Electronic Supplementary Information (ESI)
for

Regioselectivity Inversion Tuned by Iron(III) Salts in Palladium-Catalyzed Carbonylations

Zijun Huang,[a, b] Yazhe Cheng,[a] Xipeng Chen,[a] Hui-Fang Wang,*[, c] Chen-Xia Du,[d] and Yuehui Li*[, a]

[a]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P. R. China
[b]University of Chinese Academy of Sciences, Beijing 100049, P. R. China.
[c]State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China
[d]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China
E-mail: H.-F. Wang (wanghf@suda.edu.cn) or Y.Li (yhli@licp.cas.cn).

Supporting Information

1. General information

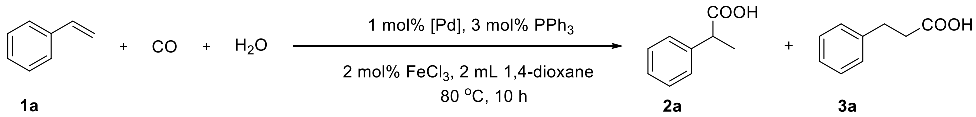
Unless otherwise stated, all the materials were purchased from commercial suppliers and were used as received. CO (99.95%) was purchased from Messer (Wujiang, China), the grade of ^{13}CO (99%, 99 atom % ^{13}C) is Sigmal (USA). Solvents were dried by solvent purification system from LC Technology Solution Inc. Flash chromatography was performed on silica gel. The products were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS spectroscopy. All ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer and Agilent 600 MHz spectrometer. The NMR chemical shift values refer to $CDCl_3$ (δ (^{1}H), 7.26 ppm; δ (^{13}C), 77.16 ppm), DMSO-d_6 (δ (^{1}H), 2.50 ppm; δ (^{13}C), 39.52 ppm), THF-d_8 (δ (^{1}H), 1.72 ppm; δ (^{13}C), 25.31 ppm). GC-MS data were obtained Shaimadzu GCMS-QP2010 SE, GC data were obtained Shaimadzu GC-2010 Plus, HRMS data were obtained on Agilent 6530 spectrometer. UV-Vis spectroscopic date were obtained Shaimadzu UV-2600. All measurements were carried out at room temperature unless otherwise stated.

2. Screening of the reaction conditions

General Procedure: The [Pd] source, ligand (PPh_3), additive, solvent (2 mL), **1a** (104 mg, 1.0 mmol) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O with syringe under nitrogen atmosphere. The vial was placed in an alloyed plate, which was then transferred into an autoclave (250 mL) under nitrogen flow. Then, the autoclave was flushed with CO gas for three times and pressurized with CO gas to 50 bar. The reaction was performed at 80 °C for 10 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then, dodecane (20 mg) and 2,6-dimethybenzoic acid (15 mg) were added into the vial. Conversion was determined by GC using dodecane as an internal standard. The yield and regioselectivity were measured by ^{1}H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard.

Firstly, different palladium sources were screened in the presence of PPh_3 and $FeCl_3$ for hydroxycarbonylation of styrene, (Table S1).

Table S1 Investigation of different palladium sources on catalytic hydroxycarbonylation of **1a**[a]

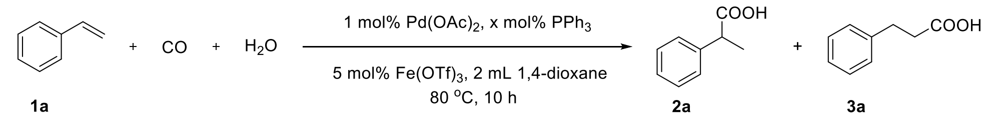


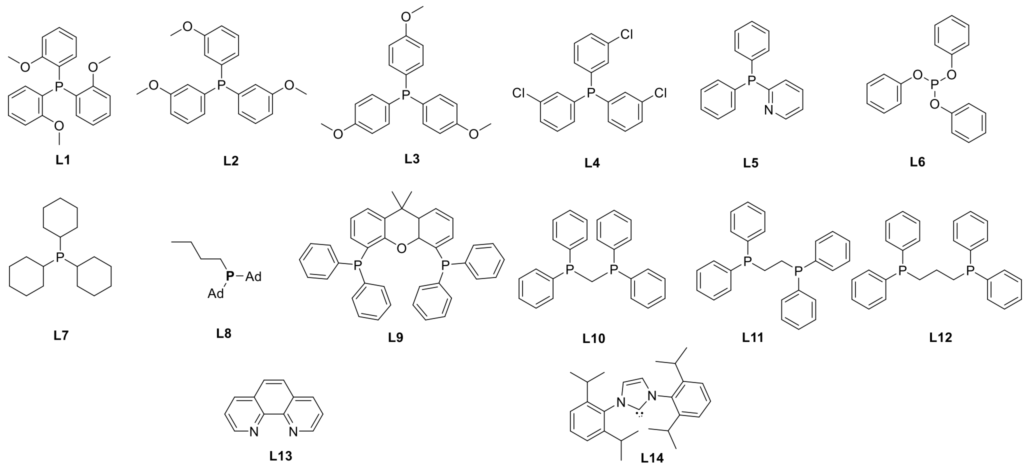
Entry	Catalyst/x mol%	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	$Pd(OAc)_2$/1	100	96 (91)[d]	>99/1
2	-	43	0	-
3	$Pd(CF_3COO)_2$/1	79	67	96/4
4	$Pd(acac)_2$/1	58	58	98/2
5	$PdCl_2$/1	100	99	99/1
6	$PdBr_2$/1	30	26	89/11
7	$PdCl_2(PPh_3)_2$/1	100	97	99/1
8	$Pd(CH_3CN)_4(OTf)_2$/1	93	87	97/3
9	$Pd(PPh_3)_4$/1	58	57	97/3

[a] Reaction conditions: **1a** (1.0 mmol), CO (50 bar), H_2O (2.0 mmol), [Pd] source (0.01 mmol), 1,4-dioxane (2.0 mL), 80 °C, 10 h. [b] Conversion was determined by GC using dodecane as an internal standard. [c] Yield and ratio of *iso*/*n* was determined by ^{1}H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d] Isolated yield. acac = 2,4-pentanedionato-O,O'. PPh_3 = triphenylphosphine. OTf = triflate.

Different regioselectivity was observed when changing the amounts of ligands (Table S2) or using different type of ligands.

Table S2 Ligand effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]



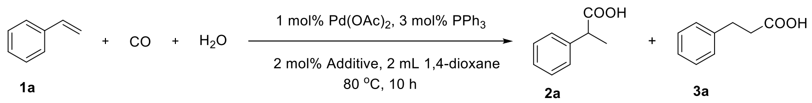


Entry	Ligand/x mol%	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	0	41	0	-
2	**PPh_3/2**	**100**	**78**	**99/1**
3	**PPh_3/3**	**100**	**96 (91)**[d]	**>99/1**
4	**PPh_3/6**	**78**	**68**	**92/8**
5	**L1**/3	56	39	99/1
6	**L2**/3	100	90	99/1
7	**L3**/3	99	96	98/2
8	**L4**/3	100	95	>99/1
9	**L5**/3	68	58	90/10
10	**L6**/3	57	11	>99/1
11	**L7**/3	42	12	>99/1
12	**L8**/3	13	4	>99/1
13	**L9**/1.5	87	79	55/45
14	**L10**/1.5	30	6	99/1
15	**L11**/1.5	33	19	67/33
16	**L12**/1.5	13	6	67/33
17	**L13**/1.5	18	6	75/25
18	**L14**/1.5	16	0	-

[a]Reaction conditions: **1a** (1.0 mmol), CO (50 bar), H_2O (2.0 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 80 °C, 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^{1}H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]Isolated yield.

As shown in Table S3 for the hydroxycarbonylation of styrene, high *iso*-regioselectivity was observed when $FeCl_3$ or $FeBr_3$ were used as the acidic additive. And, when $Fe(OTf)_3$ was used, linear product **3a** was generated as the major product (59% selectivity).

Table S3 Additive effect on Pd-catalyzed hydroxycarbonylation of **1a**.[a]

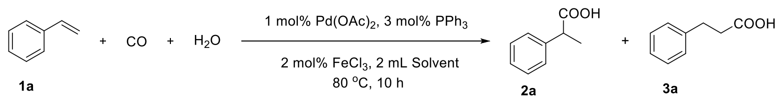


Entry	Additive/x mol%	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	**$FeCl_3$/2**	**100**	**96 (91)[d]**	**>99/1**
2	-	5	0	-
3	FeF_3/2	5	trace	-
4	**$FeBr_3$/2**	**85**	**67**	**96/4**
5	$FeCl_2$/2	5	0	-
6	**$Fe(OTf)_3$/2**	**28**	**27**	**41/59**
7	$Fe(OAc)_3$/2	5	trace	-
8[e]	$Fe(NTf)_3$ /2	5	0	-
9	$Fe_3(CO)_{12}$/2	4	0	-
10	Iron(III) citrate/2	3	0	-
11	Fe_3O_4/2	3	0	-
12	$Fe(NO_3)_3$/2	21	trace	-
13	$Fe(acac)_3$/2	4	0	-
14	LiCl/2	4	0	-
15	$MgCl_2$/2	11	trace	-
16	$CaCl_2$/2	5	trace	-
17	$ZnCl_2$/2	67	10	84/16
18	$CuCl_2$/2	100	35	>99/1
19	$NaSbF_6$/2	27	0	-
20	$(C_6F_5)_3B$/2	80	15	73/27
21	$AlCl_3$/2	100	79	99/1
22[f]	$Al(NTf)_3$/2	100	100	63/37
23	37% HCl/2	92	91	99/1
24	PTSA/2	19	trace	-
25	PTSA/2, LiCl/2	3	0	-
26[g]	$AgBF_4$/2	98	55	99/1
27[g]	$AgSbF_6$/2	18	trace	-
28[g, e]	$AgBF_4$/2	88	25	84/16
29[g, e]	$AgSbF_6$/2	6	trace	6

[a]Reaction conditions: **1a** (1.0 mmmol), CO (50 bar), H_2O (2.0 mmmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 80 °C, 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]Isolated yield. [e]$Fe(NTf)_3$ made from $FeCl_3$ and $AgNTf_2$; [f]$Al(NTf)_3$ made from $AlCl_3$ and $AgNTf_2$. NTf = trifluoromethane sulfonimide. PTSA = *p*-Toluenesulfonic acid. [g]$PdCl_2$ (0.01 mmol).[e]CO (10 bar), H_2O (1.0 mmmol), 120 °C.

Amongst the screened solvents, only 1,4-dioxane or THF was appropriate to reasonable results. When toluene was used, almost no reaction occurred (Table S4, entry 2). Probably, the solubility of water in the solvent is critical for the initiation of the reaction.

Table S4 Solvent effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]

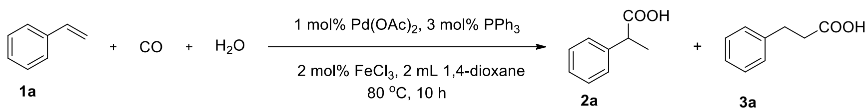


Entry	Solvent/x mL	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	1,4-dioxane/2	100	96 (91)[d]	>99/1
2	Toluene/2	35	trace	-
3	THF/2	99	76	96/4
4	CH_3CN/2	17	trace	-
5	DMF/2	15	trace	-
6	DCE/2	99	18	92/8

[a]Reaction conditions: **1a** (1.0 mmol), CO (50 bar), H_2O (2.0 mmol), $Pd(OAc)_2$ (0.01 mmol), solvent (2.0 mL), 80 °C, 10 h. [c]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]Isolated yield. THF = Tetrahydrofuran. DMF = N,N-Dimethylformamide. DCE = 1,2-Dichloroethane.

When $FeCl_3$ was used, high CO pressures are favorable. Specifically, *iso*-selectivity decreased to 58% with 1 bar of CO (Table S5, entry 4).

Table S5 Pressure effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]

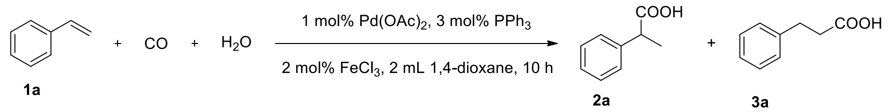


Entry	CO (bar)	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	50	100	96 (91)[d]	>99/1
2	30	99	98	93/7
3	10	62	55	93/7
4	1	14	8	58/42

[a]Reaction conditions: **1a** (1.0 mmol), CO, H_2O (2 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 80 °C, 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]Isolated yield.

When $FeCl_3$ was used, different temperature was screened, and it was found that 80 ^oC are favorable. (Table S6).

Table S6 Temperature effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]

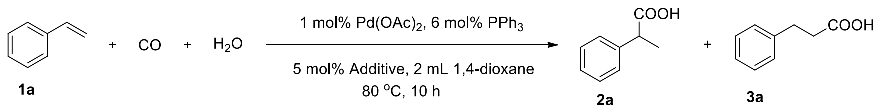


Entry	T (^oC)	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	50	40	21	>99/1
2	80	100	96 (91)[d]	>99/1
3	120	100	85	93/7

[a]Reaction conditions: **1a** (1.0 mmol), CO (50 bar), H_2O (2 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]Isolated yield.

Different metal triflates were screened, and it was found that similar regioselectivity was observed in many cases (Table S7).

Table S7 Additive effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]

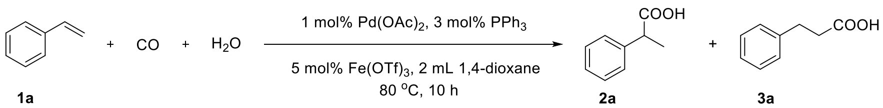


Entry	Additive/x mol%	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	$Fe(OTf)_3$/5	71	66	23/77
2	$Fe(OTf)_3$/2	28	27	41/59
3	$Zn(OTf)_2$/10	34	23	23/77
4	$Cu(OTf)_2$/10	22	11	23/77
5	LiOTf/10	19	8	44/56
6	KOTf/10	2	0	-
7	NaOTf/10	5	0	-
8	$Fe(BF_4)_2 \cdot 6H_2O$/10	6	trace	-

[a]Reaction conditions: **1a** (1.0 mmol), CO (10 bar), H_2O (2 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 80 °C, 10 h. [b]Conversion was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]**1a** (1.0 mmol), CO (10 bar), H_2O (1 mmol), $PdCl_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 120 °C, 10 h.

The highest *n*-selectivity was obtained with 10 bar of CO (71%; Table S8, entry 3). Moreover, when 6 mol% PPh_3 was used with 10 bar of CO, linear product **3a** was generated as the major product (77% selectivity; Table S8, entry 4).

Table S8 Pressure effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]

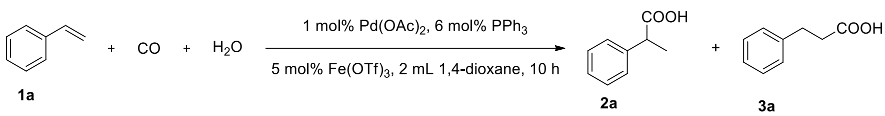


Entry	CO (bar)	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	50	70	59	33/67
2	30	68	61	33/67
3	10	61	60	29/71
4[d]	10	71	66	23/77
5	1	21	11	41/59

[a]Reaction conditions: **1a** (1.0 mmol), H_2O (2 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 80 °C, 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d]6 mol% PPh_3.

When $Fe(OTf)_3$ was used, different temperature was screened, and it was found that 120 °C are favorable (Table S9, entry2).

Table S9 Temperature effect on Pd-catalyzed hydroxycarbonylation of **1a**[a]

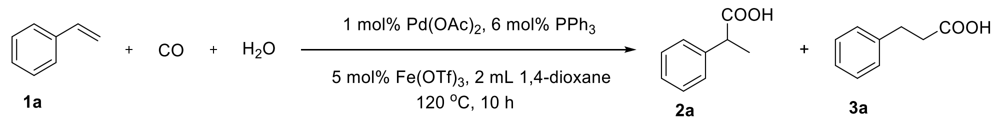


Entry	T (°C)	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	80	71	66	23/77
2	120	100	90	24/76
3	140	100	49	18/82

[a]Reaction conditions: **1a** (1.0 mmol), CO (10 bar), H_2O (2 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard.

When $Fe(OTf)_3$ was used, the highest *n*-selectivity was obtained with 1 mmol H_2O (85%; Table S10, entry1).

Table S10 Investigation of the amounts of H_2O^a

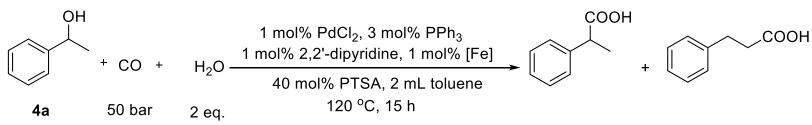


Entry	H_2O/x mmol	Conv. (%)[b]	Yield (%)[c]	*iso*/*n*[c]
1	H_2O/1	92	82(75)[d]	15/85
2	H_2O/2	100	90	24/76
3	H_2O/3	100	93	21/79

[a]Reaction conditions: **1a** (1.0 mmol), CO (10 bar), H_2O, $Pd(OAc)_2$ (0.01 mmol), 1,4-dioxane (2.0 mL), 120 °C, 10 h. [b]Conversion of **1a** was determined by GC using dodecane as an internal standard. [c]Yield and ratio of *iso*/*n* was determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [d] Isolated yield.

In carbonylation of 1-phenylethanol, it was found that the addition of PTSA is essential for the reactivity in the presence of 2,2'-dipyridine. When further adding $Fe(OTs)_3$, higher yield of 93% and *n*-selectivity of 94% were obtained (Table S11, entry 1-2). Interestingly, when $FeBr_3$ was used, the inverted *iso*-regioselectivity was obtained (87%; Table S11, entry 3).

Table S11 Palladium-catalyzed hydroxycarbonylation of alcohol[a]



Entry	Additive 1 (40 mol%)	Additive 2 (1 mol%)	Yield (%)[b]	*iso*/*n*[b]
1	PTSA	-	79	18/82
2	PTSA	$Fe(OTs)_3$	93(90)[c]	6/94
3	PTSA	$FeBr_3$	95(91)[c]	87/13
4	PTSA	$FeCl_3$	85	22/78
5	PTSA	$Fe(OTf)_3$	5	15/85
6	PTSA	$FeBr_3$ (3 mol%)	20	93/7

[a]Conditions:1 mol% $PdCl_2$, 3 mol% PPh_3, 1 mol% 2,2-dipyridyl were added into 2 mL of toluene followed by stirring at R.T. for 10 min; then **4a**, 40 mol% PTSA and Fe salts were added. [b]Yield and *iso*/*n* value were determined by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. [c]Isolated yield. OTs = tosylate.

3. Mechanism study

UV-Vis for Pd-Fe interaction study

To figure out (if there is any) the interaction of iron (III) cation with Pd center, UV-Vis spectroscopic studies were performed in water in the absence/presence of HCl or HOTf to compare the spectra between $PdCl_2$ and $FeCl_3/PdCl_2$ as long as $Pd(OTf)_2$ and $Pd(OTf)_2/Fe(OTf)_3$, respectively. Even though no clear change could be observed after the addition of $FeCl_3$ (and HCl) to the solution of $PdCl_2$ (Figure S1, left), $Fe(OTf)_3$ caused the red shift of the signal of $Pd(OTf)_2$ by 5 nm (Figure S1, right). This might be due to the fact that cationic Pd(II) center is more prone to be affected by the coordinated H_2O exposed to acidic sites of the aquo Fe(III) cations. Hence, the electronic property of Pd(II) center is influenced by Fe(III) salts in the presence of water.

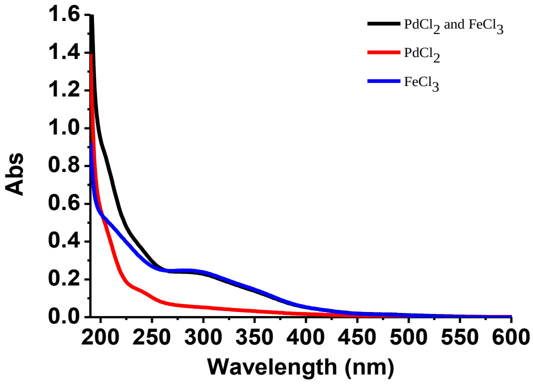


Figure S1. The interaction between $PdCl_2$ and $FeCl_3$ was studied by UV-Vis spectroscopy. UV-vis spectra of $PdCl_2$, $FeCl_3$; All spectra were measured in H_2O solutionat 25 °C and the concentrations of $PdCl_2$, $FeCl_3$ are used 0.63 mM, 63 mM, respectively.

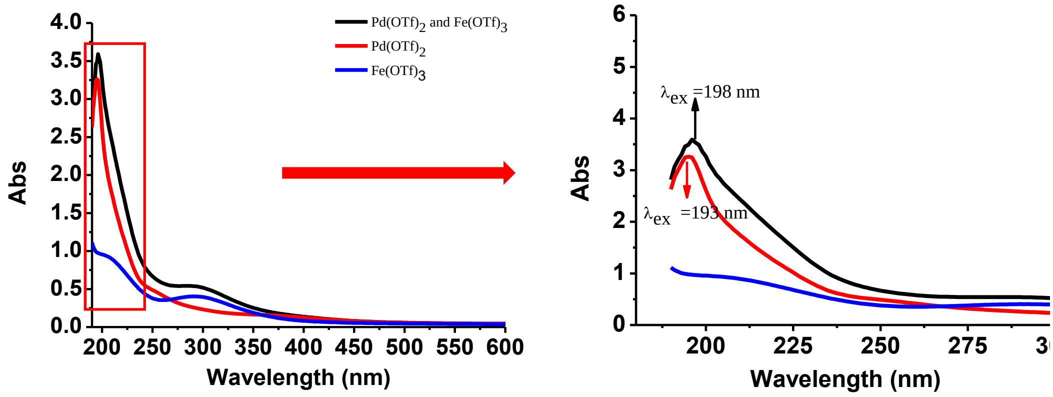
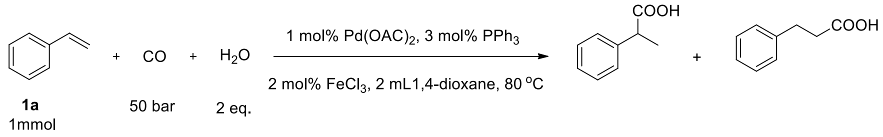


Figure S2. The interaction between $Pd(OTf)_2$ and $Fe(OTf)_3$ was studied by UV-Vis spectroscopy. UV-Vis spectra of $Pd(OTf)_2$, $Fe(OTf)_3$; All spectra were measured in H_2O solution at 25 °C and the concentrations of $Pd(OTf)_2$, $Fe(OTf)_3$ are used 1.3 mM, 0.28 mM, respectively.

Reaction profiles

Experimental procedure I: The $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), PPh_3 (0.03 mmol, 7.8 mg), $FeCl_3$(0.02 mmol, 3.2 mg, ○) or HCl (0.06 mmol, △), 1,4-dioxane (2 mL), **1a** (104 mg, 1.0 mmol), dodecane (25 mg) and a stirring bar were added into a vial (25 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (2 mmol, 36 μL) with syringe under nitrogen atmosphere. The vial was transferred into an autoclave (25 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 50 bar. The reaction was performed at 80 °C. At different time, the yield and conversion was determined by GC using dodecane as an internal standard.



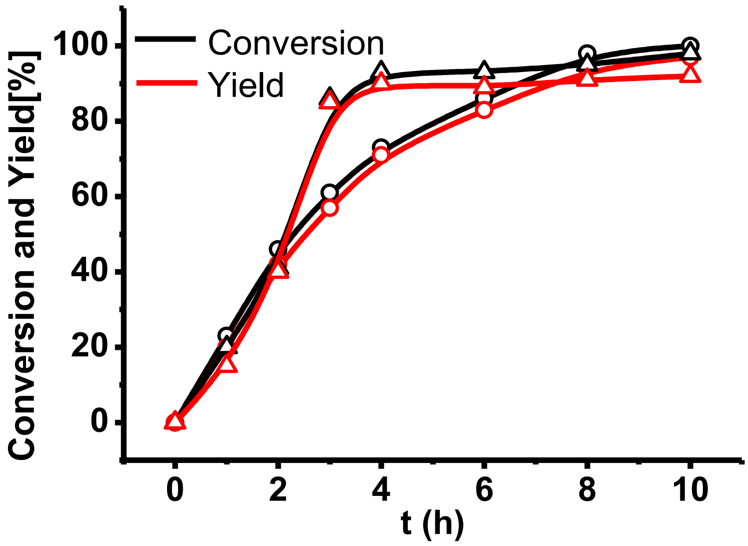


Figure S3. Kinetics of conversion and yield changes of styrene at standard condition in the presence of CO (50 bar) at different acidic additives [$FeCl_3$(0.02 mmol, 3.2 mg, ○) or HCl (0.06 mmol, △)].

Experimental procedure II**:** The $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), PPh_3 (0.06 mmol, 15.6 mg), $Fe(OTf)_3$ (0.05 mmol, 26 mg, ○) or HOTf (0.15 mmol, △), 1,4-dioxane (2 mL), **1a** (104 mg, 1.0 mmol), dodecane (25 mg) and a stirring bar were added into a vial (25 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (1 mmol, 18 μL) with syringe under nitrogen atmosphere. The vial was transferred into an autoclave (25 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 10 bar. The reaction was performed at 120 °C. At different time, the yield and conversion was determined by GC using dodecane as an internal standard.

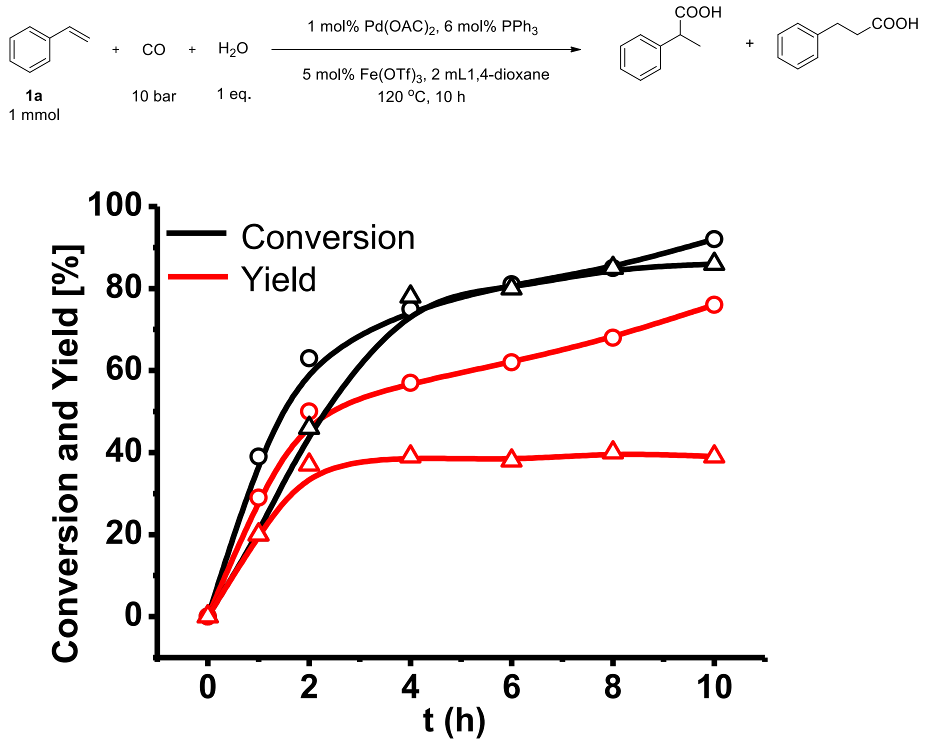


Figure S4. Kinetics of conversion and yield changes of styrene at standard condition in the presence of CO (10 bar) at different acidic additives ($Fe(OTf)_3$ (0.05 mmol, 26 mg, ○) or HOTf (0.15 mmol, △)).

***In situ* NMR study**

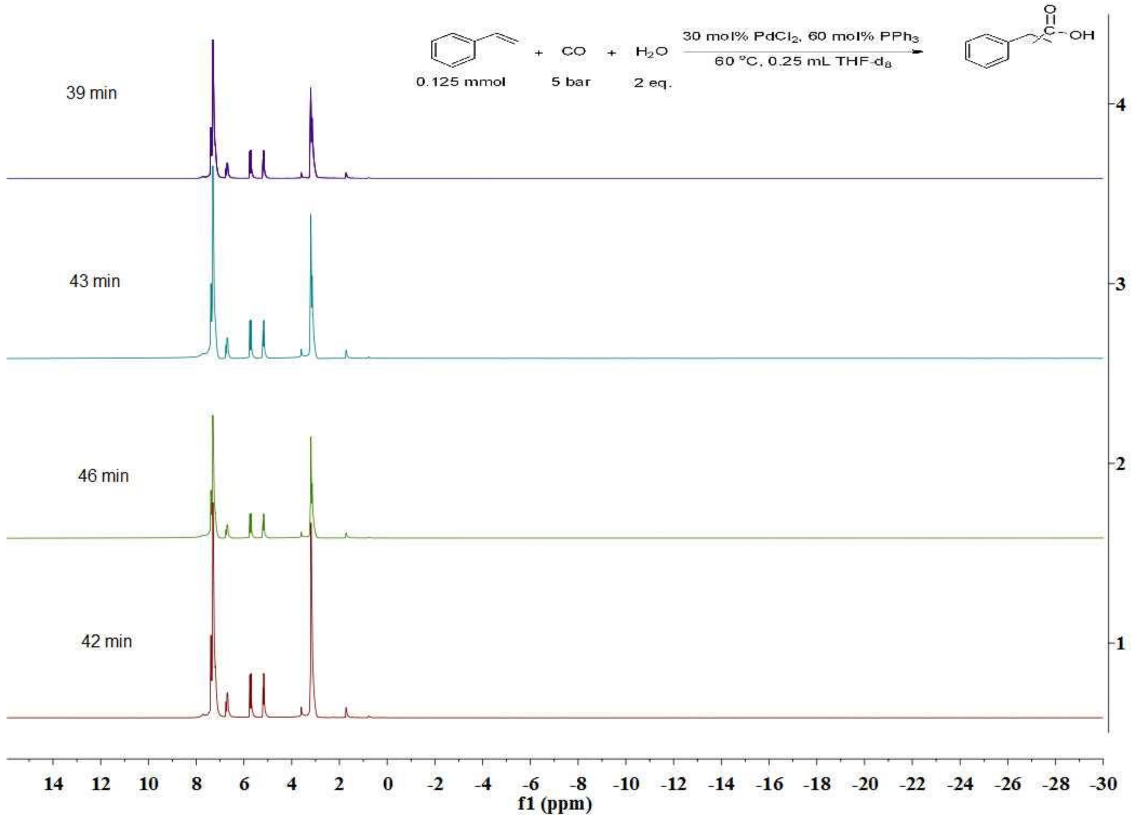


Figure S5. *In situ* ^{1}H NMR spectra

The $PdCl_2$ (0.037 mmol, 6.6 mg), PPh_3 (0.075 mmol, 19.8 mg) were added into a NMR tube. Then THF-d_8 (0.25 mL), **1a** (13 mg, 0.125 mmol) and H_2O (0.25mmol, 5 μL) were injected by syringe. At room temperature, the tube was flushed with CO gas for five times and pressurized with CO gas to 5 bar. At Bruker 400 MHz, the NMR tube was heated to 60 ^{o}C. Under such conditions, palladium hydride intermediates (-10 ~ -5 ppm) were not detected.

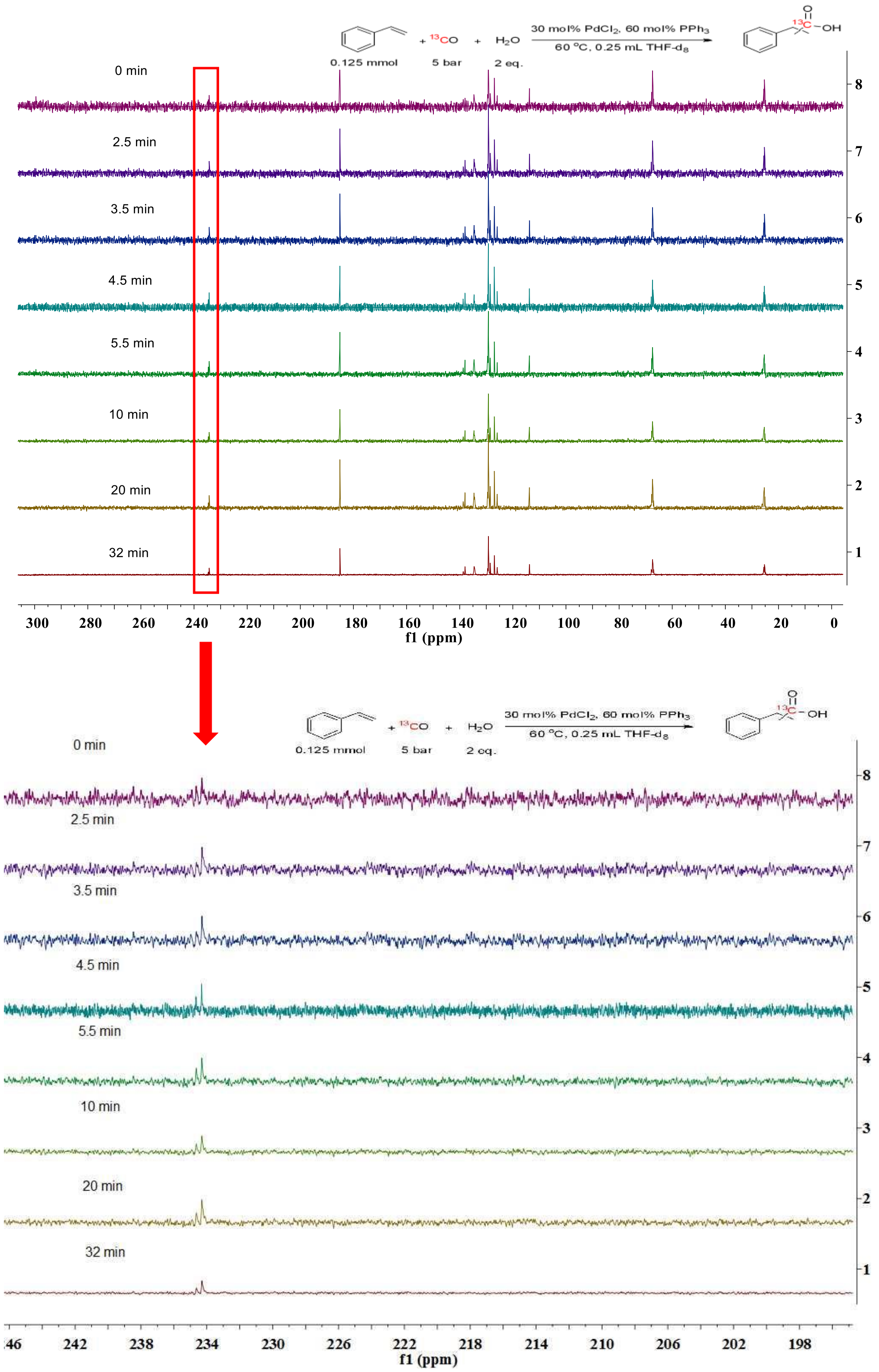


Figure S6. *In situ* ^{13}C NMR spectra

The $PdCl_2$ (0.037 mmol, 6.6 mg), PPh_3 (0.075 mmol, 19.8 mg) were added into a NMR tube in the glovebox. Then THF-d_8 (0.25 mL), **1a** (13 mg, 0.125 mmol) and H_2O (0.25 mmol, 5 μL) were injected by syringe. At room temperature, the tube was flushed with CO gas for five times and pressurized with CO gas to 5 bar. At Bruker 400 MHz, the NMR tube was heated to 60 °C. Then the ^{13}C NMR spectra were collected at different time. Under such conditions, acyl complexes (234.63, 234.29 ppm) were detected.

