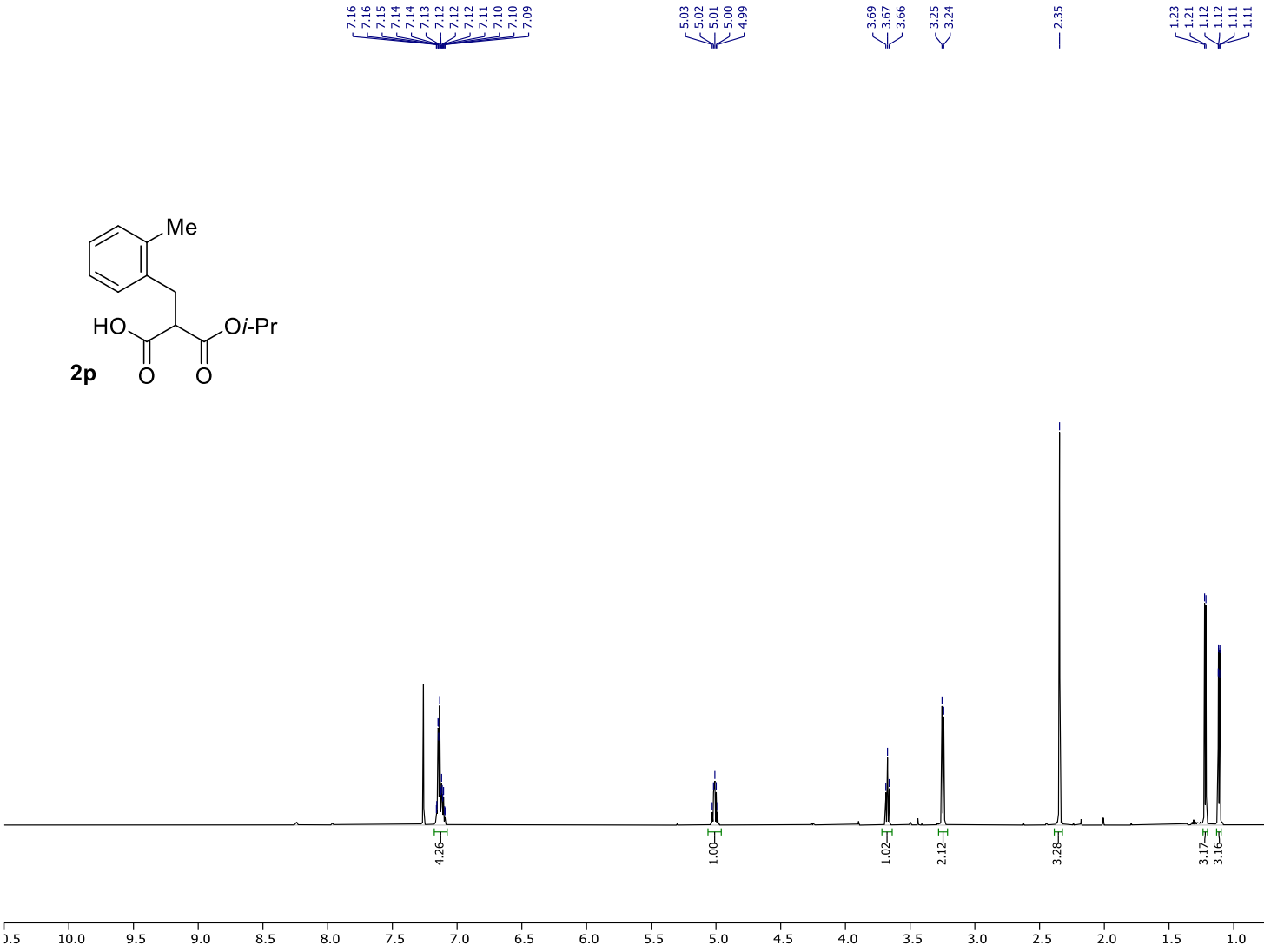

174.3
168.7
158.6
130.0
129.5
114.1
77.2 CDCl3
69.7
55.3
54.0
34.1
21.6
MeO
HO
O
O
O
Oi-Pr
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

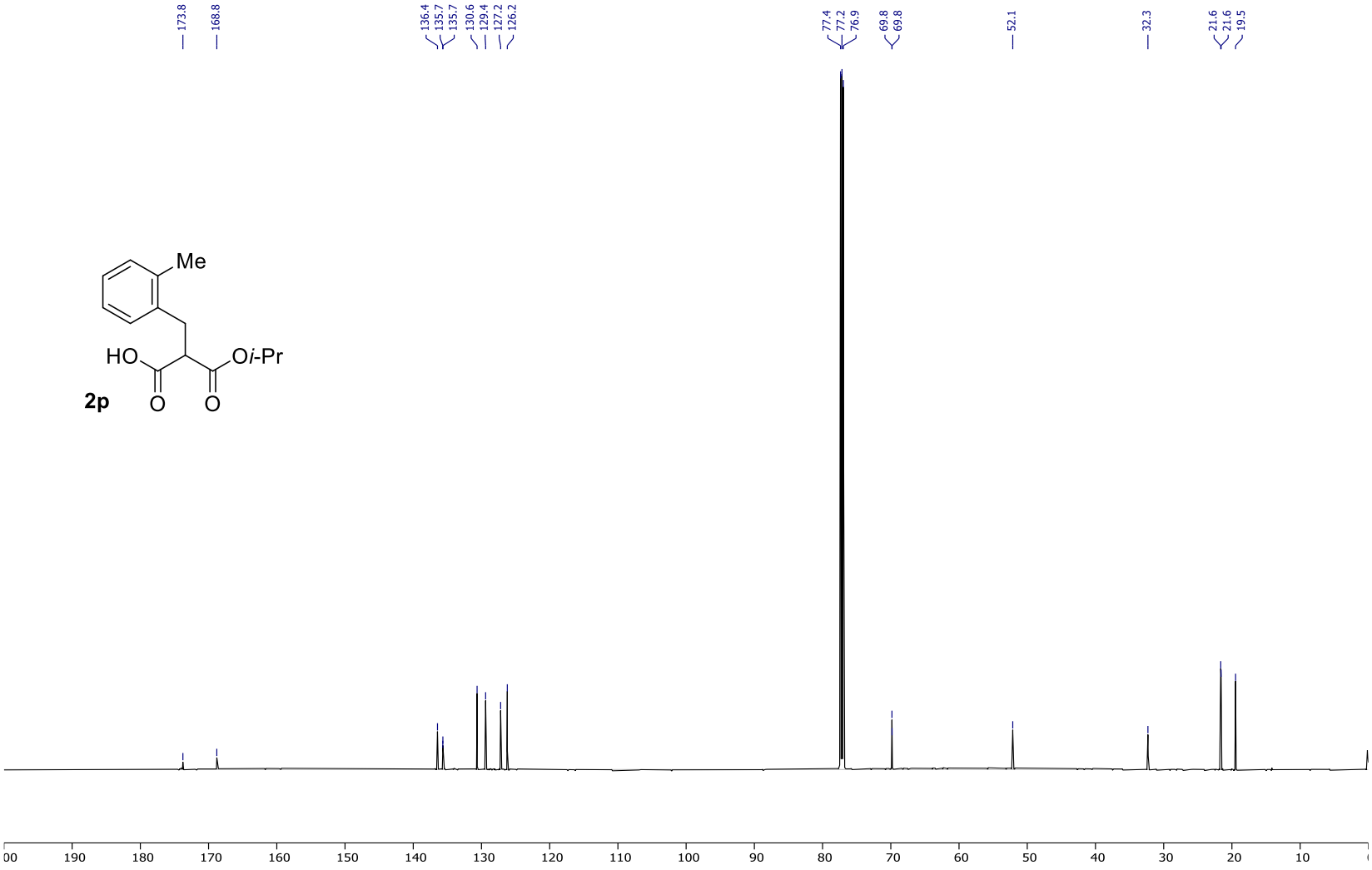
^{1}H &^{13}C NMR($CDCl_3$) of **2o**



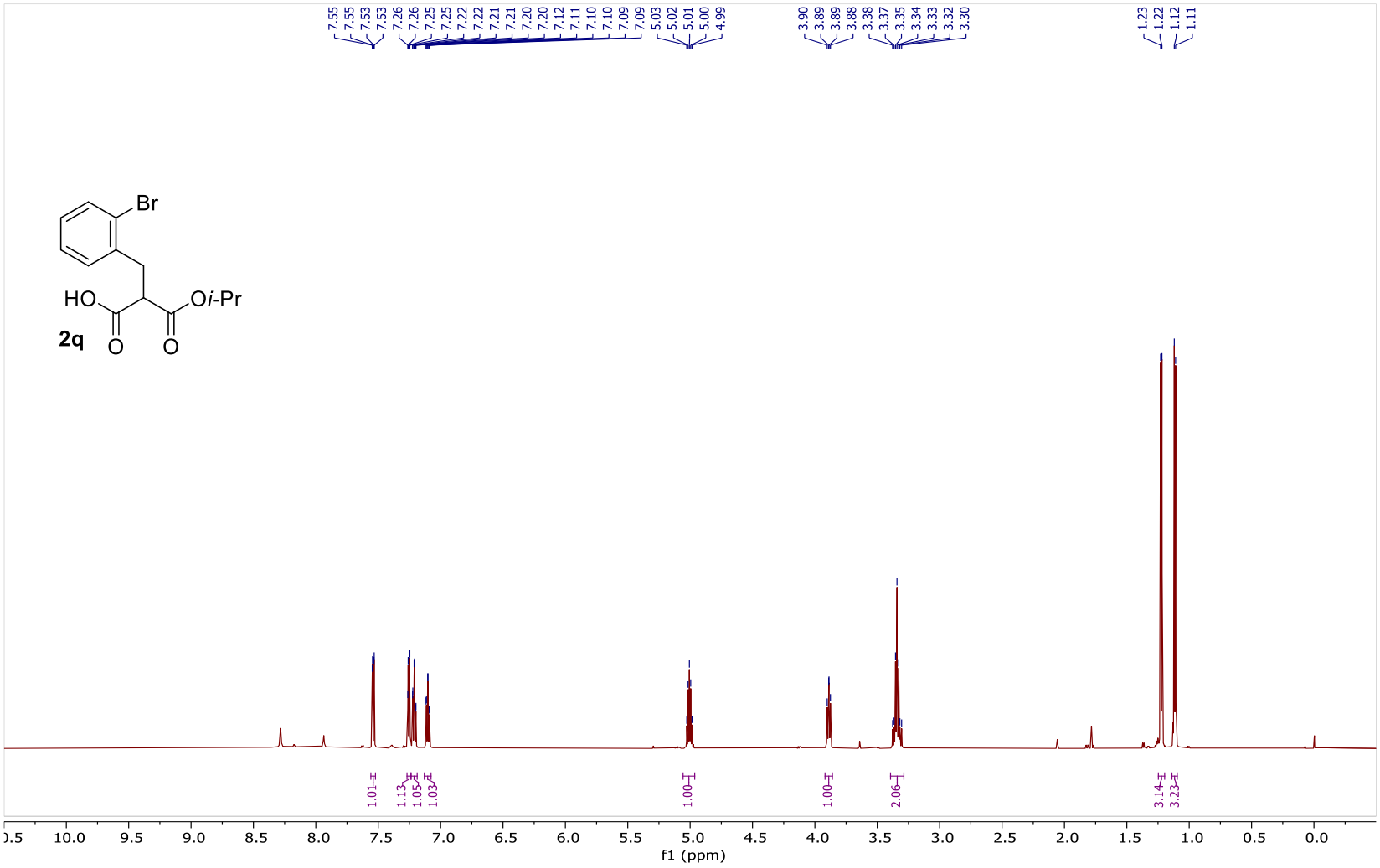

171.9
169.3
137.1
134.3
129.5
127.0
77.4
77.2
76.9
70.0
53.2
34.7
21.7
21.7
16.1
MeS
HO
O
O
O
O
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

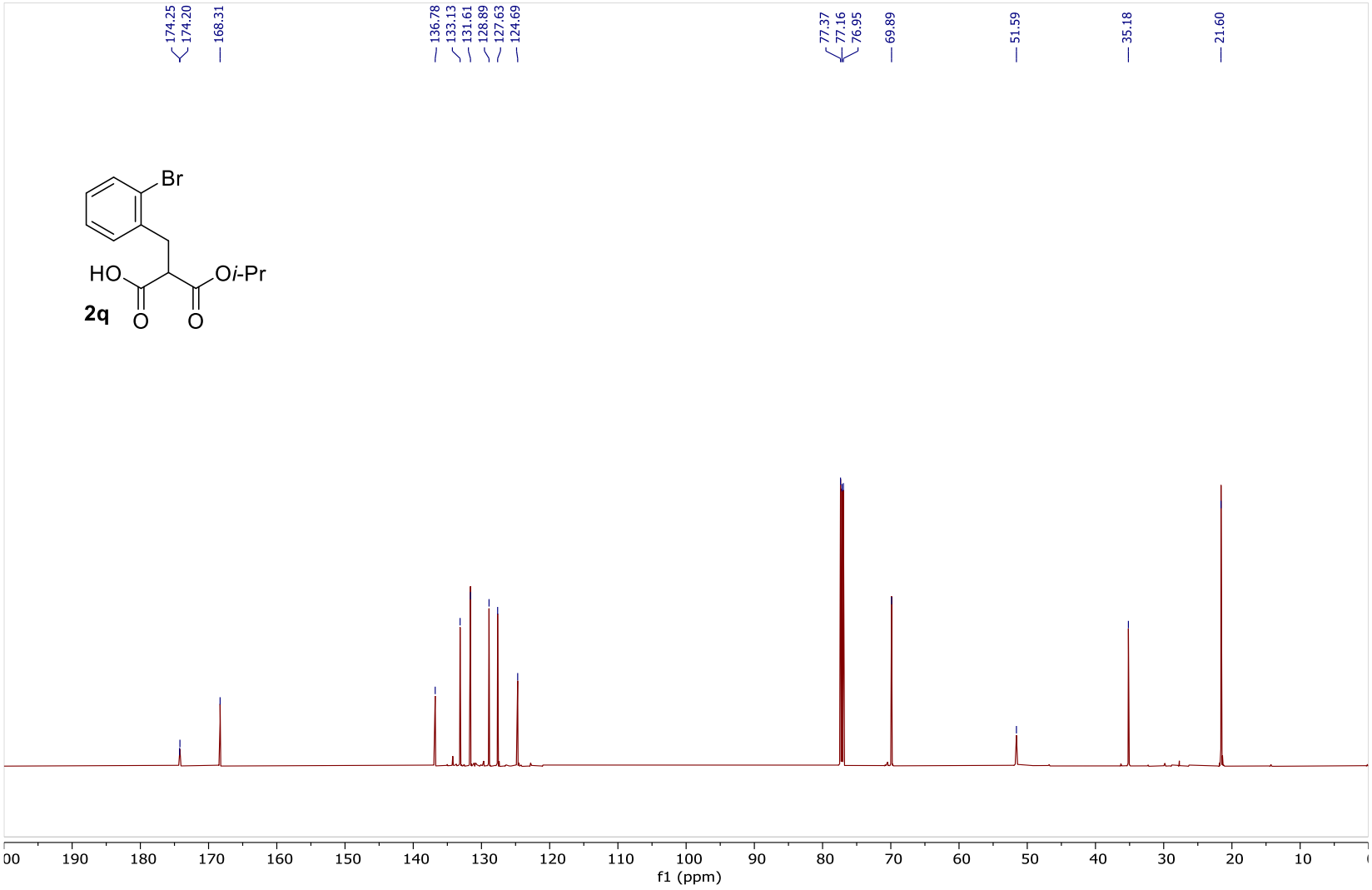
^{1}H &^{13}C NMR($CDCl_3$) of **2p**



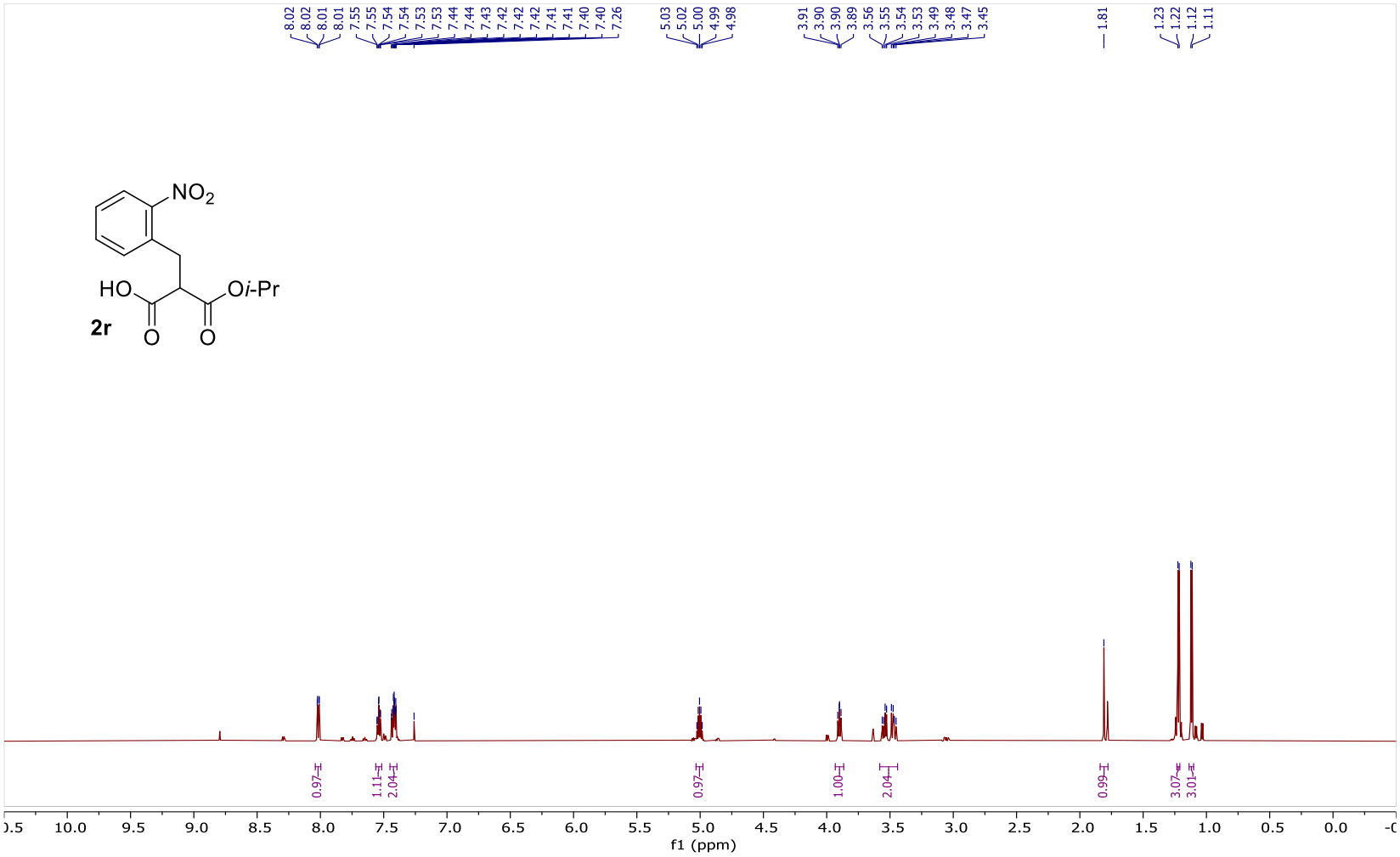

173.8
168.8
136.4
135.7
135.7
130.6
129.4
127.2
126.2
77.4
77.2
76.9
69.8
69.8
52.1
32.3
21.6
21.6
19.5
Me
HO
O
O
O
O
i-Pr
2p
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

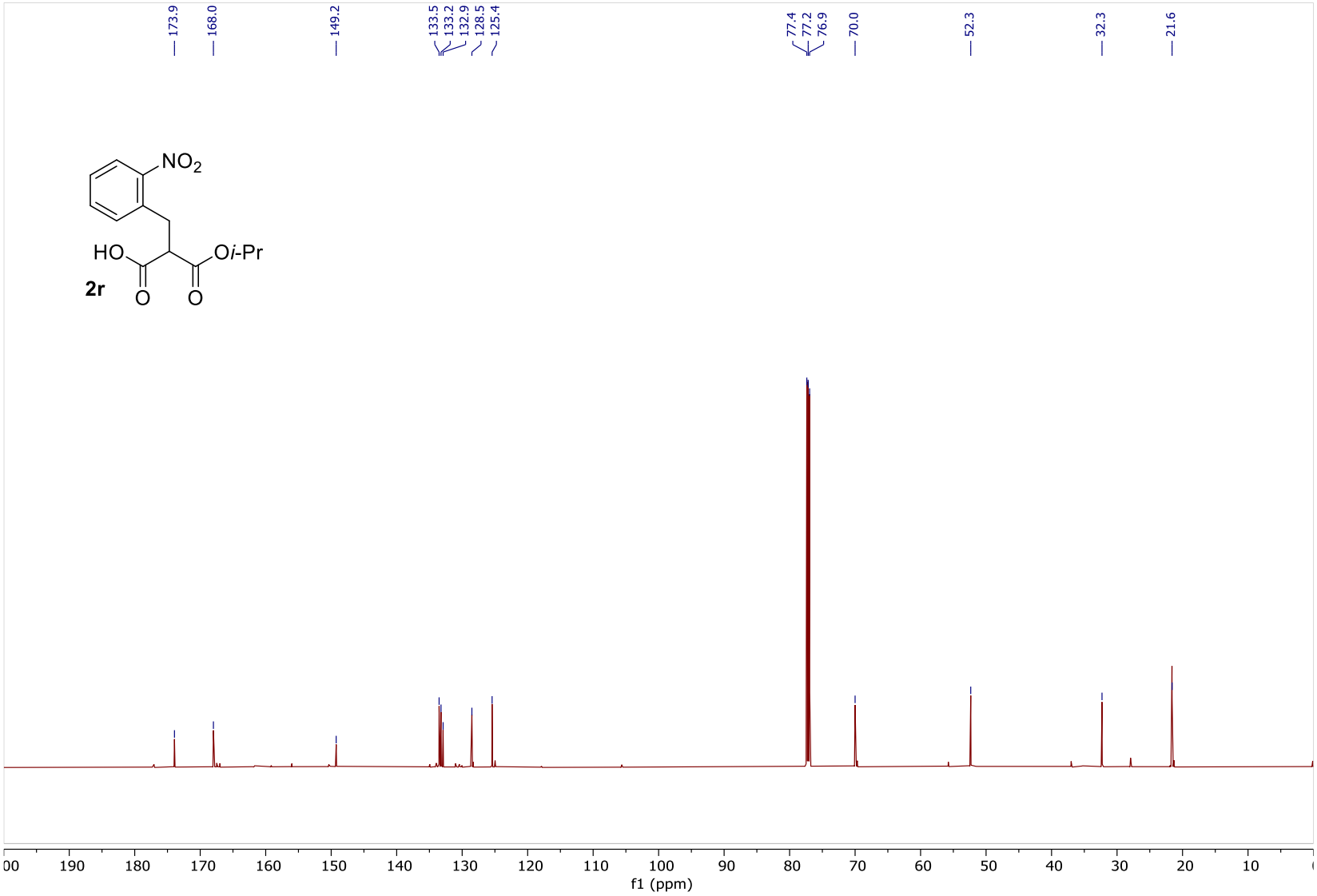
^{1}H &^{13}C NMR($CDCl_3$) of **2q**



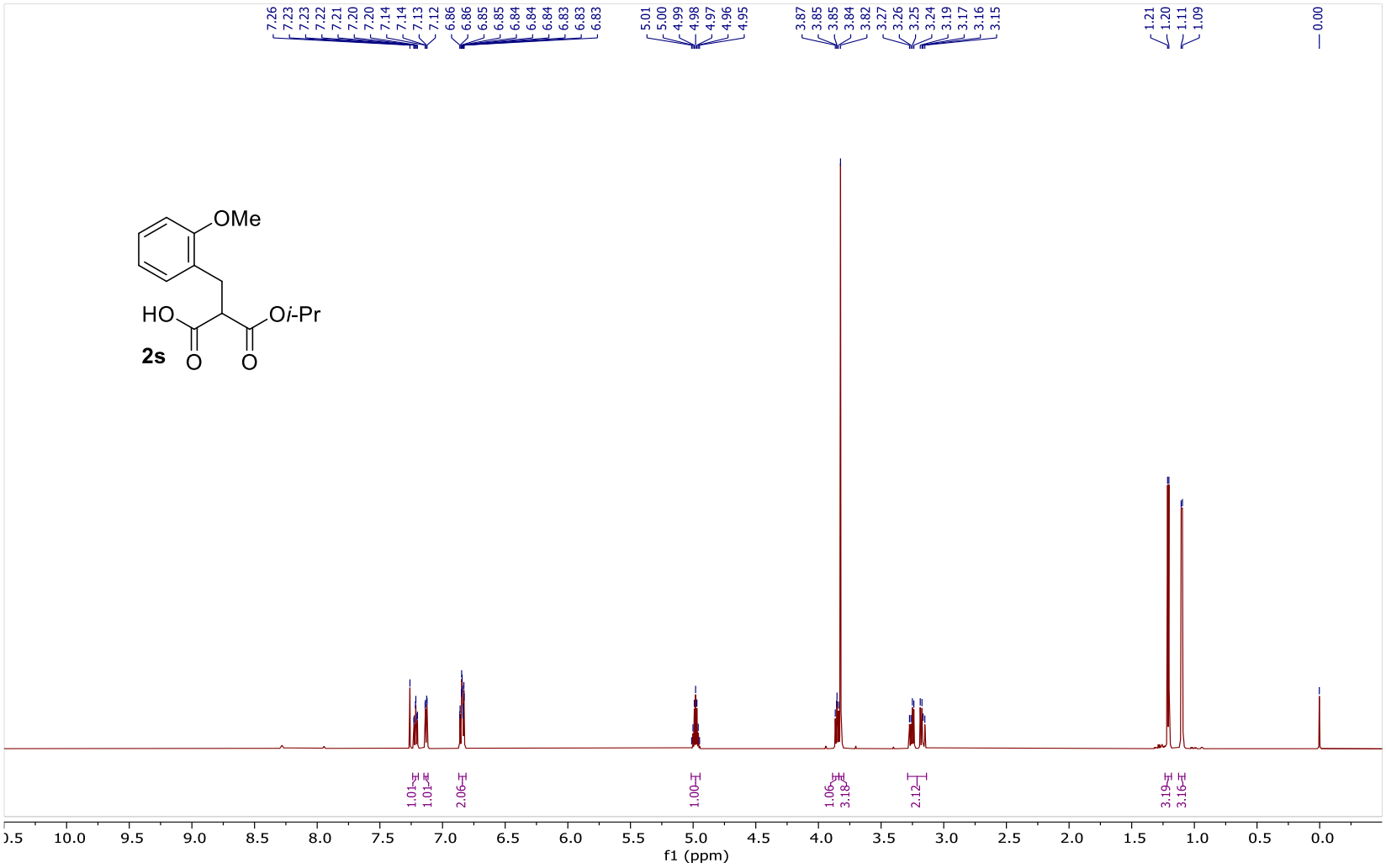

174.25
174.20
168.31
136.78
133.13
131.61
128.89
127.63
124.69
77.37
77.16
76.95
69.89
51.59
35.18
21.60
Br
HO
O
O
Oi-Pr
2q
f1 (ppm)

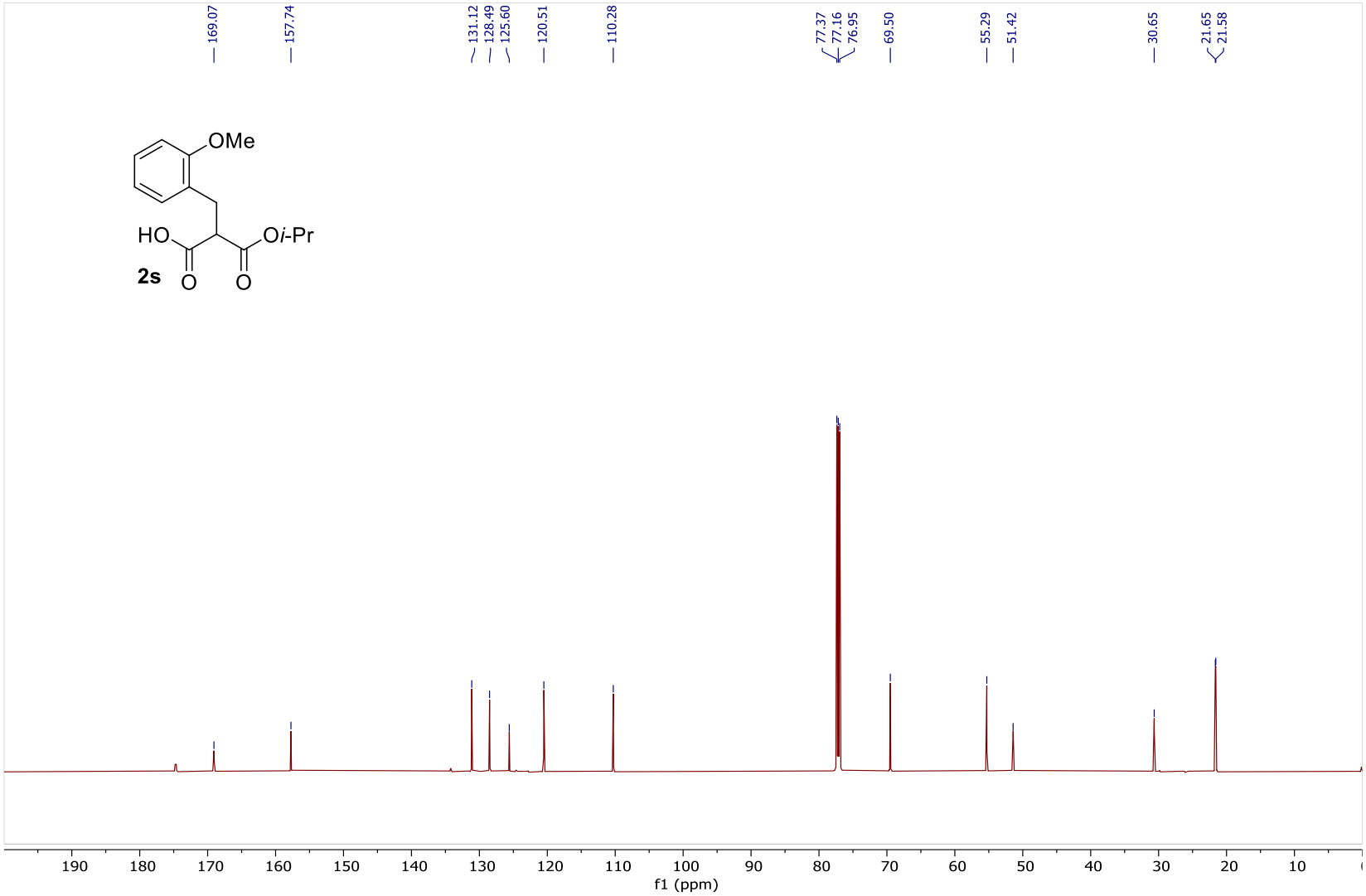
^{1}H &^{13}C NMR($CDCl_3$) of **2r**



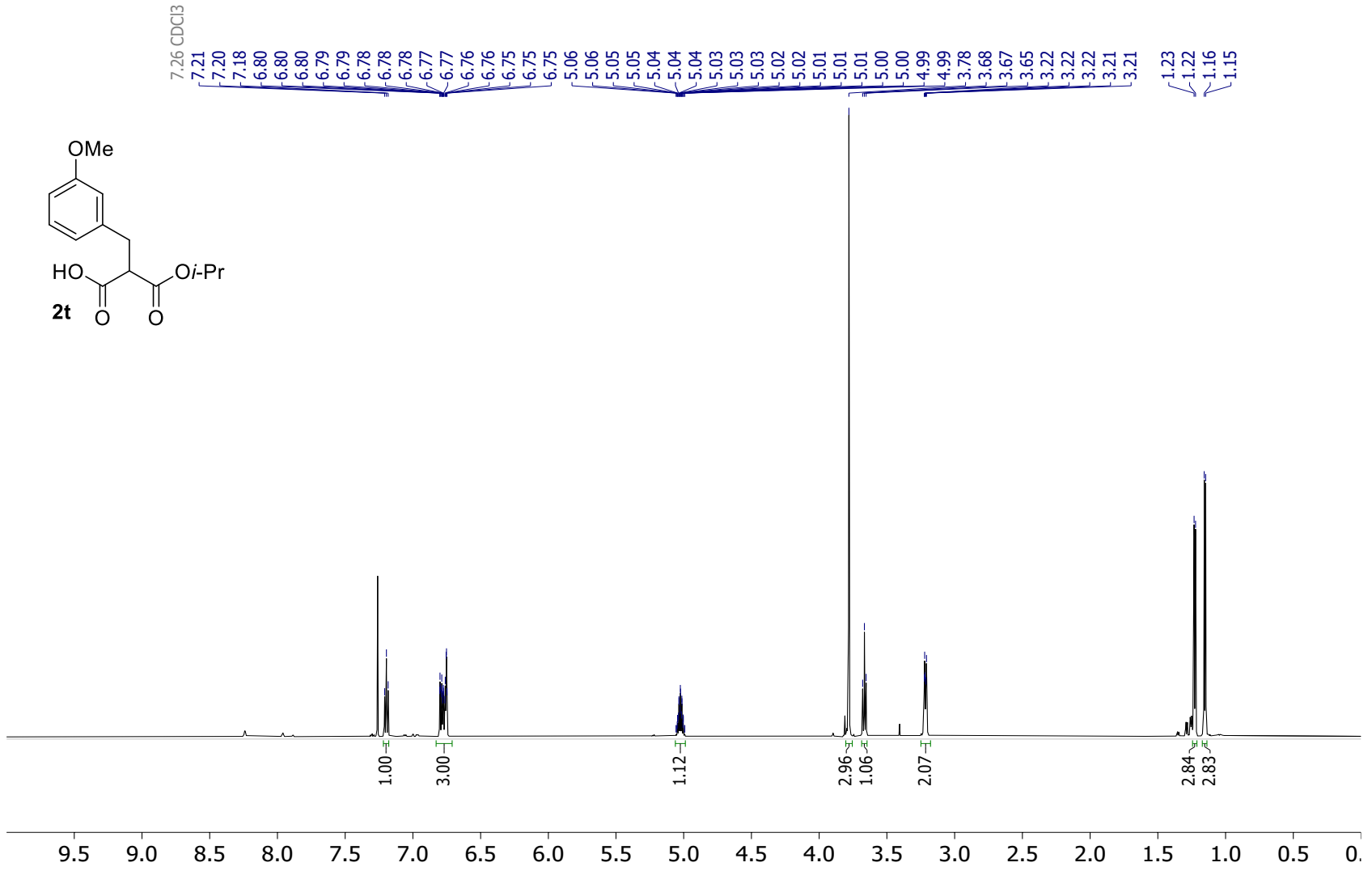

173.9
168.0
149.2
133.5
133.2
132.9
128.5
125.4
77.4
77.2
76.9
70.0
52.3
32.3
21.6
NO2
HO
O
O
Oi-Pr
2r
f1 (ppm)