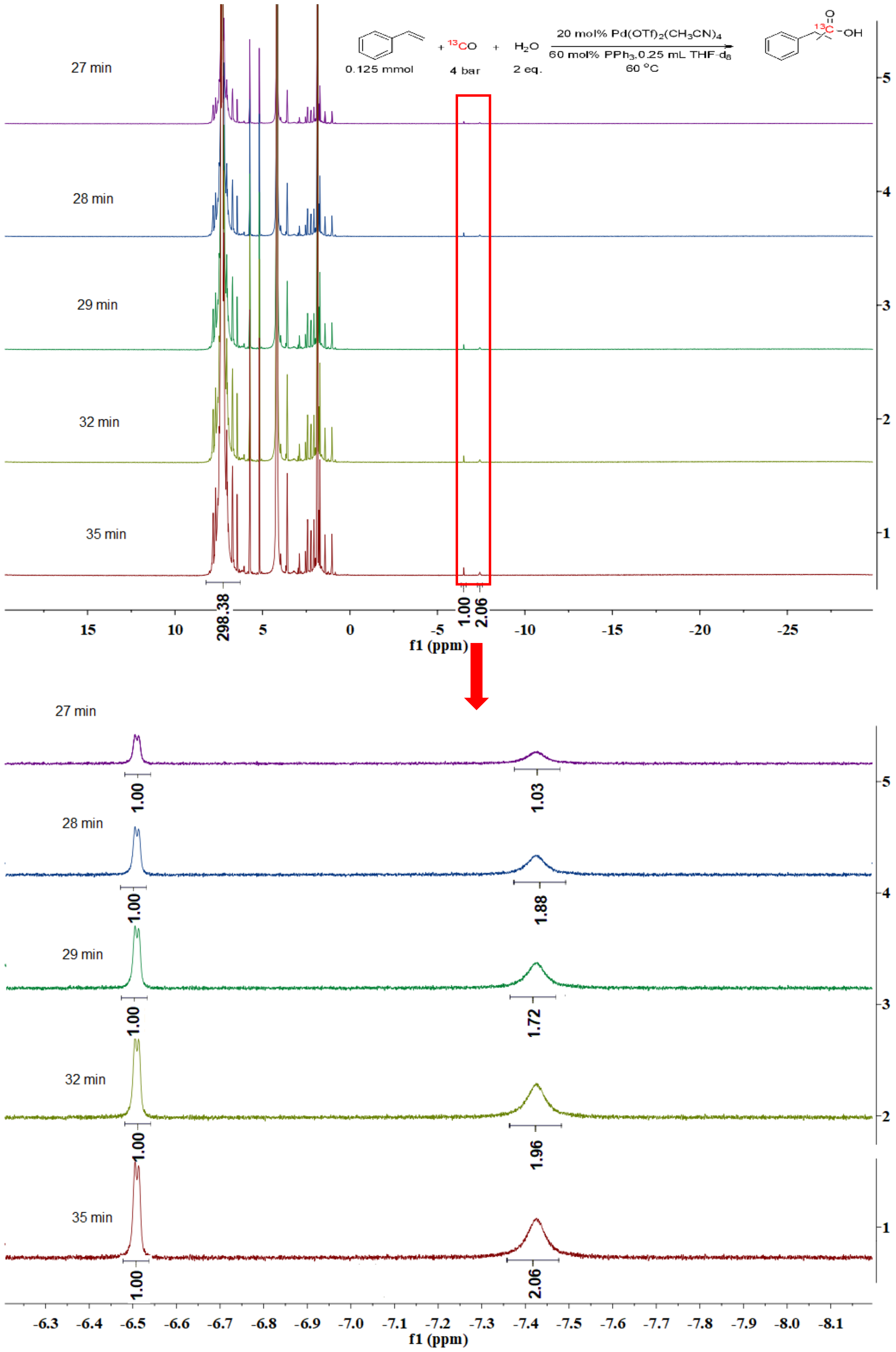


Figure S7. *In situ* ^{1}H NMR spectra

The $Pd(OTf)_2(CH_3CN)_4$ (0.025 mmol, 14.25 mg), PPh_3 (0.075 mmol, 19.6 mg) were added into a NMR tube in the glovebox. Then THF-d_8 (0.25 mL), **1a** (13 mg, 0.125 mmol) and H_2O (5 μL, 0. 25 mmol) were injected by syringe. At room temperature, the tube was flushed with CO gas for five times and pressurized with CO gas to 4 bar. Then, the NMR tube was heated to 60 ^{o}C in the Agilent 600 MHz NMR equipment. The ^{1}H NMR spectra above were collected at different time. At ca. -6.5 ppm, we can have found a double peak. Besides, we can find the other broad peak at -7.42 ppm.

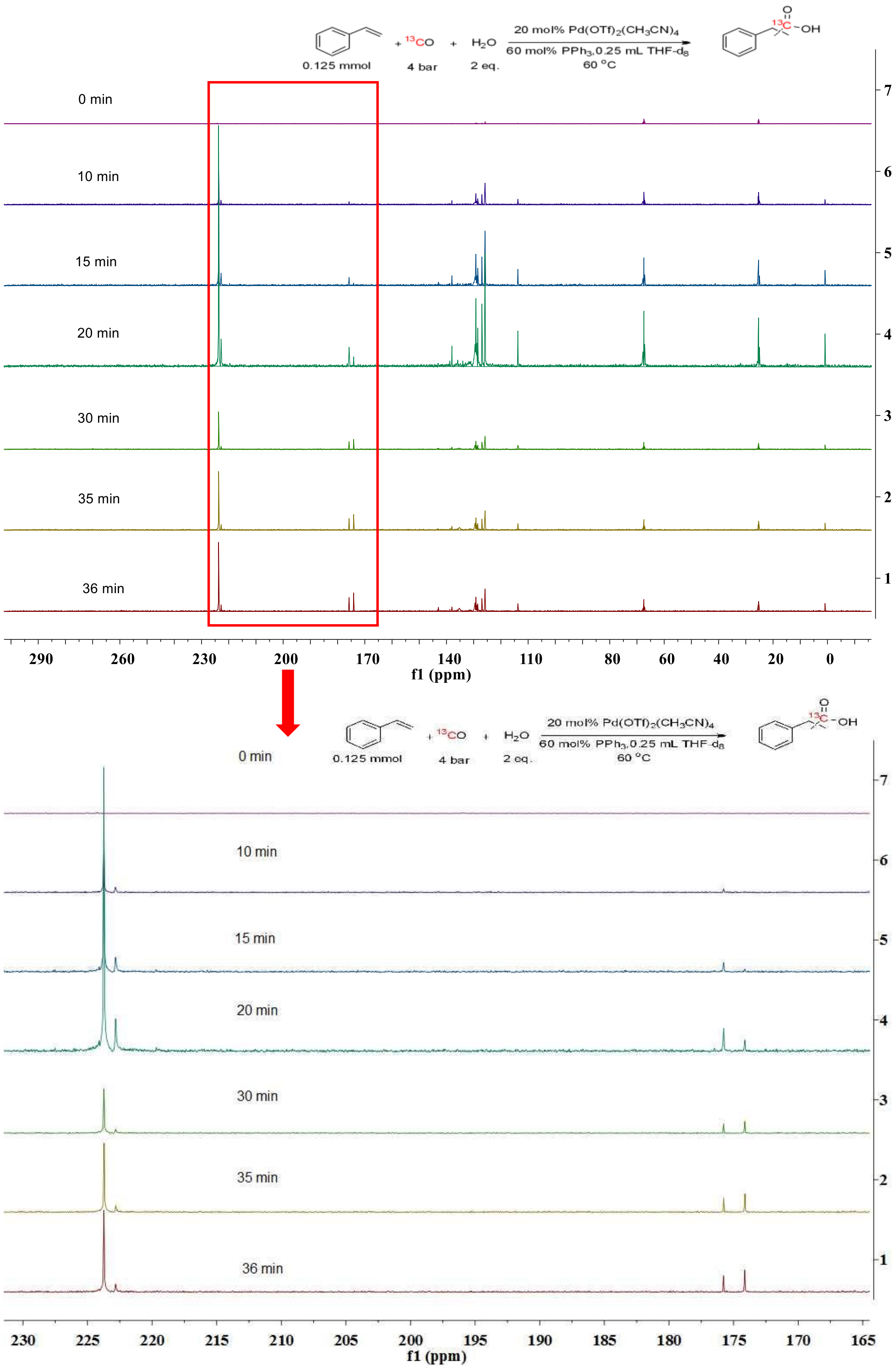
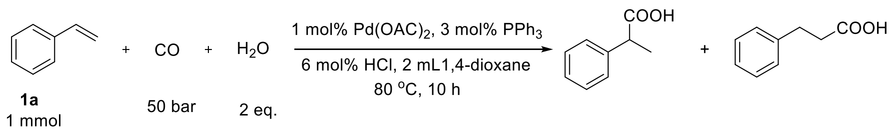


Figure S8. *In situ* ^{13}C NMR spectra

The $Pd(OTf)_2(CH_3CN)_4$ (0.025 mmol, 14.25 mg), PPh_3 (0.075 mmol, 19.6 mg) were added into a NMR tube. Then THF-d_8 (0.25 mL), **1a** (13 mg, 0.125 mmol) and H_2O (5 μL, 0. 25 mmol) were injected by syringe. At room temperature, the tube was flushed with CO gas for five times and pressurized with CO gas to 4 bar. At Agilent 600 MHz, the NMR tube was heated to 60 °C. Under such conditions, signals of acyl complexes (223.72, 222.82 ppm) were detected. Please also see the magnified spectrum for the changes of spetra.

Control experiments

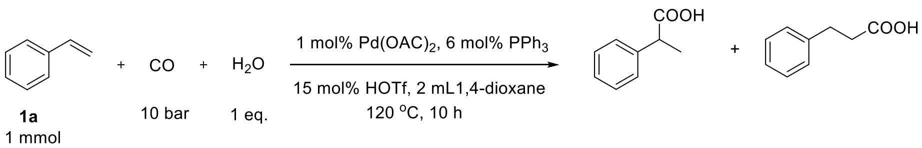
Procedure: The [Pd] source (0.01 mmol), PPh_3, additive, 1,4-dioxane (2 mL), **1a** (104 mg, 1.0 mmol) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O with syringe under nitrogen atmosphere. The vial was transferred into an autoclave (25 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas. The reaction was performed at 80 °C or 120 °C. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Conversion was determined by GC using dodecane as an internal standard. The yield and regioselectivity were measured by ^{1}H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard.



(Eq. S1)

Additive	Yield	*iso*/*n*
HCl	90 %	92/8
$FeCl_3$	96%	> 99/1

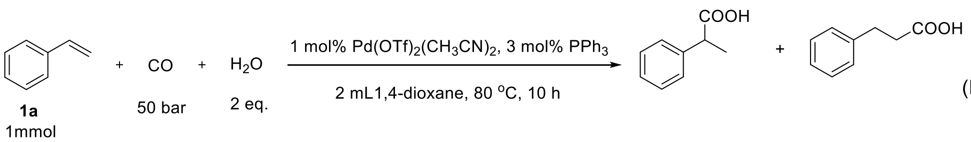
As shown in Equition S1, when 6 mol% HCl was used, the *iso*/*n* ratio decreased to 92/8.



(Eq. S2)

Additive	Yield	*iso*/*n*
HOTf	36 %	24/76
$Fe(OTf)_3$	82%	15/85

When 15 mol% HOTf was used, branch regioselectivity and the product yield of 36% were obtained.

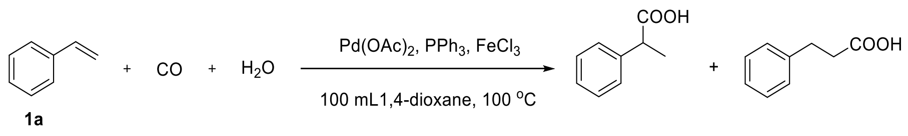


(Eq. S3)

Additive	Yield	*iso*/*n*
-	84 %	25/75
$FeCl_3$	87%	97/3

Here, when $Pd(OTf)_2(CH_3CN)$ was used as the precursor, the addition of $FeCl_3$ led to regioselectivity inversion from 25/75 to 97/3 (*iso*/*n*).

Scale-up reaction



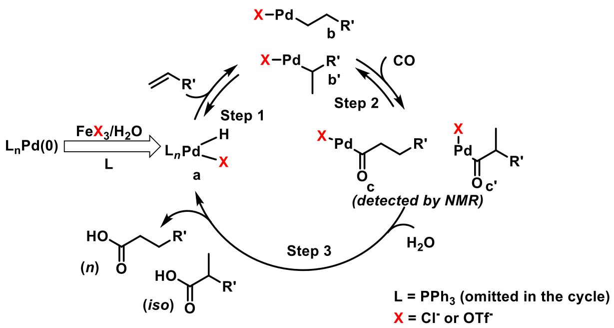
Conversion: 51%, Yield: 40%, *iso*/*n* > 99/1

Procedure: The $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), PPh_3 (0.15 mmol, 39.5 mg), $FeCl_3$ (1.28 mmol, 208 mg), 1,4-dioxane (100 mL), **1a** (62400 mg, 600.0 mmol) and a stirring bar were added into a vial (250 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O with syringe under nitrogen atmosphere. The vial was placed in an alloyed plate, which was then transferred into an autoclave (250 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 50 bar. The reaction was performed at 100 °C for 51.5 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Conversion was determined by GC using dodecane as an internal standard. The yield and regioselectivity were measured by ^1H NMR analysis of the crude reaction mixture using 2,6-dimethybenzoic acid as an internal standard. (Turnover Number (TON) = 24,000, Turnover Frequency (TOF): 24000/51.5 = 466.0 h^{-1}).

Table S12 Measuring pH value by pH meter

Entry	[Fe]/x mmol	H_2O (mmol)	1,4-dioxane (mL)	pH
1	$FeCl_3$/0.02	2	2	1.7
2	$Fe(OTf)_3$/0.05	1	2	1.1

Procedure for pH measurement: The $FeCl_3$ (0.02 mmol, 3.2 mg) or $Fe(OTf)_3$ (0.05 mmol, 26 mg), 1,4-dioxane (2 mL) were added into a vial (25 mL) in glovebox. Then H_2O (1 mmol or 2 mmol) was injected into the vial by syringe under nitrogen atmosphere. At 25 °C, the pH of mixture solutions were measured by pH meter (PHS-2F; Shanghai INESA).



Catalyst activation: the use of FeX_3 in the presence of H_2O leads to 1) slow release of proton; 2) surpress the cluster formation;
Step 1: DFT calculations clearly reveal the anion effect on the step 1. In situ NMR, Pd-H hydride signals can be observed for the reaction using $Pd(OTf)_2$;
Step 2: Insertion of CO to generate acyl Pd(II) species, Pd-acyl signals can be detected for both neutral and cationic Pd-systems under heating conditions;
Step 3: Nucleophilic addition of the water to the palldium-acyl complexes to give product (hydrolysis of Pd-acyl species) is the rate-determining step.

Scheme S1. Proposed mechanism

Computational details

All calculations were performed by Gaussian 09 D.01[1] using the range-separated hybrid WB97XD functional including dispersion correction. The dispersion correction has been proved to be critical in describing the regioselectivity of Pd-catalyzed alkoxycarbonylation reactions.[2] For geometry optimizations, we used double-zeta polarized basis set 6-31g(d) for C, H, P, Cl atoms and Lanl2dz for Pd atom (WB97XD/B1). Frequency calculations at the same level were calculated to verify either local minima or transition states and to estimate the thermal corrections Gibbs free energy at 298K. Then, single-point energies of the optimized structures was calculated with a larger triple-zeta basis set 6-311+G(d,p) (WB97XD/B2) for all atoms except Pd (Lanl2dz for Pd). Also, we carried out self-consistent reaction field (SCRF) single-point energies at WB97XD/B2 level to estimate the solvation effect (WB97XD-SCRF/B2). The polarizable continuum model (PCM) was used with 1,4-dioxane as a solvent. The Gibbs free energies (ΔG) used for our energetic discussions were estimated by sum of the single-point energies at WB97XD/B2 level and thermal corrections at 298K from frequency analysis.

To reveal the anion effect on the olefin insertion into Pd-H bond, we used L_2PdHCl and $[L_2PdH]^+$ (L=triphenyl phosphine) complexes as model catalysts to compare the different effect of Cl^- and OTf^- (OMs^-, OTs^-, etc.), respectively. Styrene was chosen as the substrate. We firstly got the optimized structures of L_2PdHCl and $[L_2Pd]^+$, both of which Pd adopt a square planar coordination geometry. Then we studied the coordination of styrene to the two [Pd] catalysts. The most stable conformations can be found in Figure S9 and Figure S10. It is shown that in $[L_2PdH(\text{styrene})]^+$ complex, C=C double bond of styrene is roughly perpendicular to the Pd-H bond , and styrene approaches the square planar of L_2PdHCl almost parallel with vinyl pointing toward Cl. Subsequently, we located the transition states of the Pd-H insertion to the C=C double bond of styrene for each catalyst with Berny algorithm encoded in G09. Two distinct insertion routes have been investigated: I) H transfer from Pd to the distal C atom of the double bond leading to a $[L_2Pd(\textit{iso}\text{-phenylethyl})]X$ (X=Cl or +) intermediate that will finally produce the branched product; II) H transfer from Pd to the proximal C atom of the double bond leading to a $[L_2Pd(\textit{n}\text{-phenylethyl})]X$ (X=Cl or +) intermediate that will finally produce the linear product. Transition states with different configurations have been located for each route and we only chose the most stable transition states for discussion and comparison.

As shown in Figure S9, the Pd-H insertion of L_2PdHCl to styrene has an energy barrier about 10.41 (8.99) kcal/mol via Path I (TS1) and 15.92 (13.96) kcal/mol via Path II (TS2). This barrier discrepancy (more or less -5 kcal/mol) corresponds to an expected *iso/n* regioselectivity about 100/0 according to Arrhenius equation, in good agreement with the experimentally observed regioselectivity when the chloride salts were used as co-catalyst. Seen from Figure S10, the Pd-H insertion of $[L_2PdH]^+$ to styrene has an energy barrier about 5.83 kcal/mol via Path I (TS1) and 5.49 kcal/mol via Path II (TS2) with the solvation effect included. Such a barrier discrepancy (0.34 kcal/mol) corresponds to an *iso/n* regioselectivity nearly 39/61. It coincides very well with the observed regioselectivity in the presence of $Fe(OTs)_3$. Our calculations indeed reproduce the observed anion effect on the regioselectivity.

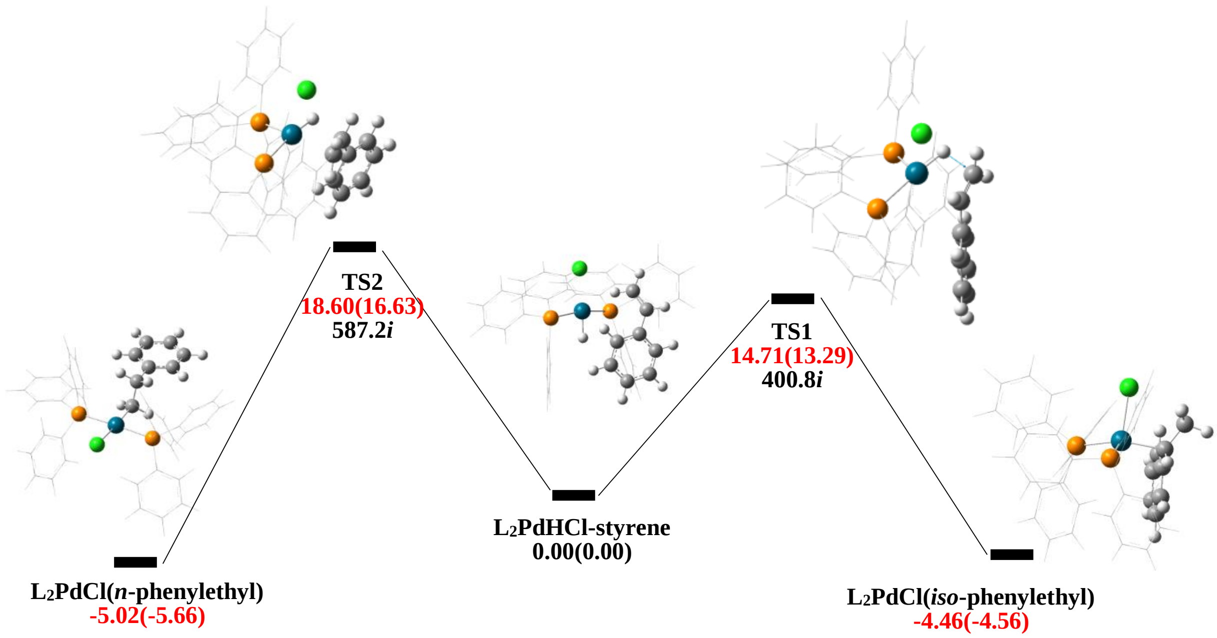


Figure S9 Calculated Gibbs free energies of Pd-H insertion into styrene in L_2PdHCl-styrene complex at WB97XD/B2 (WB97XD-SCRF/B2) level.

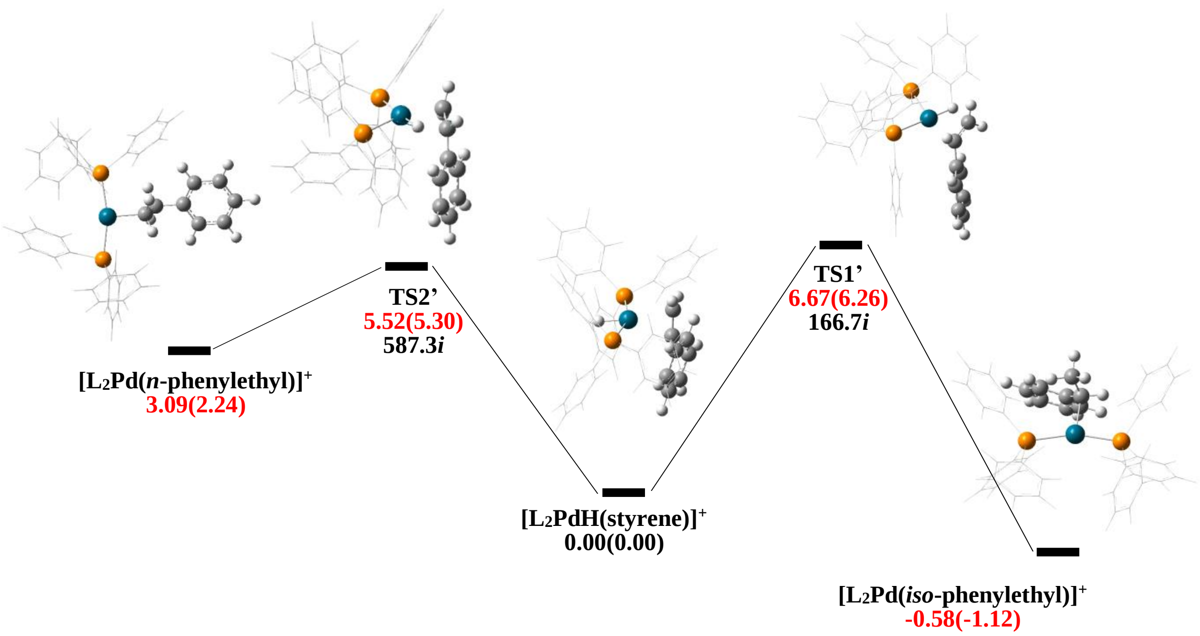


Figure S10 Calculated Gibbs free energies of Pd-H insertion into styrene in $[L_2PdH(styrene)]^+$ complex at WB97XD/B2 (WB97XD-SCRF/B2) level.

Optimized Cartesian coordinates involved in Figure S9 and Figure S10

L_2PdHCl-styreen				TS1			
C	0.2991900	-3.6584240	0.7698280	C	1.6281880	-1.3657190	-2.4015230
C	-0.6741160	-4.3904990	1.4470820	C	0.4793710	-1.7091440	-3.0876940
C	-1.9167700	-4.5997670	0.8518410	Pd	-0.0860280	-0.1834770	-1.3039010
C	-2.1776380	-4.0848990	-0.4134110	Cl	0.0213650	1.6329930	-3.4012830
C	-1.2106160	-3.3464200	-1.1074700	P	1.3716230	0.9528040	0.2327580
C	0.0330900	-3.1435790	-0.4949950	C	3.1147870	1.0965480	-0.3181910
Pd	0.1534090	0.4425850	-0.1328160	C	4.2228010	0.8555390	0.4956260
Cl	0.2631930	1.8111440	-2.1594280	C	5.5099850	0.9881230	-0.0198480
P	-2.1444110	0.7092850	0.1835850	C	5.6977540	1.3791040	-1.3425300
C	-2.5570530	2.4826130	0.3262940	C	4.5934700	1.6539170	-2.1479340
C	-3.8115860	2.9849570	-0.0335100	C	3.3053360	1.5145770	-1.6415500
C	-4.0953500	4.3379720	0.1251620	C	1.4074820	0.0816460	1.8434690
C	-3.1289290	5.1981500	0.6405660	C	0.5902370	0.4676290	2.9115400
C	-1.8754190	4.7047950	0.9928550	C	0.5025300	-0.3240930	4.0541740
C	-1.5877710	3.3537120	0.8318380	C	1.2225690	-1.5109640	4.1473140
C	-2.8712450	-0.0646440	1.6761460	C	2.0343170	-1.9059190	3.0860760
C	-2.4061270	-1.3235430	2.0680920	C	2.1210150	-1.1201220	1.9426480
C	-2.9855450	-1.9806570	3.1485980	P	-2.0846990	-0.3568300	-0.1488700
C	-4.0219960	-1.3798480	3.8585480	C	-3.5821850	0.0087740	-1.1263400
C	-4.4834100	-0.1224460	3.4782840	C	-3.4475140	0.5234490	-2.4182360
C	-3.9162420	0.5308100	2.3877690	C	-4.5873700	0.8509830	-3.1525390
P	2.4633240	0.1964920	0.0686730	C	-5.8520120	0.6648030	-2.6056110
C	3.1747020	1.7053050	0.8214930	C	-5.9882520	0.1628950	-1.3105180
C	2.7049000	2.9399970	0.3551320	C	-4.8576920	-0.1532610	-0.5687110
C	3.2268190	4.1206840	0.8726170	C	-2.3730560	0.6537950	1.3503330
C	4.2109370	4.0809270	1.8582790	C	-2.7029530	0.1305140	2.6013750
C	4.6791550	2.8555600	2.3233880	C	-2.8749370	0.9835150	3.6898840
C	4.1652530	1.6684840	1.8061580	C	-2.7104060	2.3576850	3.5390280
C	3.4261080	-0.0388800	-1.4634540	C	-2.4014860	2.8867750	2.2865310
C	4.7668990	0.3502050	-1.5509040	C	-2.2459160	2.0380280	1.1977720
C	5.4898850	0.1061020	-2.7137930	H	-1.0082240	-1.0282720	-2.2750340
C	4.8804810	-0.5269750	-3.7952670	H	0.1937270	-1.1186440	-3.9531330
C	3.5450980	-0.9105580	-3.7150120	H	0.0416520	-2.6984640	-2.9817400
C	2.8184320	-0.6617690	-2.5551460	H	4.0895810	0.5528800	1.5294140
H	1.2735620	-3.4981740	1.2203890	H	6.3666700	0.7859190	0.6166190
H	-0.4612800	-4.8018780	2.4297790	H	6.7021700	1.4795650	-1.7436630
H	-2.6832990	-5.1670600	1.3723970	H	4.7316560	1.9738340	-3.1762650

H	-3.1471820	-4.2507760	-0.8769080	H	2.4427060	1.7234480	-2.2766720
H	0.8105110	-2.6012880	-1.0252180	H	0.0039880	1.3789450	2.8551960
H	-4.5639410	2.3185410	-0.4459450	H	-0.1456460	-0.0091540	4.8662790
H	-5.0704800	4.7216310	-0.1598770	H	1.1495350	-2.1256330	5.0397980
H	-3.3496120	6.2548620	0.7596130	H	2.5969700	-2.8334690	3.1346670
H	-1.1141730	5.3749940	1.3805250	H	2.7450760	-1.4521590	1.1214660
H	-0.6002130	2.9740080	1.0806870	H	-2.4587510	0.7002350	-2.8409250
H	-1.5911200	-1.7943230	1.5260980	H	-4.4756310	1.2611920	-4.1513790
H	-2.6165260	-2.9616250	3.4324730	H	-6.7369100	0.9200830	-3.1817050
H	-4.4673890	-1.8878340	4.7090920	H	-6.9748300	0.0280480	-0.8772000
H	-5.2884380	0.3536560	4.0302910	H	-4.9636940	-0.5254910	0.4473780
H	-4.2859330	1.5098150	2.0996170	H	-2.8097830	-0.9406650	2.7380650
H	1.9386380	2.9690490	-0.4172930	H	-3.1280330	0.5676220	4.6608750
H	2.8600430	5.0738040	0.5032780	H	-2.8277560	3.0171170	4.3939640
H	4.6131910	5.0045520	2.2643470	H	-2.2651230	3.9555140	2.1541140
H	5.4466800	2.8201980	3.0907900	H	-2.0083010	2.4539770	0.2242200
H	4.5356960	0.7164710	2.1749300	C	0.9849880	2.7037070	0.6037650
H	5.2447830	0.8482100	-0.7119410	C	0.2917990	3.4438310	-0.3578510
H	6.5289450	0.4151320	-2.7779680	C	1.4373570	3.3330040	1.7681940
H	5.4447520	-0.7121510	-4.7045850	C	0.0202460	4.7916010	-0.1319560
H	3.0604760	-1.3895280	-4.5600130	H	-0.0201550	2.9697450	-1.2889250
H	1.7694820	-0.9311880	-2.5083830	C	1.1517570	4.6746720	1.9943380
C	-3.2070180	0.0970350	-1.1721890	H	2.0098780	2.7760230	2.5043510
C	-3.0861290	0.6976720	-2.4311330	C	0.4359230	5.4045800	1.0466190
C	-4.0769910	-0.9812620	-1.0025540	H	-0.5164360	5.3595430	-0.8859520
C	-3.8417310	0.2295110	-3.4996820	H	1.4970110	5.1530720	2.9061790
H	-2.3795020	1.5100440	-2.5759950	H	0.2190760	6.4546350	1.2214870
C	-4.8197350	-1.4547880	-2.0815640	C	-2.2176690	-2.0916590	0.4192870
H	-4.1725480	-1.4635670	-0.0351730	C	-3.1603950	-2.9919480	-0.0790180
C	-4.7069420	-0.8490830	-3.3289320	C	-1.2415650	-2.5482350	1.3153270
H	-3.7418660	0.7022770	-4.4721660	C	-3.1314270	-4.3277790	0.3199360
H	-5.4937360	-2.2951580	-1.9412610	H	-3.9137730	-2.6585710	-0.7859550
H	-5.2903770	-1.2177060	-4.1678420	C	-1.2254560	-3.8758740	1.7227190
C	3.0219880	-1.1717310	1.1555770	H	-0.4824920	-1.8656290	1.6852900
C	2.4995730	-1.2512650	2.4529290	C	-2.1701220	-4.7714790	1.2225560
C	3.9117050	-2.1551410	0.7205730	H	-3.8659200	-5.0218720	-0.0777230
C	2.8732580	-2.2850450	3.3016730	H	-0.4650030	-4.2073880	2.4236650
H	1.7860770	-0.5052170	2.7924900	H	-2.1528290	-5.8124810	1.5315870
C	4.2707010	-3.2036540	1.5676040	H	2.1946510	-0.5188170	-2.7774360
H	4.3263380	-2.1122500	-0.2812710	C	2.3172470	-2.2581560	-1.4473130

C	3.7569750	-3.2692900	2.8576840	C	3.6931100	-2.1024300	-1.2416240
H	2.4614510	-2.3328900	4.3052320	C	1.6418780	-3.2657000	-0.7432300
H	4.9559700	-3.9676450	1.2131120	C	4.3798610	-2.9411500	-0.3678460
H	4.0391060	-4.0850030	3.5166970	H	4.2250490	-1.3108860	-1.7628230
C	-1.5135270	-2.8454520	-2.4622320	C	2.3285760	-4.1040310	0.1248210
C	-1.0036400	-1.7464800	-3.0180210	H	0.5658060	-3.3719320	-0.8494860
H	-2.2393440	-3.4316020	-3.0247550	C	3.7020470	-3.9481160	0.3151530
H	-1.2833890	-1.4430010	-4.0213980	H	5.4459600	-2.7997070	-0.2176880
H	-0.3477100	-1.0675170	-2.4789820	H	1.7846450	-4.8732850	0.6656530
H	0.0998280	-0.3752070	1.1806130	H	4.2384050	-4.6029020	0.9958480
TS2				L_2PdCl(*iso*-phenylethyl)			
C	-4.7087770	3.5929250	0.9216560	C	2.1808690	3.6317920	-0.7385150
C	-4.5685980	3.8012100	-0.4459350	C	1.9374480	4.1817310	0.5117410
C	-3.3468700	3.5344330	-1.0621640	C	0.6439010	4.1480200	1.0487820
C	-2.2733670	3.0658610	-0.3183330	C	-0.3888970	3.5582070	0.3442120
C	-2.3977160	2.8766440	1.0621250	C	-0.1689210	3.0055490	-0.9391300
C	-3.6283050	3.1327190	1.6698950	C	1.1390070	3.0562600	-1.4713410
C	-1.2591940	2.4303580	1.9077770	C	-1.2342350	2.2653200	-1.6388760
C	0.0823980	2.6730590	1.6159850	C	-1.4503060	2.4753610	-3.1202880
Pd	-0.0788850	0.5203930	1.0515220	Pd	-0.0619280	0.6039740	-1.0639870
Cl	0.7947120	0.0136200	3.6258220	Cl	0.6814890	-0.0161320	-3.4705930
P	1.9954570	0.5176100	-0.1116290	P	-1.9384550	-0.2094120	0.0279720
C	3.1404840	1.8876520	0.3032720	C	-3.2959000	-0.6281550	-1.1246750
C	3.8536500	2.6302260	-0.6398610	C	-4.5716010	-0.9736220	-0.6609370
C	4.7521040	3.6094040	-0.2220900	C	-5.5648540	-1.3437930	-1.5590100
C	4.9540330	3.8402730	1.1352540	C	-5.2864250	-1.3918010	-2.9251150
C	4.2591370	3.0864160	2.0790260	C	-4.0134580	-1.0761720	-3.3878130
C	3.3539080	2.1138520	1.6692520	C	-3.0160210	-0.6941230	-2.4918030
C	1.6601200	0.6572420	-1.9058230	C	-2.6276600	0.9697540	1.2390200
C	1.6494800	-0.4560920	-2.7511140	C	-1.8801720	1.2238710	2.3965530
C	1.2153880	-0.3346380	-4.0701250	C	-2.2714300	2.2173350	3.2847810
C	0.7849240	0.8937290	-4.5605190	C	-3.4016700	2.9892010	3.0179010
C	0.7790400	2.0073350	-3.7204920	C	-4.1401540	2.7543910	1.8620530
C	1.2049850	1.8870740	-2.4031770	C	-3.7581710	1.7479830	0.9766780
P	-1.3017430	-1.2093620	0.0681320	P	1.7754440	-0.5220450	0.0472860
C	-2.2594850	-2.2486130	1.2230520	C	3.4006960	0.2640770	-0.2991820
C	-2.0782000	-2.0844980	2.5982510	C	3.6631420	0.6424800	-1.6200640
C	-2.7828650	-2.8952960	3.4880900	C	4.8913430	1.2063700	-1.9528280
C	-3.6635920	-3.8598400	3.0120050	C	5.8619540	1.4044290	-0.9739230