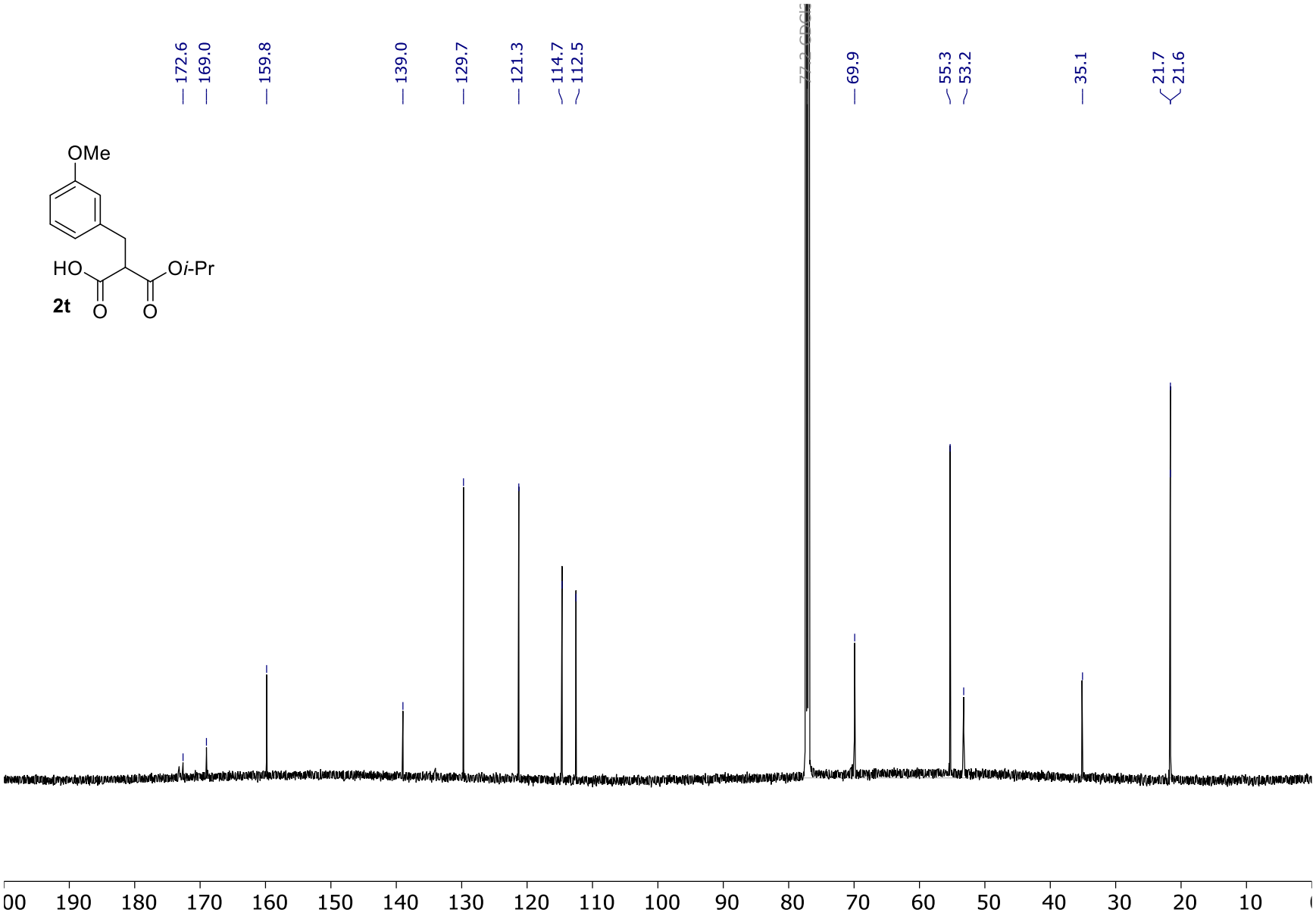
^{1}H &^{13}C NMR($CDCl_3$) of **2s**



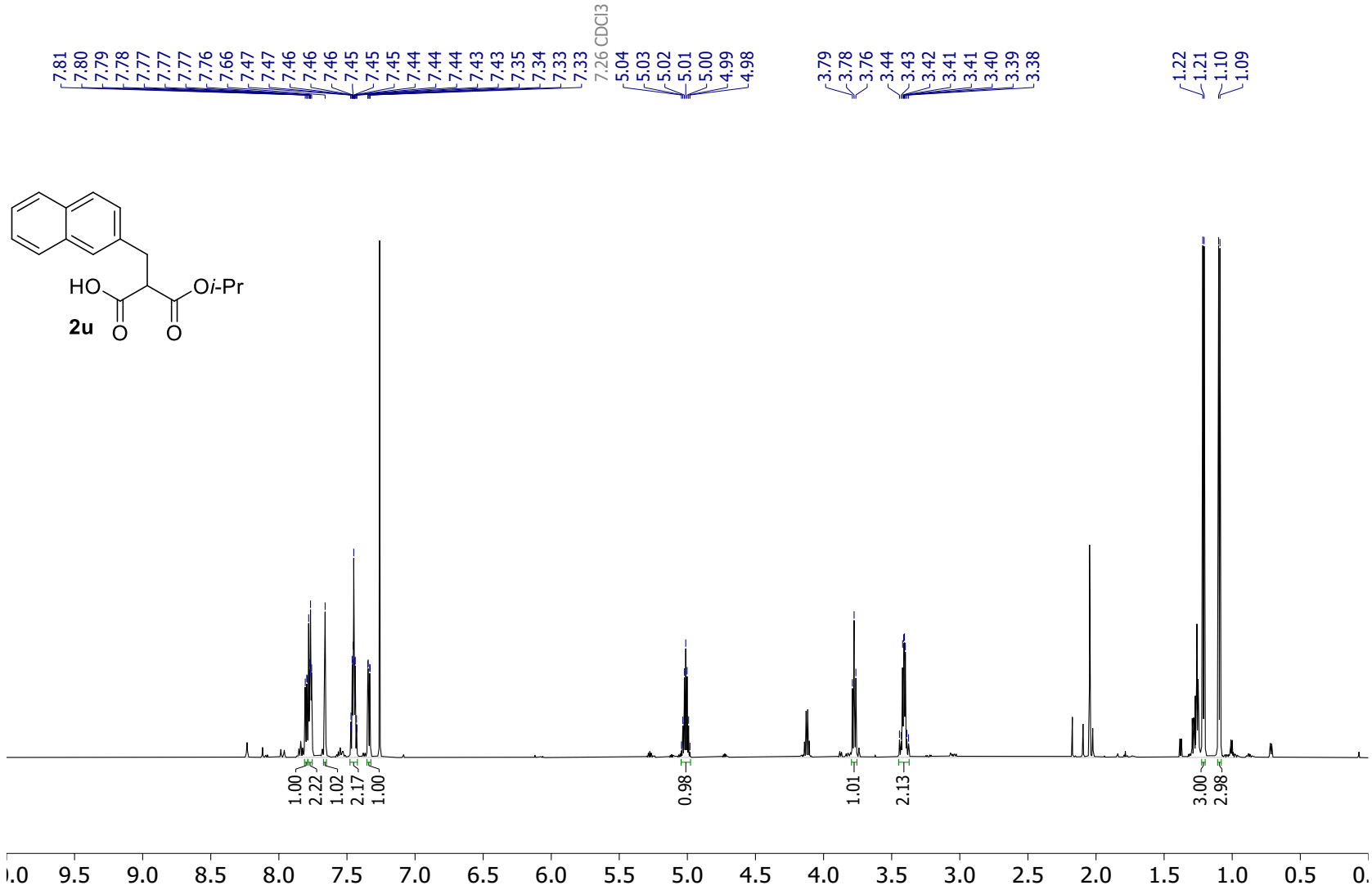

169.07
157.74
131.12
128.49
125.60
120.51
110.28
77.37
77.16
76.95
69.50
55.29
51.42
30.65
21.65
21.58
OMe
HO
O
O
O
O
i-Pr
2s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

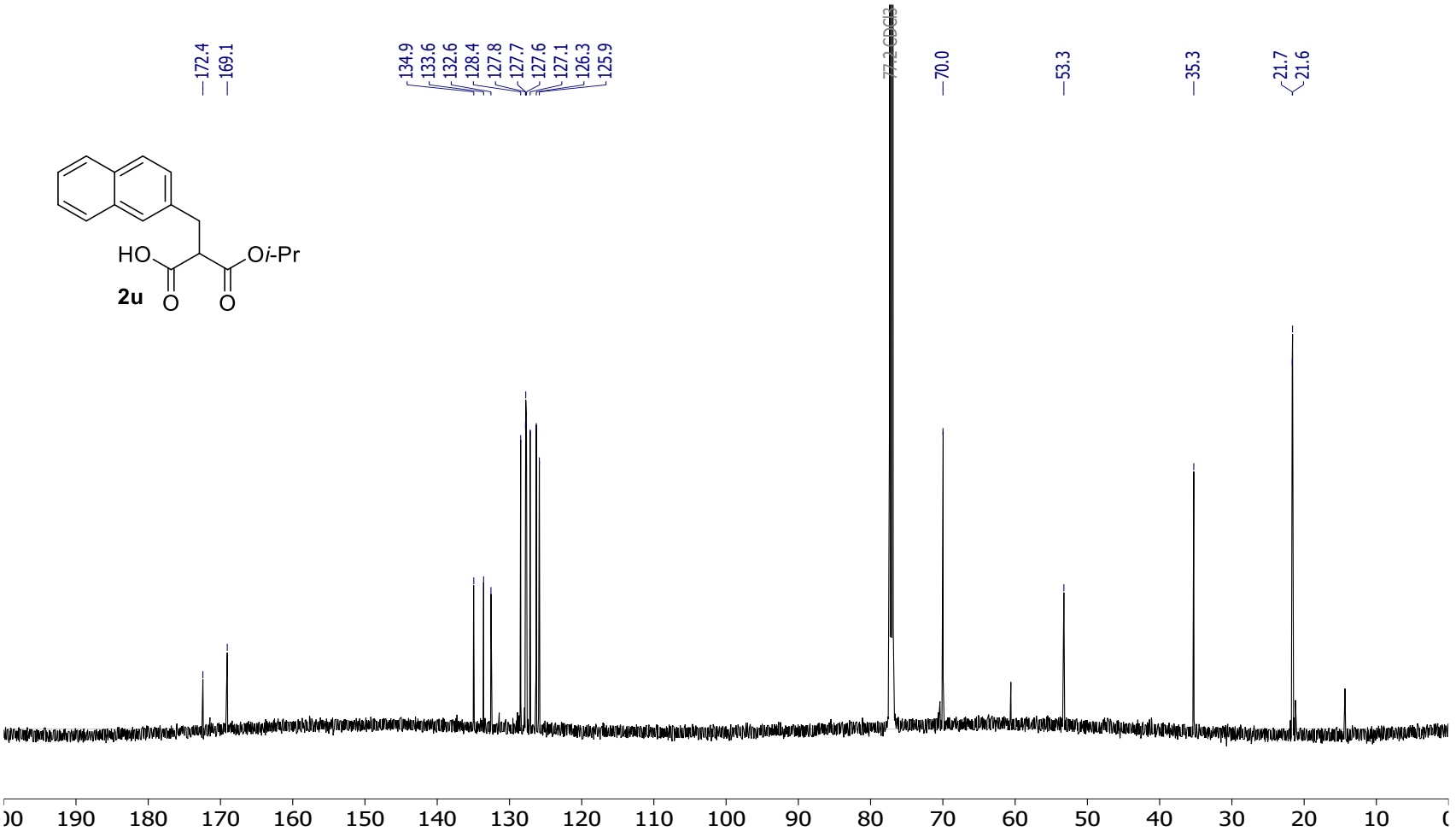
^{1}H &^{13}C NMR($CDCl_3$) of **2t**



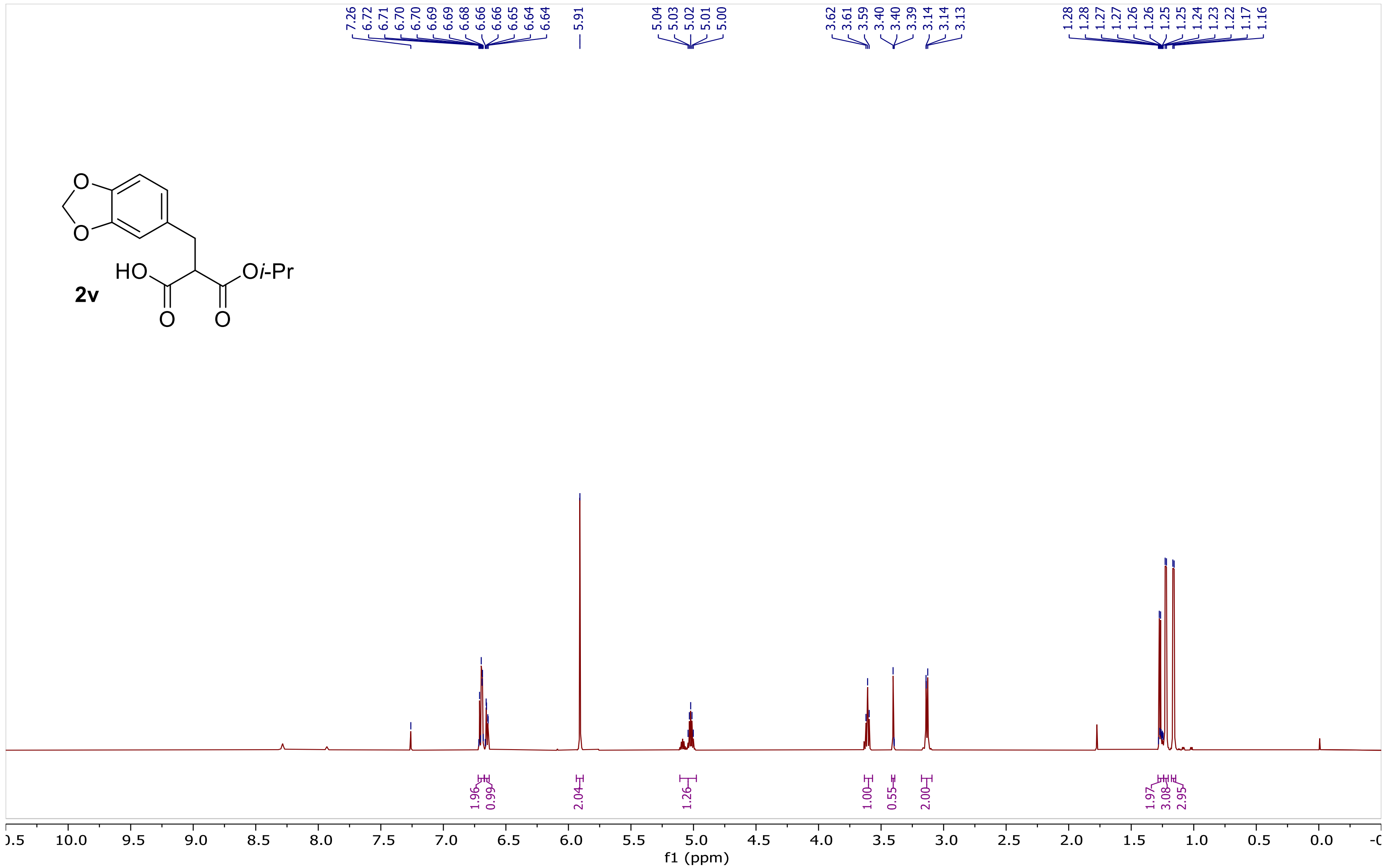

172.6
169.0
159.8
139.0
129.7
121.3
114.7
112.5
77.2
69.9
55.3
53.2
35.1
21.7
21.6
OMe
HO
O
O
O
O
i-Pr
2t
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

^{1}H &^{13}C NMR($CDCl_3$) of **2u**

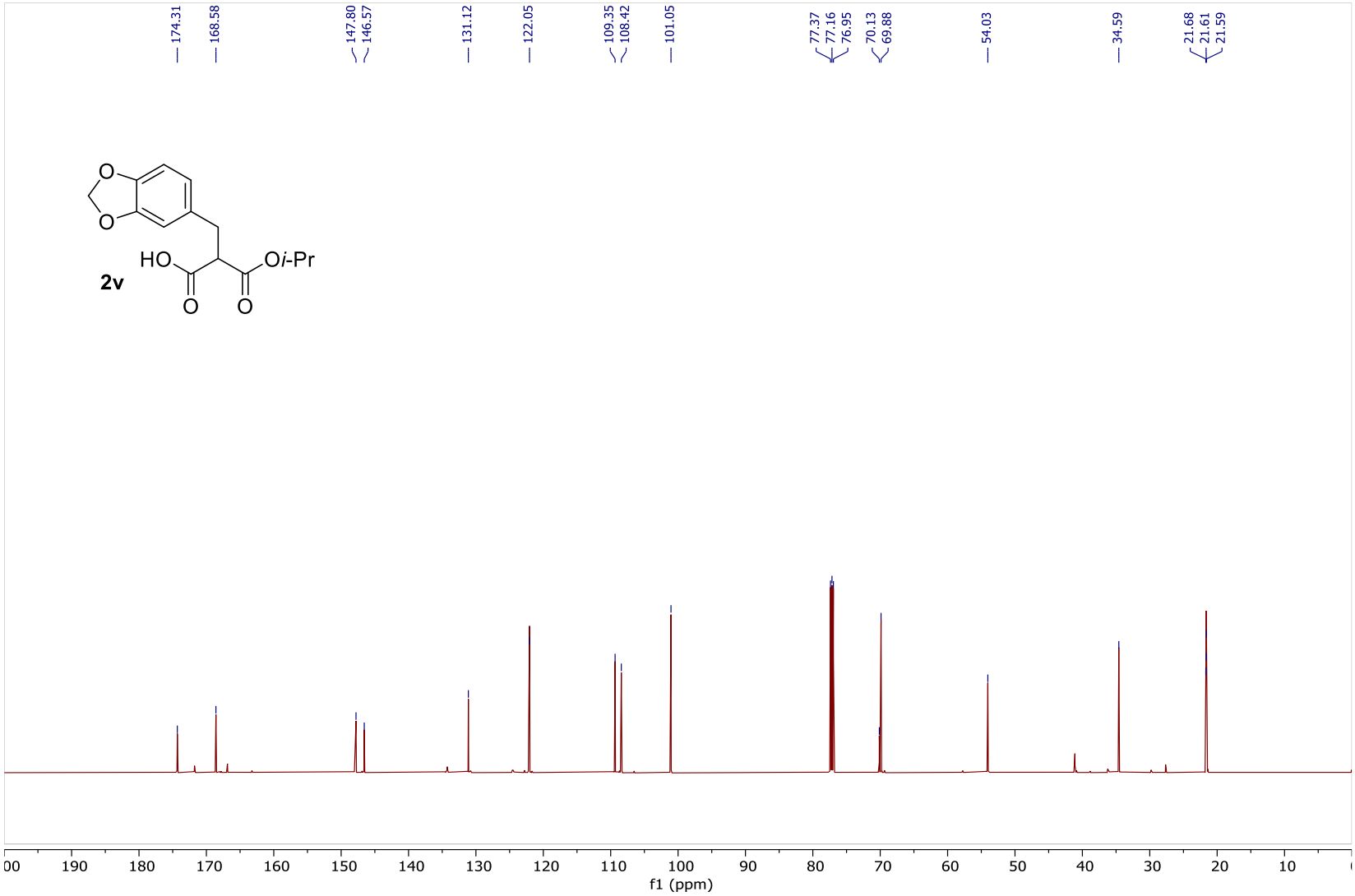


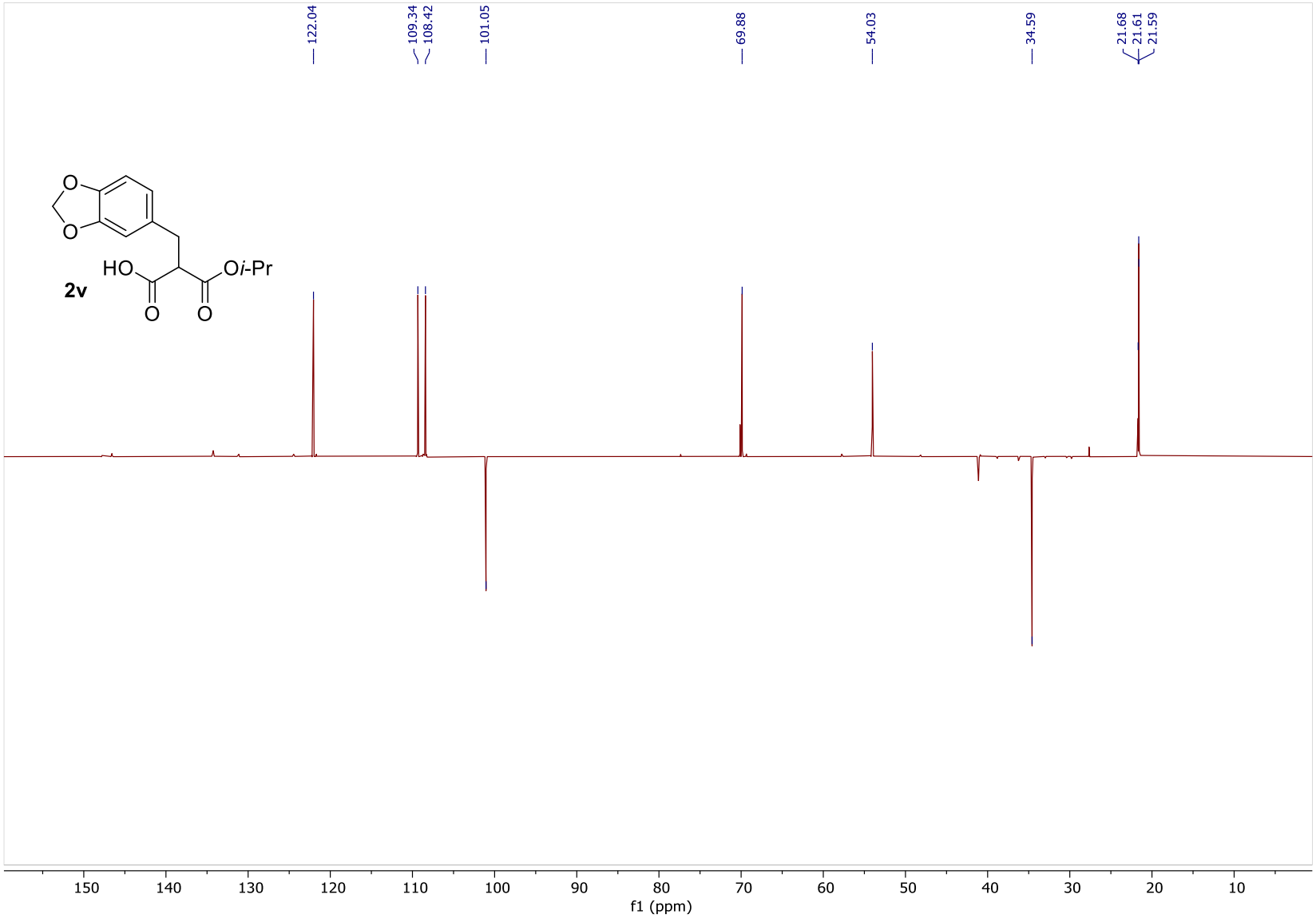

172.4
169.1
134.9
133.6
132.6
128.4
127.8
127.7
127.6
127.1
126.3
125.9
77.2 CDCl3
70.0
53.3
35.3
21.7
21.6
HO
O
O
O
O
i-Pr
2u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

^1H & ^{13}C NMR($CDCl_3$) of **2v**

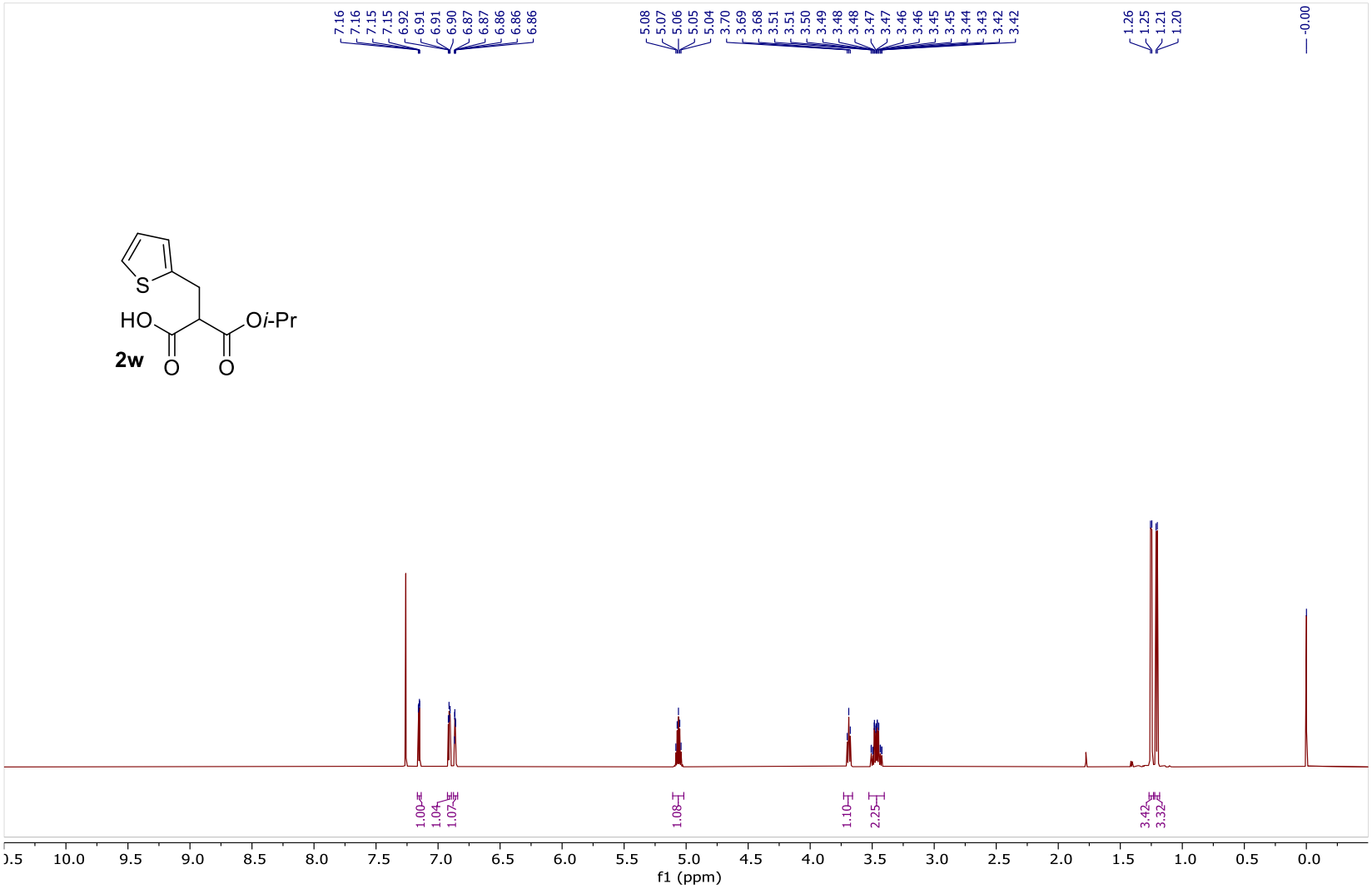


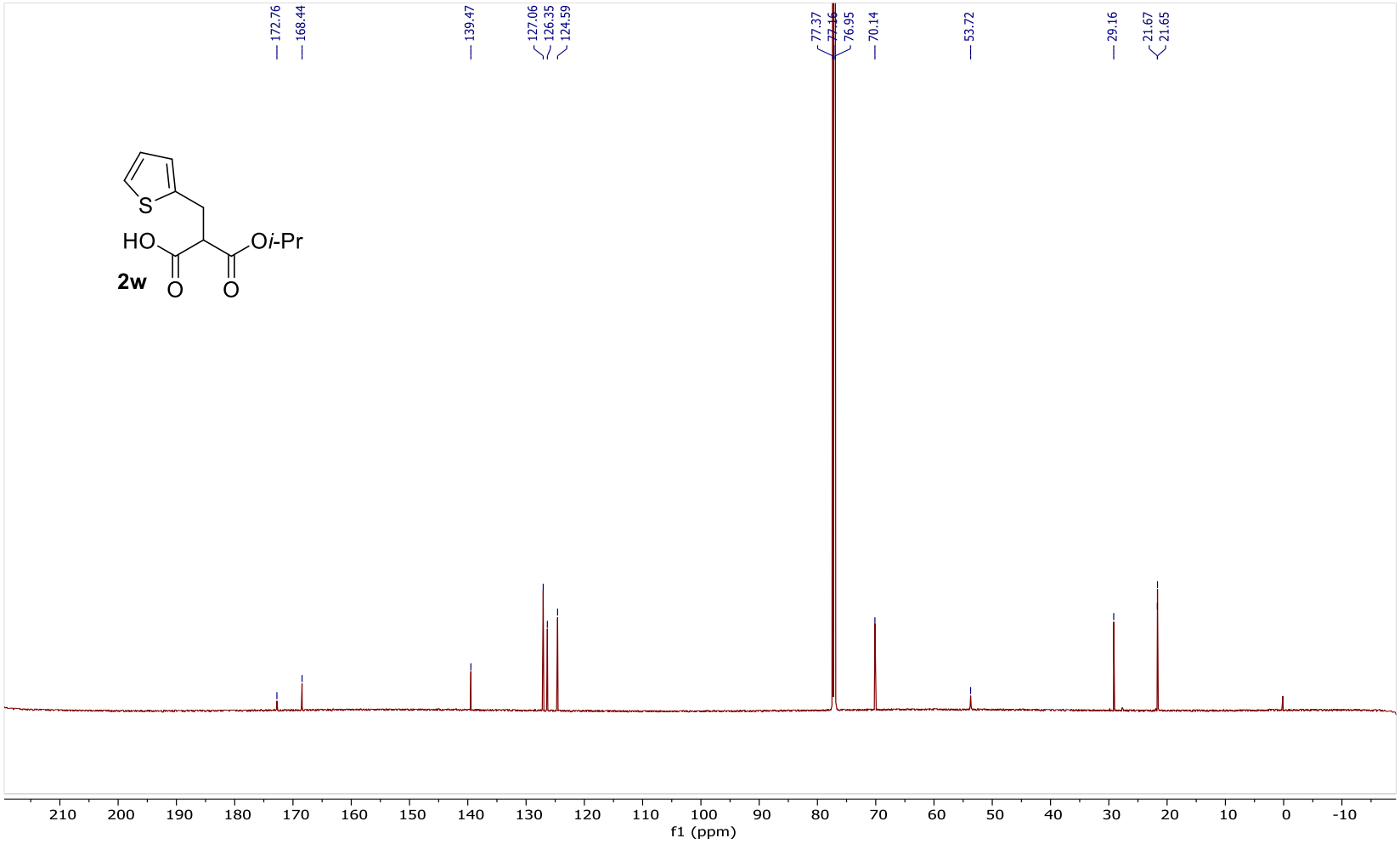
2v


174.31
168.58
147.80
146.57
131.12
122.05
109.35
108.42
101.05
77.37
77.16
76.95
70.13
69.88
54.03
34.59
21.68
21.61
21.59
HO
O
O
O
O
O*i*-Pr
2v
f1 (ppm)

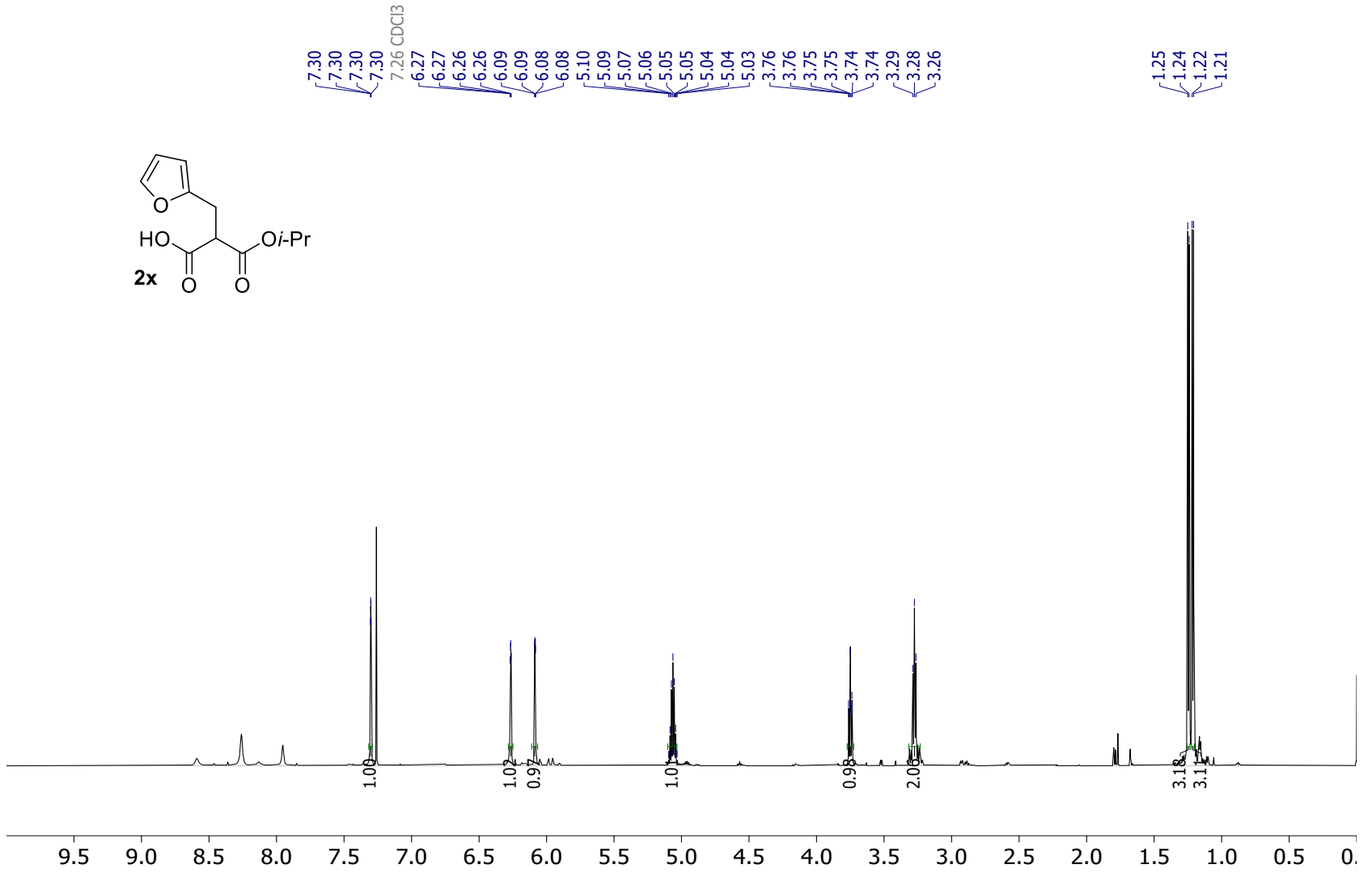

122.04
109.34
108.42
101.05
69.88
54.03
34.59
21.68
21.61
21.59
HO
O
O
O
O
O
O
i-Pr
2v
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

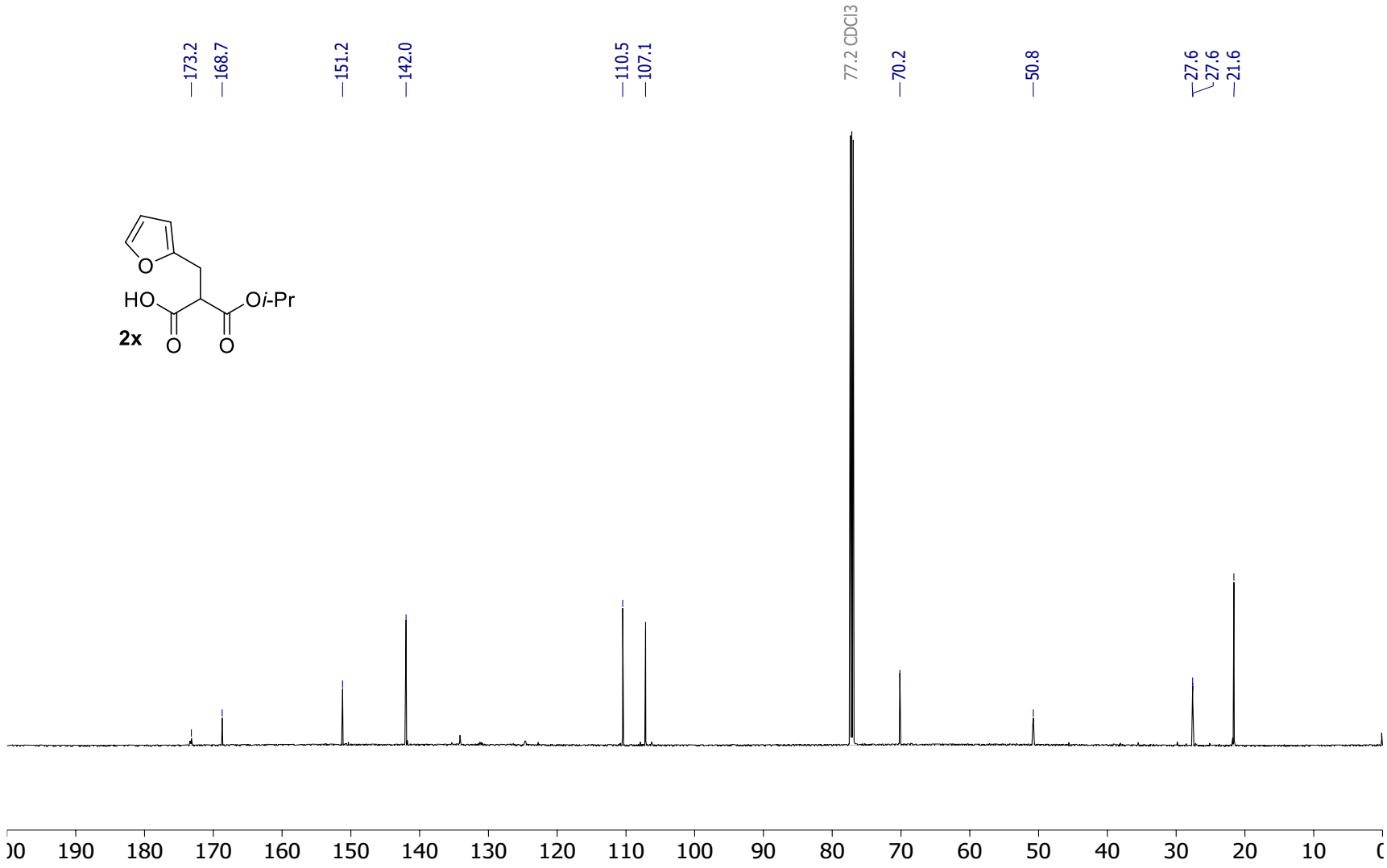
^{1}H &^{13}C NMR($CDCl_3$) of **2w**



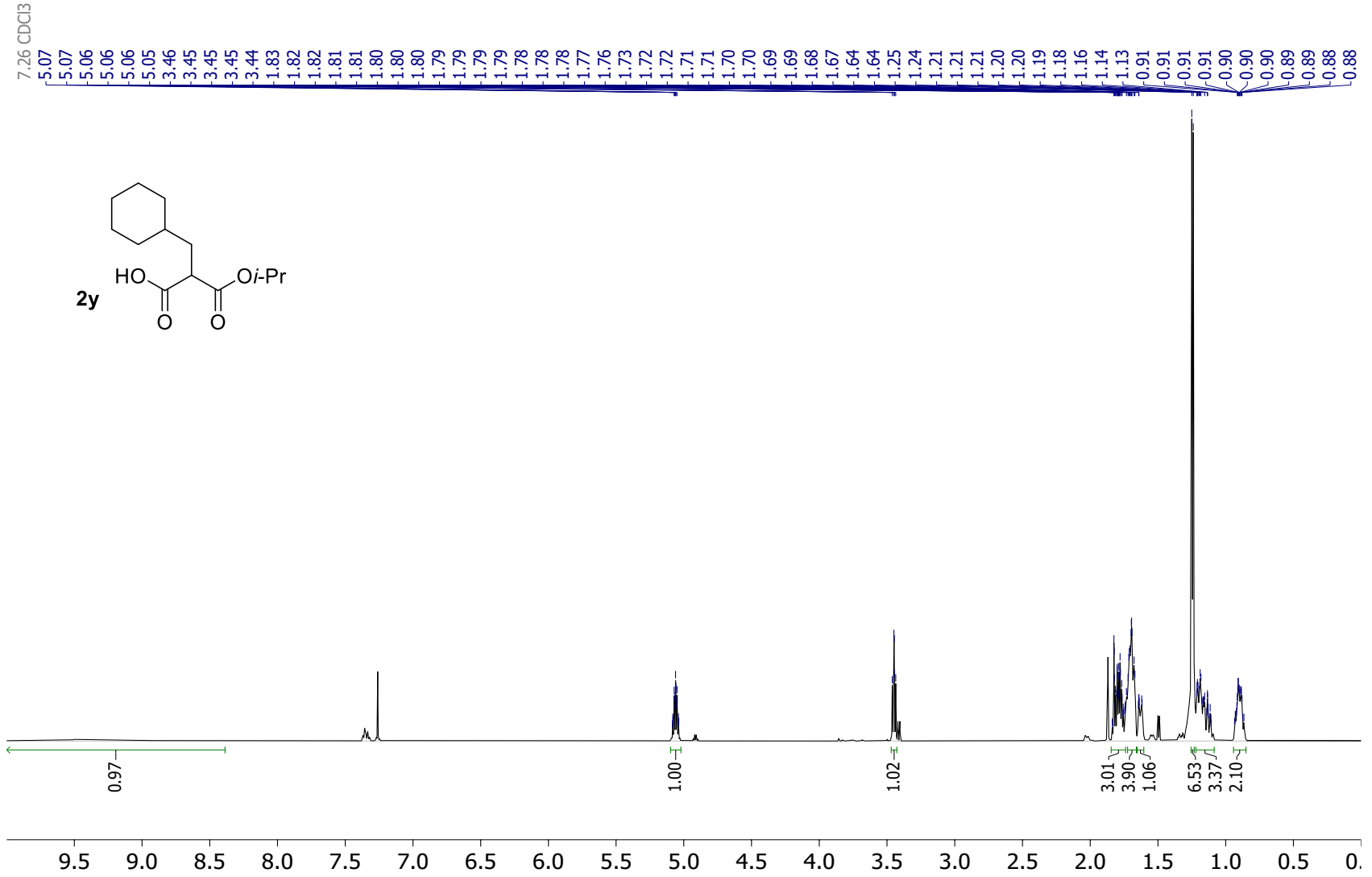

172.76
168.44
139.47
127.06
126.35
124.59
77.37
77.16
76.95
70.14
53.72
29.16
21.67
21.65
S
HO
O
O
O*i*-Pr
O
2w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