C	-3.8366660	-4.0331430	1.6378040	C	5.6080550	1.0191990	0.3399960
C	-3.1308290	-3.2368550	0.7458770	C	4.3864340	0.4426250	0.6756110
C	-0.4235050	-2.4629570	-0.9421230	C	2.1498710	-2.2908270	-0.2384710
C	-0.7495320	-2.8004600	-2.2572420	C	2.8808490	-3.0705470	0.6629050
C	0.0218260	-3.7297050	-2.9518120	C	3.1379760	-4.4085250	0.3830580
C	1.1215330	-4.3275800	-2.3414970	C	2.6875360	-4.9708530	-0.8100550
C	1.4325720	-4.0183380	-1.0185450	C	1.9942230	-4.1872560	-1.7288000
C	0.6568240	-3.0987080	-0.3230870	C	1.7255060	-2.8500400	-1.4476950
H	-5.6585150	3.7885310	1.4106080	H	3.1832120	3.6389090	-1.1549470
H	-5.4090280	4.1586460	-1.0336170	H	2.7486480	4.6369930	1.0727540
H	-3.2364010	3.6706080	-2.1332170	H	0.4493470	4.5793180	2.0267740
H	-1.3409930	2.8135080	-0.8166130	H	-1.3889250	3.5272670	0.7668110
H	-3.7393770	2.9758090	2.7399150	H	1.3323980	2.6528060	-2.4610300
H	-1.5011540	0.7048860	1.7453620	H	-2.1792390	2.3216710	-1.0953040
H	0.3621020	3.2293100	0.7250590	H	-1.8826760	3.4743960	-3.2764350
H	0.8032290	2.6343440	2.4239890	H	-2.1566890	1.7397570	-3.5130410
H	3.7143860	2.4496420	-1.7015670	H	-0.5320130	2.3879500	-3.7012040
H	5.2991360	4.1876800	-0.9610890	H	-4.7858480	-0.9544780	0.4046790
H	5.6568440	4.6027970	1.4579260	H	-6.5543560	-1.6027610	-1.1938810
H	4.4190030	3.2549840	3.1395450	H	-6.0624540	-1.6852890	-3.6260440
H	2.8137790	1.5225590	2.4095040	H	-3.7872600	-1.1275900	-4.4484160
H	1.9568100	-1.4295310	-2.3821610	H	-2.0153200	-0.4641170	-2.8545390
H	1.2046790	-1.2142470	-4.7066660	H	-0.9800070	0.6521910	2.5982240
H	0.4480800	0.9848600	-5.5888980	H	-1.6805240	2.3955600	4.1783160
H	0.4351930	2.9688880	-4.0900360	H	-3.7027120	3.7725720	3.7070450
H	1.1817300	2.7577560	-1.7525540	H	-5.0183130	3.3547390	1.6438810
H	-1.3680430	-1.3489760	2.9758780	H	-4.3406010	1.5767390	0.0765550
H	-2.6317320	-2.7677620	4.5554560	H	2.9018190	0.4975270	-2.3846780
H	-4.2134440	-4.4864910	3.7084320	H	5.0848860	1.4937490	-2.9821150
H	-4.5181600	-4.7920450	1.2648970	H	6.8162220	1.8538520	-1.2335290
H	-3.2577840	-3.3791610	-0.3244480	H	6.3638310	1.1627110	1.1069390
H	-1.5933160	-2.3306340	-2.7514500	H	4.2016970	0.1457410	1.7035760
H	-0.2349370	-3.9795800	-3.9773750	H	3.2469040	-2.6365240	1.5890870
H	1.7310890	-5.0371290	-2.8933400	H	3.6974940	-5.0108710	1.0927860
H	2.2884940	-4.4730000	-0.5293890	H	2.8892010	-6.0159740	-1.0270960
H	0.9017940	-2.8586080	0.7063810	H	1.6600180	-4.6138650	-2.6697770
C	3.1100040	-0.9140440	0.1222640	H	1.1963330	-2.2296510	-2.1698760
C	3.0337640	-1.5974900	1.3394490	C	-1.7569140	-1.7862550	0.9449370
C	4.0854000	-1.2718650	-0.8137210	C	-1.1123190	-2.8232790	0.2645490
C	3.9032230	-2.6551450	1.5956260	C	-2.2239530	-2.0088640	2.2415480

H	2.3020220	-1.2957170	2.0903490	C	-0.8969000	-4.0506220	0.8798310
C	4.9395350	-2.3391940	-0.5588210	H	-0.7603950	-2.6619090	-0.7494150
H	4.1810510	-0.7217330	-1.7454570	C	-2.0174090	-3.2420170	2.8553970
C	4.8457100	-3.0362980	0.6446270	H	-2.7358650	-1.2202020	2.7833330
H	3.8385380	-3.1777820	2.5451120	C	-1.3448310	-4.2594450	2.1830030
H	5.6859020	-2.6202260	-1.2959000	H	-0.3639840	-4.8306660	0.3443650
H	5.5191320	-3.8647800	0.8454590	H	-2.3805950	-3.4043120	3.8661940
C	-2.5236510	-0.4571510	-1.0689910	H	-1.1748800	-5.2146240	2.6710380
C	-3.8806230	-0.3618580	-0.7556650	C	1.5583200	-0.3148820	1.8558290
C	-2.0541620	0.1295430	-2.2507580	C	1.7312450	0.9706640	2.3893240
C	-4.7569100	0.2805800	-1.6275380	C	1.0683660	-1.3271230	2.6852910
H	-4.2585020	-0.7882850	0.1682700	C	1.4566970	1.2256590	3.7273190
C	-2.9338600	0.7483750	-3.1291930	H	2.0738620	1.7797230	1.7505830
H	-0.9965670	0.0941970	-2.4904790	C	0.7833060	-1.0659590	4.0244450
C	-4.2904410	0.8220850	-2.8208390	H	0.8914020	-2.3222150	2.2899380
H	-5.8088700	0.3567060	-1.3700630	C	0.9834850	0.2054320	4.5525260
H	-2.5507890	1.1831680	-4.0480370	H	1.6034170	2.2265640	4.1228770
H	-4.9793390	1.3146020	-3.5009200	H	0.3955030	-1.8649100	4.6493040
H	-1.4905000	2.2315060	2.9536520	H	0.7668120	0.4032300	5.5982670
L_2PdCl(*n*-phenylethyl)				$[L_2PdH(styrene)]^+$			
C	1.2033530	-5.8136310	0.2323710	Pd	-0.1526580	0.1032910	0.3655970
C	-0.0002000	-6.4859560	0.4329310	P	2.1344140	0.6548140	0.0114890
C	-1.2036230	-5.8133860	0.2323690	C	3.3211660	0.1341850	1.2968590
C	-1.2011260	-4.4794440	-0.1648070	C	4.3437460	-0.7793440	1.0325860
C	0.0000760	-3.7979980	-0.3691350	C	5.1921060	-1.1935380	2.0576030
C	1.2011370	-4.4796810	-0.1648060	C	5.0300990	-0.6962230	3.3470200
C	0.0001760	-2.3293400	-0.7245090	C	4.0179650	0.2248830	3.6149800
C	0.0000690	-1.4750950	0.5466820	C	3.1655960	0.6347610	2.5964380
Pd	0.0000250	0.5196340	0.0353070	C	2.4255610	2.4529860	-0.1853570
Cl	0.0001580	2.8378740	-0.8220050	C	1.5696180	3.1964410	-1.0074350
P	2.3698030	0.5669280	0.0675130	C	1.8025430	4.5483130	-1.2303090
C	3.0564960	1.1836440	-1.5097220	C	2.8906810	5.1780270	-0.6292540
C	4.2984880	1.8184380	-1.5817180	C	3.7500370	4.4459080	0.1831120
C	4.8146730	2.2075780	-2.8136310	C	3.5244110	3.0887850	0.4013010
C	4.0976370	1.9598380	-3.9814560	P	-2.4709230	0.2565650	-0.0044790
C	2.8574390	1.3306490	-3.9151590	C	-3.4845710	-0.7784900	1.1042460
C	2.3350020	0.9509540	-2.6834530	C	-3.5829580	-0.4215530	2.4557540
C	3.2877320	-1.0047180	0.3165250	C	-4.2426400	-1.2538040	3.3524580
C	3.2828860	-1.6092180	1.5809710	C	-4.8024200	-2.4522020	2.9110760

C	3.9477110	-2.8105220	1.7953350	C	-4.7065780	-2.8116720	1.5703540
C	4.6268170	-3.4295800	0.7475580	C	-4.0489010	-1.9796210	0.6666030
C	4.6289570	-2.8433380	-0.5139110	C	-2.9303840	-0.2673180	-1.6874700
C	3.9608660	-1.6391290	-0.7307280	C	-4.1894520	0.0164160	-2.2281520
P	-2.3697920	0.5668960	0.0675080	C	-4.5260320	-0.4519240	-3.4929360
C	-3.0566570	1.1838400	-1.5095650	C	-3.6137510	-1.2112910	-4.2239130
C	-2.3350730	0.9518600	-2.6833730	C	-2.3596350	-1.4959700	-3.6920360
C	-2.8576560	1.3318070	-3.9149470	C	-2.0166670	-1.0224800	-2.4289950
C	-4.0980940	1.9605340	-3.9810250	H	4.4756940	-1.1772500	0.0316340
C	-4.8152390	2.2075620	-2.8131090	H	5.9838690	-1.9047490	1.8437620
C	-4.2989050	1.8181800	-1.5813420	H	5.6943090	-1.0198320	4.1420510
C	-3.0703510	1.6566090	1.3666460	H	3.8937730	0.6248110	4.6163390
C	-4.3449390	1.4431750	1.9073230	H	2.3816420	1.3583080	2.8102420
C	-4.8544200	2.3087840	2.8704120	H	0.7232710	2.7166210	-1.4905840
C	-4.0991640	3.3963200	3.3018590	H	1.1339430	5.1106230	-1.8746270
C	-2.8346150	3.6166200	2.7643950	H	3.0694120	6.2351140	-0.7985630
C	-2.3187950	2.7524330	1.8032570	H	4.6051170	4.9272670	0.6469860
H	2.1484740	-6.3282870	0.3842870	H	4.2120850	2.5291660	1.0263340
H	-0.0003070	-7.5278350	0.7409100	H	-3.1551940	0.5155220	2.8043040
H	-2.1488460	-6.3278550	0.3842820	H	-4.3231940	-0.9673250	4.3962880
H	-2.1411460	-3.9563180	-0.3177600	H	-5.3163900	-3.1016980	3.6123730
H	2.1412660	-3.9567450	-0.3177460	H	-5.1482880	-3.7397500	1.2217170
H	-0.8832580	-2.0978480	-1.3336710	H	-3.9825570	-2.2659520	-0.3787890
H	-0.8768880	-1.7156220	1.1505800	H	-4.9052510	0.6110470	-1.6689650
H	0.8769360	-1.7155770	1.1507320	H	-5.5011330	-0.2231550	-3.9107790
H	4.8603660	2.0203790	-0.6747360	H	-3.8801990	-1.5755310	-5.2111470
H	5.7772050	2.7079700	-2.8607110	H	-1.6435560	-2.0789170	-4.2626490
H	4.5018890	2.2659860	-4.9418350	H	-1.0304670	-1.2290020	-2.0213380
H	2.2885910	1.1492470	-4.8219360	C	2.7605290	-0.0798590	-1.5329420
H	1.3537760	0.4888470	-2.6255090	C	2.2146310	-1.2832820	-1.9867940
H	2.7688880	-1.1270900	2.4086680	C	3.8112090	0.5147710	-2.2396620
H	3.9322580	-3.2658550	2.7805710	C	2.7194630	-1.8911680	-3.1319870
H	5.1451710	-4.3691350	0.9138350	H	1.4006390	-1.7527430	-1.4420200
H	5.1510900	-3.3209830	-1.3375200	C	4.3079940	-0.0925600	-3.3877150
H	3.9779270	-1.1883280	-1.7177160	H	4.2391430	1.4522750	-1.8967960
H	-1.3536640	0.4901290	-2.6256010	C	3.7639500	-1.2955780	-3.8338830
H	-2.2887270	1.1509640	-4.8217840	H	2.2929740	-2.8295480	-3.4727820
H	-4.5024560	2.2668850	-4.9412930	H	5.1208140	0.3742320	-3.9348780
H	-5.7779620	2.7076040	-2.8600120	H	4.1547130	-1.7665310	-4.7305390
H	-4.8608620	2.0195740	-0.6742870	C	-3.0952120	1.9491300	0.2494860

H	-4.9414100	0.5960060	1.5824570	C	-4.4500910	2.1851940	0.5178120
H	-5.8425210	2.1312930	3.2845890	C	-2.2149090	3.0325210	0.1616010
H	-4.4969810	4.0709950	4.0544120	C	-4.9163540	3.4861330	0.6694480
H	-2.2425180	4.4660560	3.0913800	H	-5.1405490	1.3534900	0.6262480
H	-1.3439020	2.9416200	1.3651100	C	-2.6857400	4.3328870	0.3162310
C	3.0704410	1.6567490	1.3664980	H	-1.1573230	2.8619310	-0.0143460
C	2.3187540	2.7523540	1.8034240	C	-4.0356790	4.5610400	0.5651460
C	4.3452240	1.4435430	1.9068110	H	-5.9677000	3.6605980	0.8745200
C	2.8346370	3.6165620	2.7645100	H	-1.9920480	5.1651860	0.2504180
H	1.3437060	2.9413640	1.3655530	H	-4.4024610	5.5751730	0.6887920
C	4.8547730	2.3091730	2.8698430	H	-0.2359780	0.9603960	-0.9266490
H	4.9417890	0.5965310	1.5817060	C	1.9520300	-4.5857120	-0.6353460
C	4.0993830	3.3964950	3.3016040	C	0.5931360	-4.4053580	-0.8856520
H	2.2424330	4.4658250	3.0917490	C	-0.1487580	-3.5397860	-0.0892540
H	5.8430230	2.1318650	3.2837390	C	0.4606740	-2.8372450	0.9593450
H	4.4972510	4.0711840	4.0541170	C	1.8220500	-3.0413000	1.2149240
C	-3.2876750	-1.0047960	0.3163920	C	2.5617100	-3.9065080	0.4186360
C	-3.9607790	-1.6391360	-0.7309240	H	2.5341120	-5.2624470	-1.2529210
C	-3.2828160	-1.6094180	1.5807810	H	0.1105660	-4.9433030	-1.6957610
C	-4.6288450	-2.8433810	-0.5142180	H	-1.2098170	-3.3958770	-0.2802540
H	-3.9778360	-1.1882550	-1.7178760	H	2.3031590	-2.5333040	2.0446960
C	-3.9476290	-2.8107490	1.7950380	H	3.6167100	-4.0561310	0.6252870
H	-2.7688250	-1.1273610	2.4085220	C	-0.3619720	-1.8925300	1.7352940
C	-4.6267170	-3.4297270	0.7472020	C	0.0843600	-0.8946160	2.5440000
H	-5.1509470	-3.3209720	-1.3378770	H	-1.4334990	-2.0727870	1.6922900
H	-3.9321690	-3.2661690	2.7802330	H	-0.6236570	-0.3363110	3.1500940
H	-5.1450580	-4.3693040	0.9133930	H	1.1378280	-0.7503900	2.7580610
H	0.8837660	-2.0979290	-1.3334730				
TS1’				TS2’			
C	0.8852810	-2.1471290	-2.6800450	C	-3.4780570	3.7499730	0.0108750
C	1.9753950	-1.5999970	-2.0081250	C	-2.8297820	4.7950700	0.6671460
Pd	0.0822510	-0.9231650	-0.9095800	C	-1.5090910	5.0967790	0.3487160
P	1.2844200	0.9761120	0.0279280	C	-0.8314180	4.3492890	-0.6114480
C	1.5734910	2.2479600	-1.2505060	C	-1.4696420	3.2877850	-1.2598860
C	2.0658100	3.5139610	-0.9062980	C	-2.8047640	3.0059990	-0.9488900
C	2.2760780	4.4757970	-1.8874490	C	-0.7490170	2.4656620	-2.2789400
C	1.9893450	4.1895660	-3.2212370	C	0.6419670	2.2703570	-2.2573980
C	1.4891770	2.9394080	-3.5720890	Pd	-0.1042300	0.5201620	-1.1835310
C	1.2815940	1.9747400	-2.5897910	P	2.0120990	0.1569790	-0.0996560

C	2.9183290	0.4764110	0.6696440	C	2.1429240	1.1737810	1.4093890
C	2.9549040	-0.6126140	1.5506540	C	3.0076300	0.8480240	2.4600650
C	4.1485280	-0.9986650	2.1456410	C	3.0706450	1.6578720	3.5904530
C	5.3271550	-0.3216370	1.8388460	C	2.2787650	2.8007630	3.6800450
C	5.3060590	0.7334420	0.9330370	C	1.4205040	3.1350210	2.6352110
C	4.1052290	1.1385140	0.3529950	C	1.3529750	2.3235800	1.5083040
P	-2.1045210	-0.5997090	-0.1110040	C	3.4194400	0.6399710	-1.1606230
C	-2.6585280	1.0810770	-0.5485810	C	3.3568220	0.3210340	-2.5229220
C	-2.2128440	1.6165420	-1.7623340	C	4.4160580	0.6307280	-3.3688970
C	-2.5731630	2.9051640	-2.1387410	C	5.5421730	1.2764360	-2.8625240
C	-3.3936730	3.6660140	-1.3077240	C	5.6075950	1.6032060	-1.5110910
C	-3.8559340	3.1313690	-0.1076760	C	4.5533330	1.2830380	-0.6593330
C	-3.4869380	1.8447550	0.2761690	P	-1.5820460	-1.0226720	-0.1681700
C	-2.3349970	-0.8061750	1.6826960	C	-1.3574350	-1.0772700	1.6395390
C	-3.6143850	-0.9849910	2.2254290	C	-1.0475130	0.1180430	2.2968330
C	-3.7757390	-1.1103150	3.6002120	C	-0.7892360	0.1245850	3.6629870
C	-2.6647950	-1.0693410	4.4418420	C	-0.8511240	-1.0661120	4.3844860
C	-1.3906800	-0.9108720	3.9063600	C	-1.1840820	-2.2553660	3.7394330
C	-1.2270370	-0.7863860	2.5307030	C	-1.4349020	-2.2653990	2.3699430
H	0.7091920	-3.2181980	-2.6419660	C	-1.4943060	-2.7456850	-0.7389660
H	2.3991390	-0.6724580	-2.3879790	C	-2.6033540	-3.5967400	-0.6605430
H	2.2732570	3.7505170	0.1333900	C	-2.4803640	-4.9322810	-1.0290000
H	2.6602800	5.4523600	-1.6105180	C	-1.2545730	-5.4254530	-1.4728740
H	2.1506770	4.9440800	-3.9847540	C	-0.1507180	-4.5810420	-1.5553980
H	1.2582390	2.7154780	-4.6088870	C	-0.2711310	-3.2428830	-1.1963090
H	0.8725120	1.0068660	-2.8675220	H	-4.5097900	3.5086360	0.2454670
H	2.0464890	-1.1708920	1.7643000	H	-3.3566000	5.3789840	1.4152770
H	4.1626760	-1.8408790	2.8294120	H	-1.0062770	5.9268170	0.8355930
H	6.2629710	-0.6265300	2.2966040	H	0.1905550	4.6124110	-0.8681750
H	6.2251610	1.2533390	0.6812360	H	-3.3128280	2.1807330	-1.4418230
H	4.1013360	1.9702330	-0.3441310	H	-1.2626870	2.3198710	-3.2285120
H	-1.5672330	1.0280410	-2.4086550	H	1.1432280	1.9302630	-3.1590030
H	-2.2052390	3.3177950	-3.0726630	H	1.2664880	2.8155300	-1.5559420
H	-3.6720540	4.6749930	-1.5954830	H	3.6227720	-0.0452900	2.4034450
H	-4.4967560	3.7217980	0.5397620	H	3.7409890	1.3943100	4.4023830
H	-3.8251710	1.4511930	1.2292270	H	2.3304810	3.4284240	4.5643440
H	-4.4817400	-1.0379470	1.5730770	H	0.7953840	4.0207400	2.6962750
H	-4.7685110	-1.2489720	4.0162350	H	0.6561200	2.5788220	0.7148010
H	-2.7949830	-1.1724590	5.5144750	H	2.4734480	-0.1734360	-2.9225050
H	-0.5220950	-0.8866070	4.5568460	H	4.3594870	0.3761880	-4.4226070

H	-0.2333820	-0.6714250	2.1126550	H	6.3660220	1.5279290	-3.5229250
C	0.5608570	1.9474210	1.4086570	H	6.4831370	2.1075350	-1.1148110
C	-0.4578230	2.8655100	1.1305970	H	4.6171640	1.5418090	0.3929370
C	0.9723630	1.7706280	2.7335240	H	-0.9928910	1.0473320	1.7368900
C	-1.0658290	3.5739160	2.1612190	H	-0.5251180	1.0551390	4.1553560
H	-0.7721800	3.0444480	0.1071500	H	-0.6427970	-1.0670510	5.4498650
C	0.3567700	2.4774430	3.7619200	H	-1.2408210	-3.1822590	4.3017940
H	1.7794270	1.0867140	2.9736780	H	-1.6629370	-3.2019940	1.8714980
C	-0.6674730	3.3759580	3.4799120	H	-3.5599740	-3.2161740	-0.3139230
H	-1.8520630	4.2841330	1.9259730	H	-3.3425470	-5.5890490	-0.9704800
H	0.6877850	2.3301560	4.7852310	H	-1.1620340	-6.4691450	-1.7567290
H	-1.1449550	3.9278530	4.2834890	H	0.8059110	-4.9600270	-1.9005470
C	-3.3756540	-1.7055860	-0.8242890	H	0.5917470	-2.5882270	-1.2625690
C	-4.5474890	-1.2158930	-1.4026130	C	2.4016070	-1.5540960	0.4156000
C	-3.1760240	-3.0879100	-0.7322470	C	1.8234970	-2.0788670	1.5771300
C	-5.5068820	-2.1032850	-1.8899040	C	3.1627830	-2.3906890	-0.4076500
H	-4.7174780	-0.1466920	-1.4803820	C	1.9841660	-3.4231520	1.8937140
C	-4.1381480	-3.9681110	-1.2089470	H	1.2519170	-1.4403470	2.2423170
H	-2.2656740	-3.4774390	-0.2816300	C	3.3215420	-3.7355030	-0.0847120
C	-5.3058200	-3.4752190	-1.7919270	H	3.6376880	-1.9989090	-1.3014540
H	-6.4126990	-1.7154990	-2.3450620	C	2.7256100	-4.2565170	1.0604650
H	-3.9787790	-5.0386220	-1.1272700	H	1.5256490	-3.8160230	2.7957260
H	-6.0552330	-4.1636410	-2.1695080	H	3.9203470	-4.3736450	-0.7271840
H	-0.6587420	-2.1169300	-1.6409180	H	2.8482790	-5.3062750	1.3076100
H	0.4522080	-1.6303830	-3.5319770	C	-3.3292270	-0.5273660	-0.4065030
C	2.8563550	-2.4099960	-1.1422710	C	-4.1054580	-0.0293400	0.6387940
C	4.2309230	-2.1576880	-1.1505330	C	-3.8638220	-0.5748230	-1.7008070
C	2.3599640	-3.4539220	-0.3511950	C	-5.3981110	0.4329460	0.3903780
C	5.0961750	-2.9495180	-0.4051910	H	-3.7082480	0.0093190	1.6477550
H	4.6239750	-1.3380150	-1.7453920	C	-5.1546090	-0.1234600	-1.9430100
C	3.2246010	-4.2351620	0.4054110	H	-3.2672470	-0.9654280	-2.5222210
H	1.2897240	-3.6461360	-0.3170030	C	-5.9224120	0.3905660	-0.8961510
C	4.5962370	-3.9896150	0.3736630	H	-5.9943430	0.8217450	1.2100860
H	6.1624050	-2.7482010	-0.4268590	H	-5.5649030	-0.1713750	-2.9468320
H	2.8292920	-5.0399880	1.0174000	H	-6.9287580	0.7499110	-1.0866780
H	5.2716240	-4.6059540	0.9587180	H	-1.4375530	0.8993920	-1.9784530
$[L_2Pd($*iso*-phenylethyl$)]^+$				$[L_2Pd($*n*-phenylethyl$)]^+$			
C	-2.6847100	3.8036790	0.3149380	C	2.1468930	-5.6668790	0.8729500
C	-2.0969770	4.5733110	-0.6867990	C	1.1547540	-6.6254600	0.6774310

C	-0.7359150	4.4345670	-0.9592040	C	-0.0385610	-6.2674830	0.0557410
C	0.0216790	3.5127620	-0.2492670	C	-0.2384520	-4.9555600	-0.3657130
C	-0.5660840	2.7020200	0.7360960	C	0.7511680	-3.9901750	-0.1759380
C	-1.9268360	2.8808740	1.0251530	C	1.9446280	-4.3575190	0.4507380
C	0.2660040	1.7000260	1.4350030	C	0.5265560	-2.5479030	-0.5772470
C	-0.1467740	1.2371560	2.8121460	C	0.0897670	-1.7620860	0.6531120
Pd	0.1842020	-0.0182870	0.2371470	Pd	-0.2254530	0.2016020	0.1926830
P	-2.1730740	-0.5872880	-0.0020390	P	2.0764780	0.7245960	0.0383840
C	-2.8710940	0.0549420	-1.5606520	C	2.4769480	1.1003430	-1.7004420
C	-3.9417680	-0.5777440	-2.2030150	C	3.4858370	2.0058360	-2.0441890
C	-4.4731370	-0.0373170	-3.3684440	C	3.7689810	2.2578810	-3.3826530
C	-3.9416510	1.1367390	-3.9008370	C	3.0510790	1.6080800	-4.3847240
C	-2.8741690	1.7673420	-3.2690680	C	2.0446320	0.7058310	-4.0493260
C	-2.3367170	1.2266720	-2.1044720	C	1.7551700	0.4552700	-2.7115940
C	-3.4136600	-0.2041240	1.2780630	C	3.3007310	-0.5039730	0.5909590
C	-3.2311990	-0.7355670	2.5612660	C	3.3041740	-0.8753050	1.9422470
C	-4.1214230	-0.4244170	3.5827140	C	4.2061480	-1.8262070	2.4046450
C	-5.1972460	0.4266690	3.3337170	C	5.1052470	-2.4213600	1.5201840
C	-5.3841930	0.9556840	2.0601120	C	5.0979110	-2.0644800	0.1750790
C	-4.4982920	0.6407670	1.0320050	C	4.1988530	-1.1076770	-0.2921940
P	2.5109590	-0.0884030	0.0499280	P	-2.5389450	0.2368340	0.0876400
C	3.2108150	0.8597010	-1.3357390	C	-3.4174760	-0.5116360	-1.3073300
C	2.3655190	1.6106600	-2.1561770	C	-3.2500180	-1.8845820	-1.5220490
C	2.8835190	2.3011170	-3.2497040	C	-3.9131200	-2.5106370	-2.5715260
C	4.2448100	2.2388220	-3.5290350	C	-4.7387030	-1.7678440	-3.4134750
C	5.0910400	1.4754130	-2.7243990	C	-4.9068350	-0.4012570	-3.2035700
C	4.5774070	0.7819060	-1.6360920	C	-4.2496860	0.2301380	-2.1514230
C	2.9474810	-1.8155280	-0.3621520	C	-2.2983440	2.0111100	-0.2823770
C	3.7633040	-2.6248250	0.4299000	C	-2.6195340	3.0163710	0.6387910
C	4.0092310	-3.9438240	0.0542500	C	-2.2305710	4.3294610	0.3977280
C	3.4486310	-4.4599640	-1.1099280	C	-1.5065830	4.6526100	-0.7508220
C	2.6452460	-3.6513130	-1.9128170	C	-1.1751720	3.6600820	-1.6683270
C	2.3956310	-2.3356400	-1.5414540	C	-1.5647380	2.3423300	-1.4377380
H	-3.7384950	3.9232840	0.5462730	H	3.0818380	-5.9406060	1.3528310
H	-2.6929470	5.2907790	-1.2419500	H	1.3126560	-7.6484390	1.0045400
H	-0.2651980	5.0537630	-1.7165870	H	-0.8130030	-7.0116080	-0.1041990
H	1.0845070	3.4124600	-0.4524620	H	-1.1694310	-4.6829930	-0.8591280
H	-2.3994250	2.2966730	1.8065520	H	2.7208620	-3.6111210	0.6008310
H	1.3186140	1.9876970	1.4194130	H	-0.2335490	-2.4866680	-1.3646250
H	-0.1495350	2.1063060	3.4852350	H	-0.8390400	-2.1531710	1.0748510

H	0.5693600	0.5147150	3.2109680	H	0.8621630	-1.7567270	1.4266450
H	-1.1463220	0.7963730	2.8375200	H	4.0436010	2.5211390	-1.2676870
H	-4.3578730	-1.4948500	-1.7961680	H	4.5501990	2.9644790	-3.6440790
H	-5.3027210	-0.5327360	-3.8629580	H	3.2742610	1.8072730	-5.4281710
H	-4.3604640	1.5565980	-4.8101630	H	1.4842340	0.1985320	-4.8283840
H	-2.4560470	2.6815000	-3.6789450	H	0.9653750	-0.2456850	-2.4507800
H	-1.5052320	1.7239600	-1.6141770	H	2.6106140	-0.4073440	2.6373010
H	-2.3965090	-1.4045380	2.7592340	H	4.2074490	-2.1032030	3.4539600
H	-3.9768320	-0.8470610	4.5719540	H	5.8099930	-3.1638960	1.8808550
H	-5.8910360	0.6729310	4.1312580	H	5.7950300	-2.5275990	-0.5157980
H	-6.2250320	1.6130150	1.8615360	H	4.2054710	-0.8313070	-1.3420840
H	-4.6489720	1.0608400	0.0424810	H	-2.6045830	-2.4638500	-0.8664100
H	1.2996130	1.6458780	-1.9469980	H	-3.7819430	-3.5753620	-2.7358930
H	2.2220350	2.8826130	-3.8840700	H	-5.2508800	-2.2555070	-4.2368880
H	4.6491900	2.7756580	-4.3813270	H	-5.5507770	0.1759810	-3.8592780
H	6.1505860	1.4146090	-2.9511710	H	-4.3811030	1.2965870	-1.9921560
H	5.2361400	0.1736280	-1.0218820	H	-3.1748370	2.7703930	1.5389760
H	4.2172850	-2.2323780	1.3339920	H	-2.4966230	5.1054550	1.1085230
H	4.6470900	-4.5665540	0.6734240	H	-1.2048700	5.6796580	-0.9300050
H	3.6447990	-5.4880380	-1.3973340	H	-0.6131270	3.9043120	-2.5638450
H	2.2196630	-4.0425350	-2.8318000	H	-1.3230820	1.5774380	-2.1723100
H	1.7843660	-1.7038950	-2.1836070	C	2.4543090	2.2477340	0.9650620
C	-2.2361910	-2.4084320	-0.1561970	C	1.4513690	3.2188510	1.0671080
C	-1.1052040	-3.0629030	-0.6555490	C	3.7085180	2.4888810	1.5343070
C	-3.3616710	-3.1627580	0.1911380	C	1.7024230	4.4195800	1.7206710
C	-1.0950990	-4.4438170	-0.8135460	H	0.4706300	3.0464580	0.6289210
H	-0.2134300	-2.4986510	-0.9240110	C	3.9532520	3.6902490	2.1937410
C	-3.3519430	-4.5456200	0.0312870	H	4.4915420	1.7391610	1.4698050
H	-4.2427070	-2.6741870	0.5971830	C	2.9535940	4.6552910	2.2863220
C	-2.2218820	-5.1868410	-0.4707360	H	0.9186090	5.1671750	1.7915080
H	-0.2042720	-4.9341530	-1.1939110	H	4.9270740	3.8707200	2.6376760
H	-4.2295250	-5.1236800	0.3034020	H	3.1488450	5.5905950	2.8013910
H	-2.2181780	-6.2658290	-0.5894450	C	-3.5928330	0.1067610	1.5515630
C	3.4187650	0.3720170	1.5575390	C	-4.9869220	0.0446740	1.4535600
C	4.3132050	1.4442550	1.6031200	C	-2.9779000	0.0951240	2.8085830
C	3.1128190	-0.3190060	2.7393590	C	-5.7574430	-0.0164090	2.6095350
C	4.9102170	1.8044300	2.8096530	H	-5.4679720	0.0362610	0.4798480
H	4.5482340	2.0019550	0.7023330	C	-3.7547700	0.0414260	3.9613330
C	3.7196980	0.0364300	3.9374740	H	-1.8930120	0.1266020	2.8805090
H	2.3985390	-1.1392900	2.7200000	C	-5.1429370	-0.0150620	3.8604320

C	4.6200070	1.1004440	3.9734580	H	-6.8387430	-0.0686360	2.5335190
H	5.6061640	2.6368010	2.8352100	H	-3.2770080	0.0326190	4.9355920
H	3.4854250	-0.5109770	4.8449720	H	-5.7484300	-0.0649950	4.7599870
H	5.0904270	1.3813380	4.9102800	H	1.4553520	-2.1337610	-0.9851610

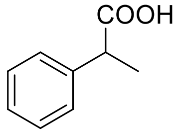
4. Characterization data

4.1 General procedure: $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), PPh_3 (0.03 mmol, 7.8 mg), $FeCl_3$ (0.02 mmol, 3.2 mg), 1,4-dioxane (2 mL), **1** (1.0 mmol) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (2 mmol, 36 μL) with syringe under nitrogen atmosphere. The vial was placed in an alloyed plate, which was then transferred into an autoclave (250 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 50 bar. The reaction was performed at 80 °C for 10 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Remove the solvent under vacuum and the residue was directly purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10/1 - 3/1) to give the desired carboxylic acid **2** or carboxylic acid **3**. After sealed, the vial was brought out of the glovebox followed by addition of H_2O with syringe under nitrogen atmosphere.

Experimental procedure for 2 (**2j, 2o**)**:** $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), PPh_3 (0.03 mmol, 7.8 mg), $FeCl_3$(0.02 mmol, 3.2 mg), 1,4-dioxane (2 mL), **1** (1mmol, **1j, 1o**) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (2 mmol, 36 μL) with syringe under nitrogen atmosphere. At room temperature, the autoclave pressurized with CO gas to 50 bar. The reaction was performed at 100 °C for 15 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Remove the solvent under vacuum, and the residue was directly purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10/1-3/1) to give the product **2j** or **2o**.

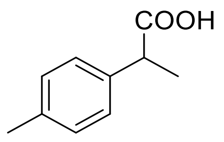
Experimental procedure for 2 (2l, 2t, 2u, 2x): $Pd(OAc)_2$ (0.02 mmol, 4.4 mg), PPh_3 (0.06 mmol, 15.6 mg), $FeCl_3$ (0.04 mmol, 6.4 mg), 1,4-dioxane (2 mL), **1** (1 mmol, **1l, 1t, 1u, 1x**) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (2 mmol, 36 μL) with syringe under nitrogen atmosphere. At room temperature, the autoclave pressurized with CO gas to 50 bar.The reaction was performed at 120 °C for 15 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Remove the solvent under vacuum, and the residue was directly purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10/1-3/1) to give the product **2** (**2l, 2t, 2u, 2x**).

2-phenylpropionic acid, **2a**



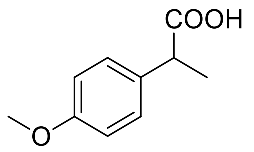
Colourless oil; 91% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) 7.37-7.16 (m, 5H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 139.8, 128.8, 127.7, 127.5, 45.5, 18.2. Data are in accordance with those reported in ref. [3, 4, 5, 6, 7].

2-(4-methylphenyl) propanoic acid, **2b**



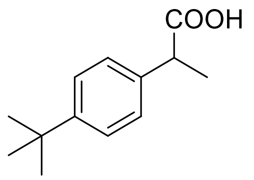
White solid; m.p. 31-32 °C; 90% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 7.19-7.15 (m, 4H), 3.70 (q, *J* = 7.0 Hz, 1H), 2.33 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.5, 137.2, 136.9, 129.5, 127.6, 45.2, 21.1, 18.2. Data are in accordance with those reported in ref. [4, 5].

2-(4-methoxyphenyl) propanoic acid, **2c**



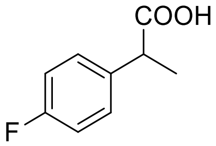
Yellow solid; m.p. 52-53 °C; 71% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, br, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 3.76 (d, *J* = 6.9 Hz, 1H), 1.56 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 158.9, 131.9, 128.7, 114.1, 55.3, 44.6, 18.2. Data are in accordance with those reported in ref. [4].

2-(4-(tert-butyl) phenyl) propanoic acid, **2d**



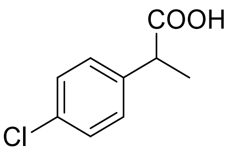
White solid, mp. 90-91 °C; 91% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 4H), 3.71 (q, *J* = 6.9 Hz, 1H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.5, 150.3, 136.7, 127.4, 125.7, 45.0, 34.6, 31.4, 18.1. Data are in accordance with those reported in ref. [5].

2-(4-fluorophenyl) propionic acid, **2e**



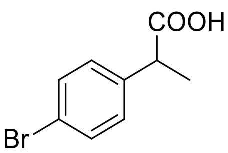
Colourless oil; 72% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 1H), 7.28-6.99 (m, 4H), 3.83-3.55 (m, 1H), 1.49 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 162.2(d, *J* = 246 Hz), 135.5 (d, *J* = 3.0 Hz), 129.3 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21 Hz), 44.8, 18.3. Data are in accordance with those reported in ref. [4].

2-(4-chlorophenyl) propionic acid, **2f**



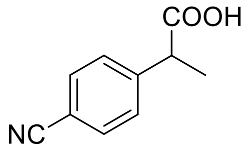
White solid, m.p. 47-49 °C; 86% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 4H), 3.74-3.64 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 138.2, 133.4, 129.1, 128.9, 44.9, 18.2. Data are in accordance with those reported in ref. [5, 8].