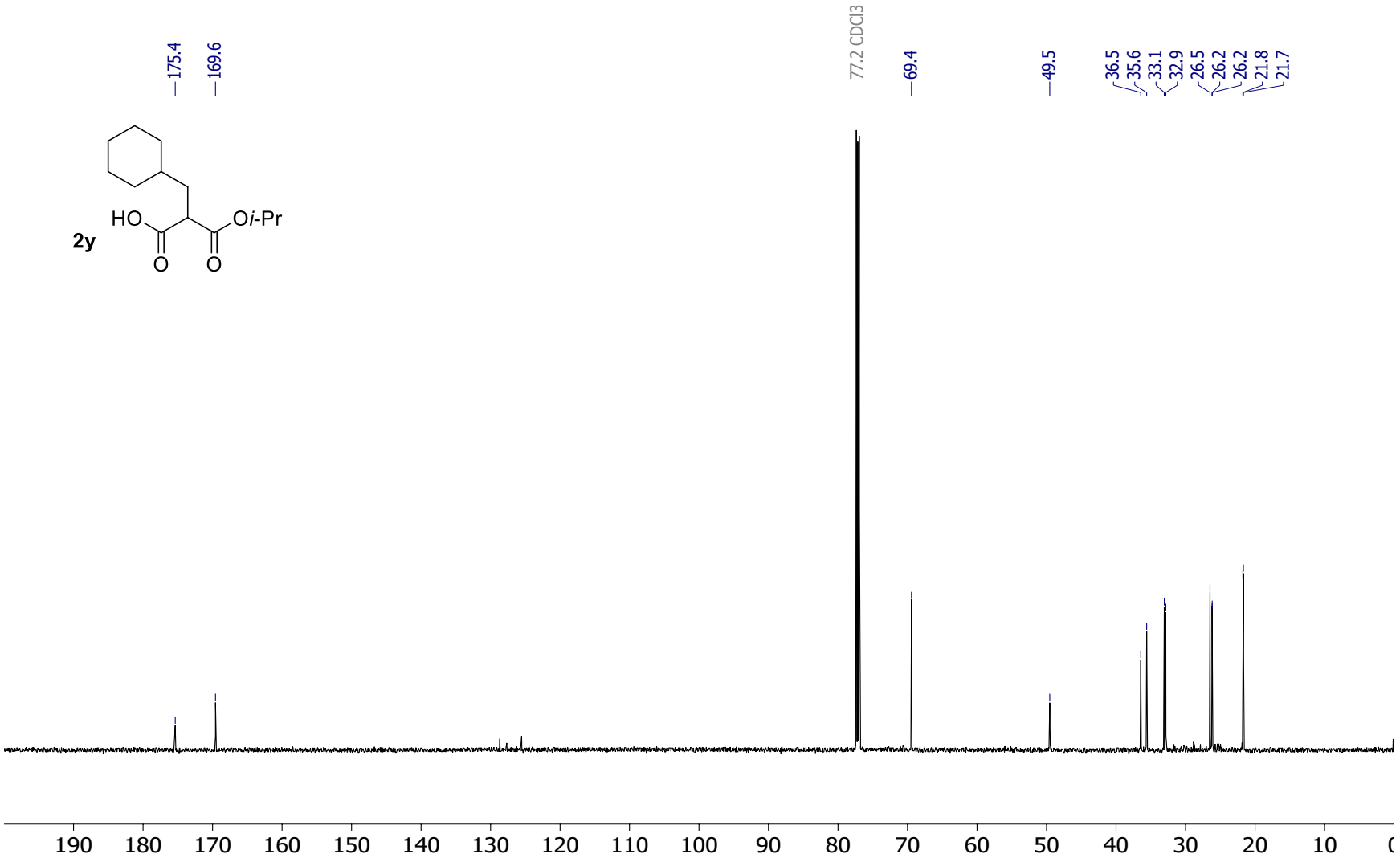
^{1}H &^{13}C NMR($CDCl_3$) of **2x**



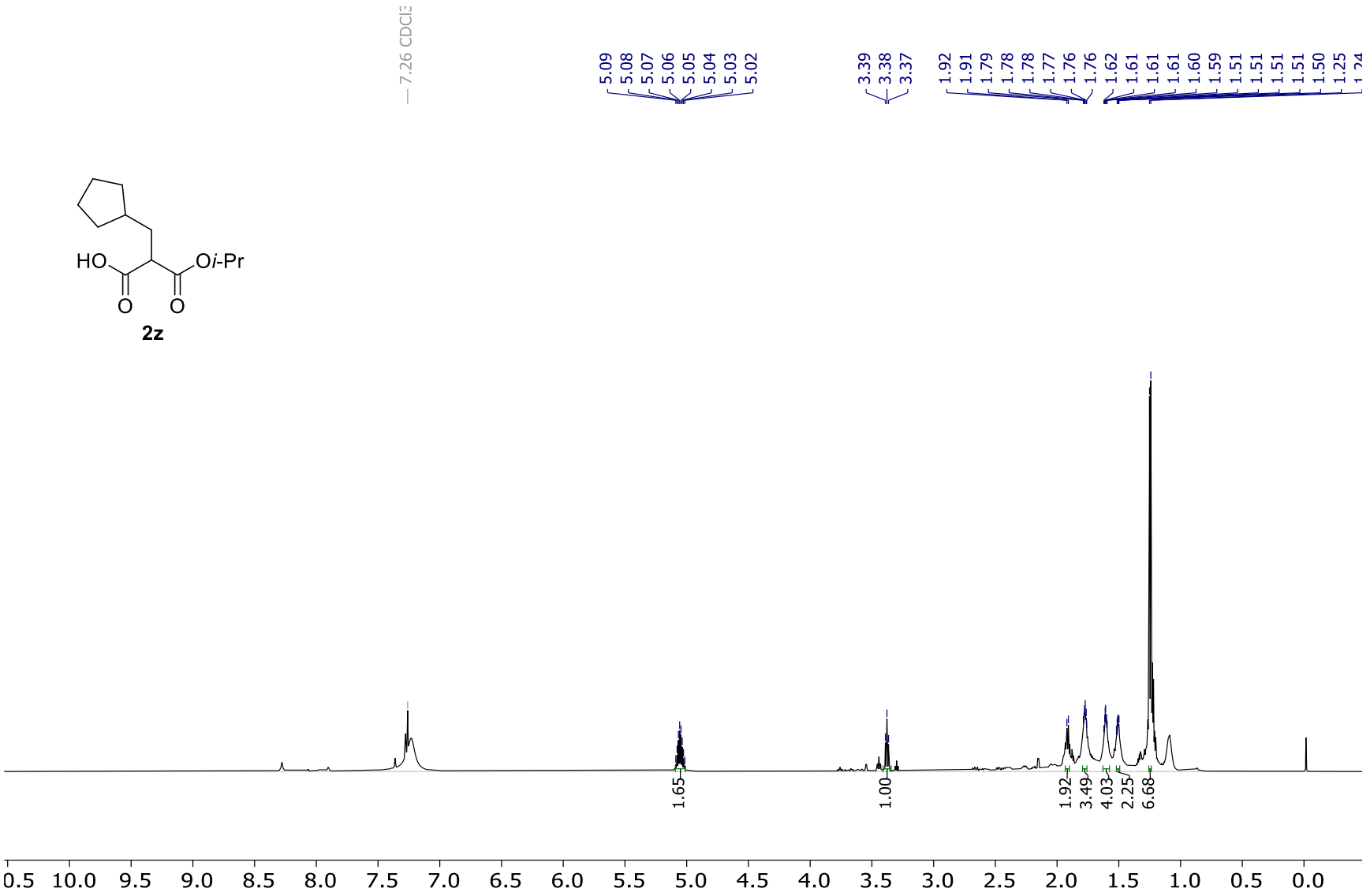

173.2
168.7
151.2
142.0
110.5
107.1
77.2 CDCl3
70.2
50.8
27.6
27.6
21.6
HO
O
Oi-Pr
O
O
2x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

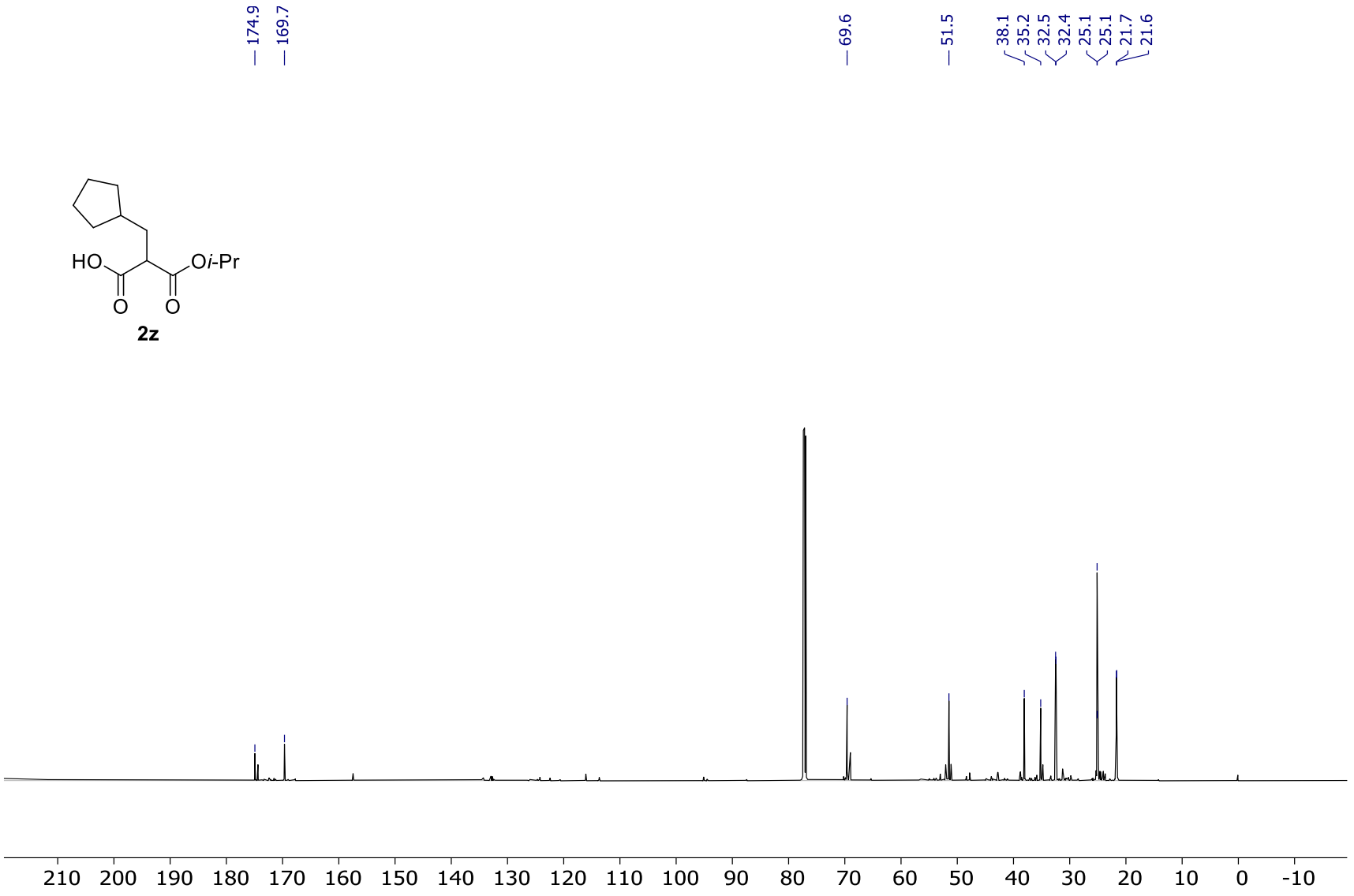
^{1}H &^{13}C NMR($CDCl_3$) of **2y**


7.26 CDCl3
5.07 5.07 5.06 5.06 5.06 5.05 3.46 3.45 3.45 3.45 3.44 1.83 1.82 1.82 1.81 1.81 1.80 1.80 1.80 1.79 1.79 1.79 1.79 1.78 1.78 1.78 1.77 1.76 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.68 1.67 1.64 1.64 1.25 1.24 1.21 1.21 1.21 1.20 1.20 1.19 1.18 1.16 1.14 1.13 0.91 0.91 0.91 0.90 0.90 0.90 0.89 0.89 0.88 0.88
HO
O
O
O*i*-Pr
2y
0.97
1.00
1.02
3.01
3.90
1.06
6.53
3.37
2.10
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.

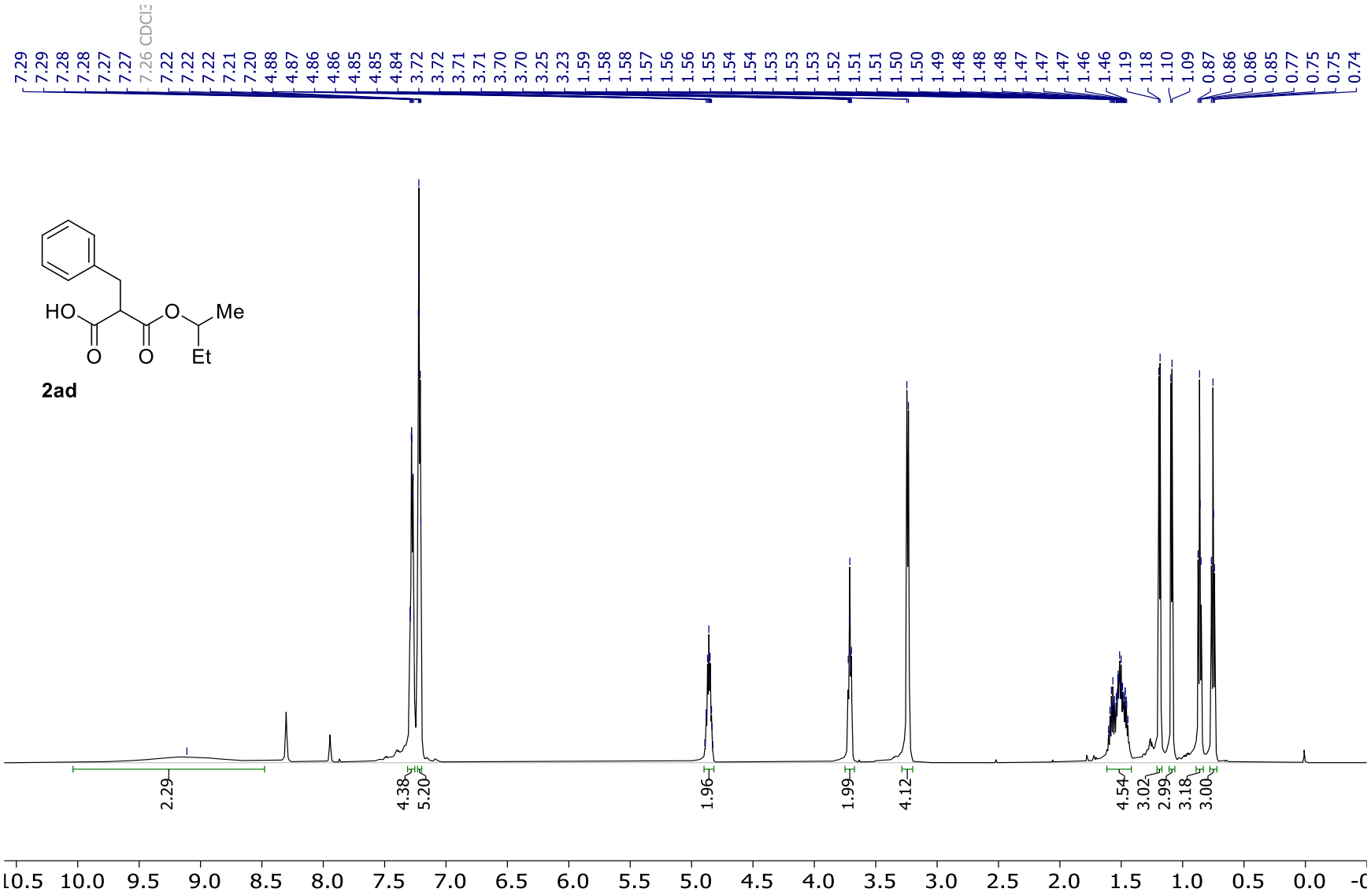


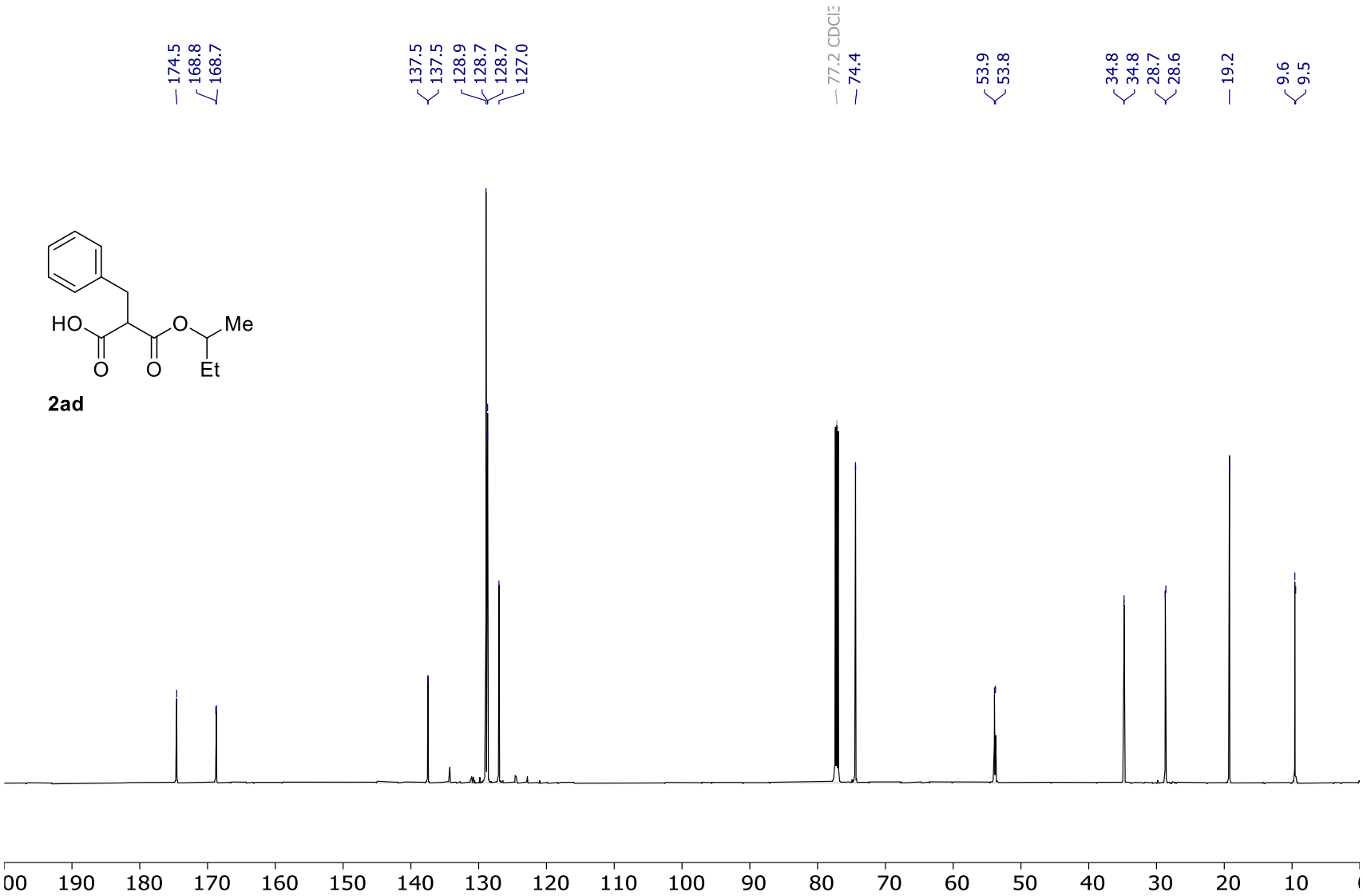
^{1}H &^{13}C NMR($CDCl_3$) of **2z**


7.26 CDCl3
5.09
5.08
5.07
5.06
5.05
5.04
5.03
5.02
3.39
3.38
3.37
1.92
1.91
1.79
1.78
1.78
1.77
1.76
1.76
1.62
1.61
1.61
1.61
1.60
1.59
1.51
1.51
1.51
1.51
1.50
1.25
HO
O
O
Oi-Pr
2z
1.65
1.00
1.92
3.49
4.03
2.25
6.68
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

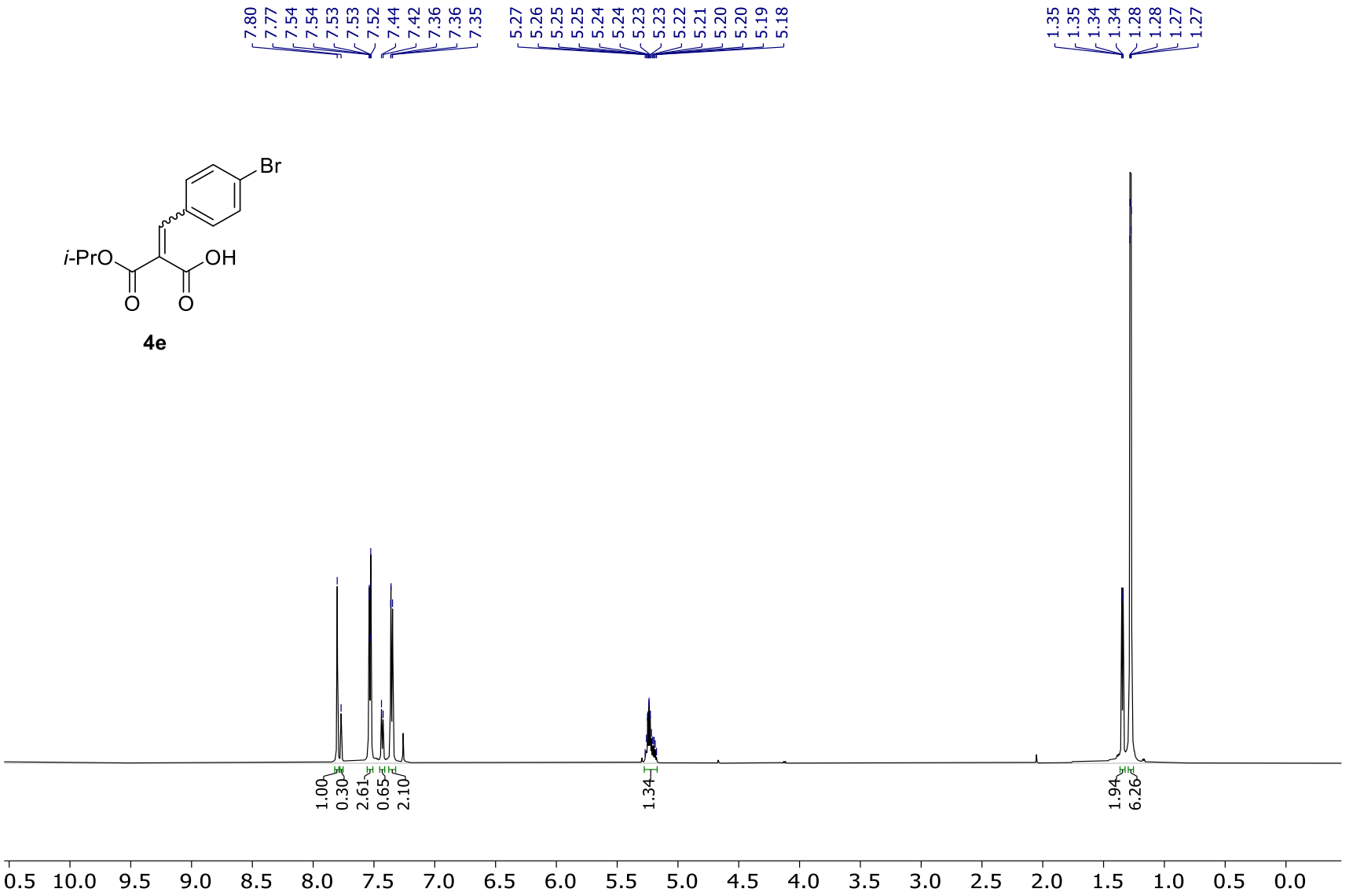

174.9
169.7
69.6
51.5
38.1
35.2
32.5
32.4
25.1
25.1
21.7
21.6
HO
O
O
O*i*-Pr
O
2z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

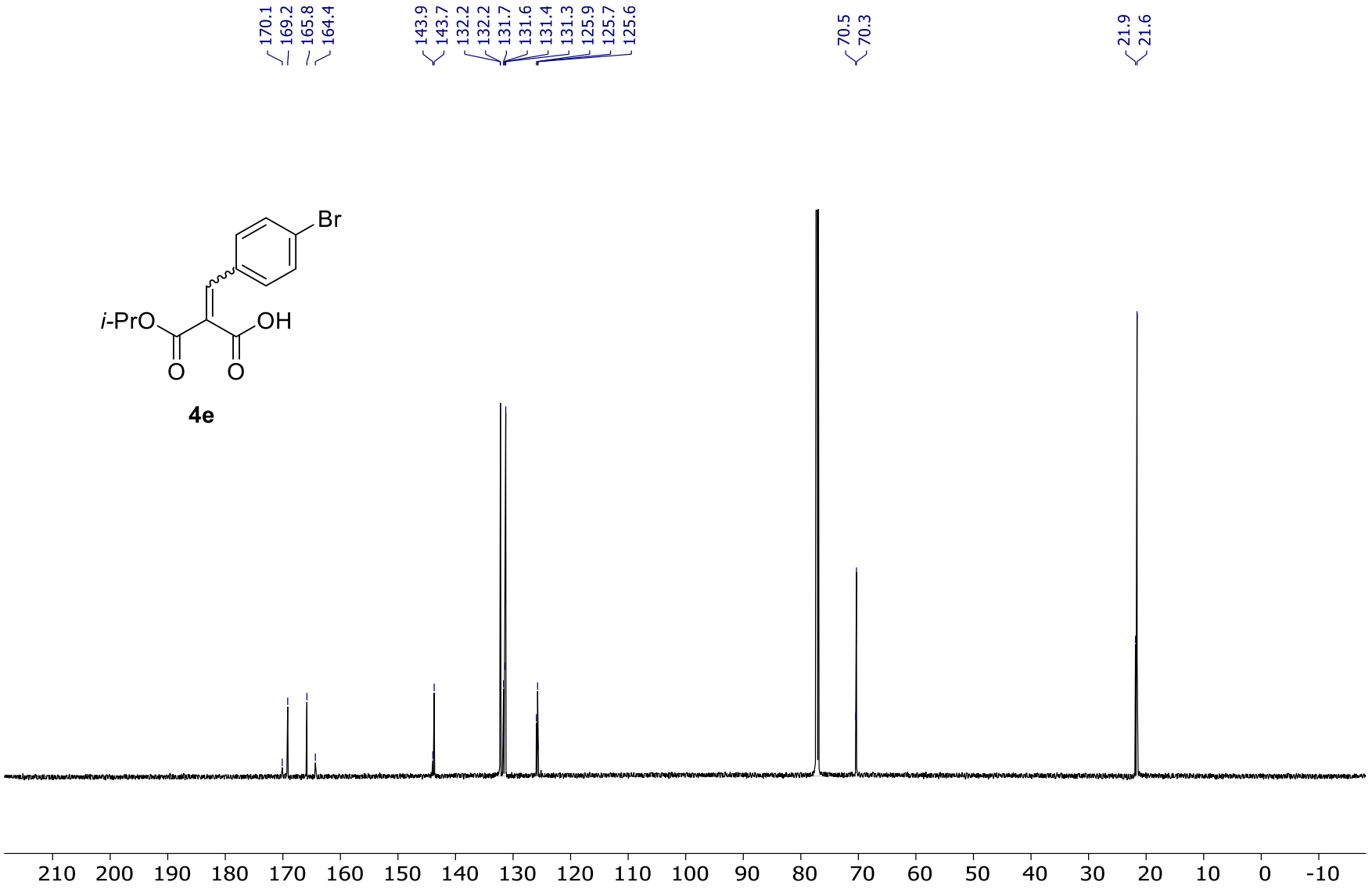
^{1}H &^{13}C NMR($CDCl_3$) of **2ad**



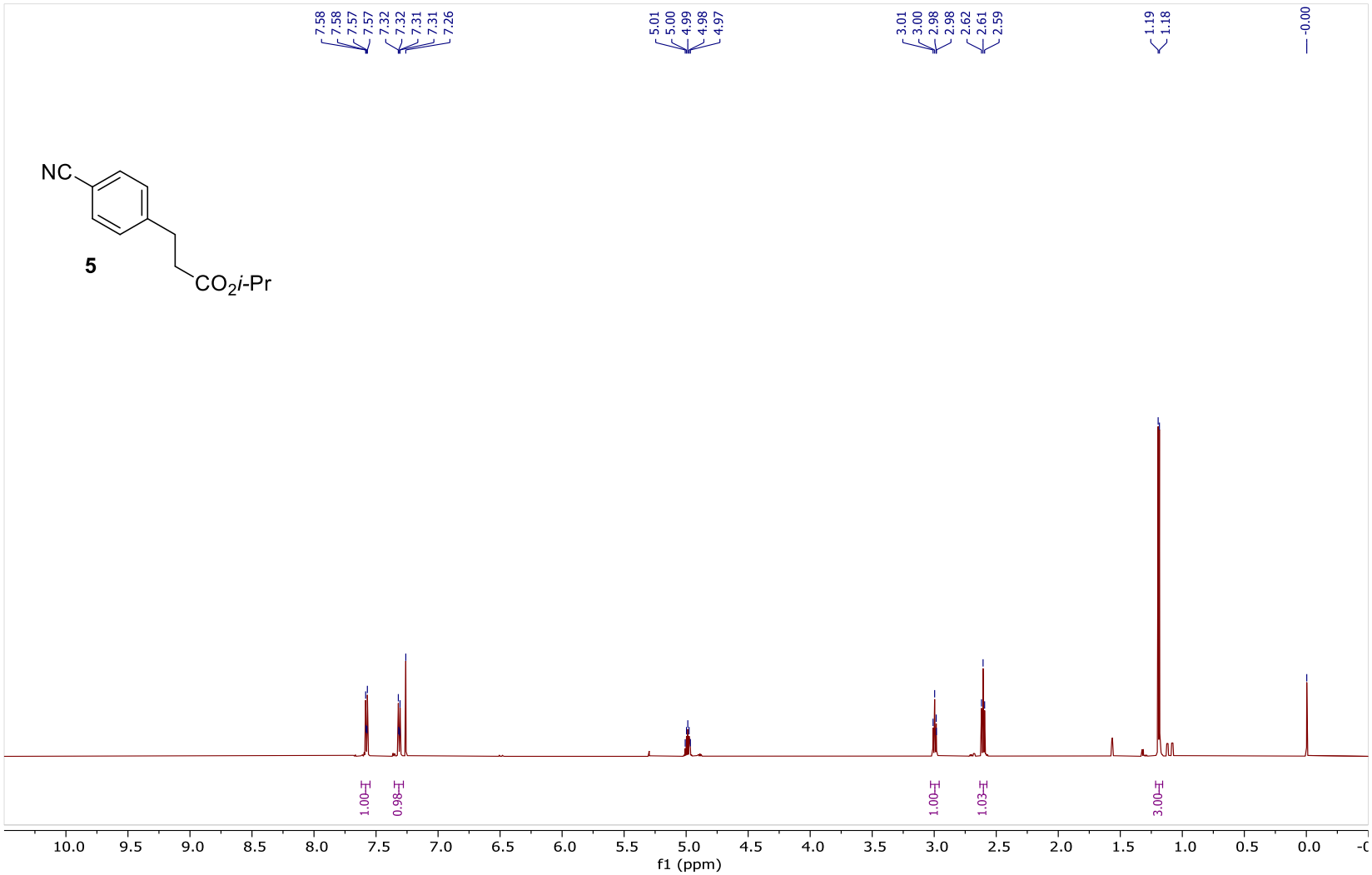

174.5
168.8
168.7
137.5
137.5
128.9
128.7
128.7
127.0
77.2 CDCl3
74.4
53.9
53.8
34.8
34.8
28.7
28.6
19.2
9.6
9.5
HO
O
O
O
Et
Me
2ad
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

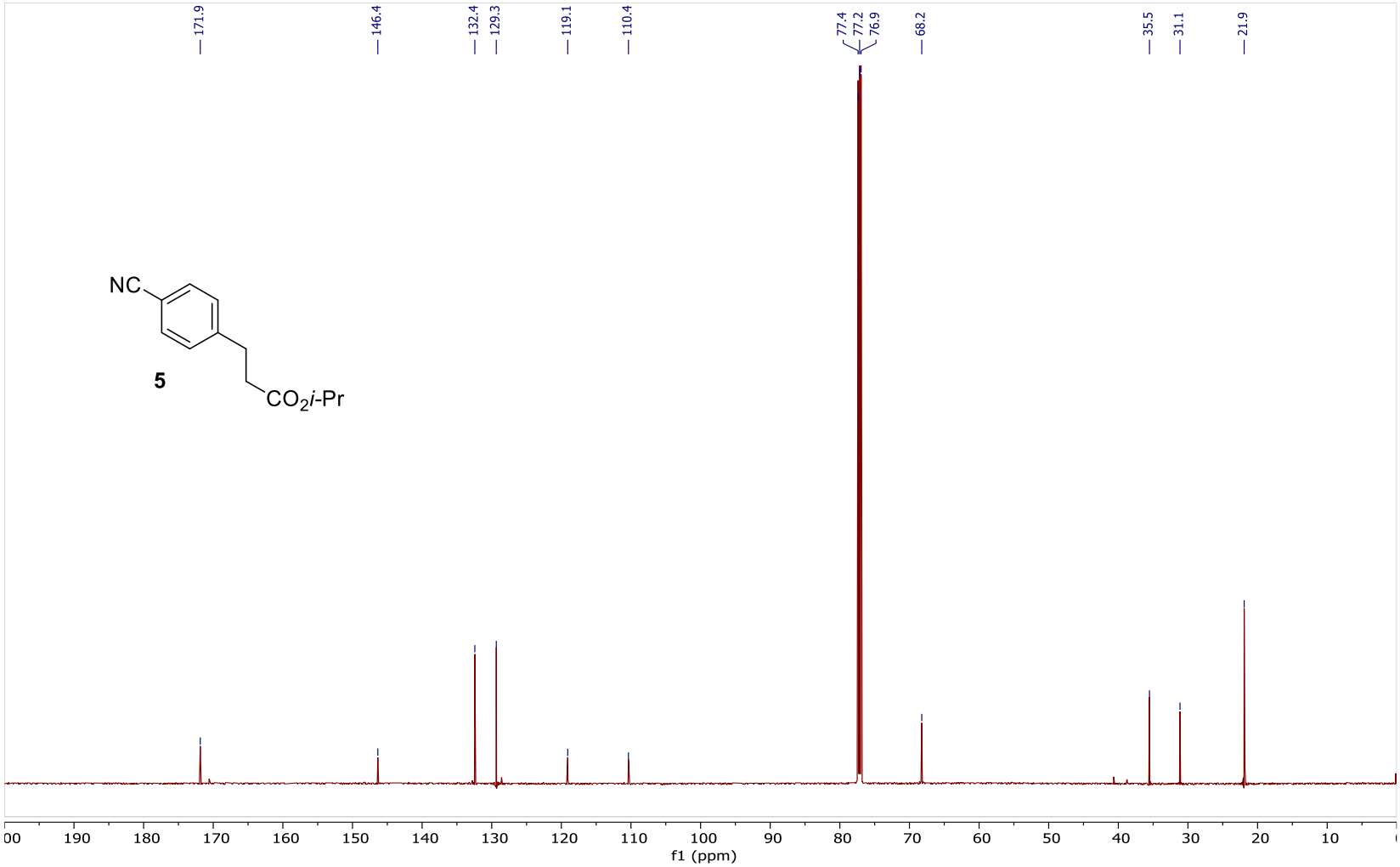
^{1}H, ^{13}C NMR($CDCl_3$) of **4e**

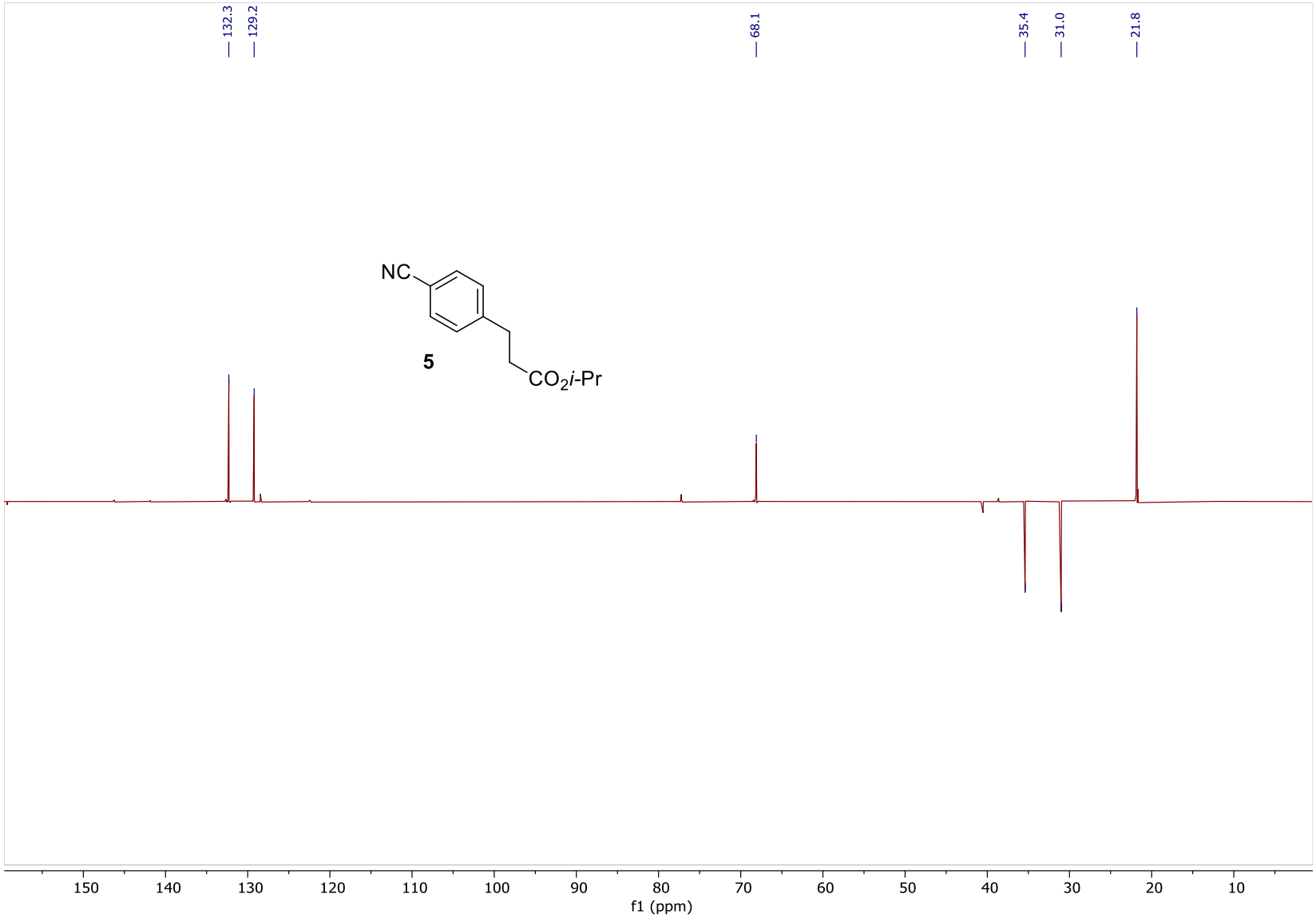



170.1
169.2
165.8
164.4
143.9
143.7
132.2
132.2
131.7
131.6
131.4
131.3
125.9
125.7
125.6
70.5
70.3
21.9
21.6
Br
i-PrO
OH
O
O
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