2-(4-bromophenyl) propanoic acid, **2g**



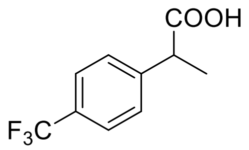
White solid; m.p. 66-67 °C; 85% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 3.70 (q, *J* = 6.9 Hz, 1H), 1.49 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 138.6, 131.8, 129.4, 121.4, 44.8, 18.0. Data are in accordance with those reported in ref. [9].

2-(4-cyanophenyl) propanoic acid, **2h**



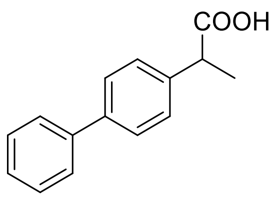
Yellow solid; m.p. 103-105 ºC. 67% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, br, 1H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.46 (d, *J* = 13.0 Hz, 2H), δ 3.80 (q, *J* = 7.8, 10.7 Hz, 1H), 1.58 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 144.9, 132.6, 128.7, 118.7, 111.5, 45.5, 18.0. Data are in accordance with those reported in ref. [6, 7].

2-(4-(trifluoromethyl) phenyl) propanoic acid, **2i**



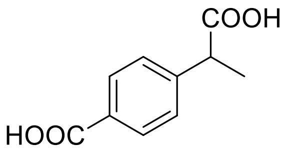
Colorless oil; 64% yield, *iso*/*n* = 100/0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 3.81 (q, *J* = 7.1 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 143.6, 129.9 (q, *J* = 33 Hz), 128.2, 125.6 (q, *J* = 3.3 Hz), 122.7 (q, *J* = 270 Hz), 45.3, 18.0. Data are in accordance with those reported in ref. [6].

2-phenylpropanoic acid, **2j**



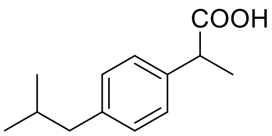
White solid; m.p. 134-136 °C; 70% yield, *iso*/*n* = 97/3; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.41 (s, br, 1H), 7.65-7.60 (m, 4H), 7.50-7.32 (m, 5H), 3.73 (q, *J* = 6.9 Hz, 1H), 1.41 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.4, 140.5, 140.0, 138.8, 128.9, 128.1, 127.4, 126.8, 126.6, 44.4, 18.5. Data are in accordance with those reported in ref. [4, 5].

2-(4-carboxyphenyl) propionic acid, **2k**



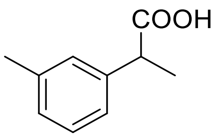
Yellow oil; 56% yield, *iso*/*n* = 97/3; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (s, 2H), 7.91 (d, *J* = 6.0 Hz, 2H), 7.40 (d, *J* = 5.9 Hz, 2H), 3.77 (d, *J* = 5.2 Hz, 1H), 1.37 (d, *J* = 4.5 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.0, 167.3, 146.3, 129.7, 129.4, 127.8, 44.8, 18.4. Data are in accordance with those reported in ref. [10].

2-(4-isobutylphenyl) propionic acid, **2l**



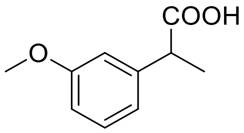
White solid; 77-78 ºC; 92% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 3.76 (q, *J* = 6.7 Hz, 1H), 2.50 (d, *J* = 6.9 Hz, 2H), 1.95-1.85 (m, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 140.9, 136.9, 129.4, 127.3, 45.1, 44.9, 30.2, 22.4, 18.1. HRMS (ESI): Calcd. for $C_{13}H_{17}O_2$ $[M]^+$: 205.12340, Found: 205.1232.

2-(3-methylphenyl) propanoic acid, **2m**



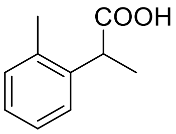
Yellow oil; 91% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, br, 1H), 7.27-7.06 (m, 4H), 3.78-3.61 (m, 1H), 2.33 (s, 3H), 1.49 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 139.8, 138.4, 128.7, 128.4, 128.3, 124.7, 45.5, 21.5, 18.2. Data are in accordance with those reported in ref. [4, 5].

2-(3-methoxyphenyl) propanoic acid, **2n**



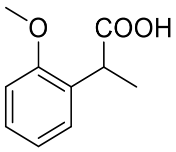
Yellow oil; 96% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (s, br, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 6.96-6.76 (m, 3H), 3.79 (s, 3H), 3.72 (q, *J* = 7.0 Hz, 1H), 1.51 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 159.8, 141.3, 129.7, 120.0, 113.5, 112.7, 55.2, 45.5, 18.1. Data are in accordance with those reported in ref. [4, 5, 6].

2-(2-methylphenyl) propanoic acid, **2p**



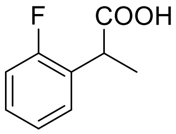
White solid; m.p. 75-76 °C; 94% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.26-7.15 (m, 3H), 3.98 (q, *J* = 7.0 Hz, 1H), 2.38 (s, 3H), 1.49 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.52, 138.41, 136.03, 130.65, 127.32, 126.65, 126.5, 41.25, 19.75, 17.60. Data are in accordance with those reported in ref. [4, 5, 11].

2-(2-methoxyphenyl) propanoic acid, **2q**



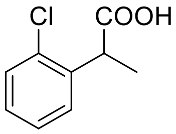
White solid; m.p. 94-96 °C; 96% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, br, 1H), 7.24-7.40 (m, 2H), 6.99-7.76 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.80 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H). 4.07 (q, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 156.7, 128.8, 128.4, 128.0, 120.8, 110.7, 55.4, 39.2, 16.9. Data are in accordance with those reported in ref. [4, 5].

2-(2-fluorophenyl) propionic acid, **2r**



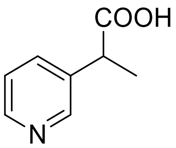
Colorless oil; 86% yield, *iso*/*n* = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, br, 1H), 7.50-7.24 (m, 2H), 7.24-7.01 (m, 2H), 4.13 (q, *J* = 6.9 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 161.7, 159.2, 128.9 (q, *J* =8.3 Hz), 127.2 (d, *J* = 15.1 Hz), 124.4 (*J* = 3.8 Hz), 115.6 (d, *J*= 23.0 Hz), 38.54, 17.23. Data are in accordance with those reported in ref. [12].

2-(2-chlorphenyl) propionic acid, **2s**



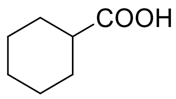
Colorless oil; 92% yield, *iso*/*n* = 93/7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 2H), 7.30-7.23 (m, 2H), 4.31 (q, *J* = 6.8 Hz, 1H), 1.56 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 137.7, 134.0, 129.8, 128.7, 128.6, 127.3, 42.1, 17.4. Data are in accordance with those reported in ref. [6, 12].

2-pyridyl propionic aicd**, 2t**



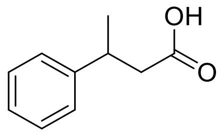
White solid; m.p. 84-85 °C; 73% yield, *iso*/*n* > 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.59 (s, 1H), 8.48 (d, *J* = 4.1 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.41-7.28 (m, 1H), 3.78 (q, *J* = 6.8 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 146.9, 145.7, 138.1, 137.3, 124.2, 43.5, 18.4. HRMS (ESI): calcd. for $C_8H_8NO_2$ 150.05550, Found: 150.0558.

Boxylic acid, **2u**



Colorless oil; 86% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 2.40-1.32 (m, 1H), 1.99-1.95 (m, 2H), 1.82-1.78 (m, 2H), 1.69-1.66 (m, 2H), 1.53-1.38 (m, 2H), 1.29-1.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 42.9, 28.7, 25.7, 25.3. Data are in accordance with those reported in ref. [12].

3-phenylbutanoic acid, **2x**



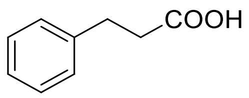
Colorless oil; 79% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 3H), 3.41-3.32 (m, 1H), 2.79-2.64 (m, 2H), 1.32 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.92, 145.50, 128.63, 126.77, 126.56, 42.69, 36.19, 21.92. Data are in accordance with those reported in ref. [13].

4.2 General procedure: $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), PPh_3 (0.06 mmol, 15.6 mg), $Fe(OTf)_3$ (0.05 mmmol, 26 mg), 1,4-dioxane (2 mL), **1** (1.0 mmol) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (1 mmol, 18 μL) with syringe under nitrogen atmosphere. The vial was placed in an alloyed plate, which was then transferred into an autoclave (250 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 10 bar. The reaction was performed at 120 °C for 10 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The regioselectivity was measured by ^1H NMR analysis. Remove the solvent under vacuum and the residue was directly purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10/1-3/1) to give the desired carboxylic acid **2** or carboxylic acid **3**.

Experimental procedure for 3 (**3u, 3x**)**:** $Pd(OTf)_2(CH_3CN)_4$ (0.01 mmol, 2.2 mg), PPh_3 (0.06 mmol, 15.6 mg), $FeCl_3$ (0.02 mmol, 3.2 mg), 1,4-dioxane (2 mL), **1** (**1u, 1x**, 1.0 mmol) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (1 mmol, 18 μL) with syringe under nitrogen atmosphere. The vial was placed in an alloyed plate, which was then transferred into an autoclave (250 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 10 bar. The reaction was performed at 120 °C for 10 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The regioselectivity was measured by ^1H NMR analysis. Remove the solvent under vacuum and the residue was directly purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10/1-3/1) to give the desired carboxylic acid.

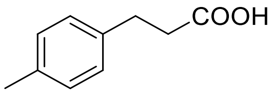
Experimental procedure for 3z, 3aa, 3ab, 3ac: $Pd(OAc)_2$ (0.01 mmol, 2.3 mg), PPh_3 (0.06 mmol, 15.6 mg), $Fe(OTf)_3$ (0.05 mmol, 25.6 mg), 1,4-dioxane (1 mL), **1** (**1z, 1aa, 1ab, 1ac**) and a stirring bar were added into a vial (5 mL) in glovebox. After sealed, the vial was brought out of the glovebox followed by addition of H_2O (3 mmol, 54 μL) with syringe under nitrogen atmosphere. The vial was placed in an alloyed plate, which was then transferred into an autoclave (250 mL) under nitrogen atmosphere. At room temperature, the autoclave was flushed with CO gas for five times and pressurized with CO gas to 50 bar. The reaction was performed at 120 °C for 15 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The regioselectivity was measured by GC analysis. Remove the solvent under vacuum and the residue was directly purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 50/1-10/1) to give the desired aliphatic carboxylic acid.

3-phenylpropionic acid, **3a**



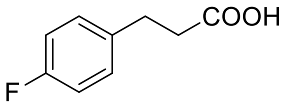
75% yield, *iso*/*n* =15/85; ^1H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, br, 1H), 7.37-7.30 (m, 3H), 7.28-7.20 (m, 2H), 2.97 (t, J = 7.8 Hz, 2H), 2.69 (t, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 140.2, 128.6, 128.3, 126.5, 35.7, 30.6. Data are in accordance with those reported in ref. [5, 14, 15].

3-(4-methylphenyl) propanoic acid, **3b**



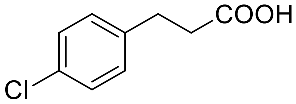
72% yield, *iso*/*n* = 16/84; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.12 (m, 4H), 2.97 (t, J = 7.7 Hz, 2H), 2.71 (t, J = 7.7 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 137.2, 136.0, 129.4, 128.4, 35.9, 30.23, 21.1. Data are in accordance with those reported in ref. [5, 15].

3-(4-fluorophenyl) propionic acid, **3e**



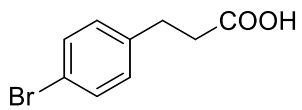
85% yield, *iso*/*n* = 17/83; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (m, 2H), 7.05-7.00 (m, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 161.6 (d, J = 242.8 Hz), 135.8 (d, J = 3.3 Hz), 129.8 (d, J = 7.9 Hz), 115.4 (d, J = 21.1 Hz), 35.9, 29.8. Data are in accordance with those reported in ref. [15].

3-(4-chlorophenyl) propionic acid, **3f**



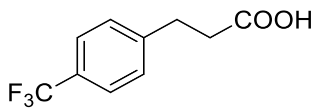
89% yield, *iso*/*n* = 11/89; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.3 Hz, 2H), 7.18 (d, J = 7.7 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 138.6, 132.2, 129.8, 128.7, 35.6, 29.9. Data are in accordance with those reported in ref. [5, 16].

3-(4-bromophenyl) propanoic acid, **3g**



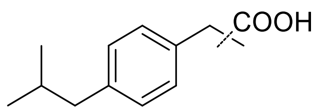
67% yield, *iso*/*n* = 23/77; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.17, 139.16, 131.73, 130.18, 120.30, 35.47, 30.03. Data are in accordance with those reported in ref. [15].

3-(4-trifluromethylphenyl) propanoic acid, **3i**



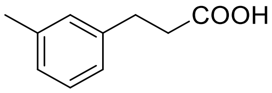
80% yield, *iso*/*n* = 15/85; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 179.0, 144.3, 129.1 (q, *J* =30.3Hz), 128.2, 125.6 (q, *J* =3.8 Hz), 123.0 (q, *J* =270 Hz), 35.2, 30.4. Data are in accordance with those reported in ref. [15].

3-(4-isobutylphenyl) propionic acid, **3l**



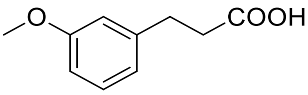
84% yield, *iso*/*n* = 31/69; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, br, 1H), 7.11-7.05 (m, 4H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.43 (d, *J* = 6.1 Hz, 2H), 1.88-1.78 (m, 1H), 0.89 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 139.8, 137.4, 129.3, 128.0, 45.1, 35.8, 30.3, 30.2, 22.4.

3-(3-methylphenyl) propanoic acid, **3m**



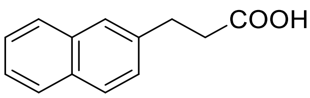
70% yield, *iso*/*n* = 19/81; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 1H), 7.14-7.00 (m, 3H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 140.2, 138.3, 129.2, 128.6, 127.2, 125.4, 35.8, 30.6, 21.5. Data are in accordance with those reported in ref. [5, 17].

3-(3-methoxyphenyl) propanoic acid, **3n**



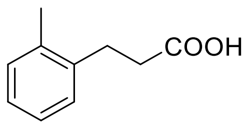
86% yield, *iso*/*n* = 19/81; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, *J* = 10.9, 1H), 6.90-6.78 (m, 3H), 3.80 (s, 3H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.69 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 159.7, 141.9, 129.6, 120.7, 114.1, 111.7, 55.2, 35.6, 30.8. Data are in accordance with those reported in ref. [5, 14].

3-naphthalen-2-yl propanoic acid, **3o**



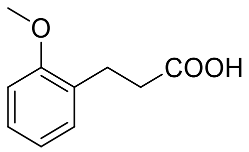
68% yield, *iso*/*n* = 16/84; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, br, 1H), 7.57-7.06 (m, 7H), 3.04 (t, *J* = 7.8 Hz, 2H), 2.77 (t, *J* = 7.8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 140.2, 128.8, 128.6, 128.3, 127.7, 127.5, 126.4, 35.7, 30.6. Data are in accordance with those reported in ref. [14].

3-(2-methylphenyl) propanoic acid, **3p**



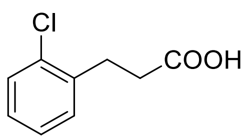
77% yield, *iso*/*n* = 6/94; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, br, 1H), 7.15 (s, 4H), 3.06-2.88 (m, 2H), 2.76-2.60 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 138.3, 136.1, 130.5, 128.5, 126.6, 126.3, 34.5, 28.0, 19.4. Data are in accordance with those reported in ref. [5, 15, 18].

3-(2-methoxyphenyl) propanoic acid, **3q**



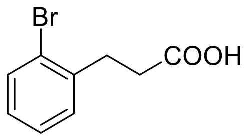
45% yield, *iso*/*n* = 20/80; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, br, 1H), 7.34-7.22 (m, 2H), 6.99-6.89 (m, 2H), 3.89 (s, 3H), 3.03 (t, J = 7.8 Hz, 2H), 2.75 (t, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 157.5, 130.0, 128.5, 127.8, 120.5, 110.3, 55.2, 34.1, 26. Data are in accordance with those reported in ref. [5].

3-(2-chlorophenyl) propionic acid, **3s**



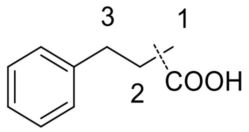
White solid; m.p. 85-86 °C; 76% yield, *iso*/*n* = 1/99; ^{1}H NMR (400 MHz, $CDCl_3$), 7.41-7.24 (m, 4H), 3.12 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 137.8, 134.1, 130.6, 129.7, 128.1, 127.1, 33.8, 28.7. Data are in accordance with those reported in ref. [5].

3-(2-bromophenyl) propanoic acid, **3y**



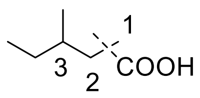
White solid; 99-102 °C; 68% yield, *iso*/*n* = 2/98; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, br, 1H), 7.42-7.21 (m, 4H), 3.13 (t, J = 7.7 Hz, 2H), 2.78 (t, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 137.7, 134.0, 130.54, 129.7, 128.1, 127.1, 33.8, 28.7. Data are in accordance with those reported in ref. [19].

4-phenylbutanoic acid, **3z**



89% yield, 1/2/3 = 82/17/1 (The regioselectivity was measured by GC analysis); **3z**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.24 (t, J = 7.6 Hz, 3H), 2.72 (t, J = 7.5 Hz, 2H), 2.42 (t, J = 7.5 Hz, 2H), 2.05-1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 141.4, 128.7, 128.6, 126.2, 35.2, 33.6, 26.4. Data are in accordance with those reported in ref. [20].

4-methylhexanoic acid, **3aa**



53% yield, 1/2/3 = 93/2/5 (The regioselectivity was measured by GC analysis); **3aa**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47-2.24 (m, 2H), 1.72-1.64 (m, 1H), 1.47-1.33 (m, 3H), 1.20-1.12 (m, 1H), 0.89-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 33.9, 31.9, 31.2, 29.1, 18.8, 11.3. Data are in accordance with those reported in ref. [21].

5. References:

(1) M. J. Frisch, W. G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, T. Ishida, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin,V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman,V. J. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

(2) H. Li, K. Dong, H. Jiao, H. Neumann, R. Jackstell, M. Beller, *Nature Chem.*, 2016, **8**, 1159.

(3) J. E. Milne, T. Storz, J. T. Colyer, *J. Org. Chem*., 2011, **76**, 9519.

(4) M. D. Greenhalgh, S. P. Thomas, *J. Am. Chem. Soc.*, 2012, **134**, 11900.

(5) (a) W. Liu, W. Ren, Y. Shi, et al. *Org. Lett.*, 2017, **19**, 1748.

(6) C. M. Williams, J. B. Johnson, T. Rovis, *J. Am. Chem. Soc.*, 2008, **130**, 14936.

(7) M. Ohkoshi, J. Michinishi, H. Senboku, *Tetrahedron*, 2010, **66**, 7732.

(8) A. Aramini, M. R. Sablone, G. Bianchini, et al., *Tetrahedron*, 2012, **65**, 2015.

(9) T. Muller, L. Johann, E. D. Charvet, et al. *J. Am. Chem. Soc.*, 2011, **133**, 11557.

(10) T. M. Konrad, J. T. Durrani, M. L. Clarke, *Chem. Commun.*, 2013, **49**, 3306.

(11) I. Shiina, K. Nakata, M. Itagaki, et al. *J. Am. Chem. Soc.*, 2010, **132**, 11629.

(12) (a) A. Mai, M. Artico, J. A. Este, et al. *J. Med. Chem.*, 2007, **50**, 5412. (b) J. Li, D. Liu, W. Zhang, *Org. Lett.*, 2016, **18**, 2122.

(13) L. R. Cafiero, T. S. Snowden, *Org. Lett.*, 2008, **10**, 3853.

(14) Y. Zhang, J. Jiao, Flowers, II, R. A. *J. Org. Chem.*, 2006, **71**, 4516.

(15) N. R. Vautravers, B. Breit, *Synlett*, 2011, **17**, 2517.

(16) A. J. Pearson, K. Lee, *J. Org. Chem.*, 1994, **59**, 2257.

(17) J. B. Arterburn, M. Pannala, R. M. Chamberlin, et al., *Tetrahedron Lett*., 2000, **41**, 7847.

(18) M. Lima, K. A. D. Castro, H. Rhee, *Appl. Organometal. Chem.*, 2011, **25**, 1.

(19) A. Stößel, M. Gütschow, C. E. Müller, et al. G. *J. Med. Chem.*, 2013, **56**, 4580.

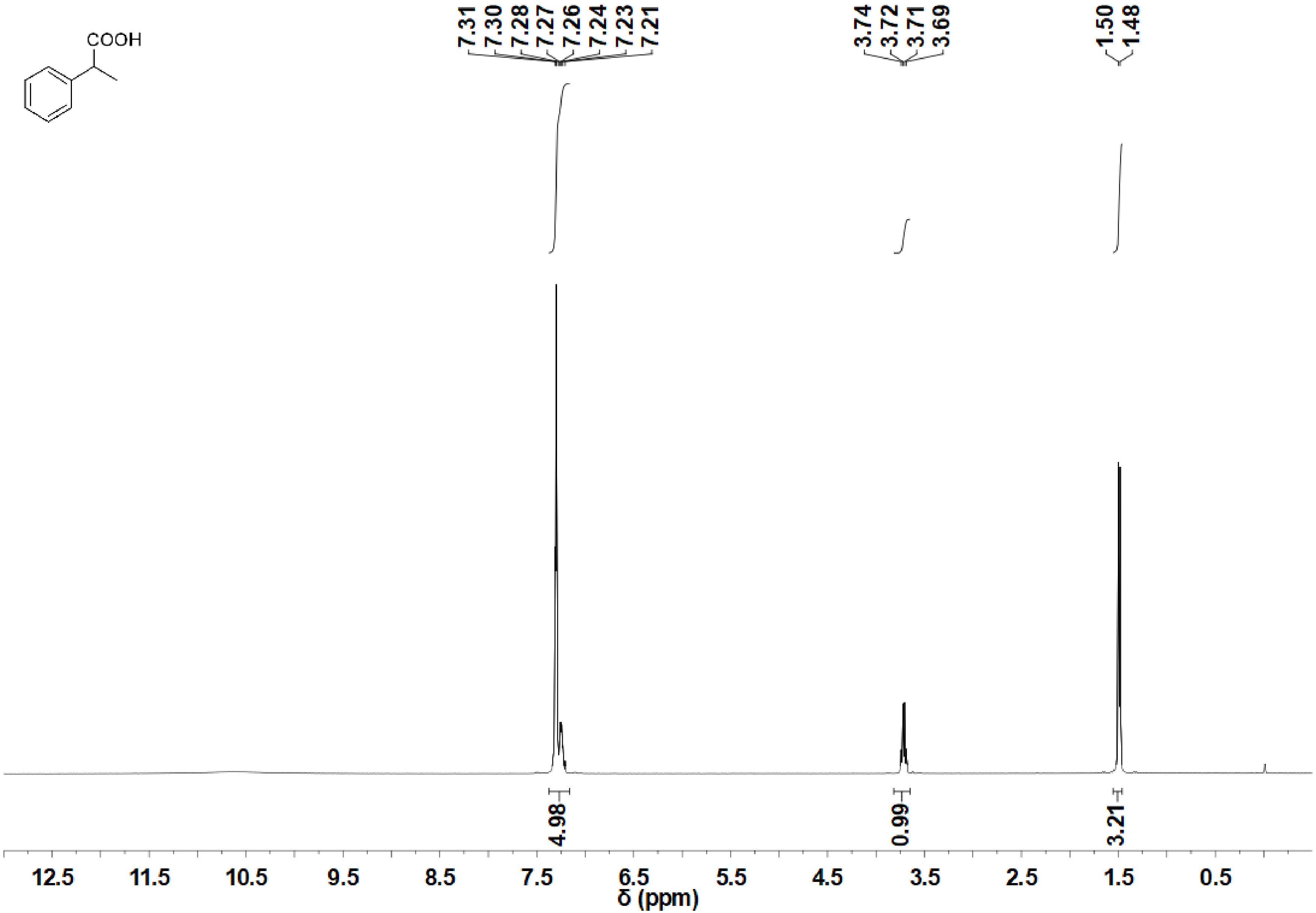
(20) A. C. Bonaparte, M. P. Betush, S. S. Murphree, et al. *Org. Lett*., 2011, **13**, 1447.

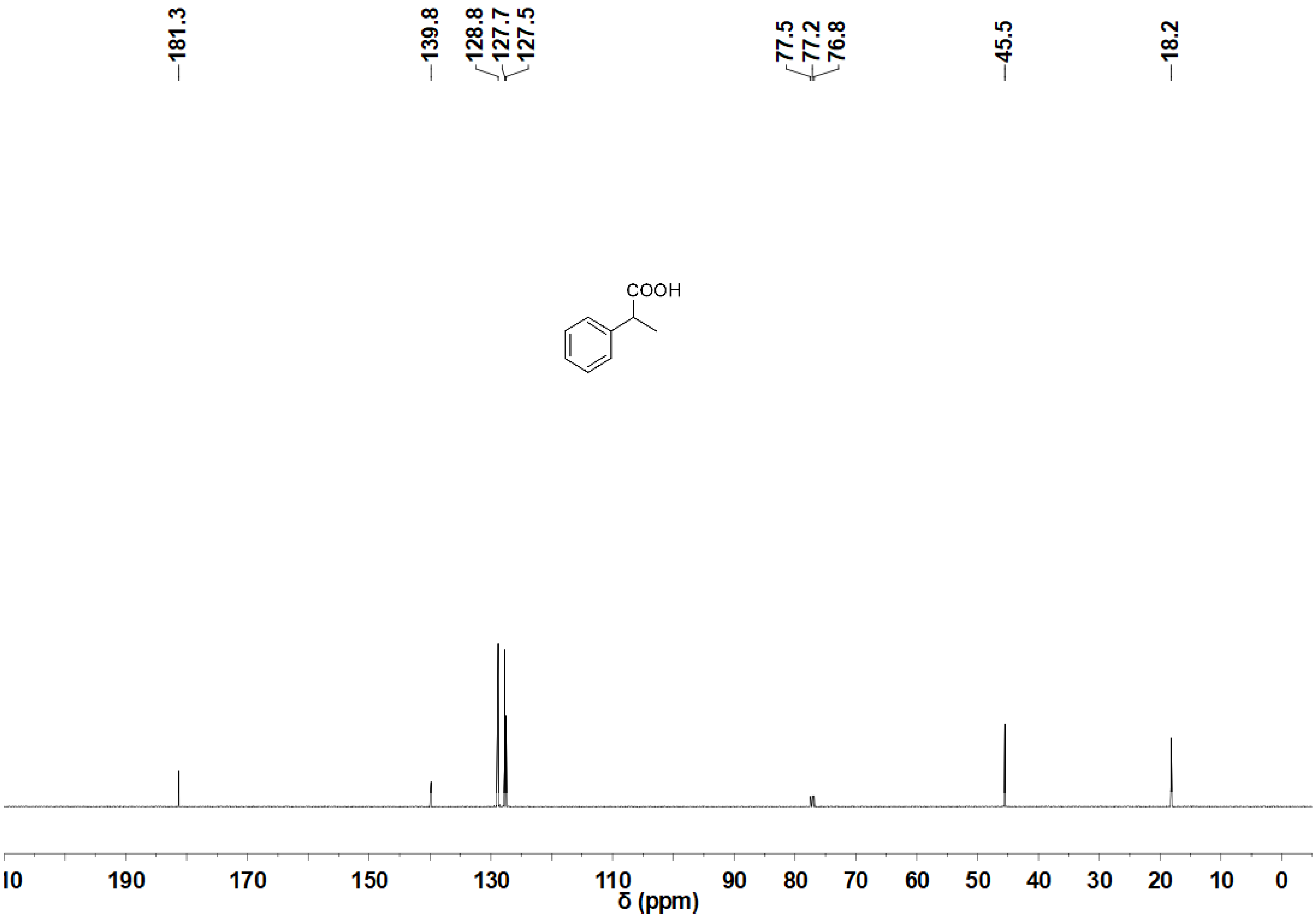
(21) K. Mori, S. Kuwahara, H. Ueda, *Tetrahedron*, 1983, **39**, 2439.

6. Copies of product spectra

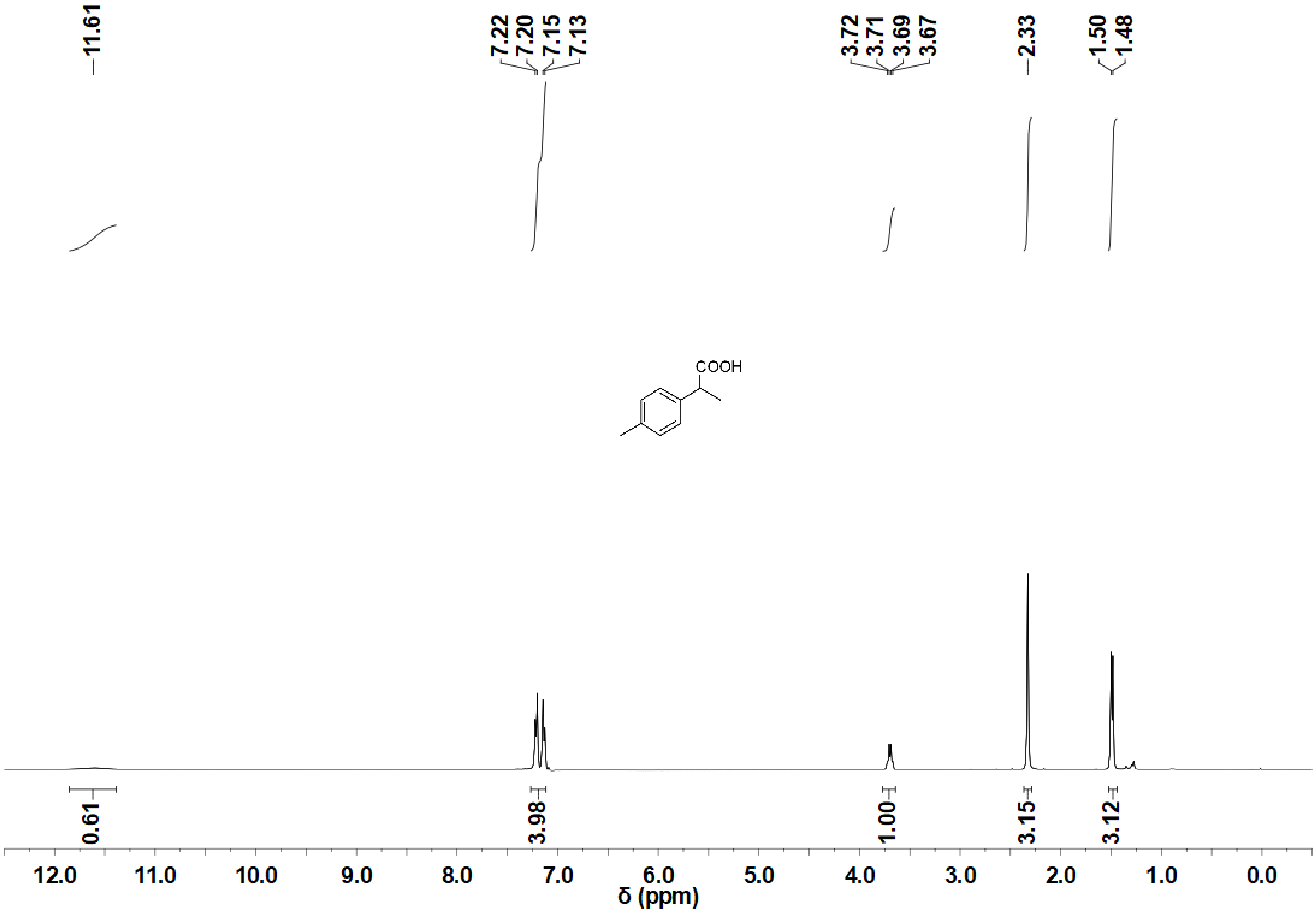
2-phenylpropionic acid, **2a**

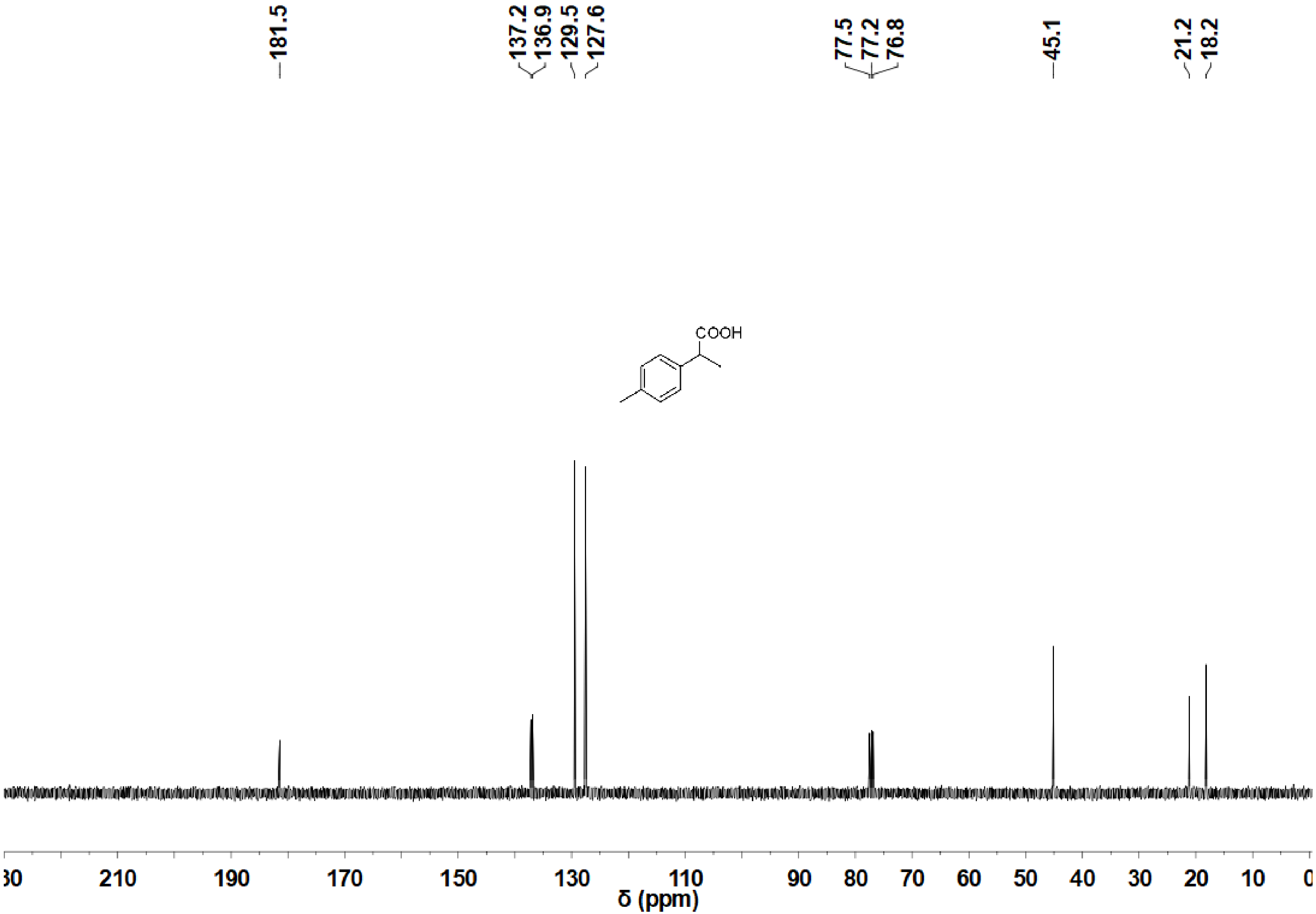
400 MHz, $CDCl_3$



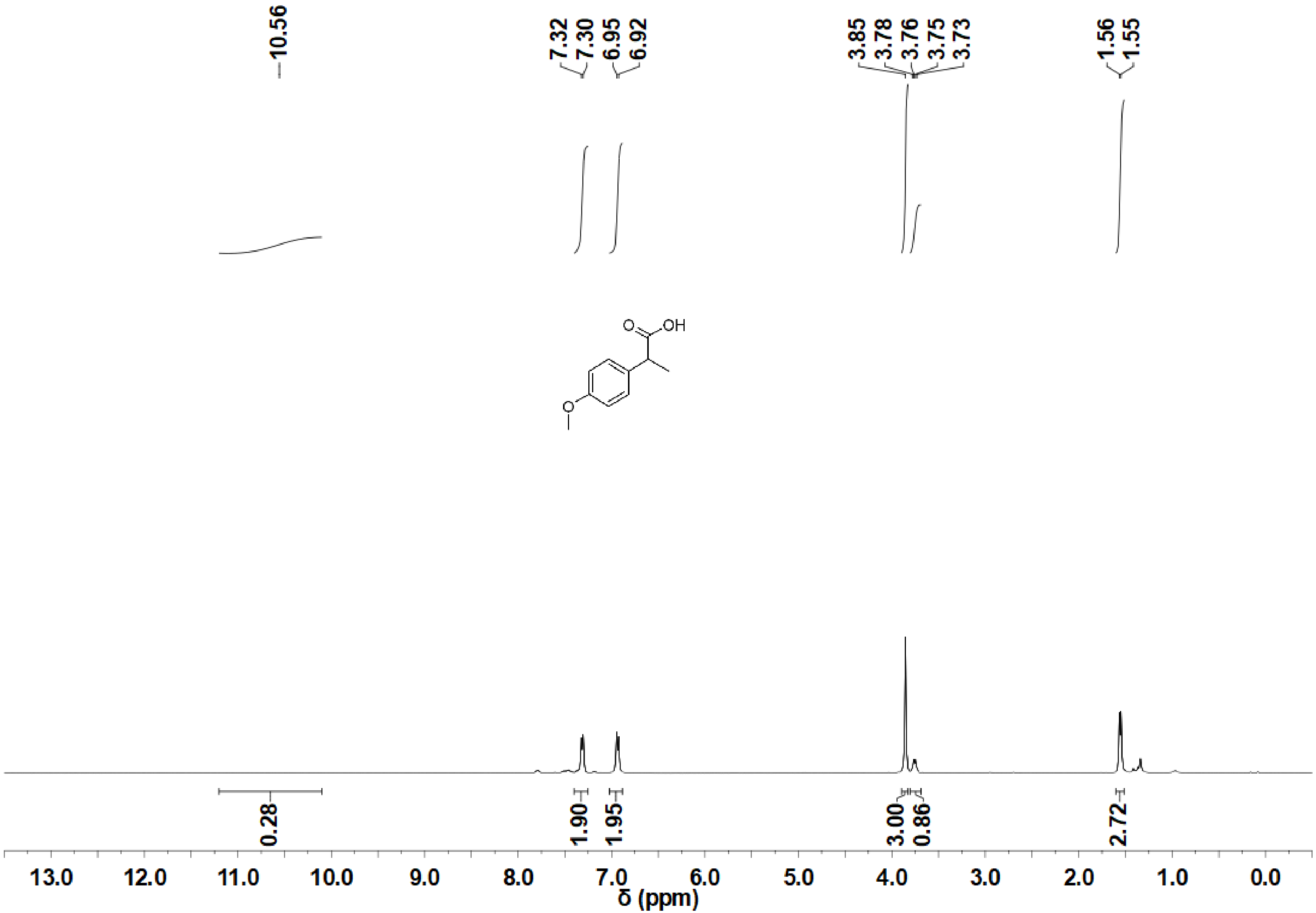

181.3
139.8
128.8
127.7
127.5
77.5
77.2
76.8
45.5
18.2
COOH
δ (ppm)

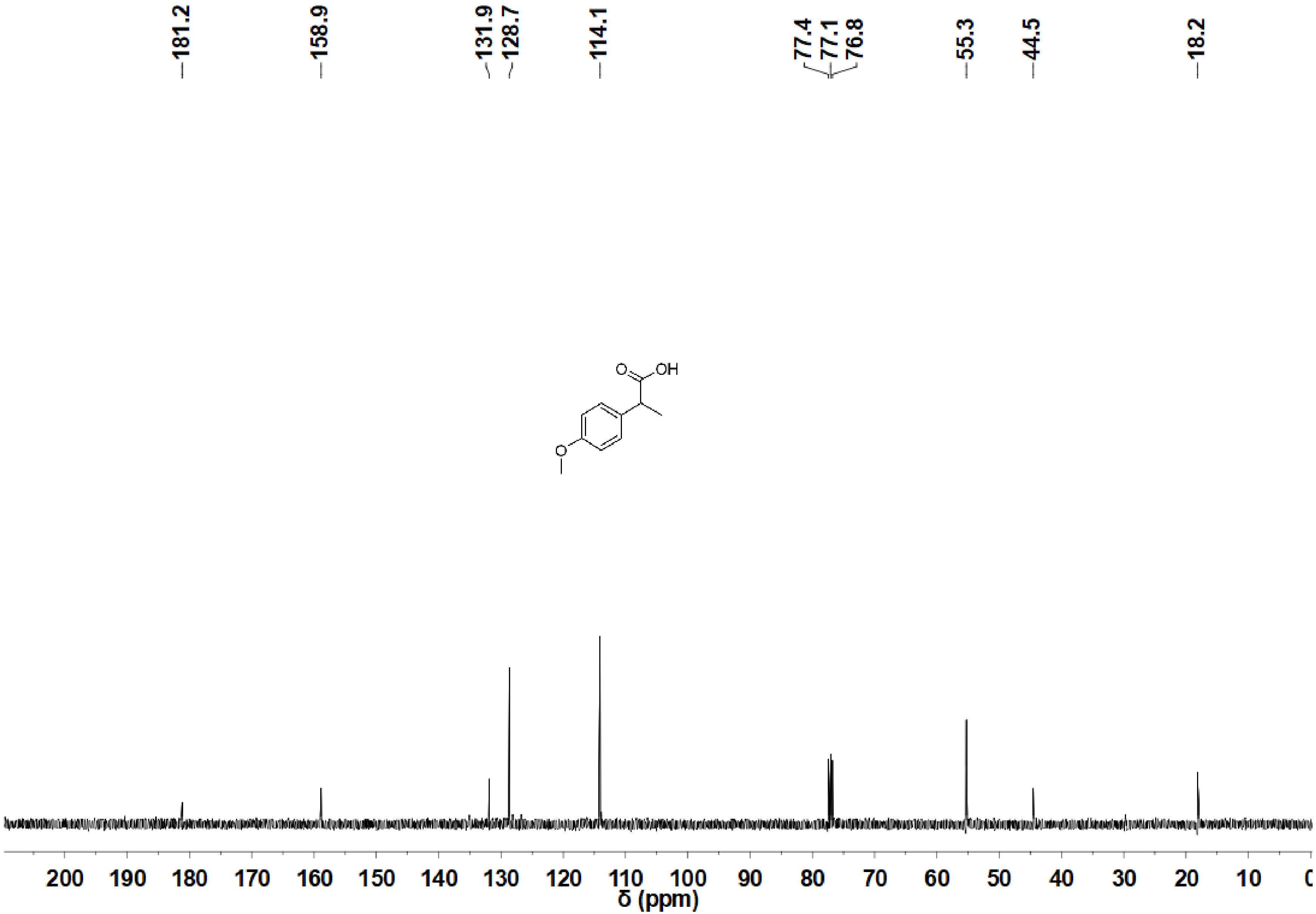
2-(4-methylphenyl) propanoic acid, **2b**
400 MHz, $CDCl_3$



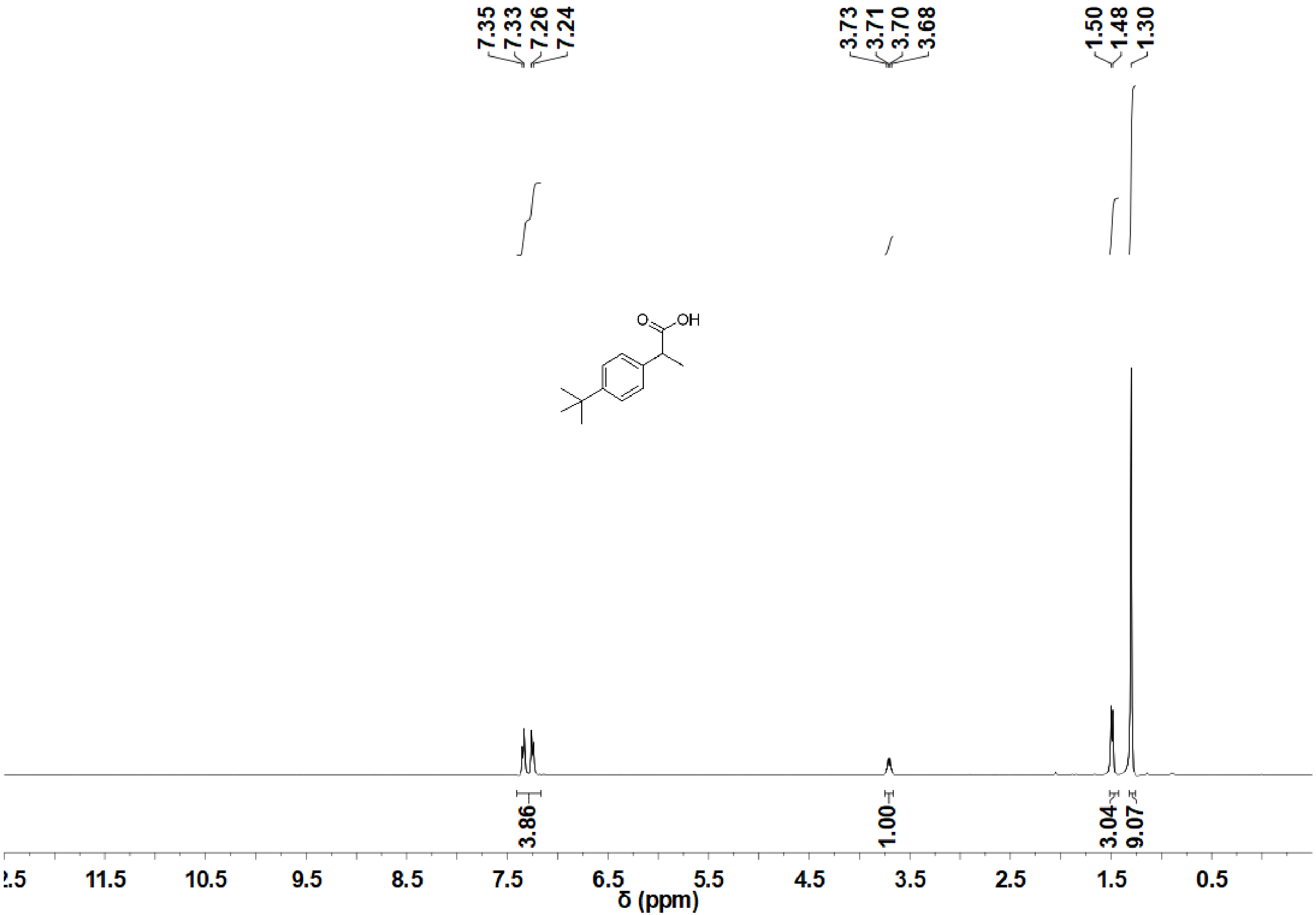

181.5
137.2
136.9
129.5
127.6
77.5
77.2
76.8
45.1
21.2
18.2
COOH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

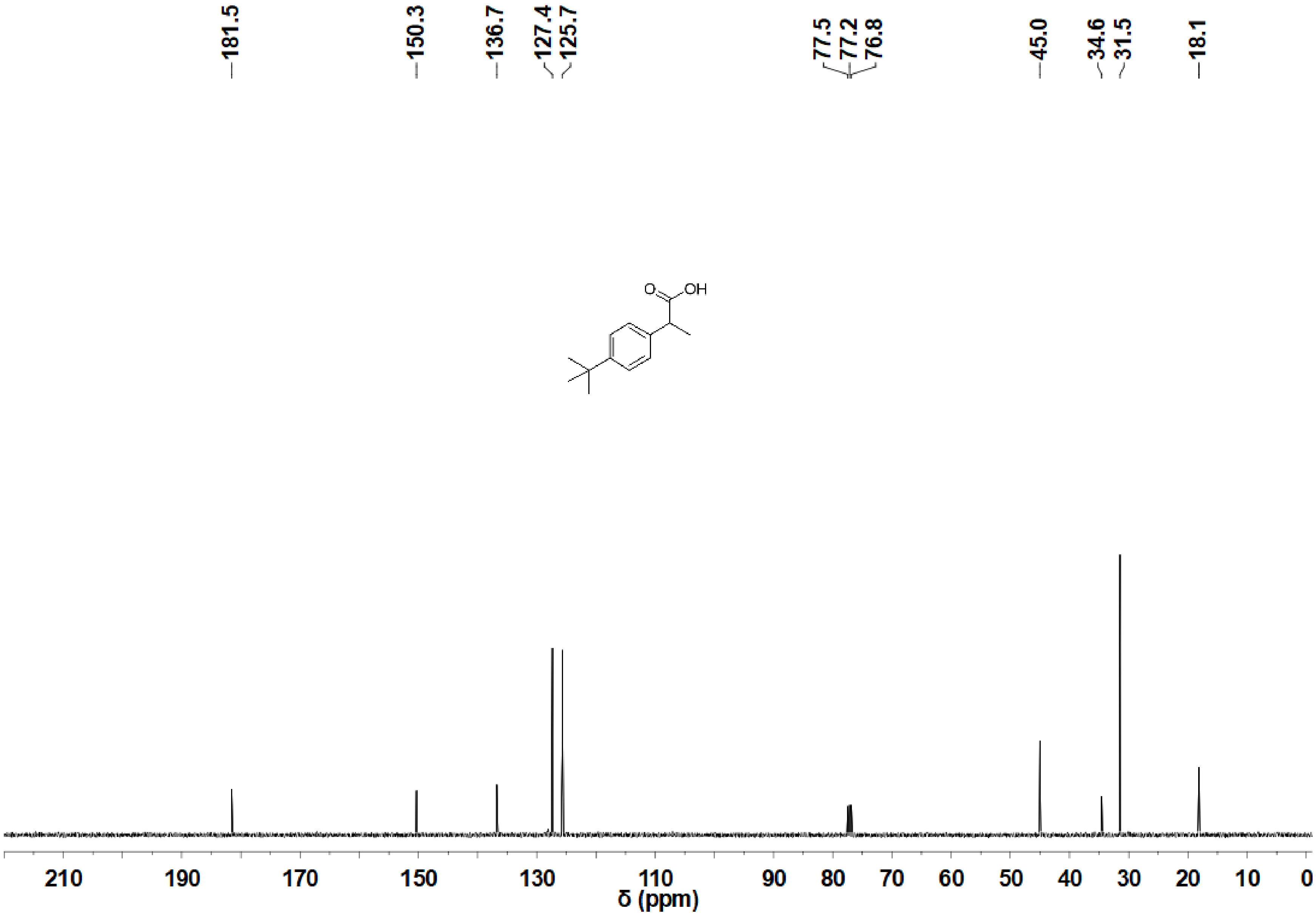
2-(4-methoxyphenyl) propanoic acid, **2c**
400 MHz, $CDCl_3$



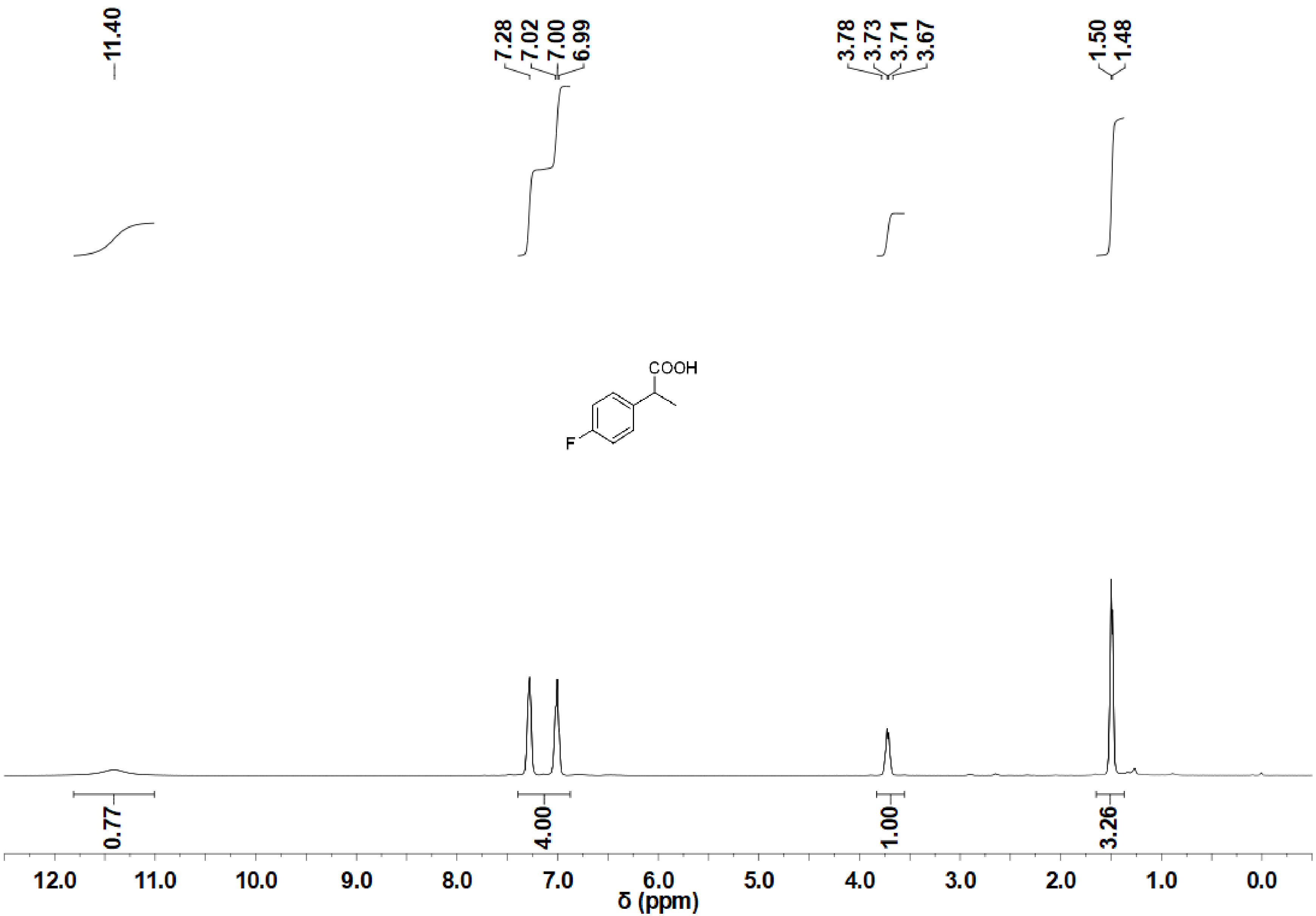

181.2
158.9
131.9
128.7
114.1
77.4
77.1
76.8
55.3
44.5
18.2
OH
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)

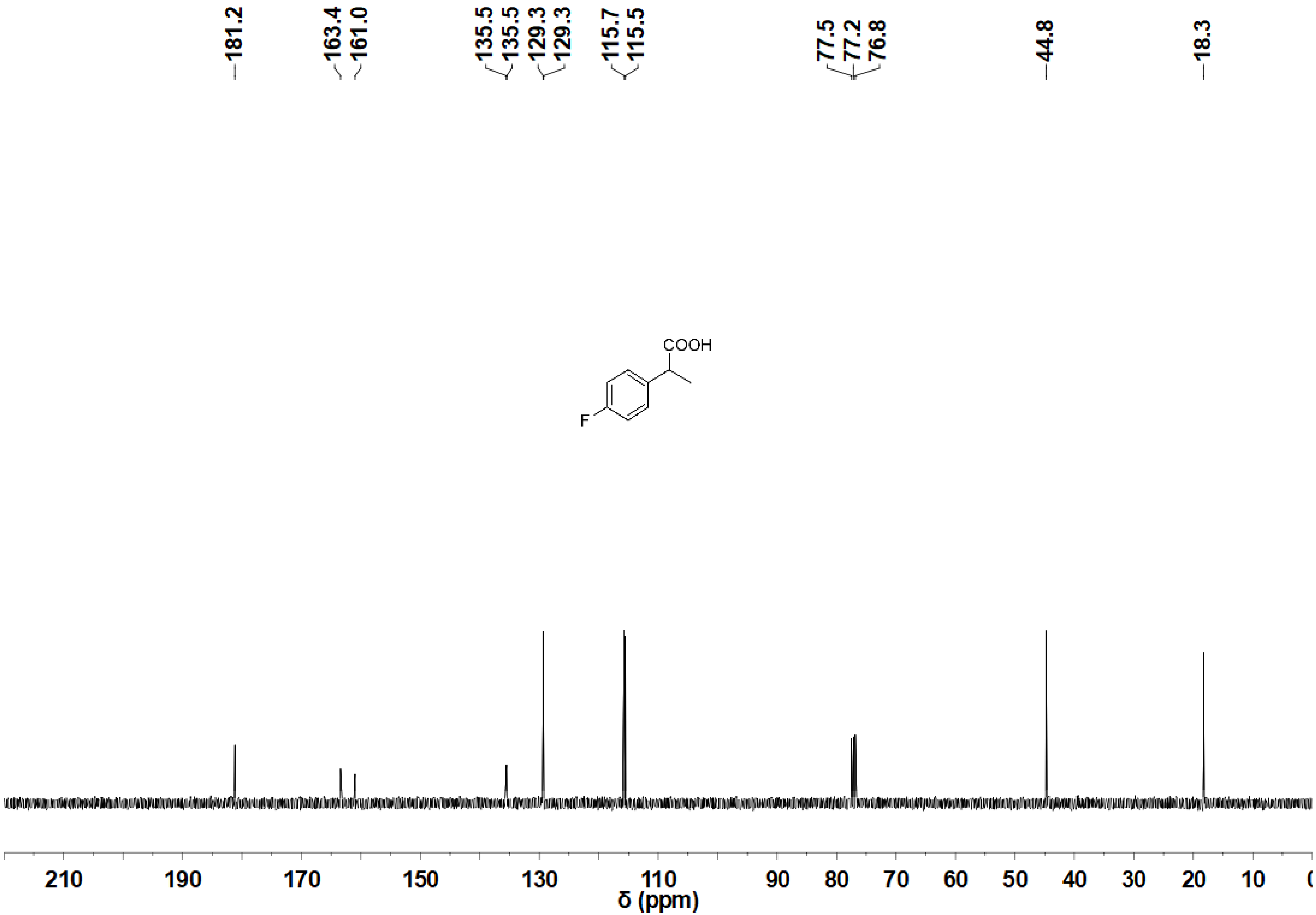
2-(4-(tert-butyl) phenyl) propanoic acid, **2d**
400 MHz, $CDCl_3$



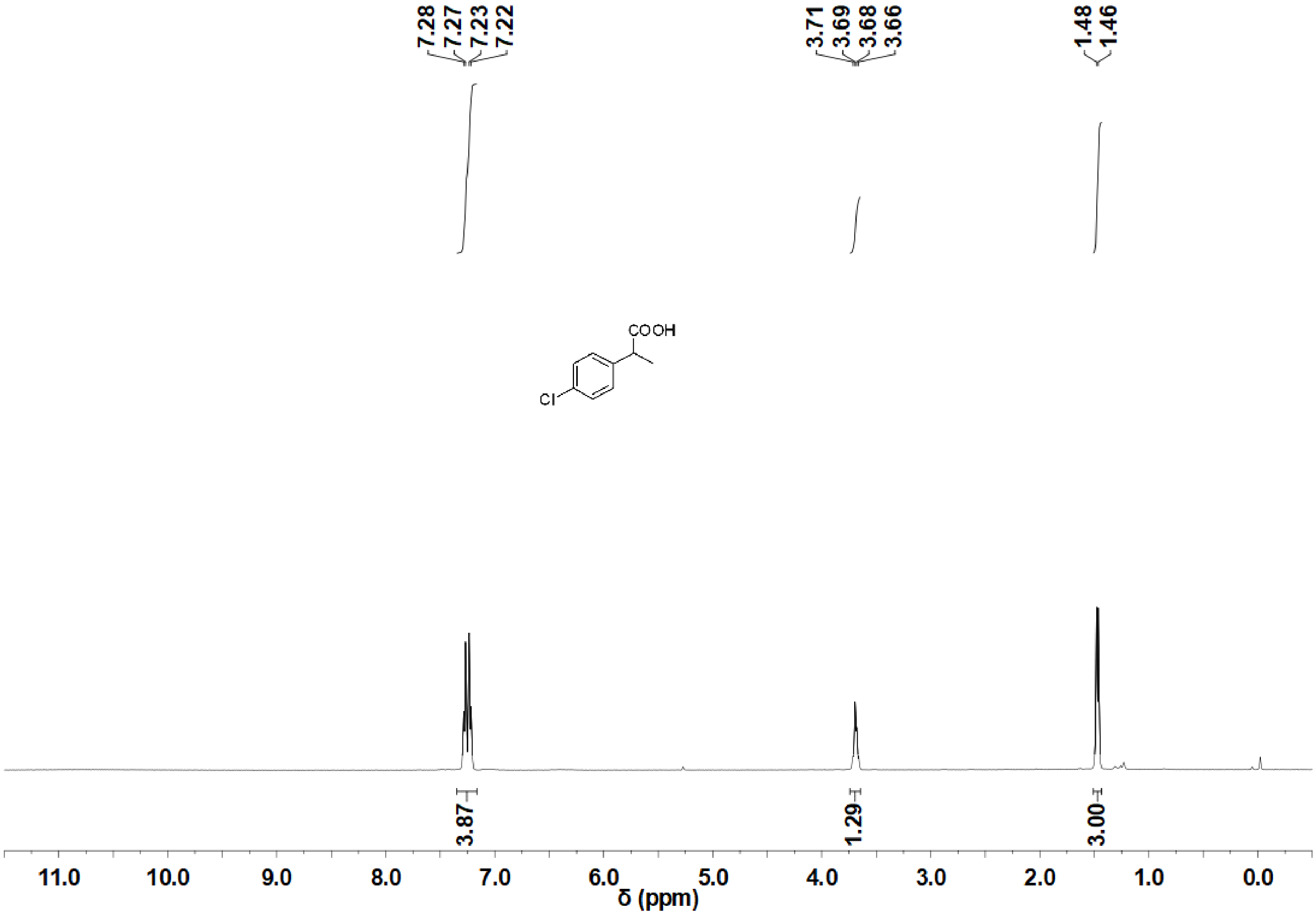

181.5
150.3
136.7
127.4
125.7
77.5
77.2
76.8
45.0
34.6
31.5
18.1
O
OH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

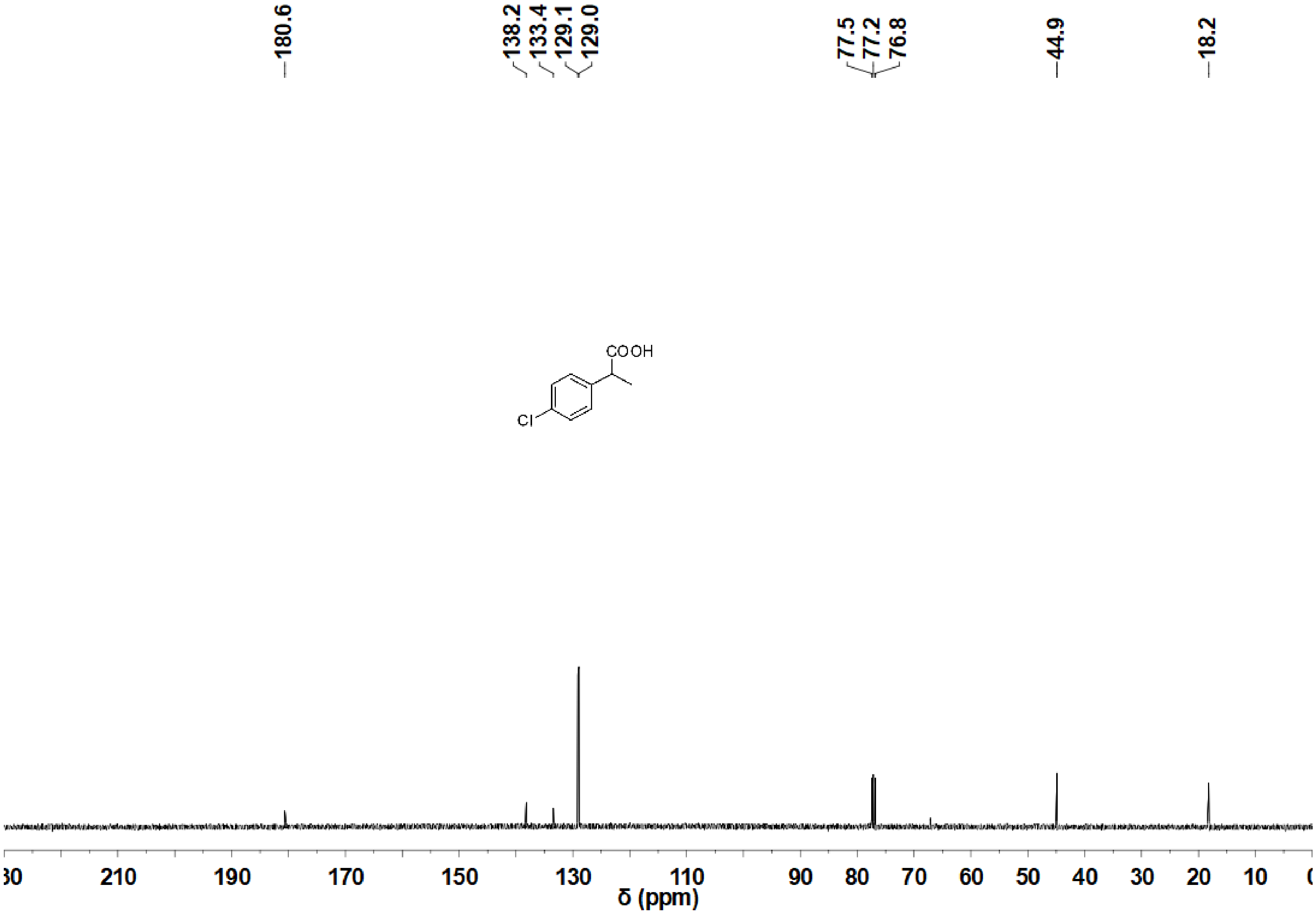
2-(4-fluorophenyl) propionic acid, **2e**
400 MHz, $CDCl_3$




181.2
163.4
161.0
135.5
135.5
129.3
129.3
115.7
115.5
77.5
77.2
76.8
44.8
18.3
COOH
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
δ (ppm)

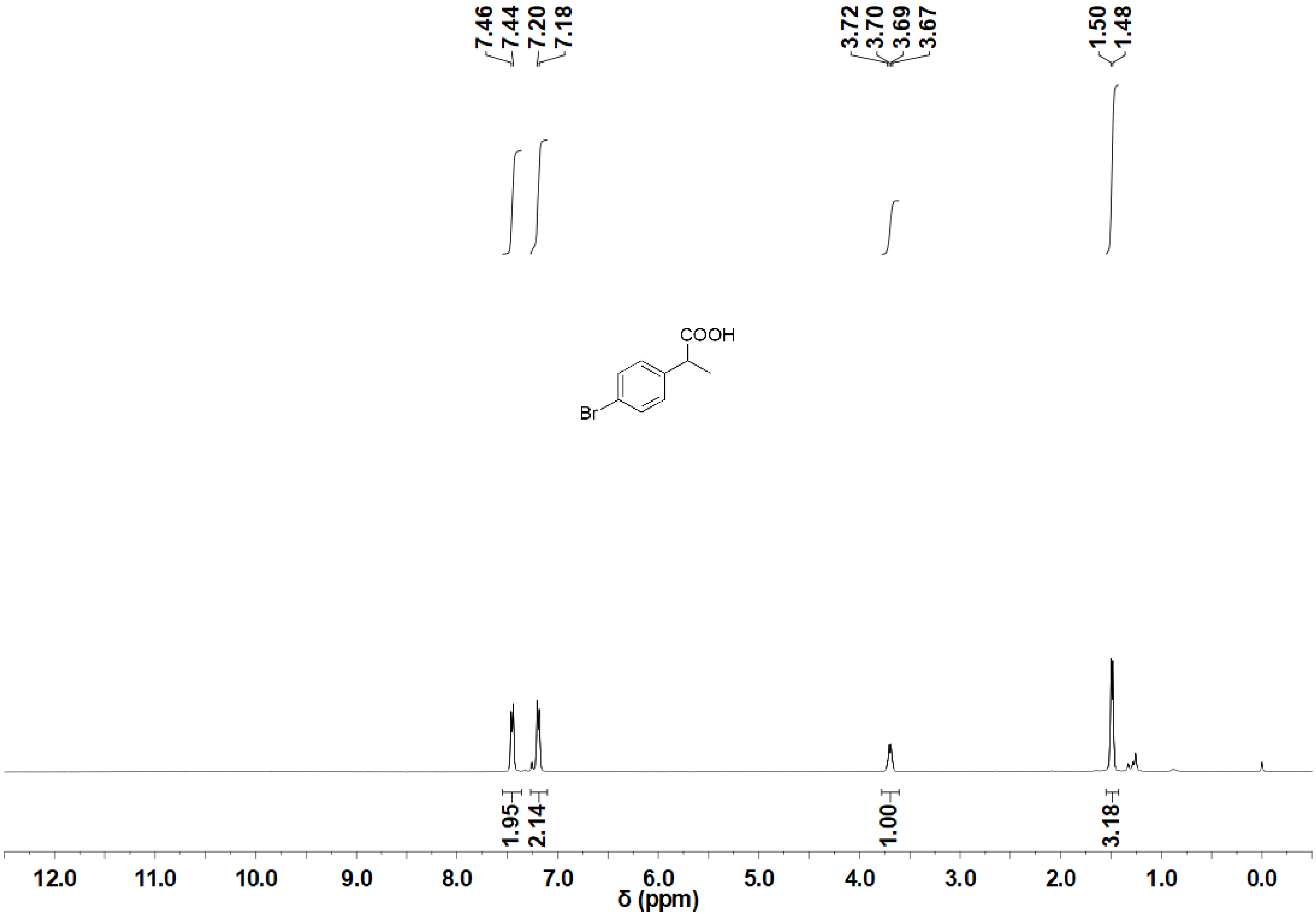
2-(4-chlorophenyl) propionic acid, **2f**
400 MHz, $CDCl_3$