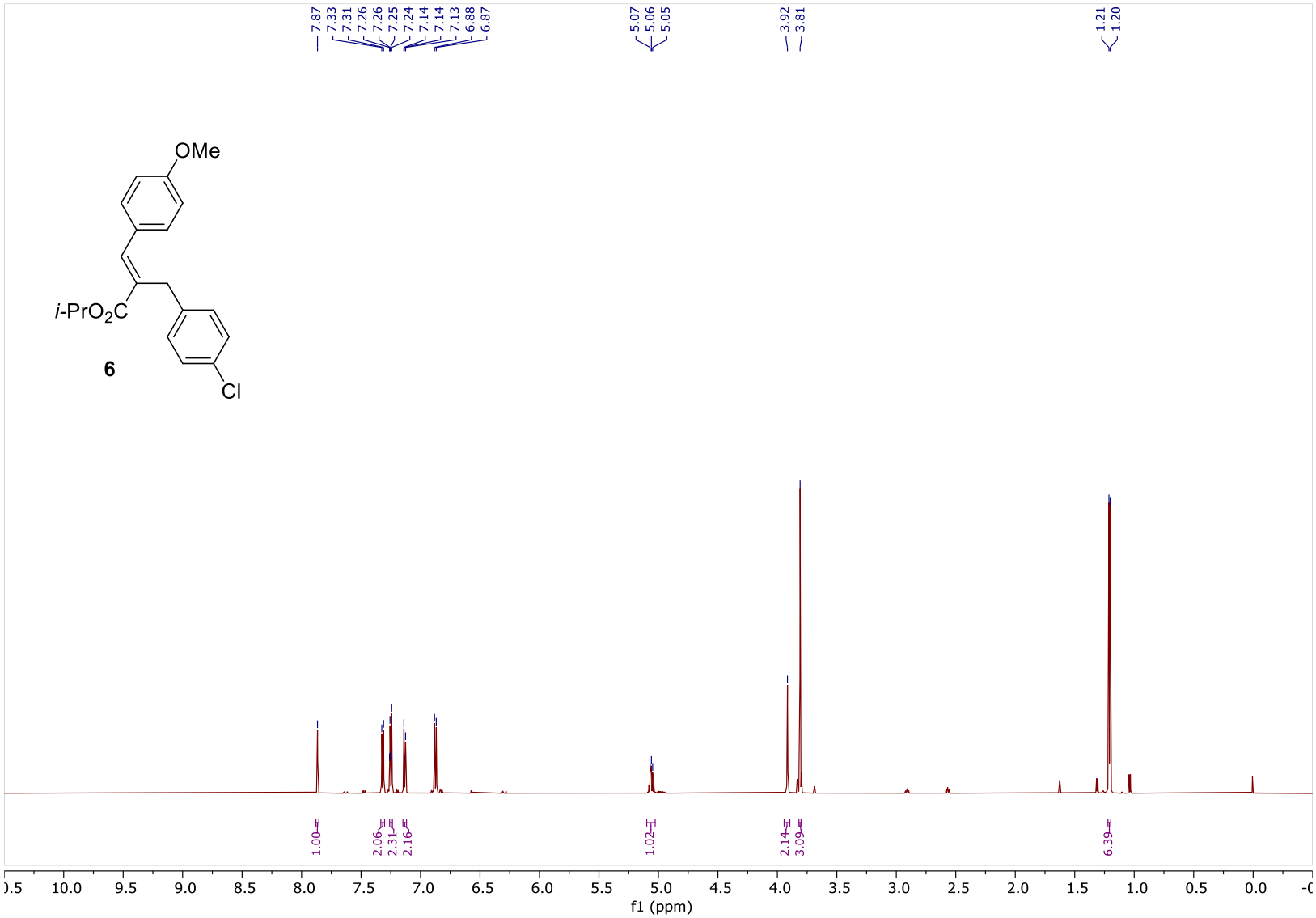
^{1}H, ^{13}C, DEPT-135 Spectra of **5**

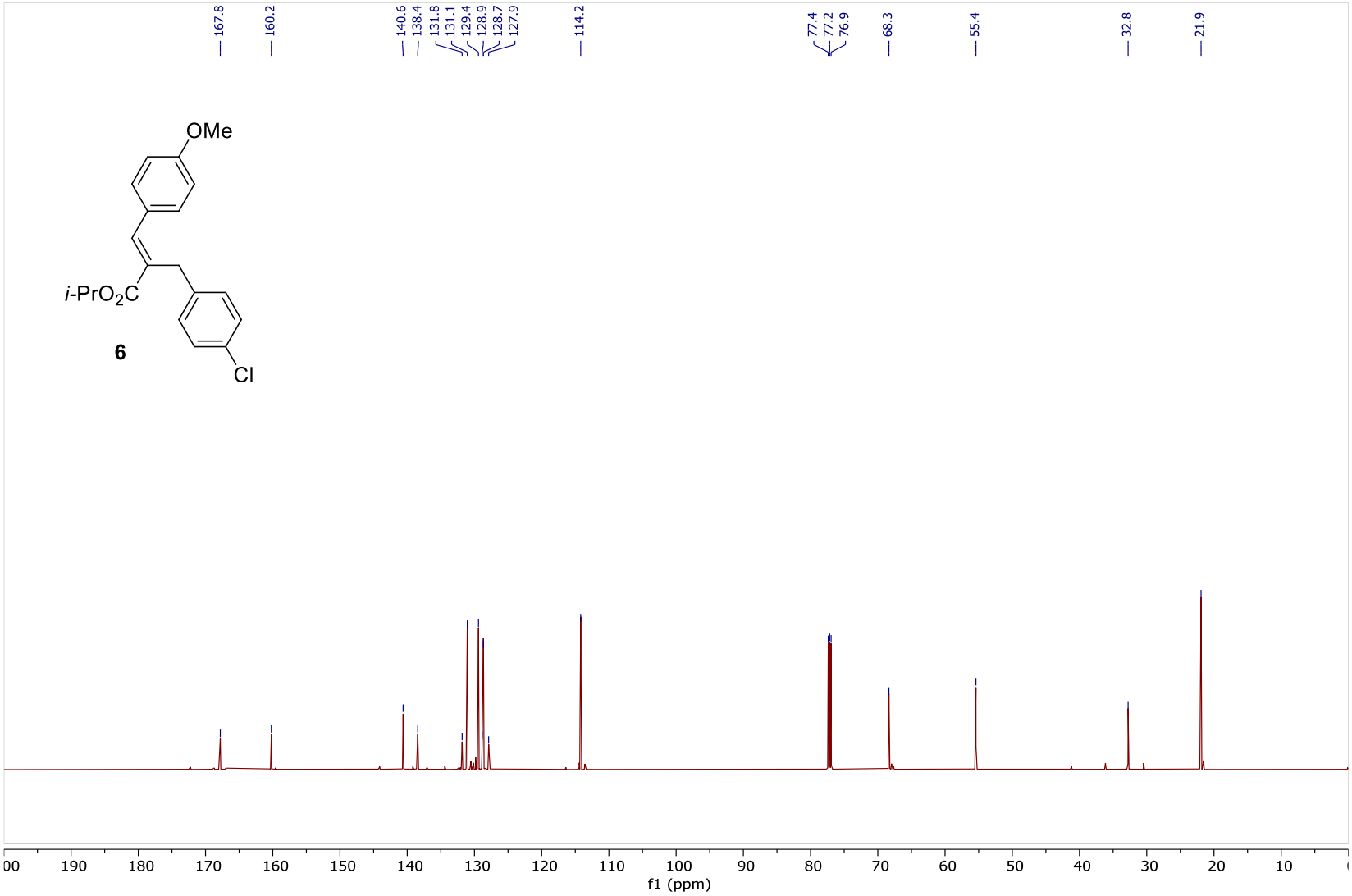


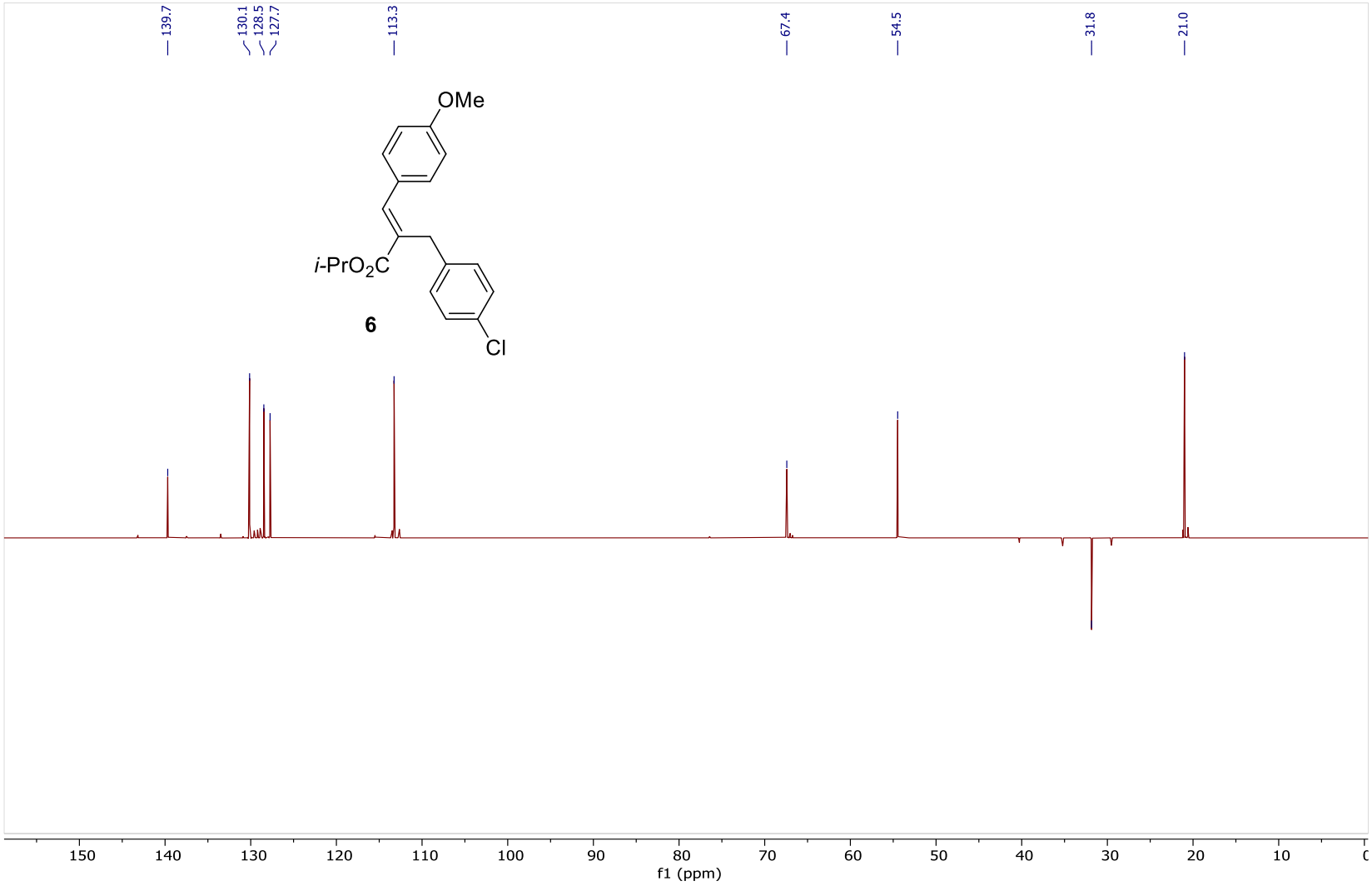

171.9
146.4
132.4
129.3
119.1
110.4
77.4
77.2
76.9
68.2
35.5
31.1
21.9
NC
5
CO2i-Pr
f1 (ppm)

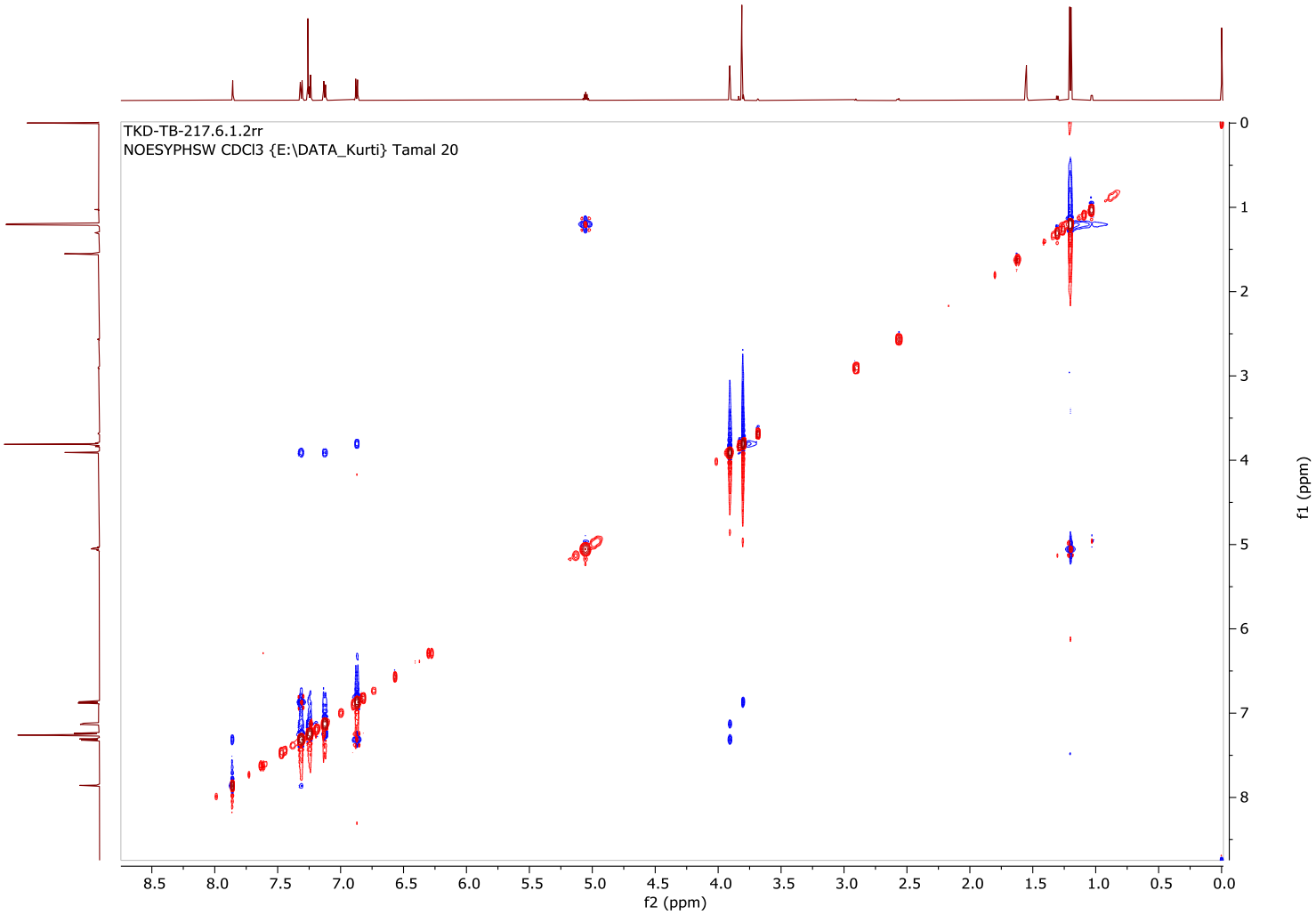

132.3
129.2
68.1
35.4
31.0
21.8
NC
5
CO2i-Pr
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H, ^{13}C, DEPT-135 & NOESY NMR of **6**