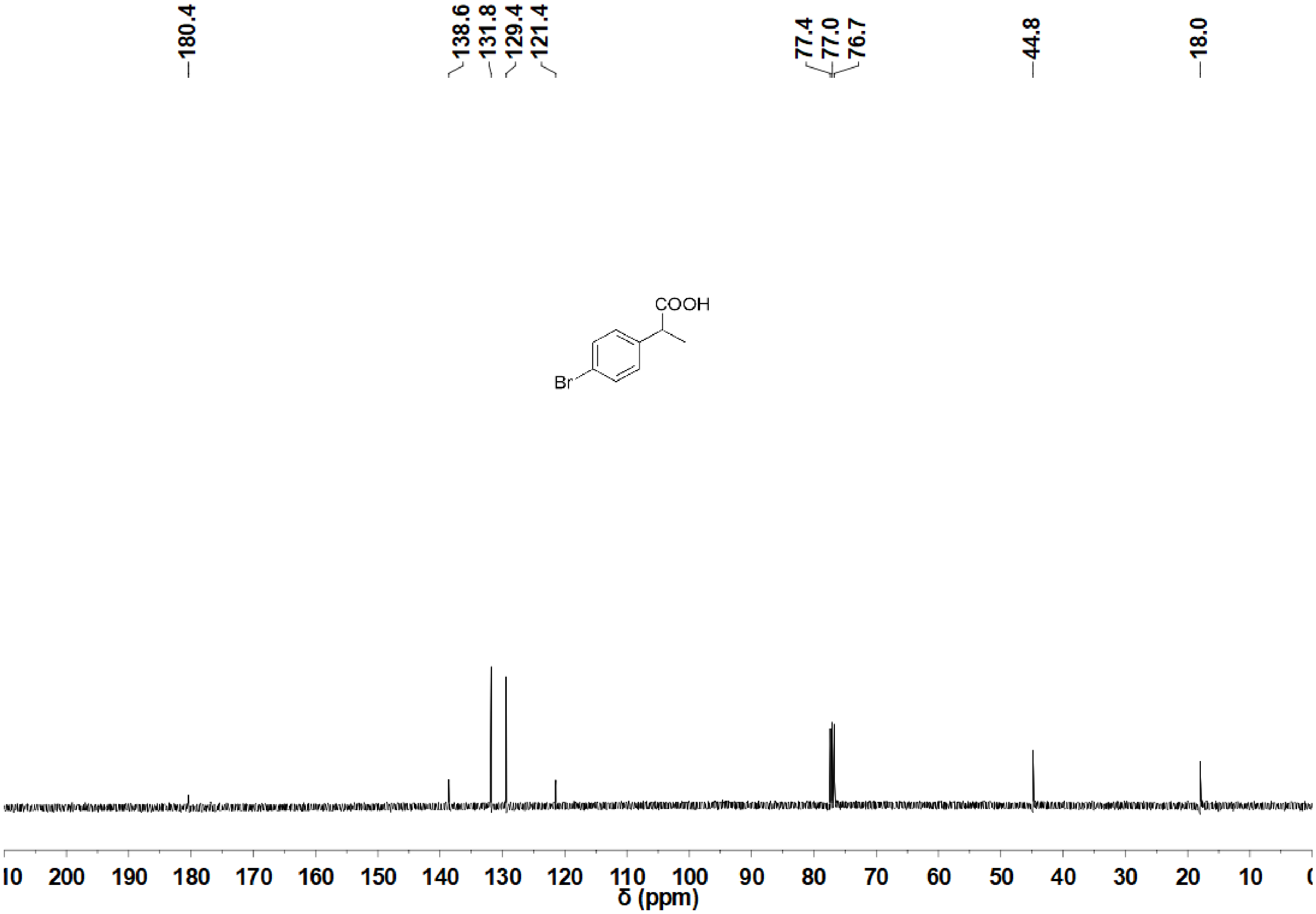




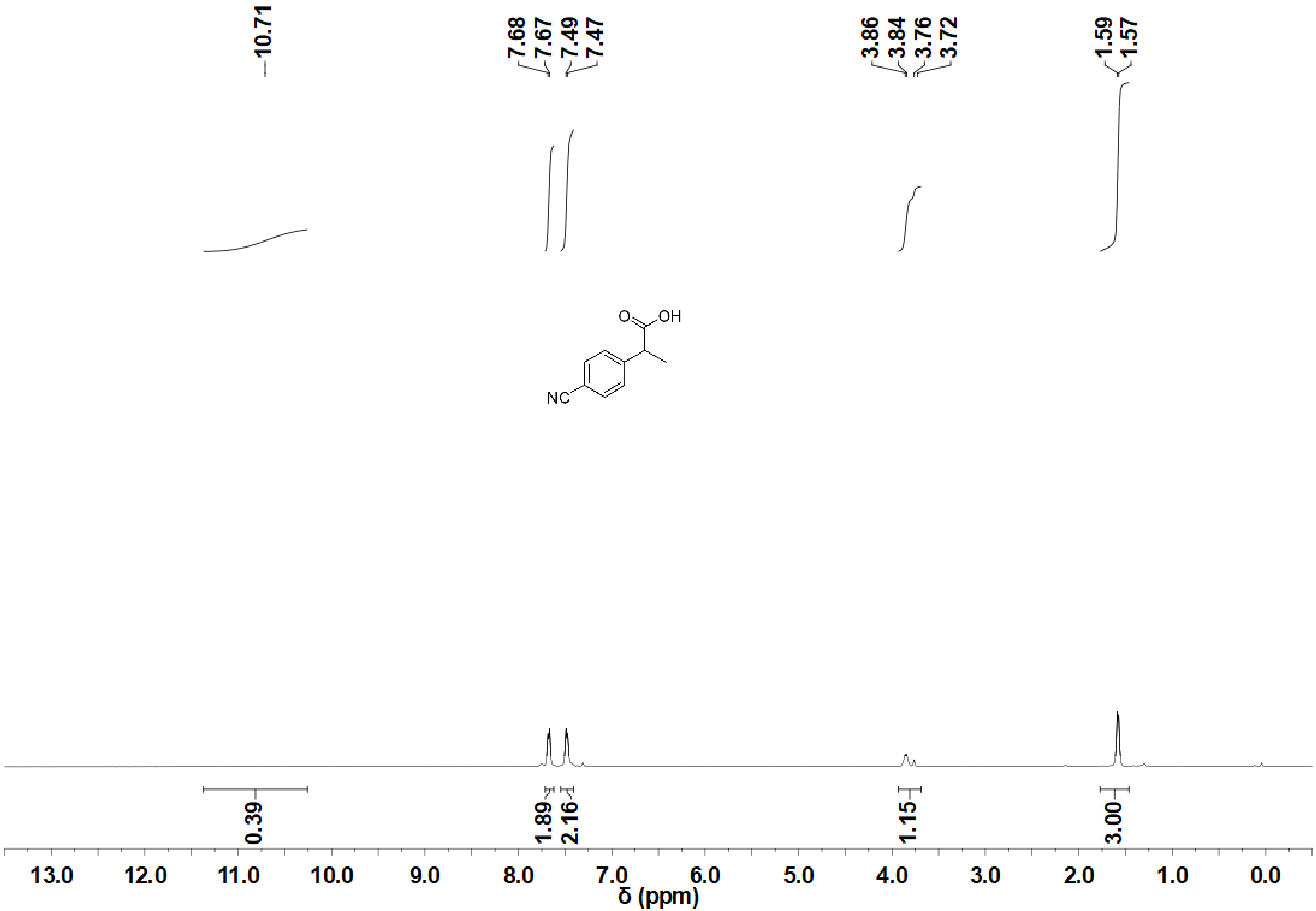
180.6
138.2
133.4
129.1
129.0
77.5
77.2
76.8
44.9
18.2
COOH
Cl
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

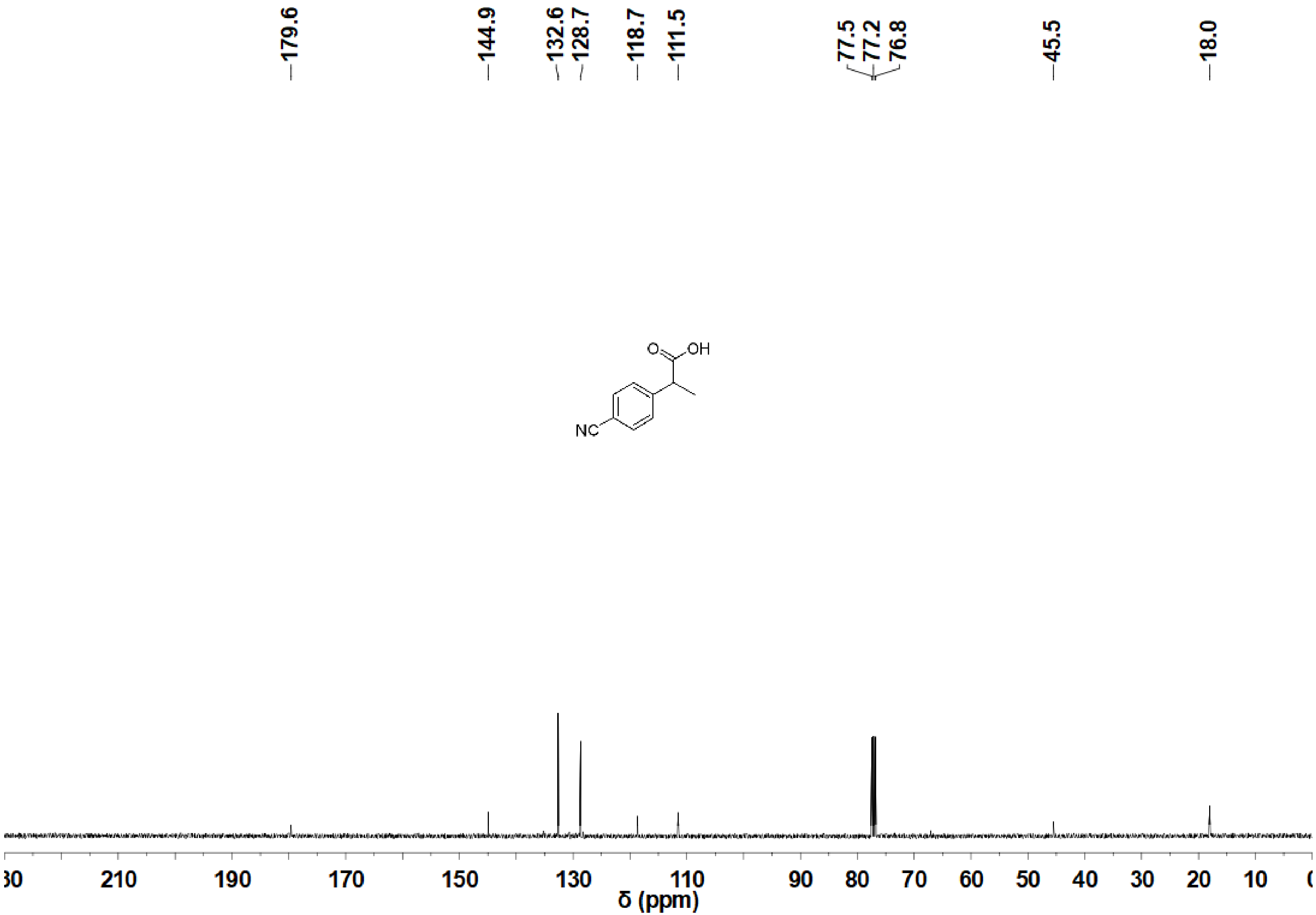
2-(4-bromophenyl) propanoic acid, **2g**
400 MHz, $CDCl_3$




180.4
138.6
131.8
129.4
121.4
77.4
77.0
76.7
44.8
18.0
COOH
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)

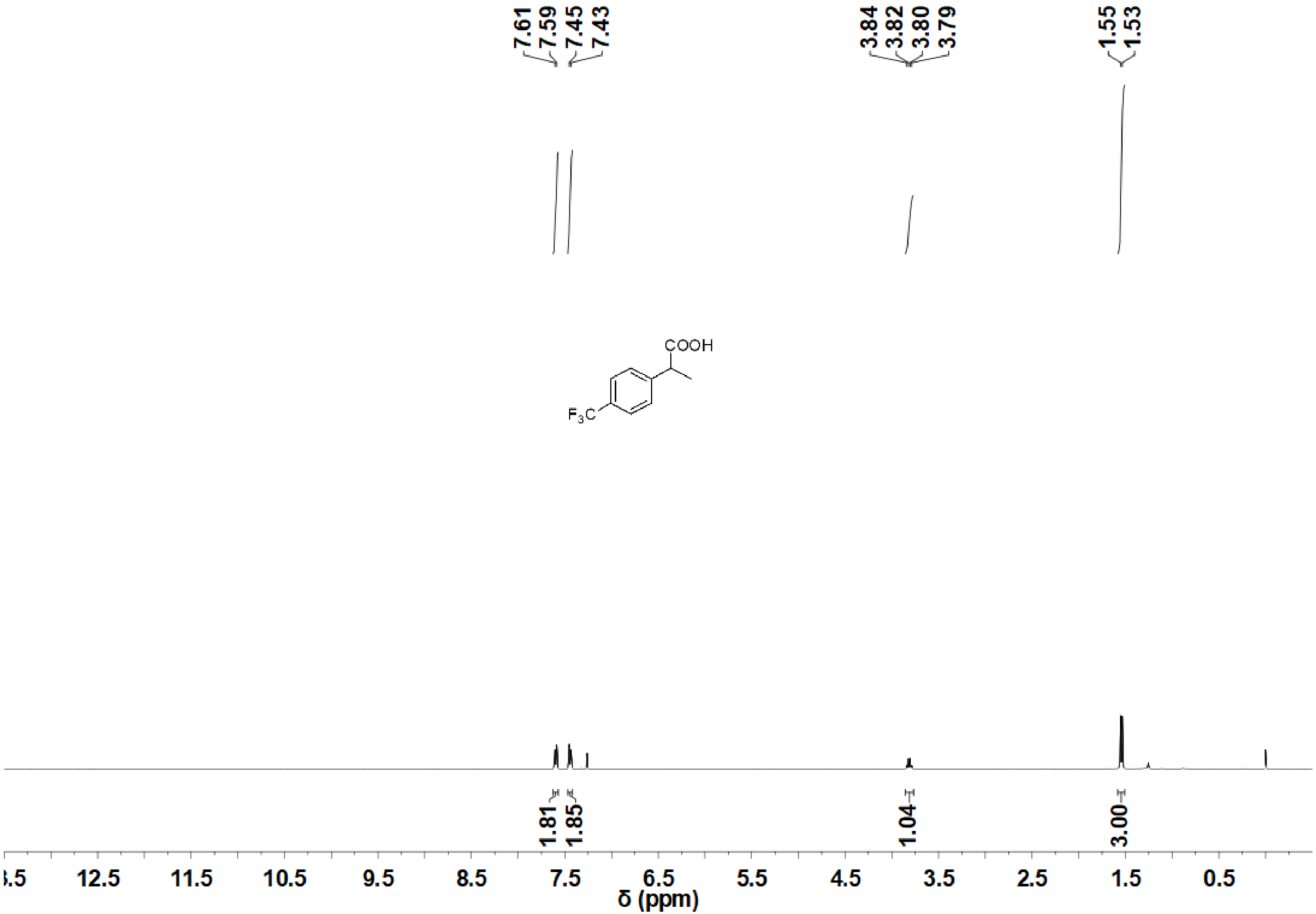
2-(4-cyanophenyl) propanoic acid, **2h**
400 MHz, $CDCl_3$

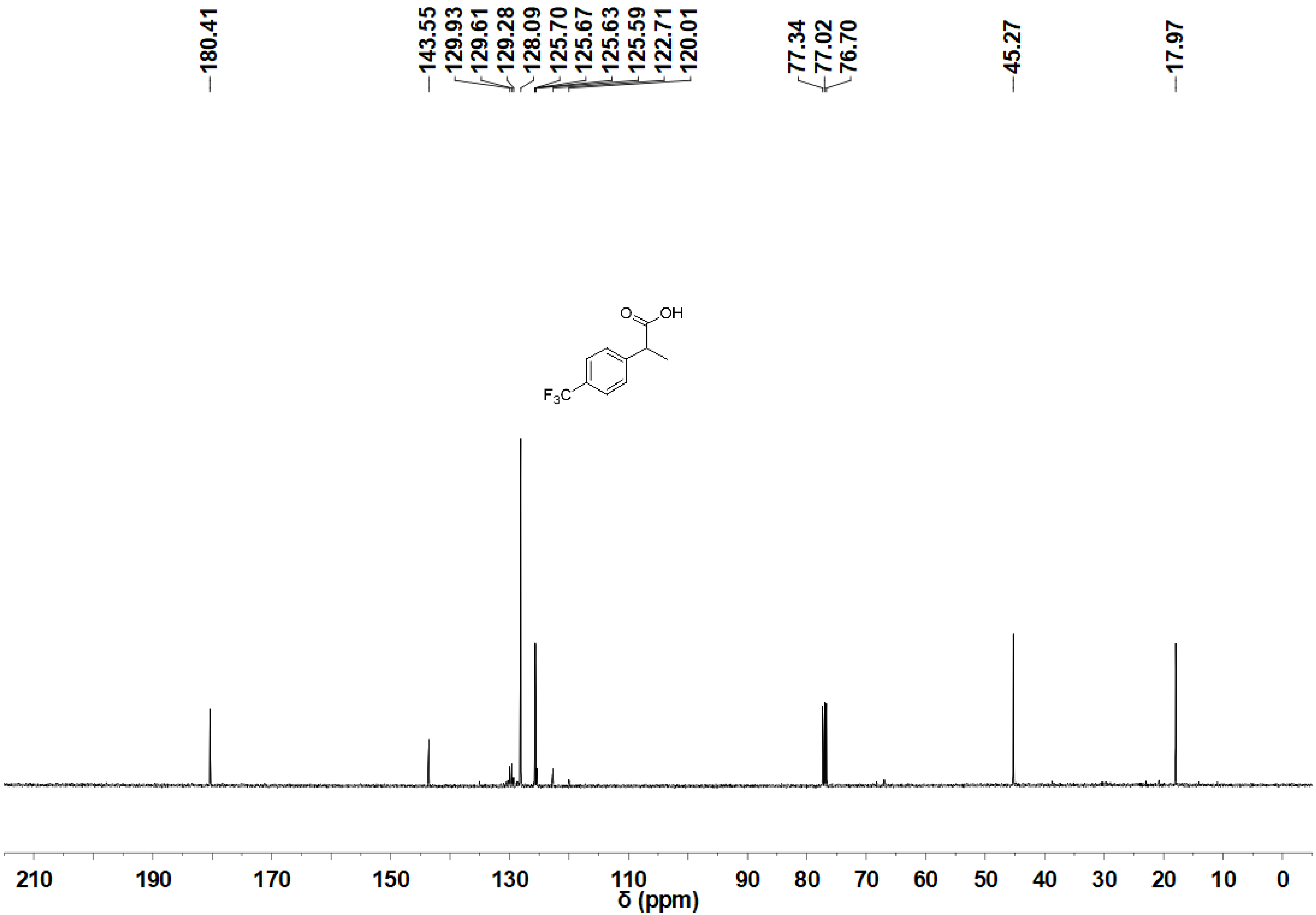



179.6
144.9
132.6
128.7
118.7
111.5
77.5
77.2
76.8
45.5
18.0
O
OH
NC
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

2-(4-(trifluoromethyl) phenyl) propanoic acid, **2i**

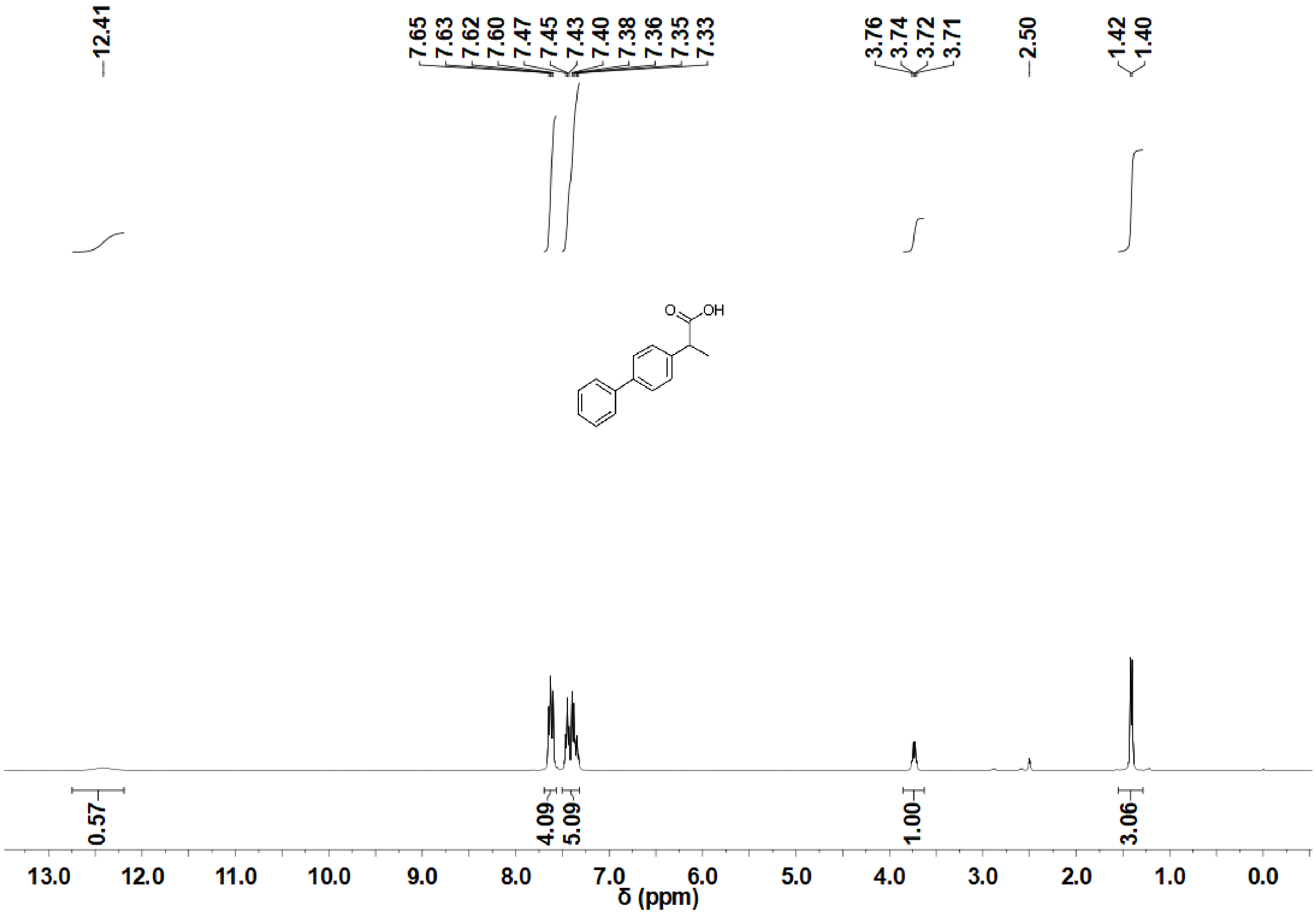
400 MHz, $CDCl_3$

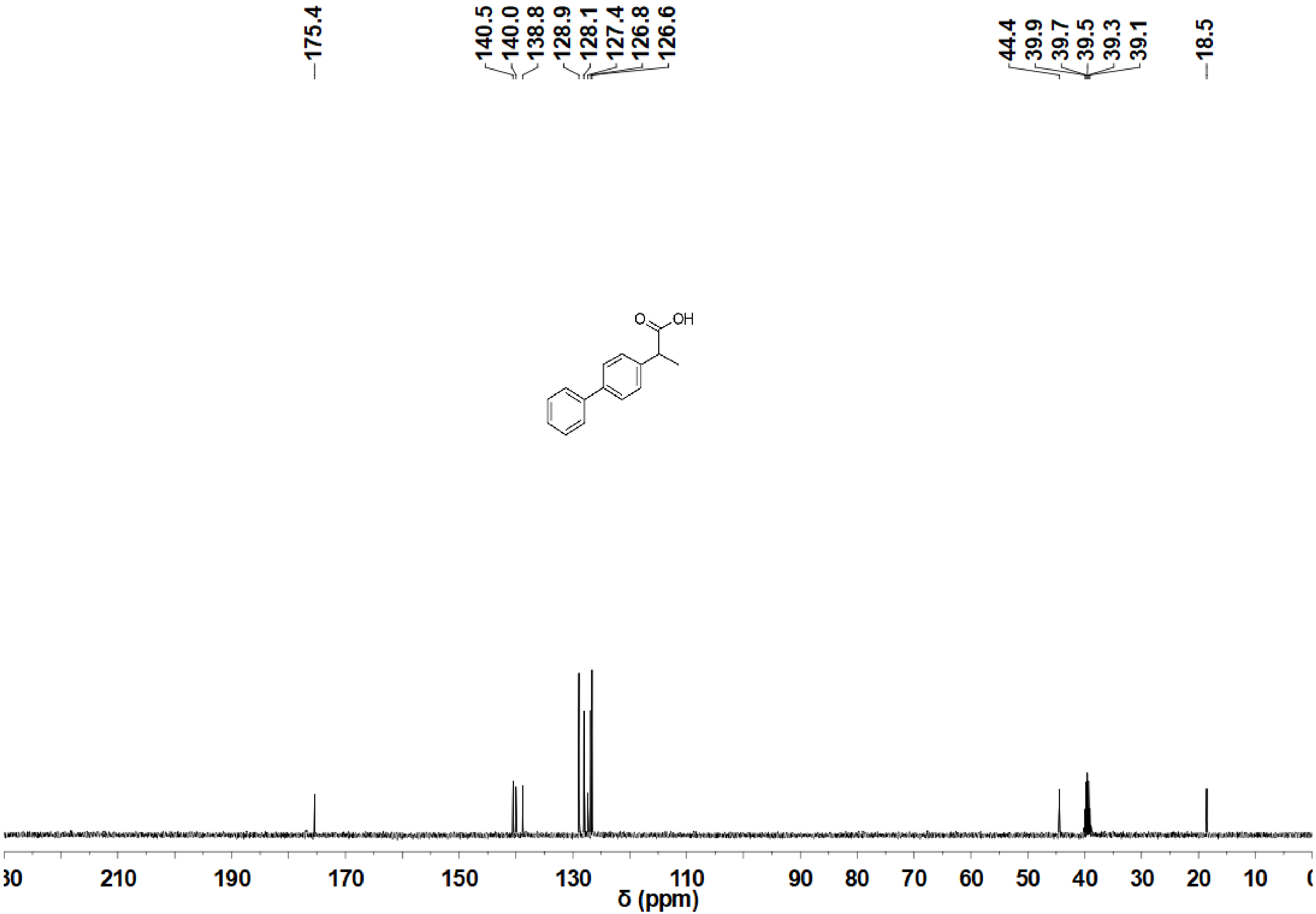




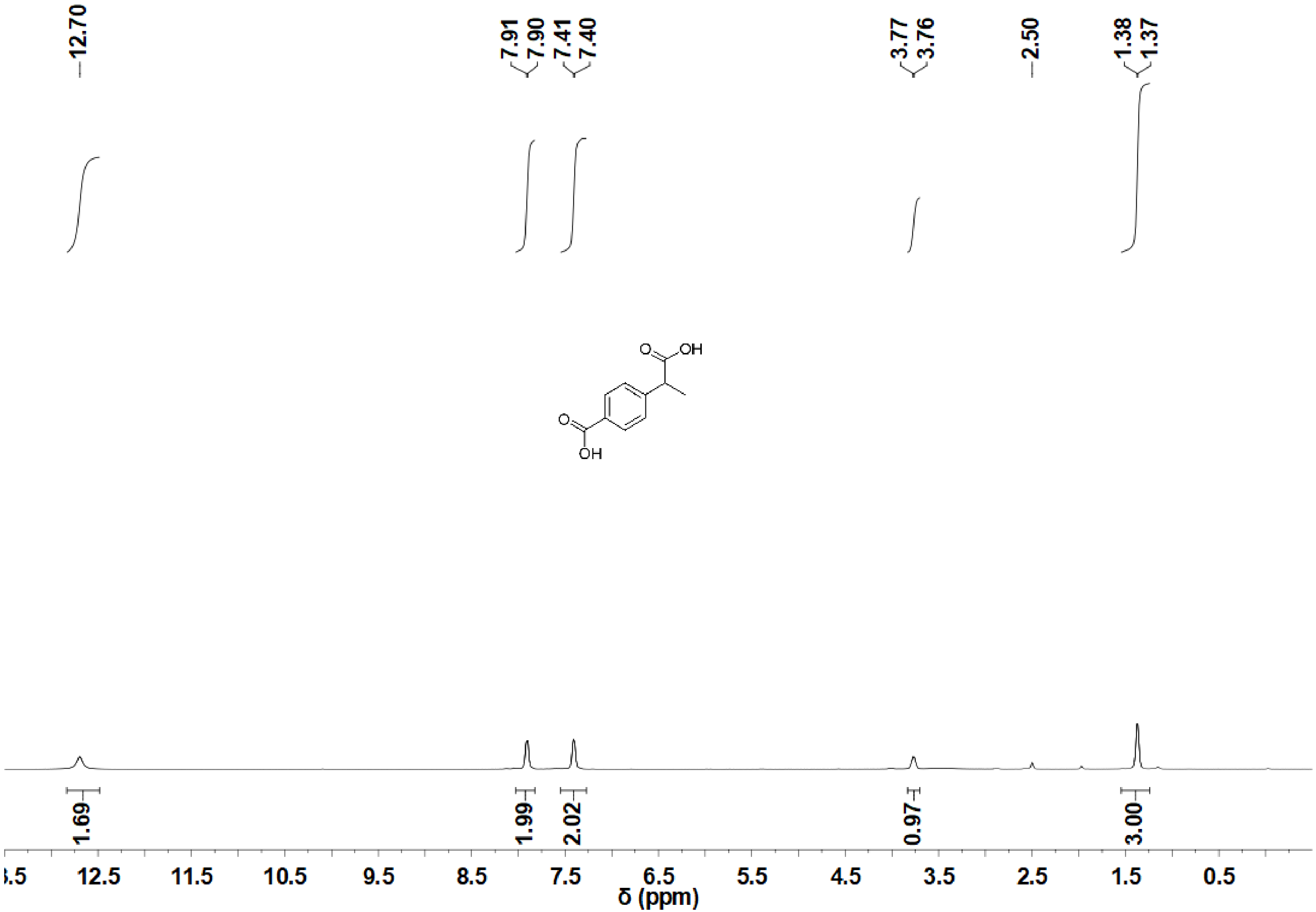
180.41
143.55
129.93
129.61
129.28
128.09
125.70
125.67
125.63
125.59
122.71
120.01
77.34
77.02
76.70
45.27
17.97
O
OH
F3C
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

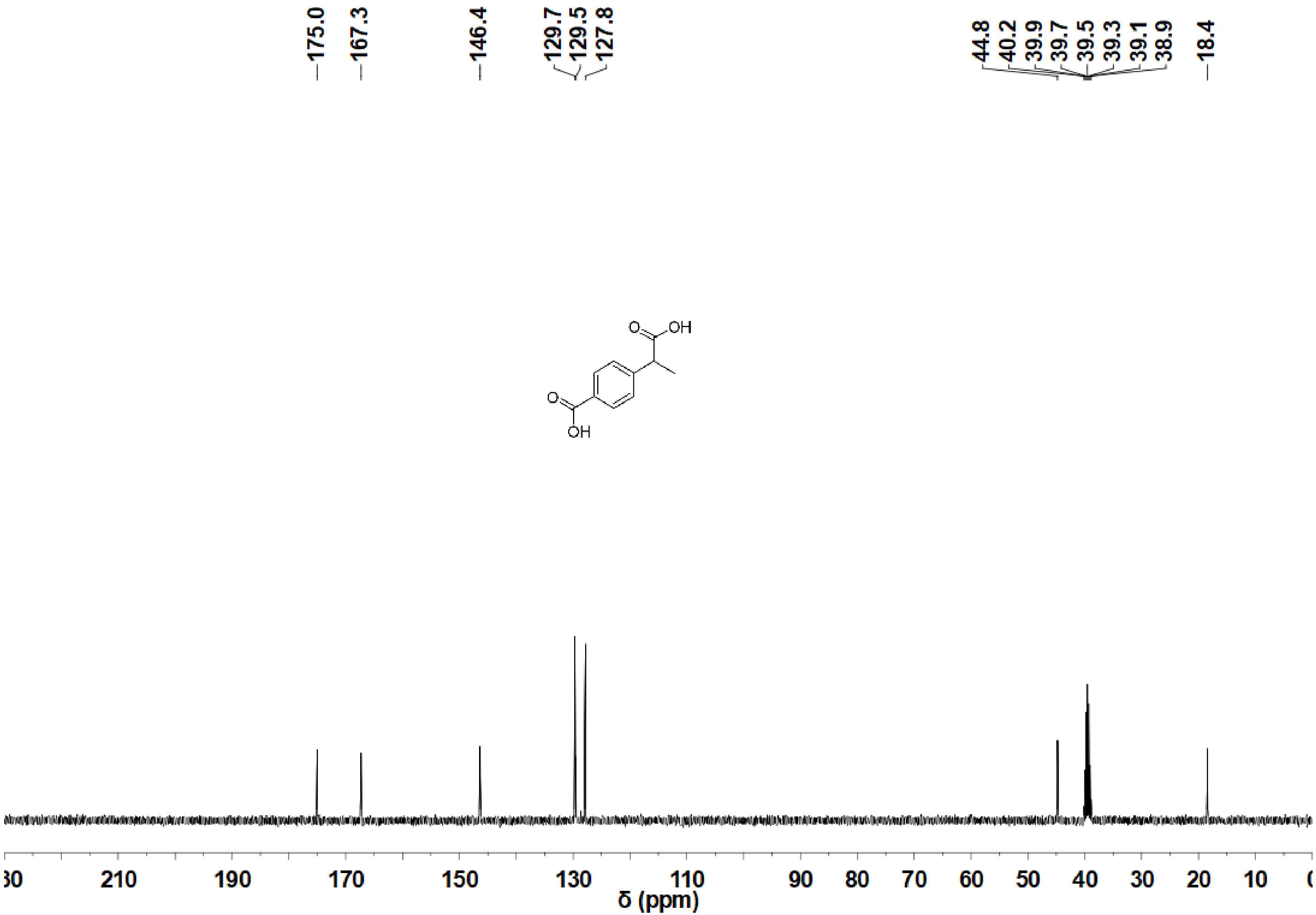
2-phenylpropanoic acid, **2j**
400 MHz, DMSO-d_6



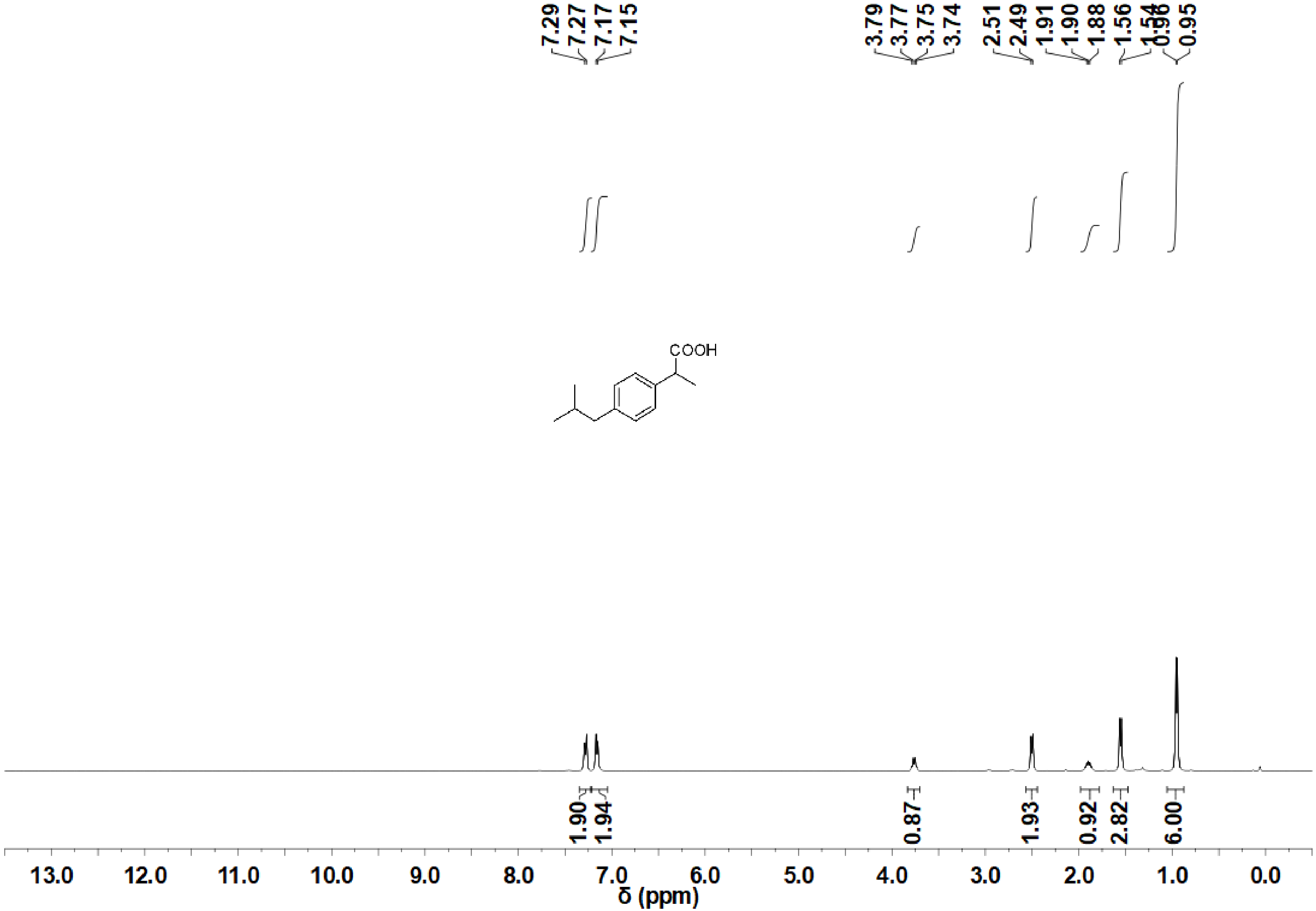

175.4
140.5
140.0
138.8
128.9
128.1
127.4
126.8
126.6
44.4
39.9
39.7
39.5
39.3
39.1
18.5
OH
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

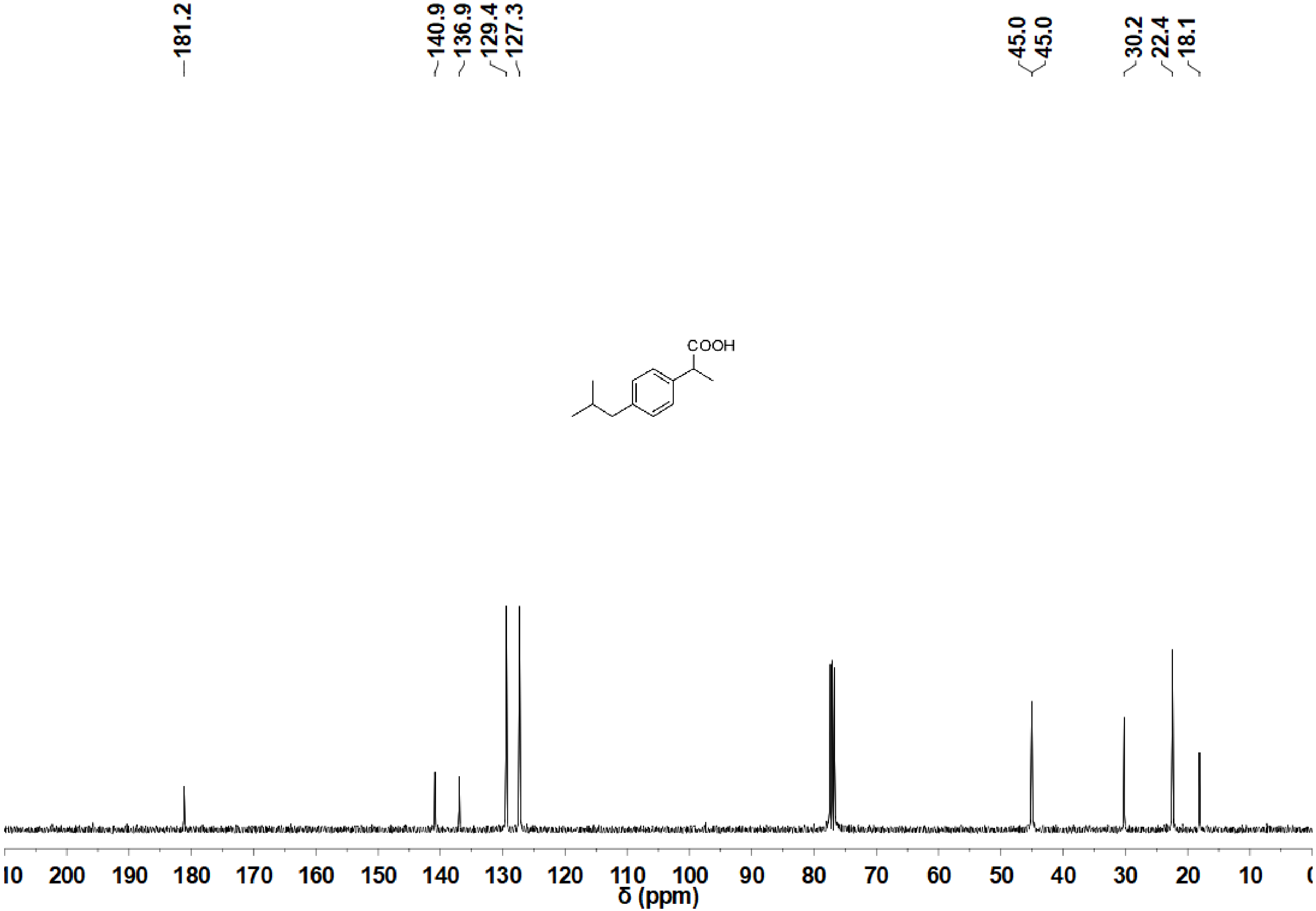
2-(4-carboxyphenyl) propionic acid, **2k**
400 MHz, DMSO-d_6




175.0
167.3
146.4
129.7
129.5
127.8
44.8
40.2
39.9
39.7
39.5
39.3
39.1
38.9
18.4
OH
O
OH
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

2-(4-isobutylphenyl) propionic acid, **2l**
400 MHz, $CDCl_3$




181.2
140.9
136.9
129.4
127.3
45.0
45.0
30.2
22.4
18.1
COOH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)

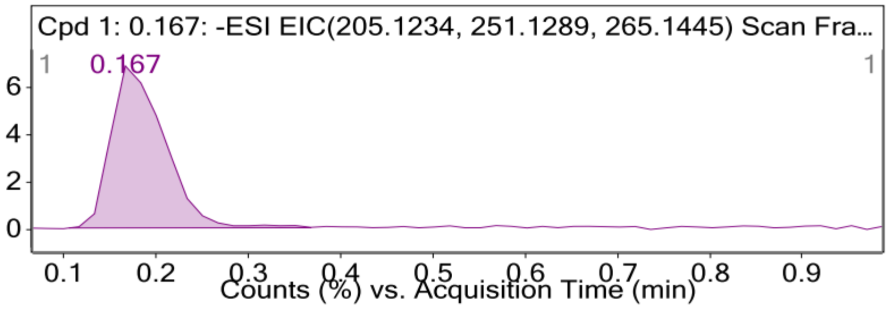
Qualitative Compound Report

Data File	HZJ-4-16-4+.d	**Sample Name**	HZJ-4-16-4
Sample Type	Sample	**Position**	Vial 24
Instrument Name	6530 QTOF LC/MS	**Acq Method**	my-MS.m
Acquired Time	5/18/2017 10:44:22 AM	**IRM Calibration Status**	Success

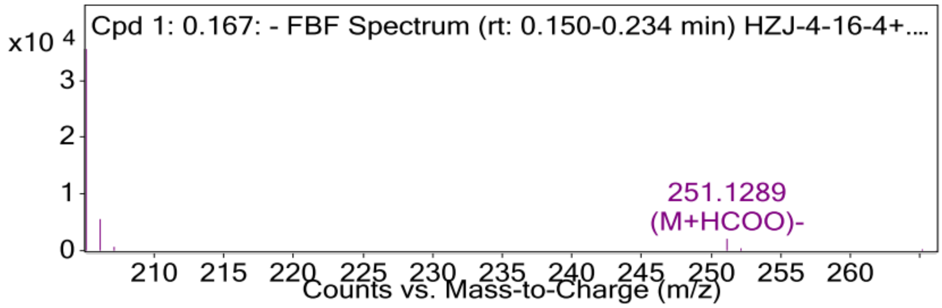
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 0.167	0.167	206.1306	35544	C13 H18 O2	206.1307	-0.41

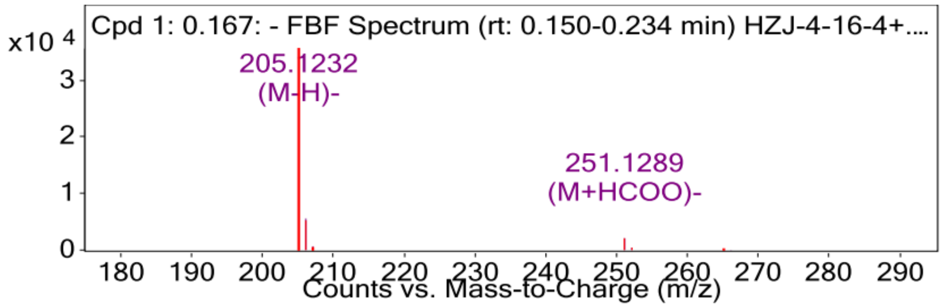
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: 0.167	205.1232	0.167	Find By Formula	206.1306



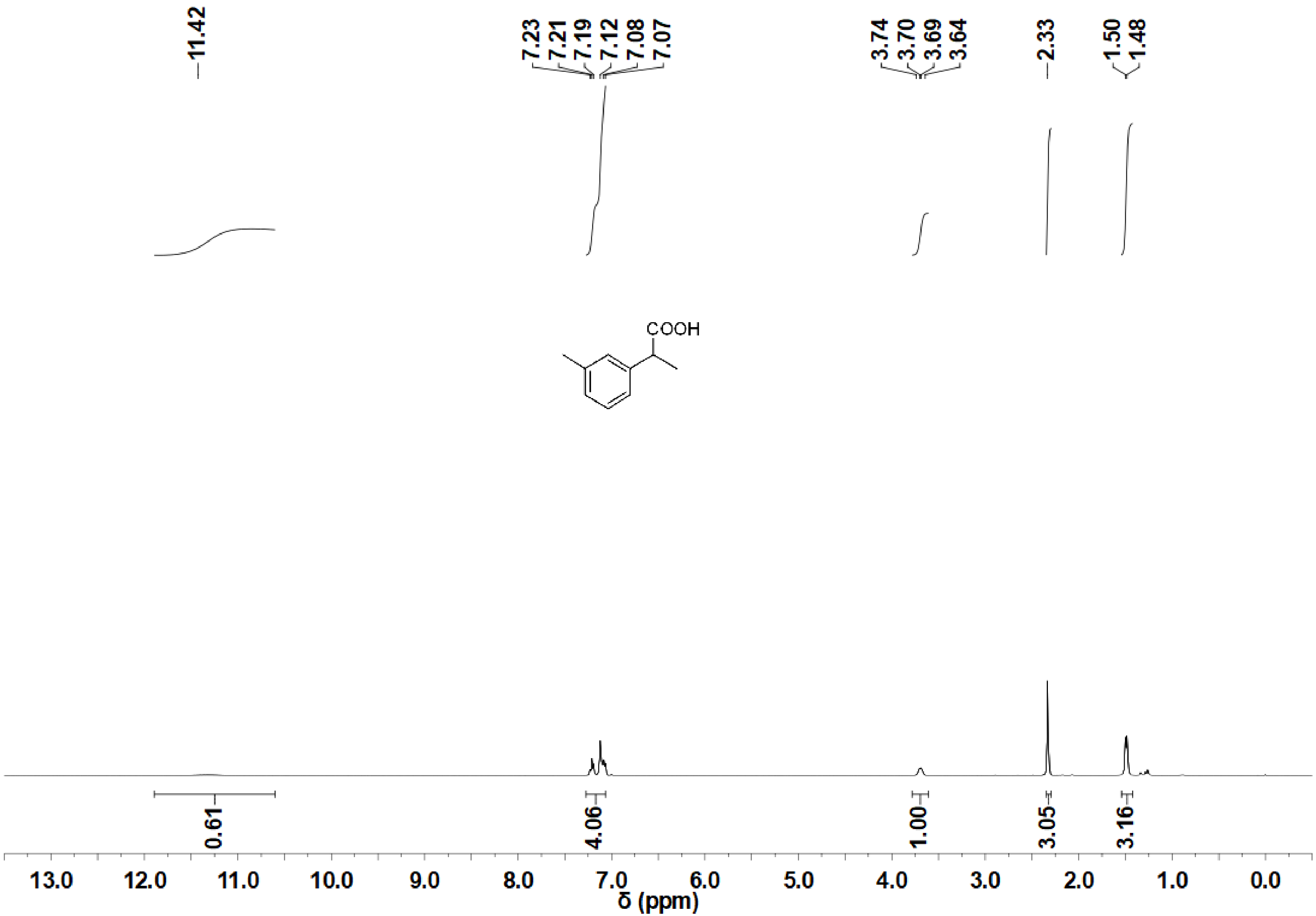
MS Spectrum

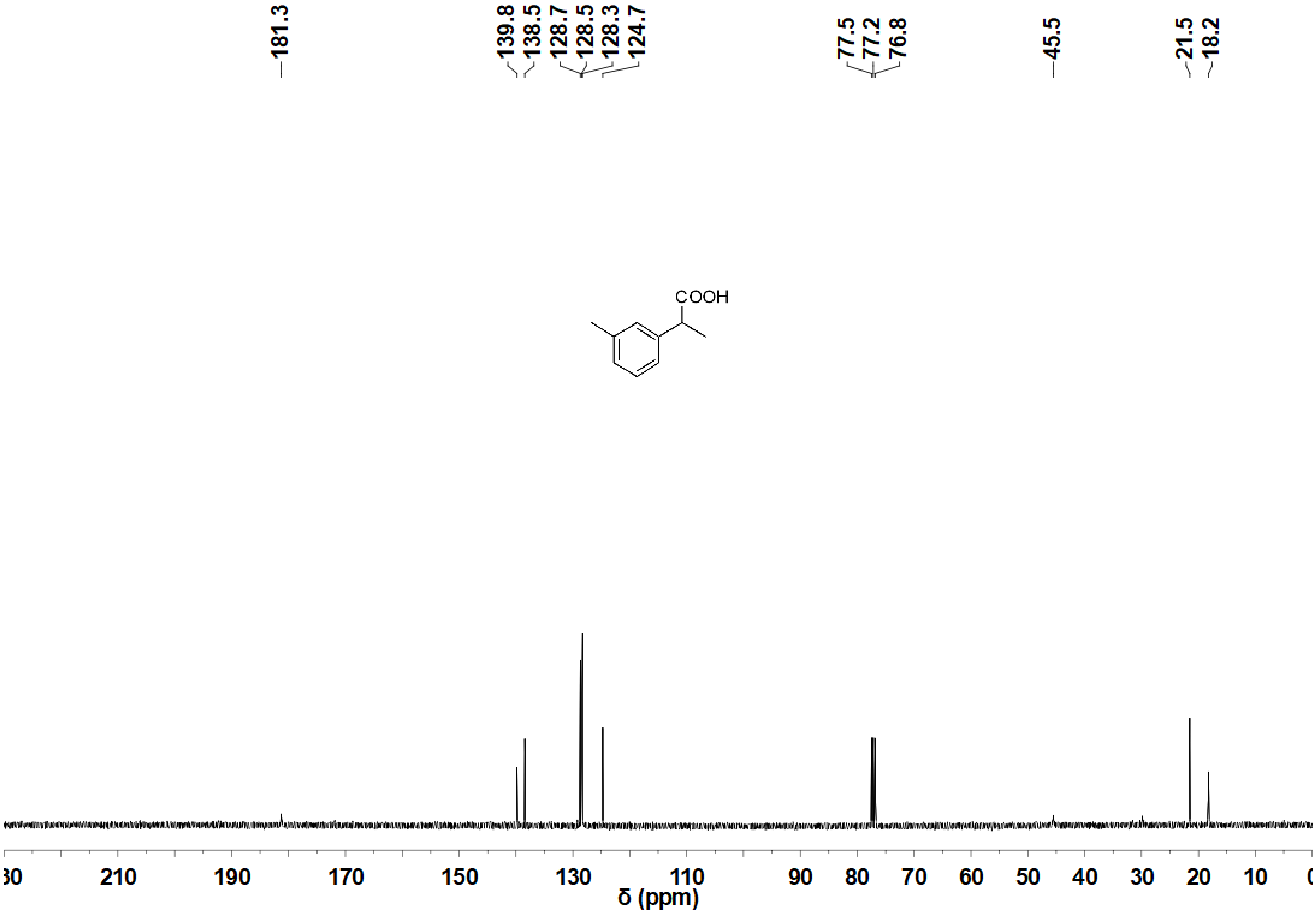


MS Zoomed Spectrum

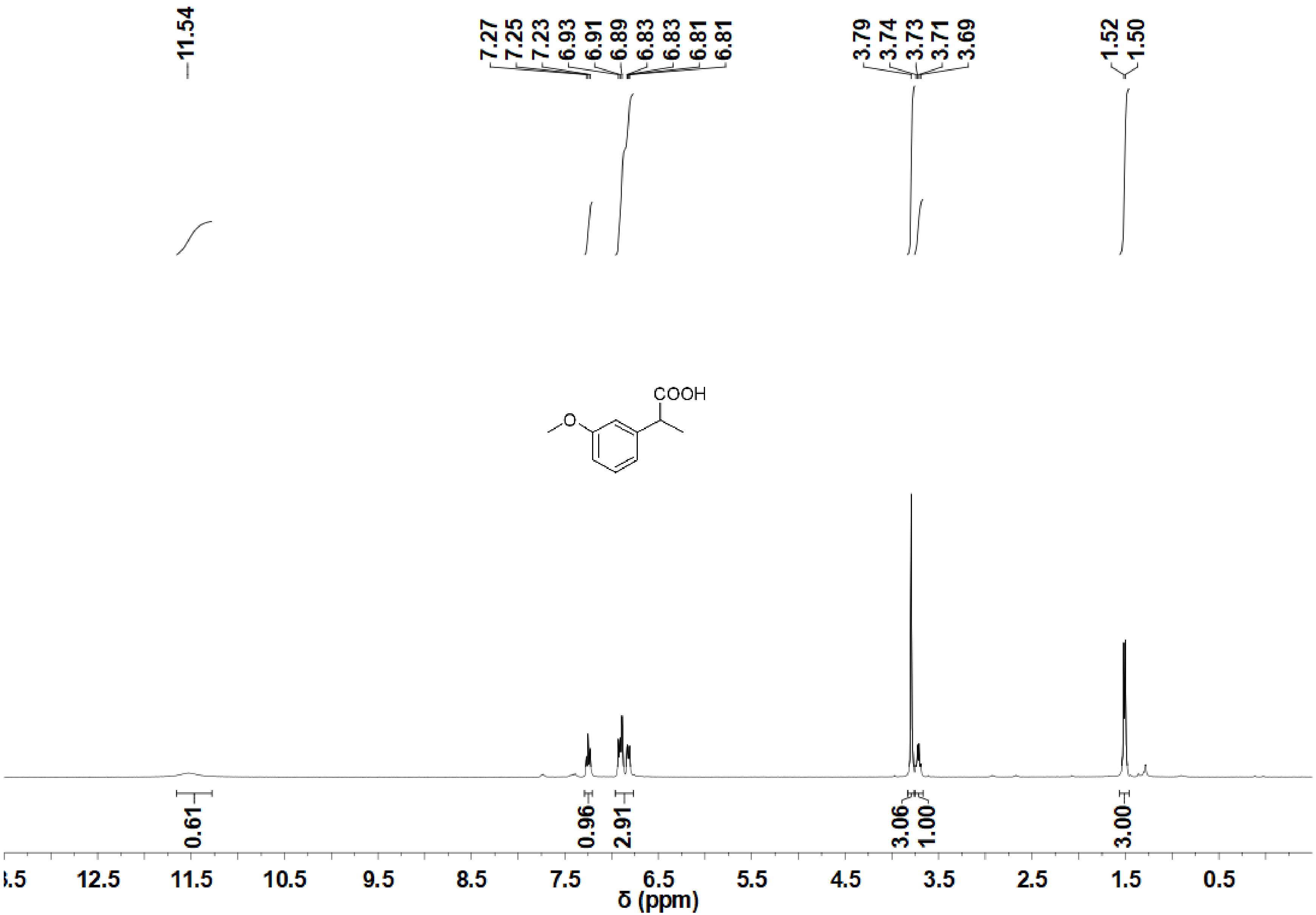


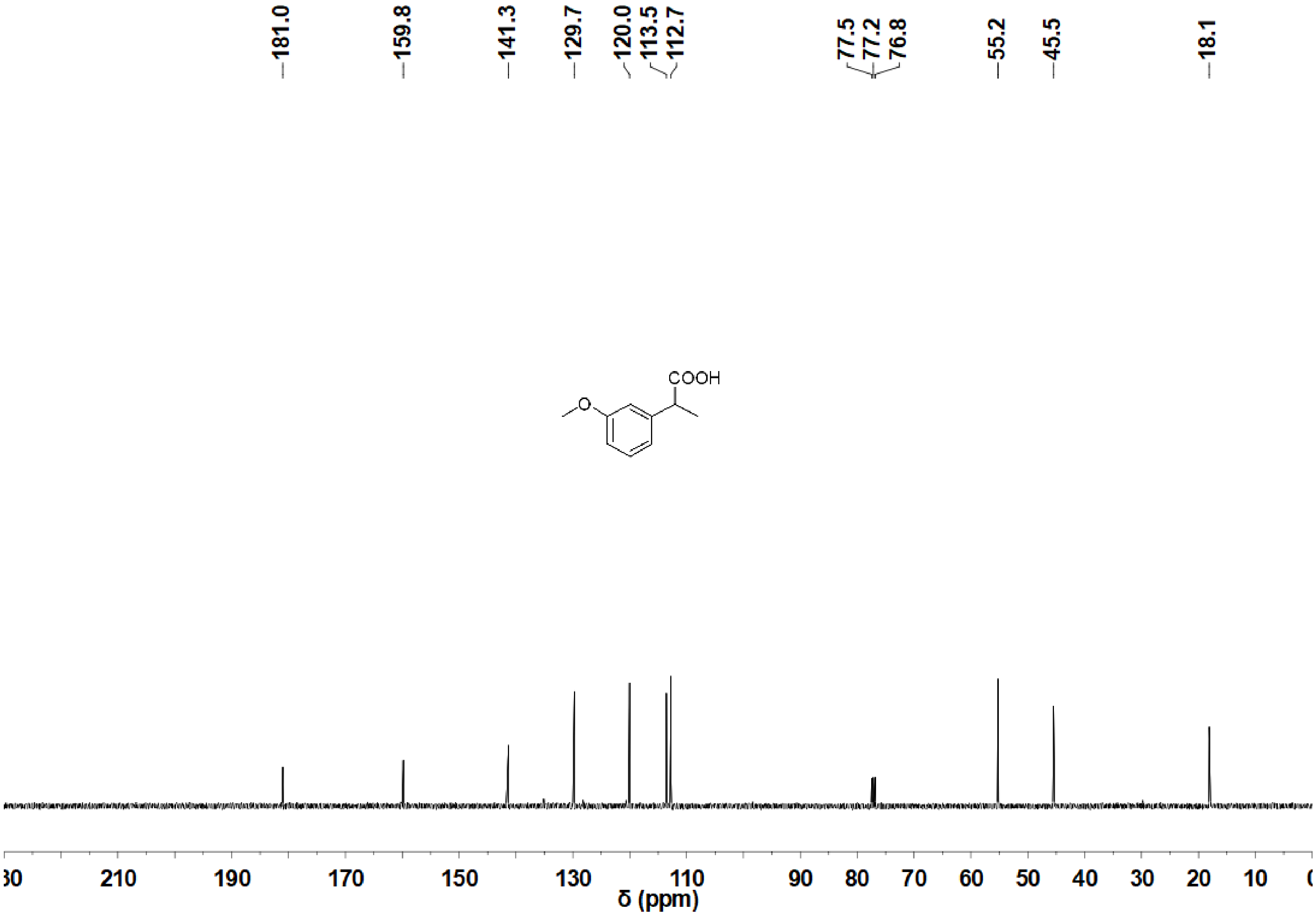
2-(3-methylphenyl) propanoic acid, **2m**
400 MHz, $CDCl_3$



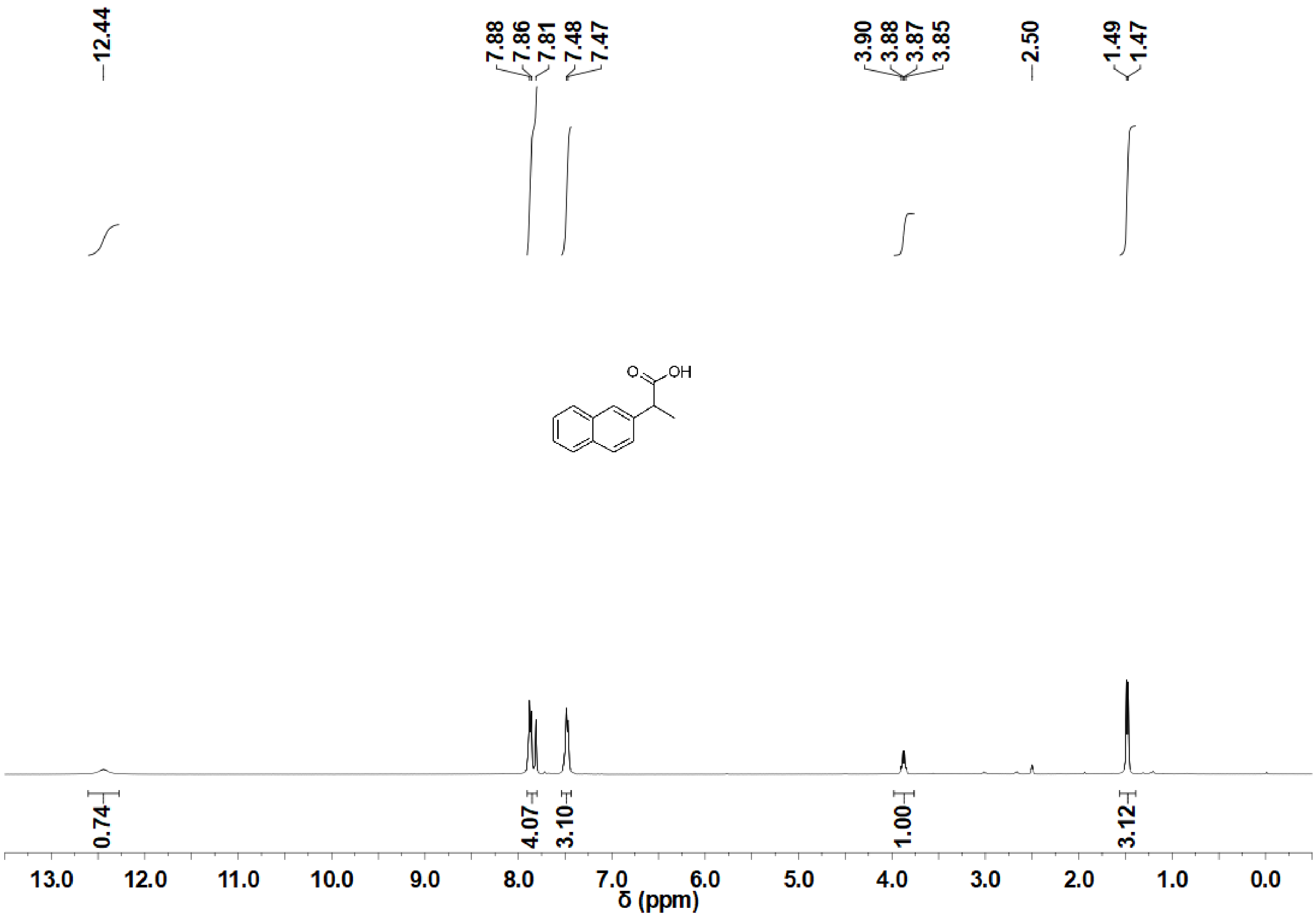

181.3
139.8
138.5
128.7
128.5
128.3
124.7
77.5
77.2
76.8
45.5
21.5
18.2
COOH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

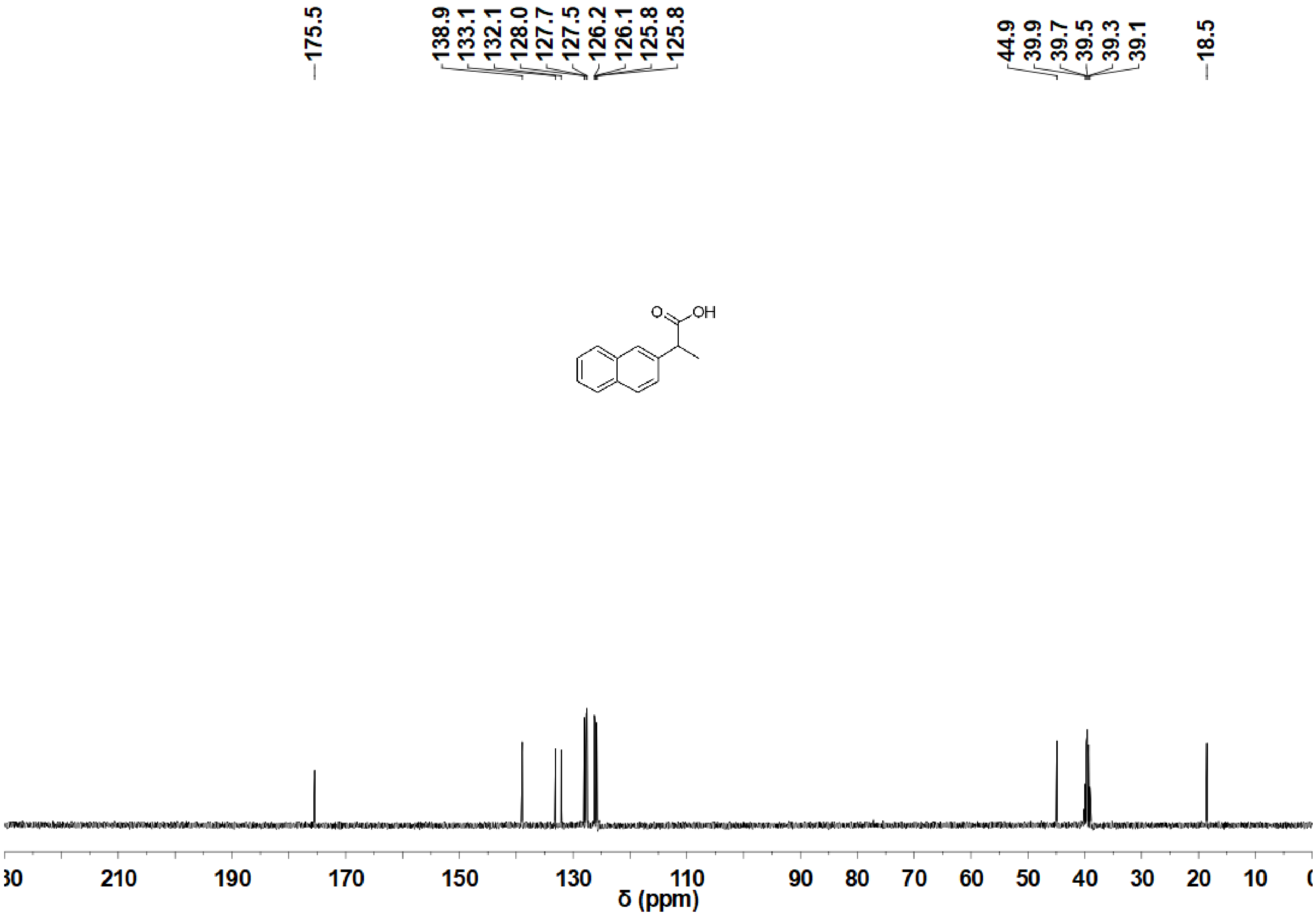
2-(3-methoxyphenyl) propanoic acid, **2n**
400 MHz, $CDCl_3$



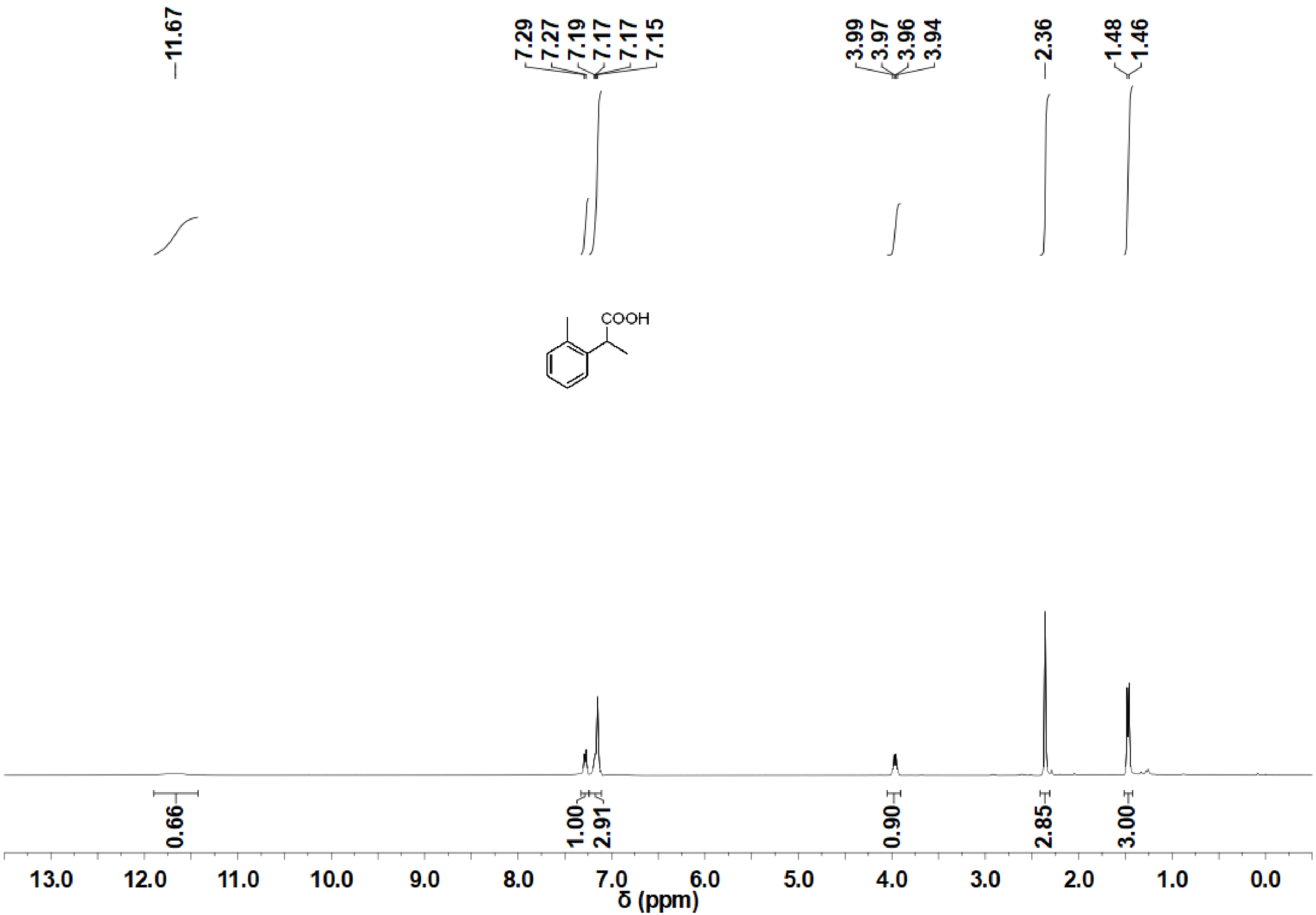

181.0
159.8
141.3
129.7
120.0
113.5
112.7
77.5
77.2
76.8
55.2
45.5
18.1
COOH
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

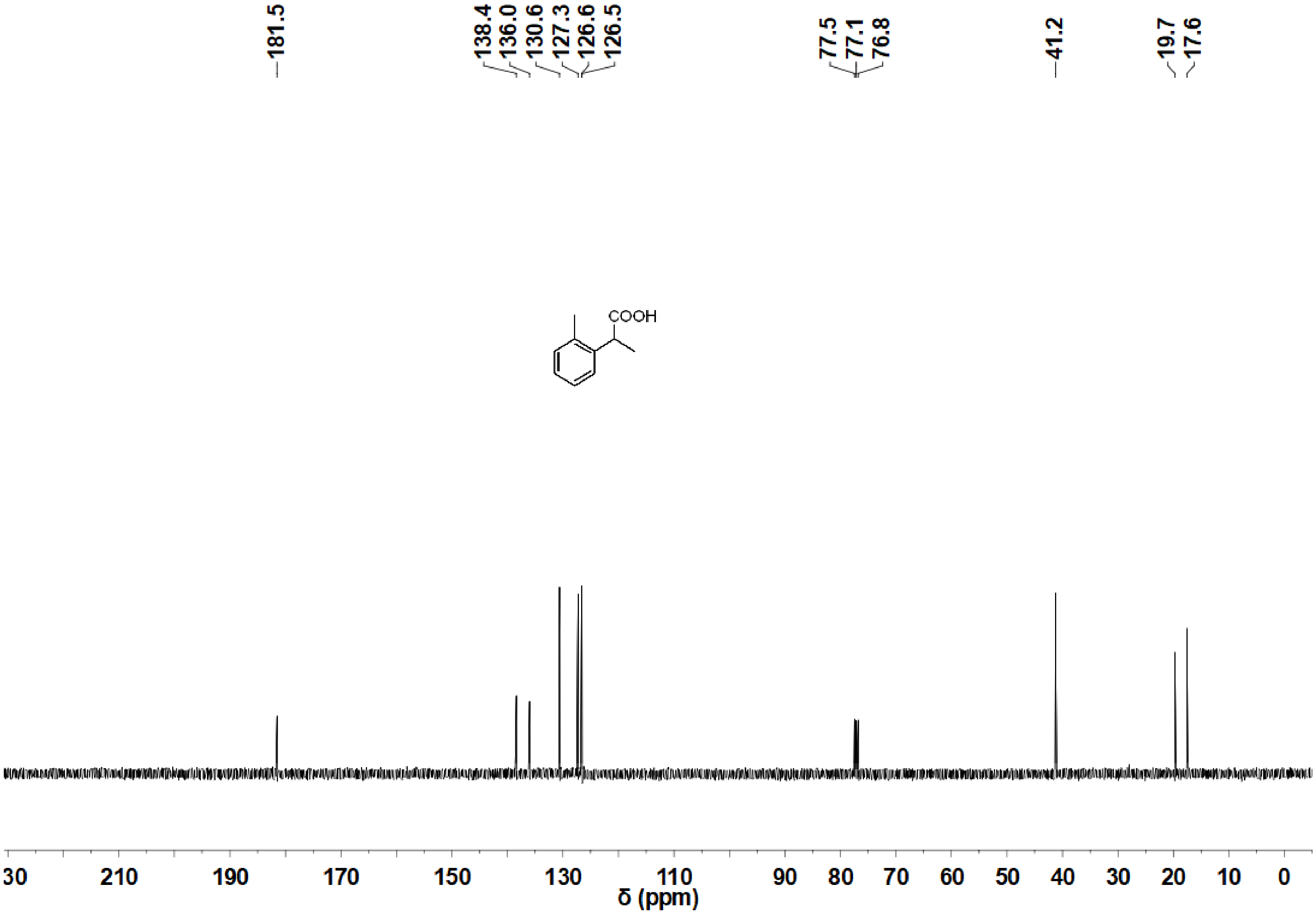
2-(2-naphthyl) propanoic acid, **2o**
400 MHz, DMSO-d_6