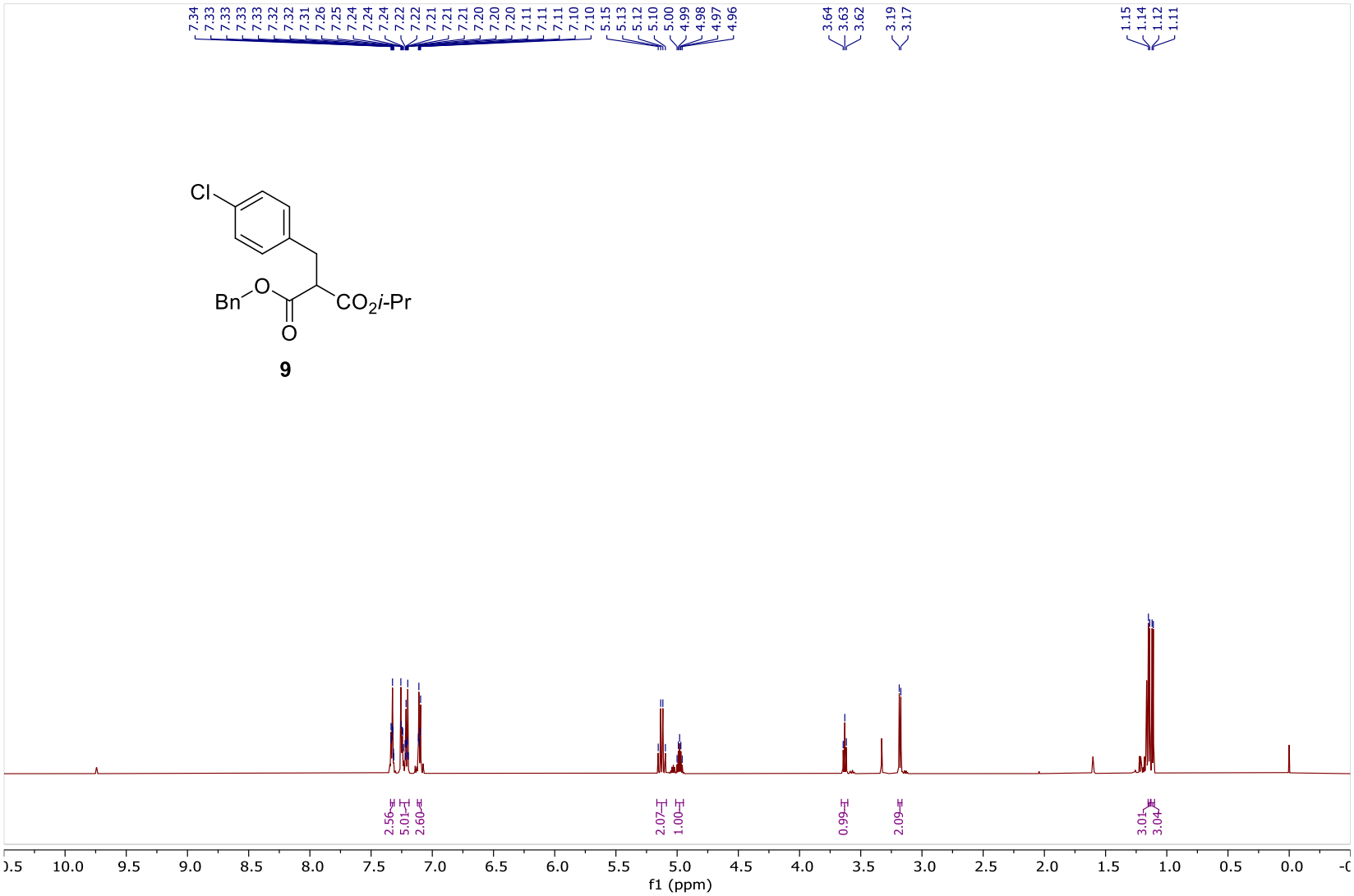


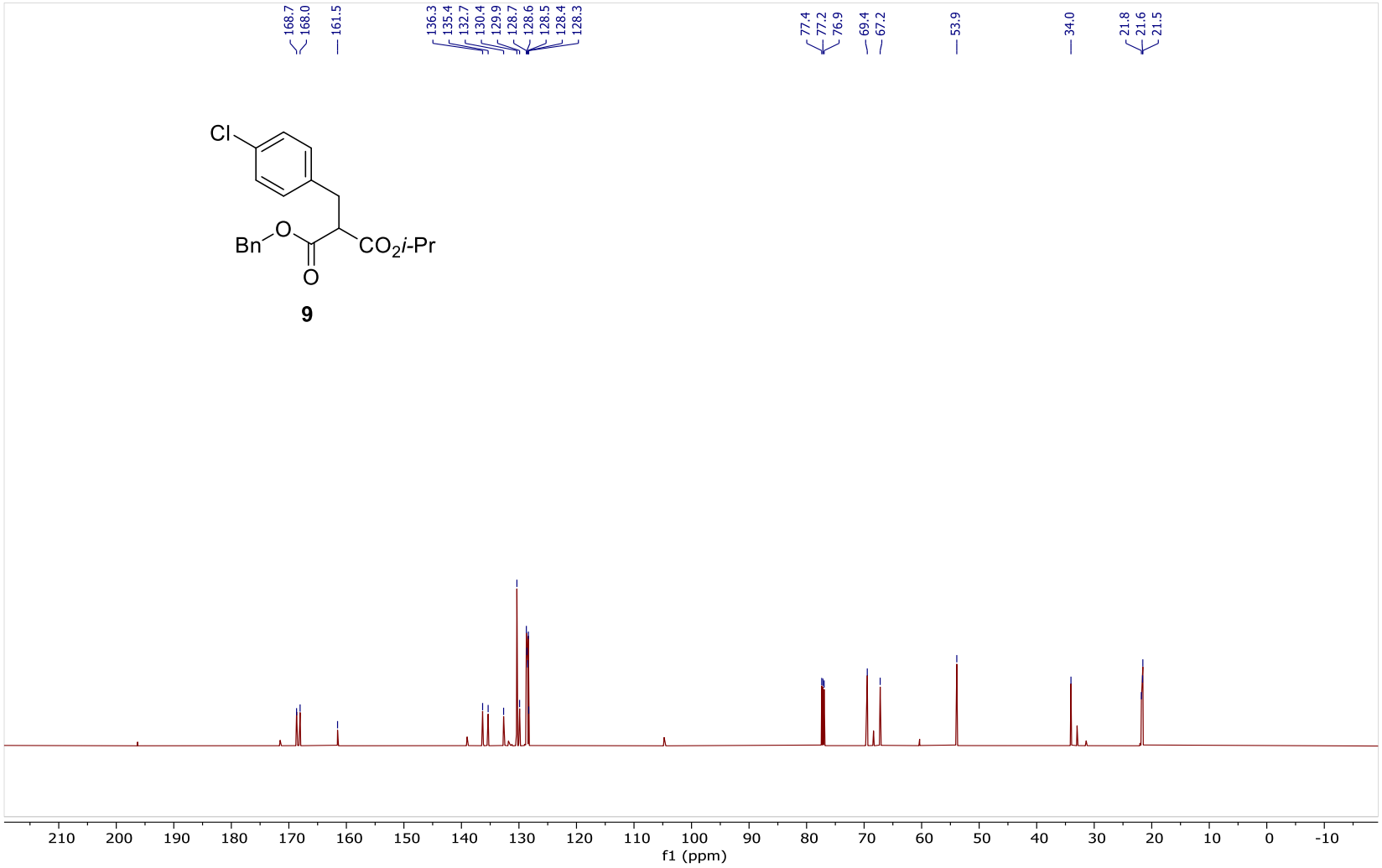

167.8
160.2
140.6
138.4
131.8
131.1
129.4
128.9
128.7
127.9
114.2
77.4
77.2
76.9
68.3
55.4
32.8
21.9
OMe
i-PrO2C
6
Cl
f1 (ppm)

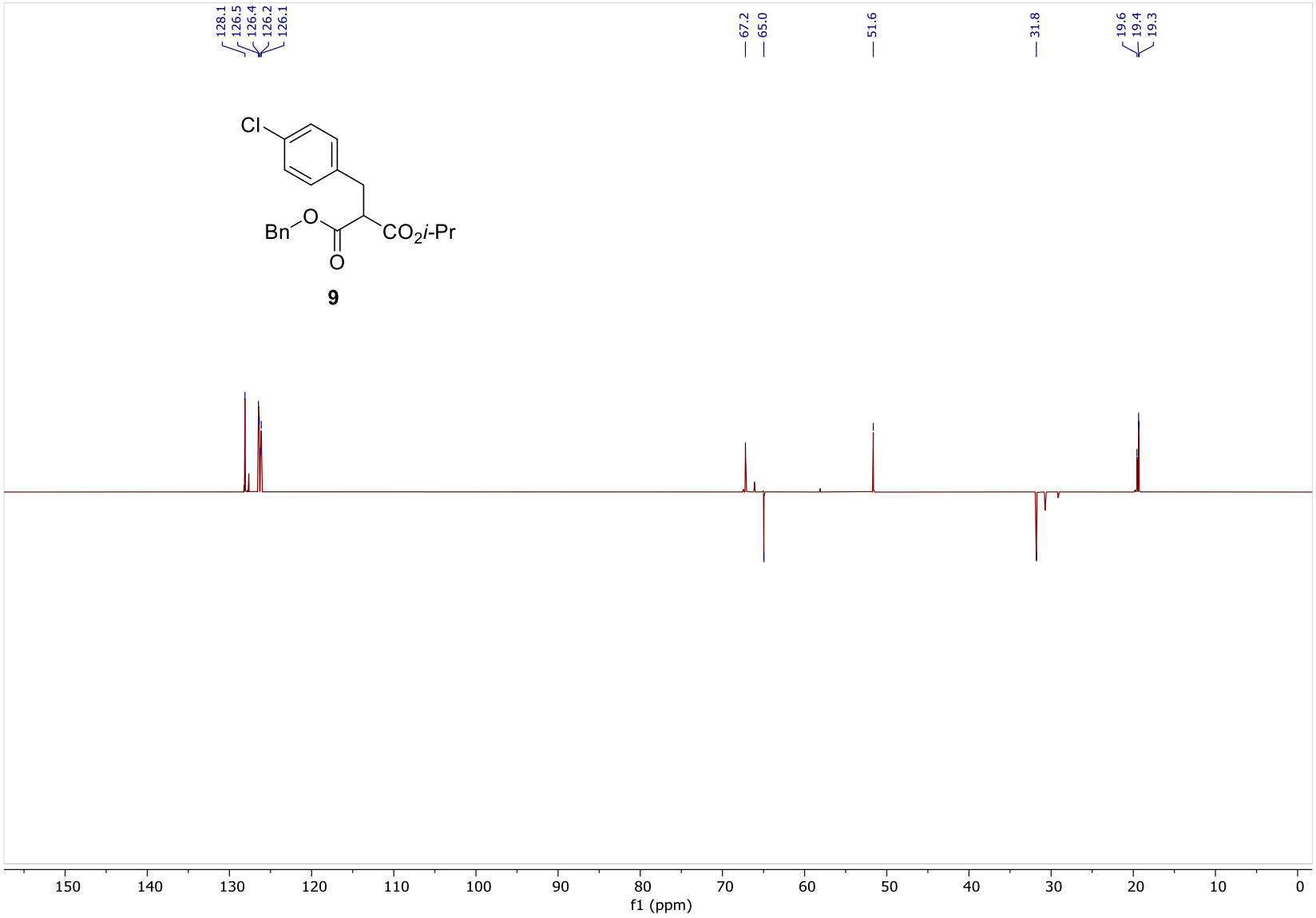

139.7
130.1
128.5
127.7
113.3
67.4
54.5
31.8
21.0
OMe
i-PrO2C
6
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TKD-TB-217.6.1.2rr
NOESYPHSW CDCl3 {E:\DATA_Kurti} Tamal 20
f2 (ppm)
f1 (ppm)

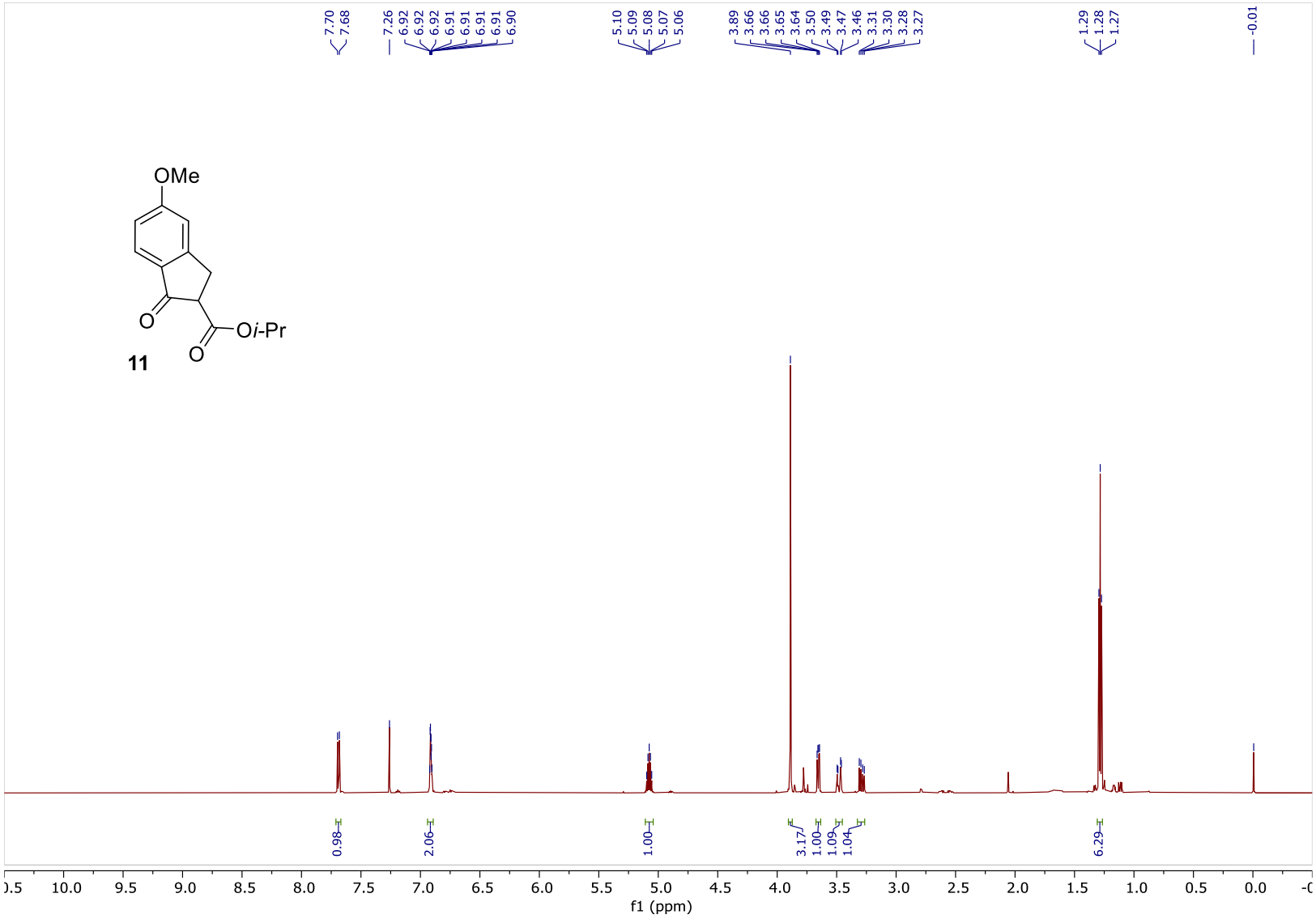
^{1}H,^{13}C, DEPT-135 Spectra of **9**

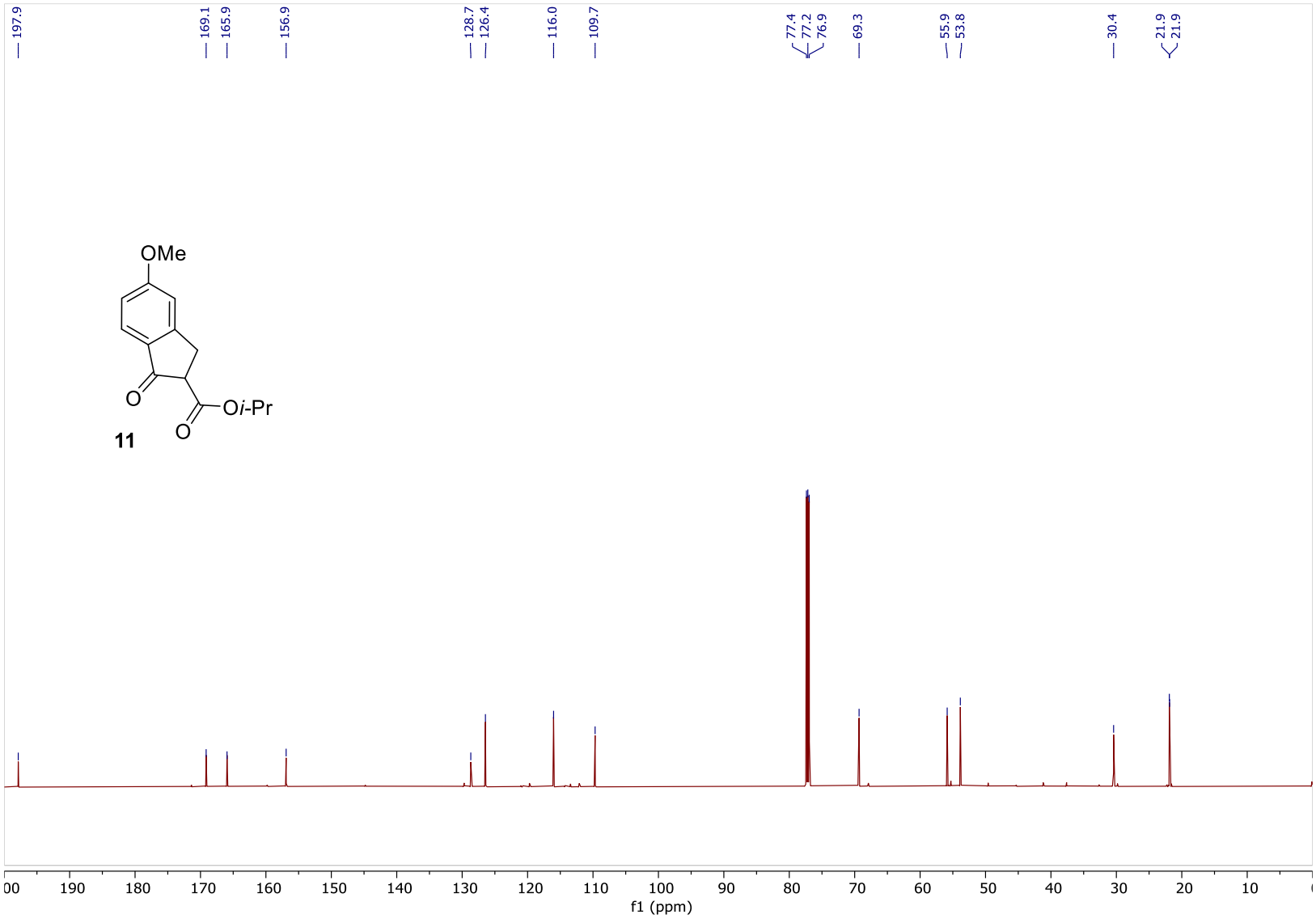


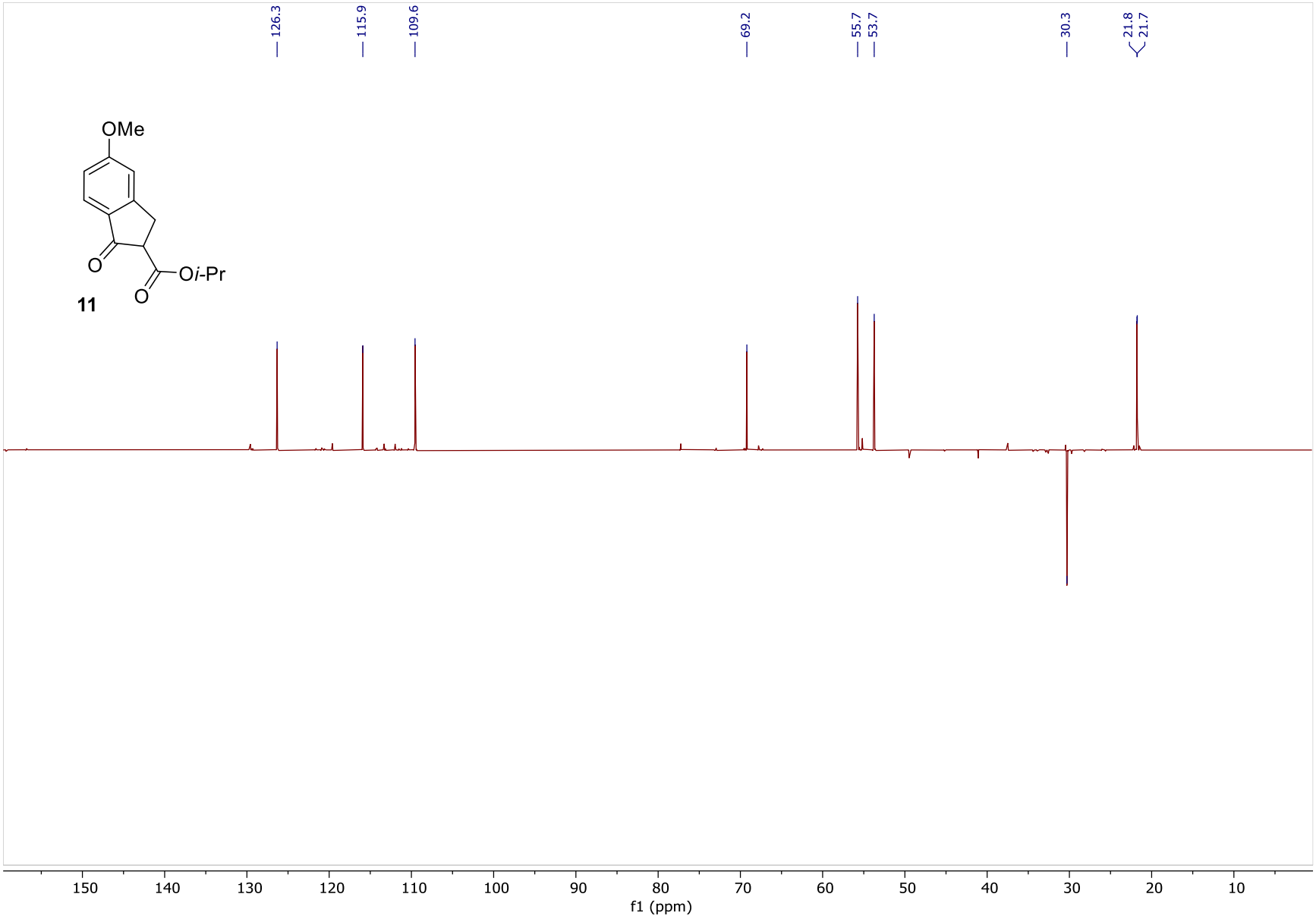

168.7
168.0
161.5
136.3
135.4
132.7
130.4
129.9
128.7
128.6
128.5
128.4
128.3
77.4
77.2
76.9
69.4
67.2
53.9
34.0
21.8
21.6
21.5
Cl
Bn
O
O
CO2i-Pr
O
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


128.1
126.5
126.4
126.2
126.1
67.2
65.0
51.6
31.8
19.6
19.4
19.3
Cl
Bn
O
O
CO2i-Pr
O
9
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H and ^{13}C Spectra of **11**




197.9
169.1
165.9
156.9
128.7
126.4
116.0
109.7
77.4
77.2
76.9
69.3
55.9
53.8
30.4
21.9
21.9
OMe
O
O
O*i*-Pr
11
f1 (ppm)


126.3
115.9
109.6
69.2
55.7
53.7
30.3
21.8
21.7
OMe
O
O
O*i*-Pr
11
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)