175.5
138.9
133.1
132.1
128.0
127.7
127.5
126.2
126.1
125.8
125.8
44.9
39.9
39.7
39.5
39.3
39.1
18.5
O
OH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

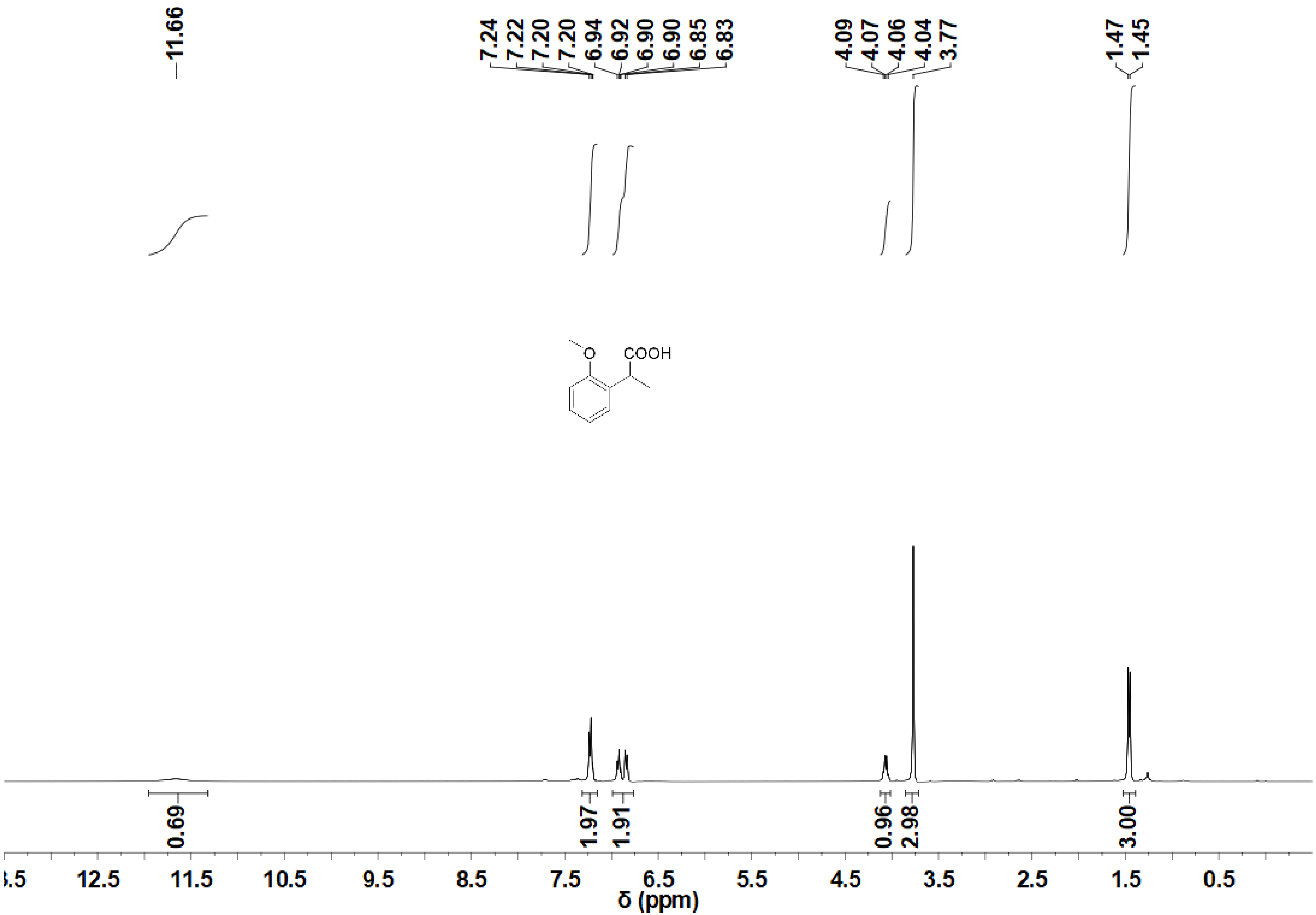
2-(2-methylphenyl) propanoic acid, **2p**
400 MHz, , $CDCl_3$

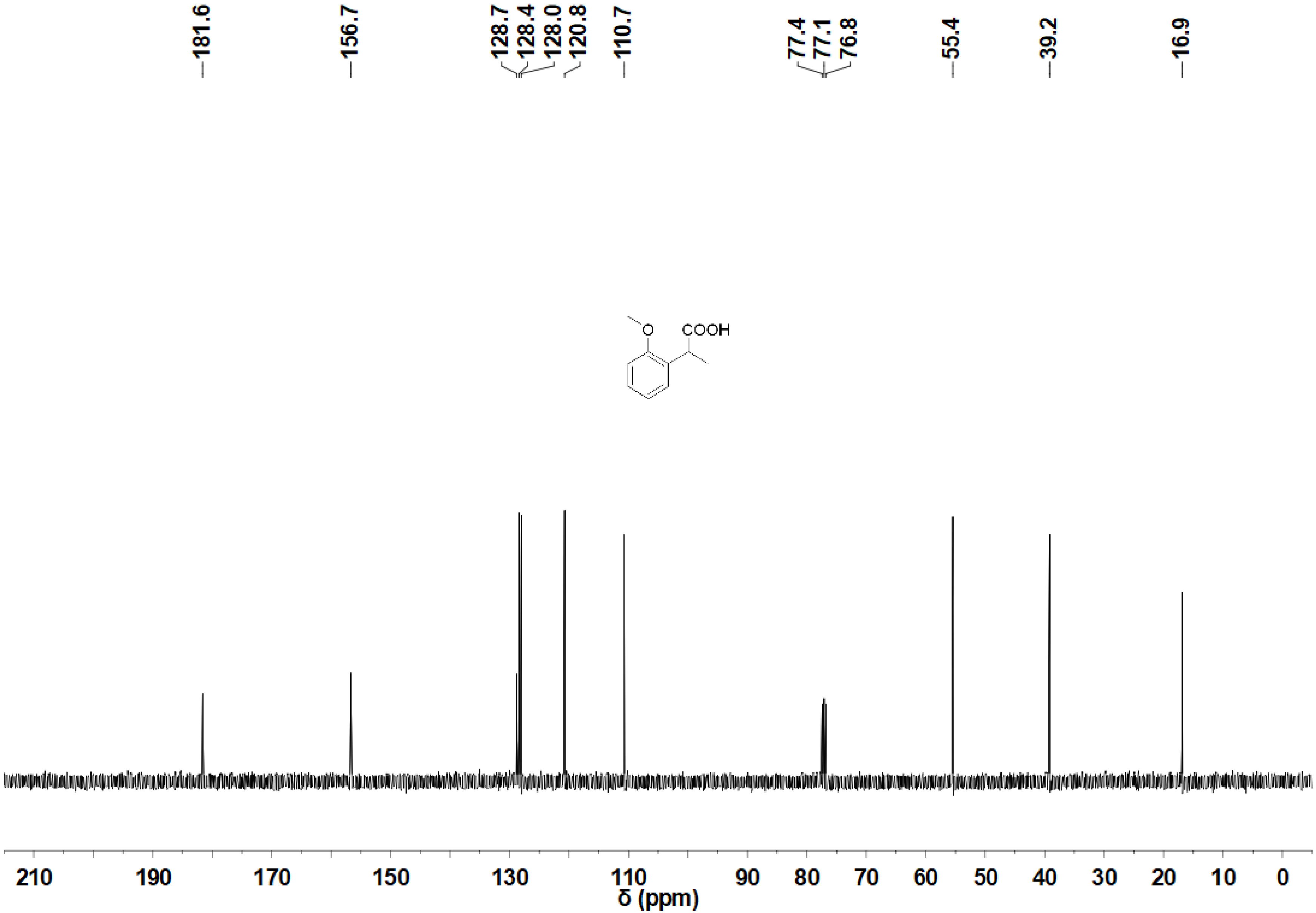




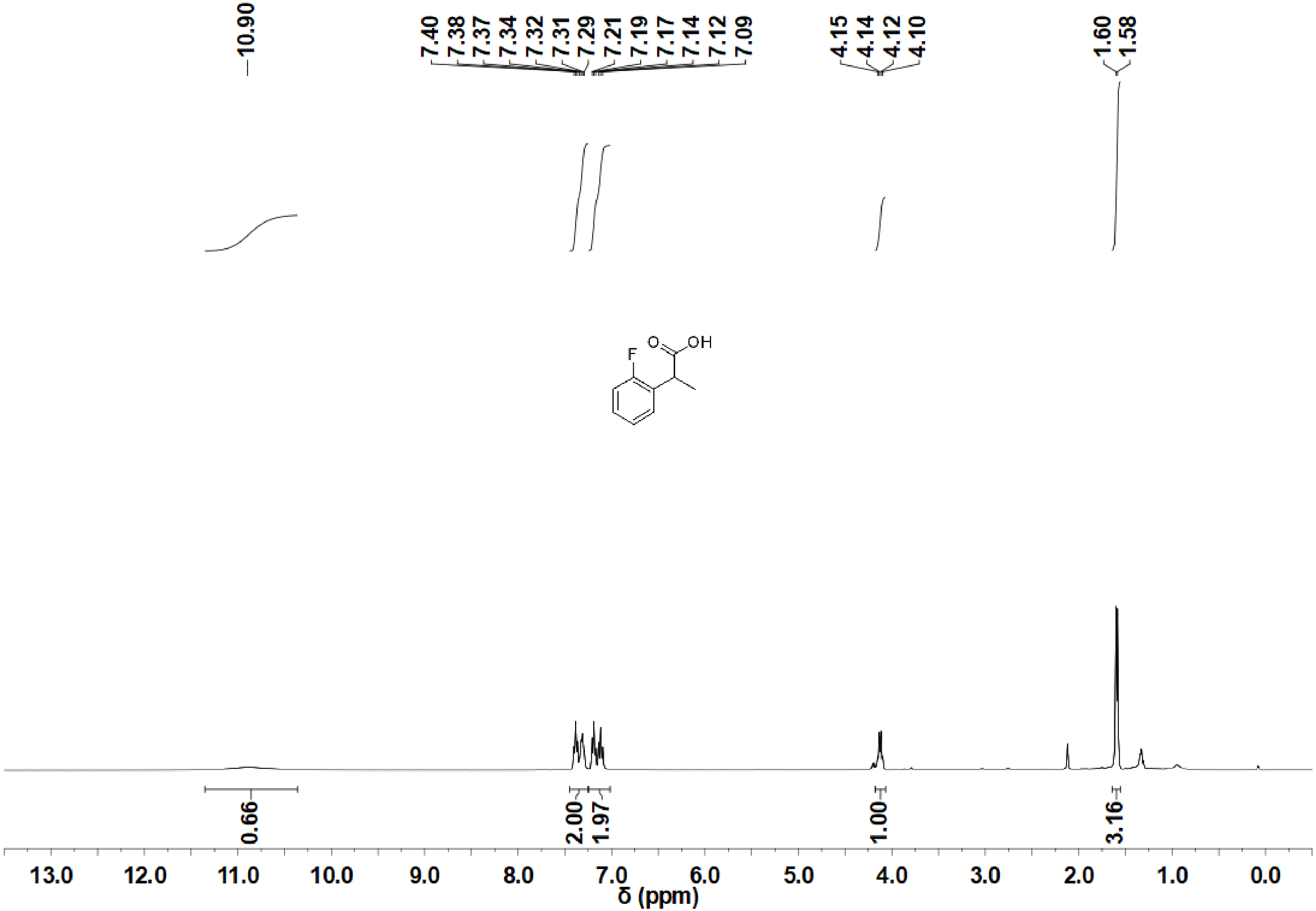
181.5
138.4
136.0
130.6
127.3
126.6
126.5
77.5
77.1
76.8
41.2
19.7
17.6
COOH
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

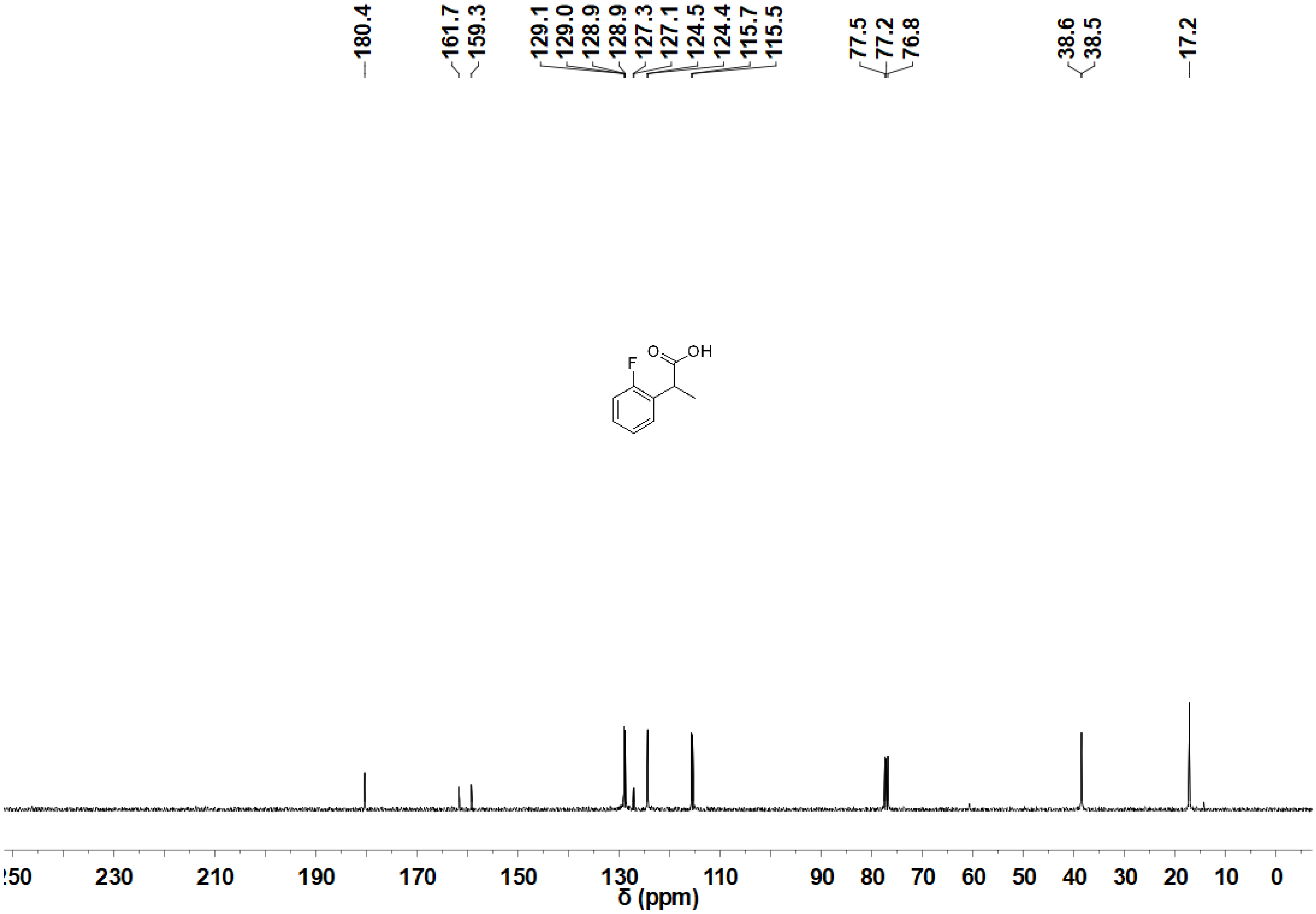
2-(2-methoxyphenyl)propanoic acid, **2q**
400 MHz , $CDCl_3$



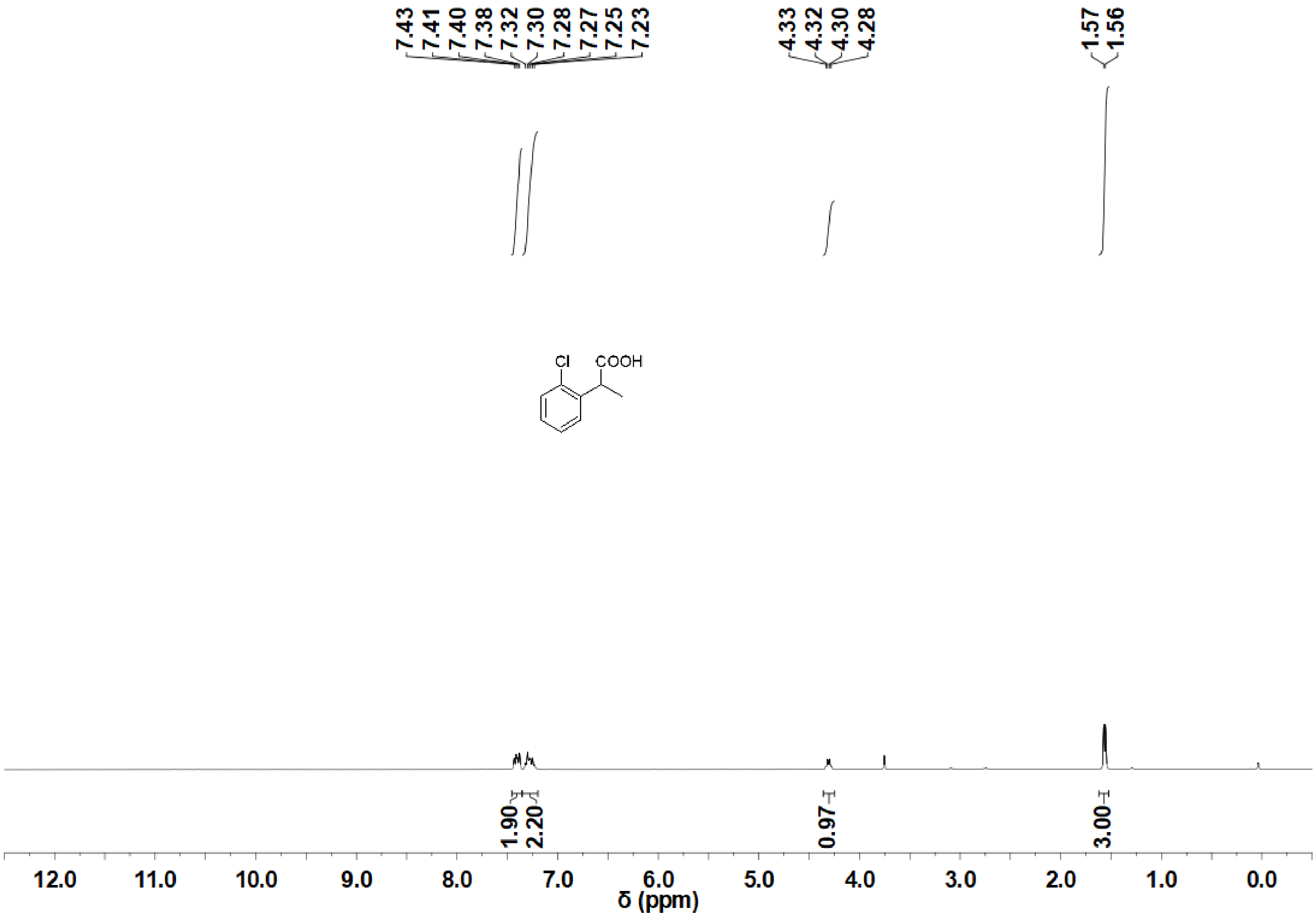

181.6
156.7
128.7
128.4
128.0
120.8
110.7
77.4
77.1
76.8
55.4
39.2
16.9
O
COOH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

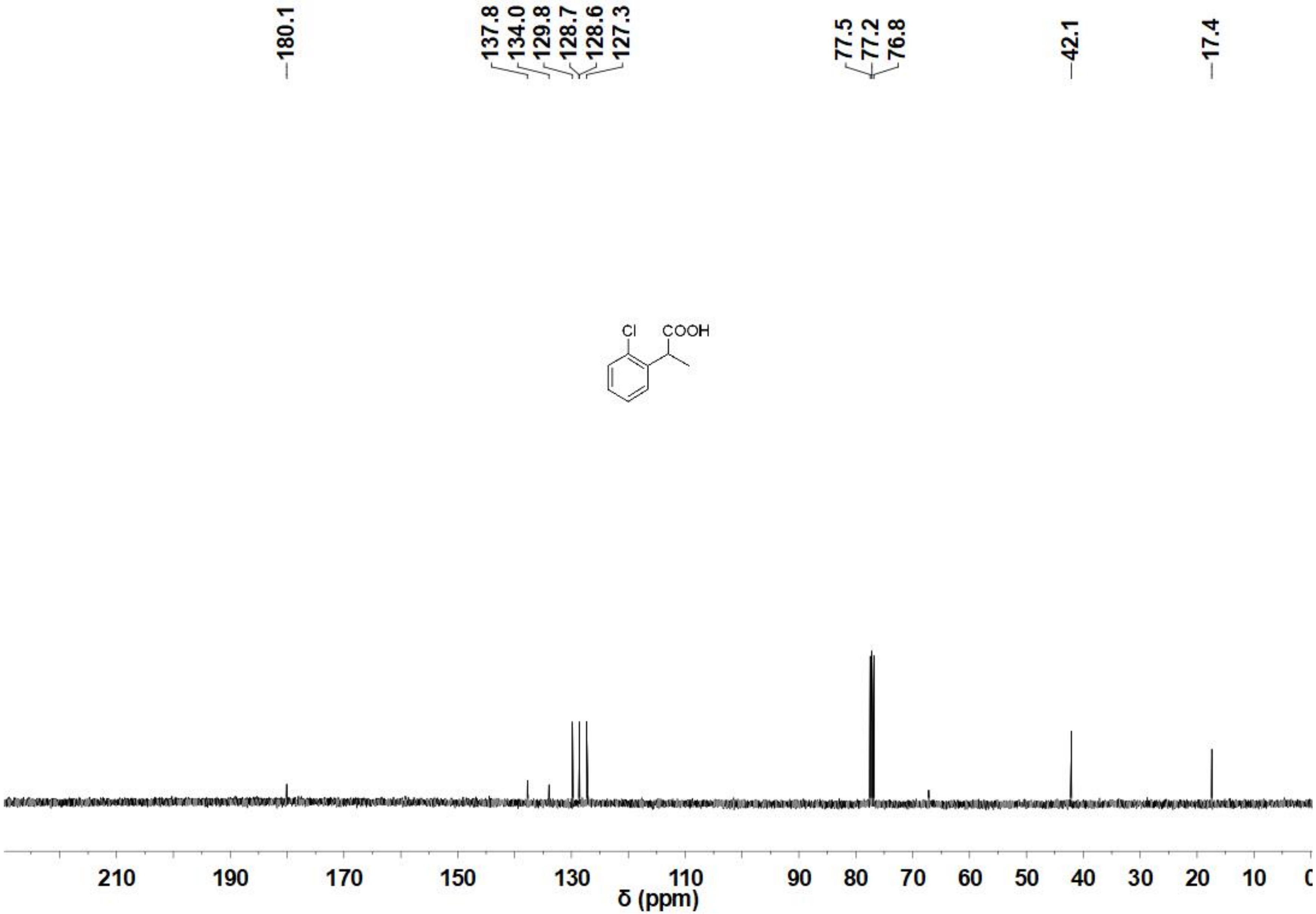
2-(2-fluorophenyl) propionic acid, **2r**
400 MHz, $CDCl_3$



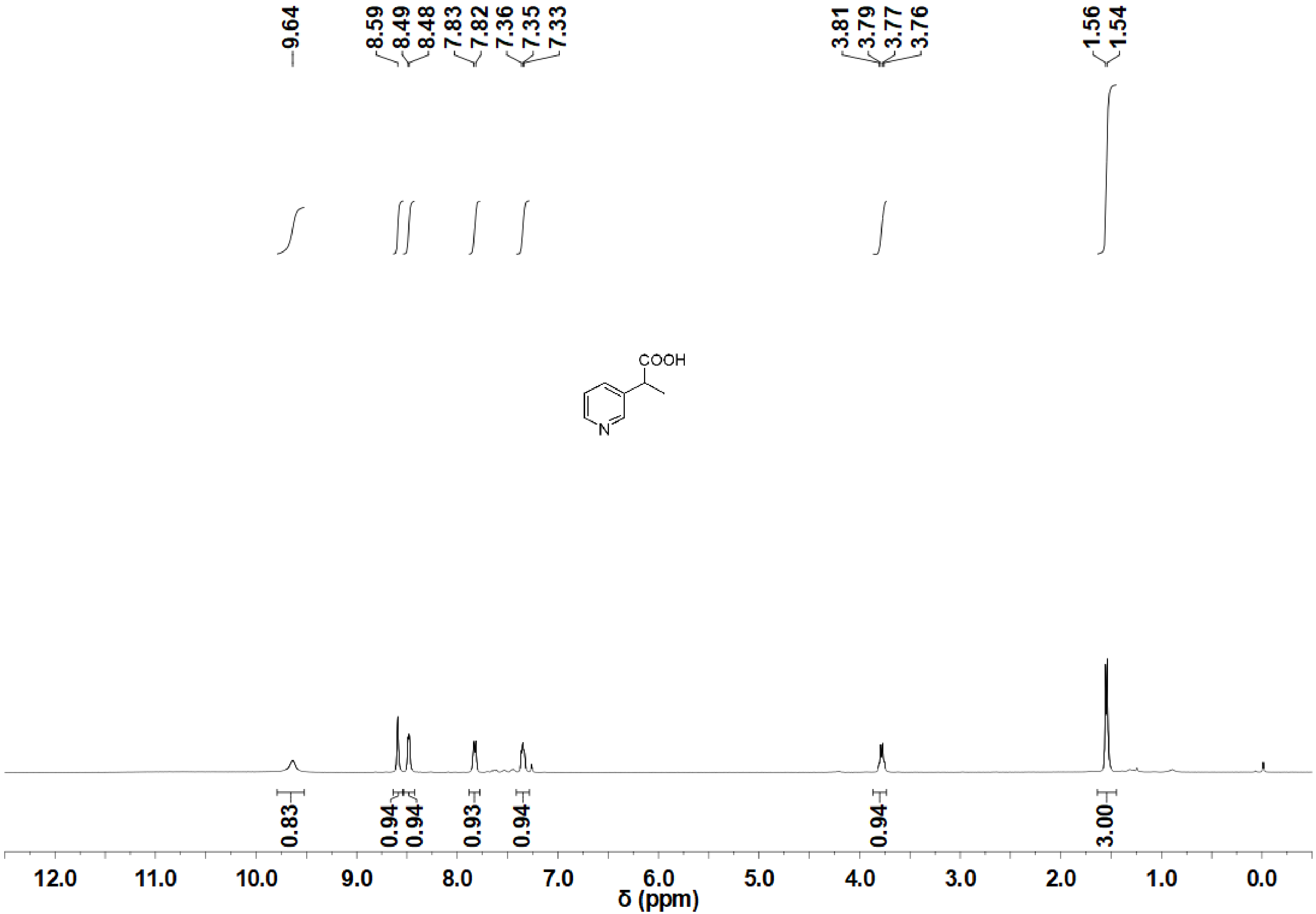

180.4
161.7
159.3
129.1
129.0
128.9
128.9
127.3
127.1
124.5
124.4
115.7
115.5
77.5
77.2
76.8
38.6
38.5
17.2
F
O
OH
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

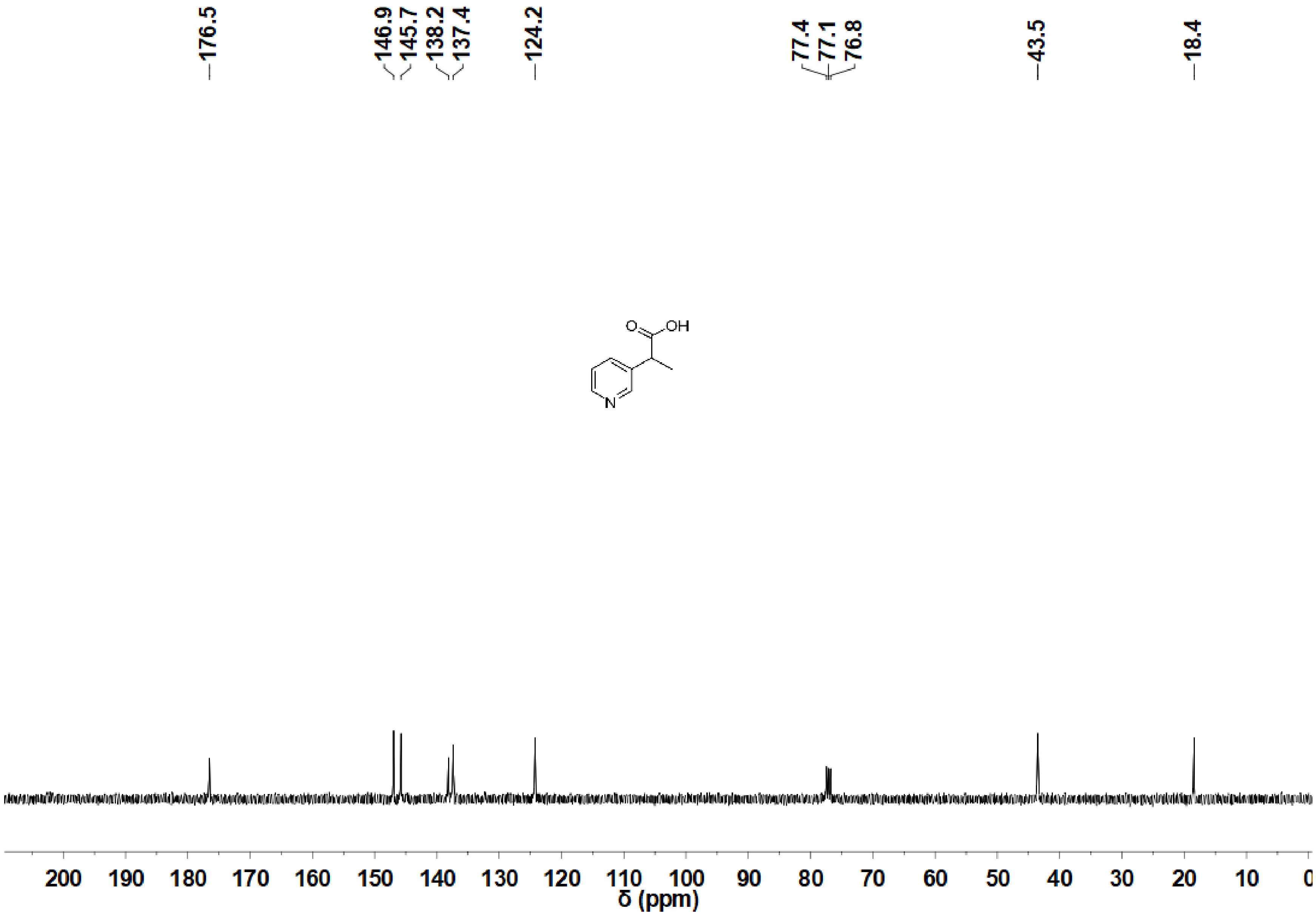
2-(2-chlorphenyl) propionic acid, **2s**
400 MHz, $CDCl_3$




180.1
137.8
134.0
129.8
128.7
128.6
127.3
77.5
77.2
76.8
42.1
17.4
Cl
COOH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

2-pyridyl propionic aicd, **2t**
400 MHz, $CDCl_3$




176.5
146.9
145.7
138.2
137.4
124.2
77.4
77.1
76.8
43.5
18.4
O
OH
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

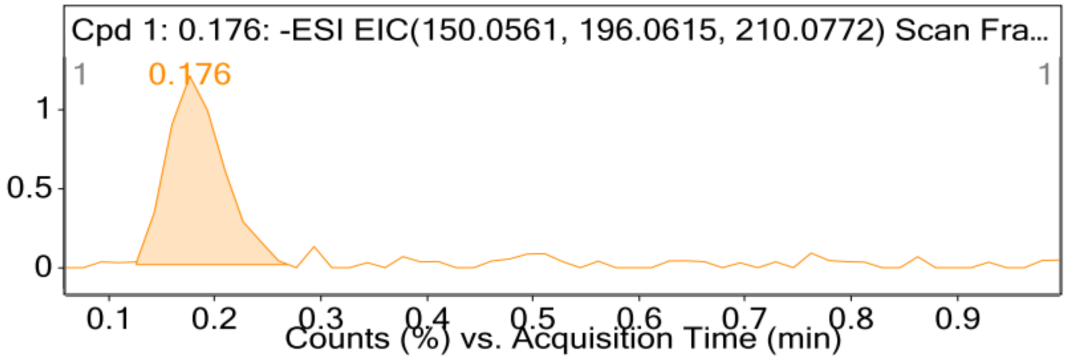
Qualitative Compound Report

Data File	HZJ-3-11-3+.d	**Sample Name**	HZJ-3-11-3
Sample Type	Sample	**Position**	Vial 25
Instrument Name	6530 QTOF LC/MS	**Acq Method**	my-MS.m
Acquired Time	5/18/2017 10:46:44 AM	**IRM Calibration Status**	Success

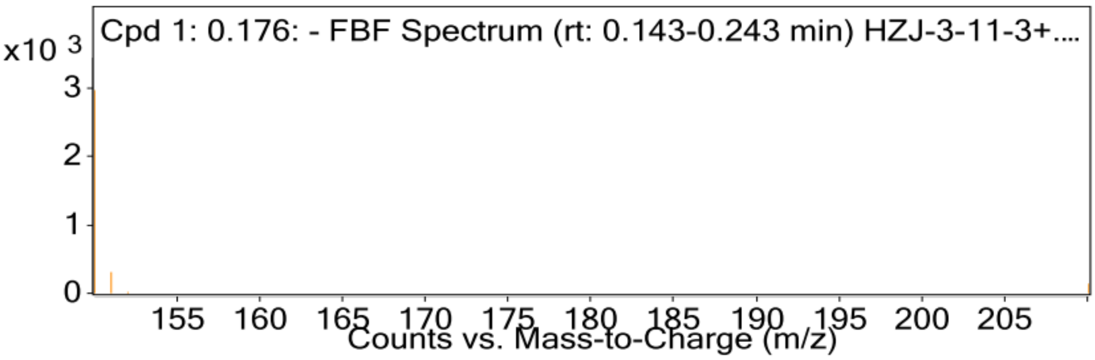
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 0.176	0.176	151.0633	2973	C8 H9 N O2	151.0633	-0.43

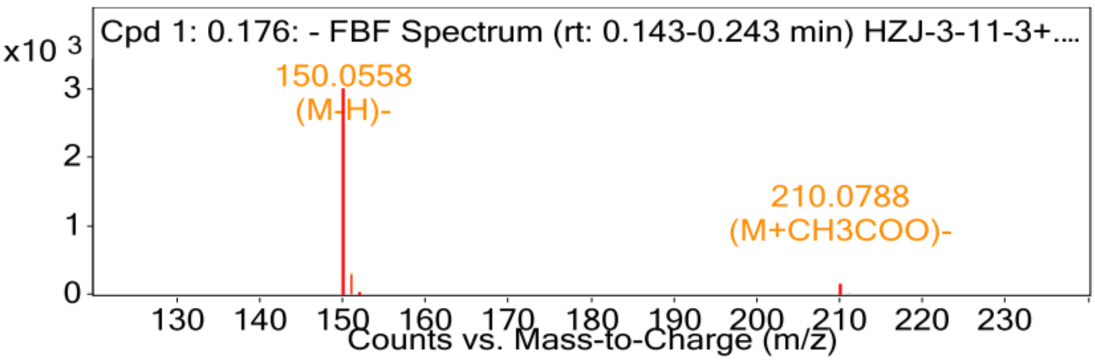
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: 0.176	150.0558	0.176	Find By Formula	151.0633



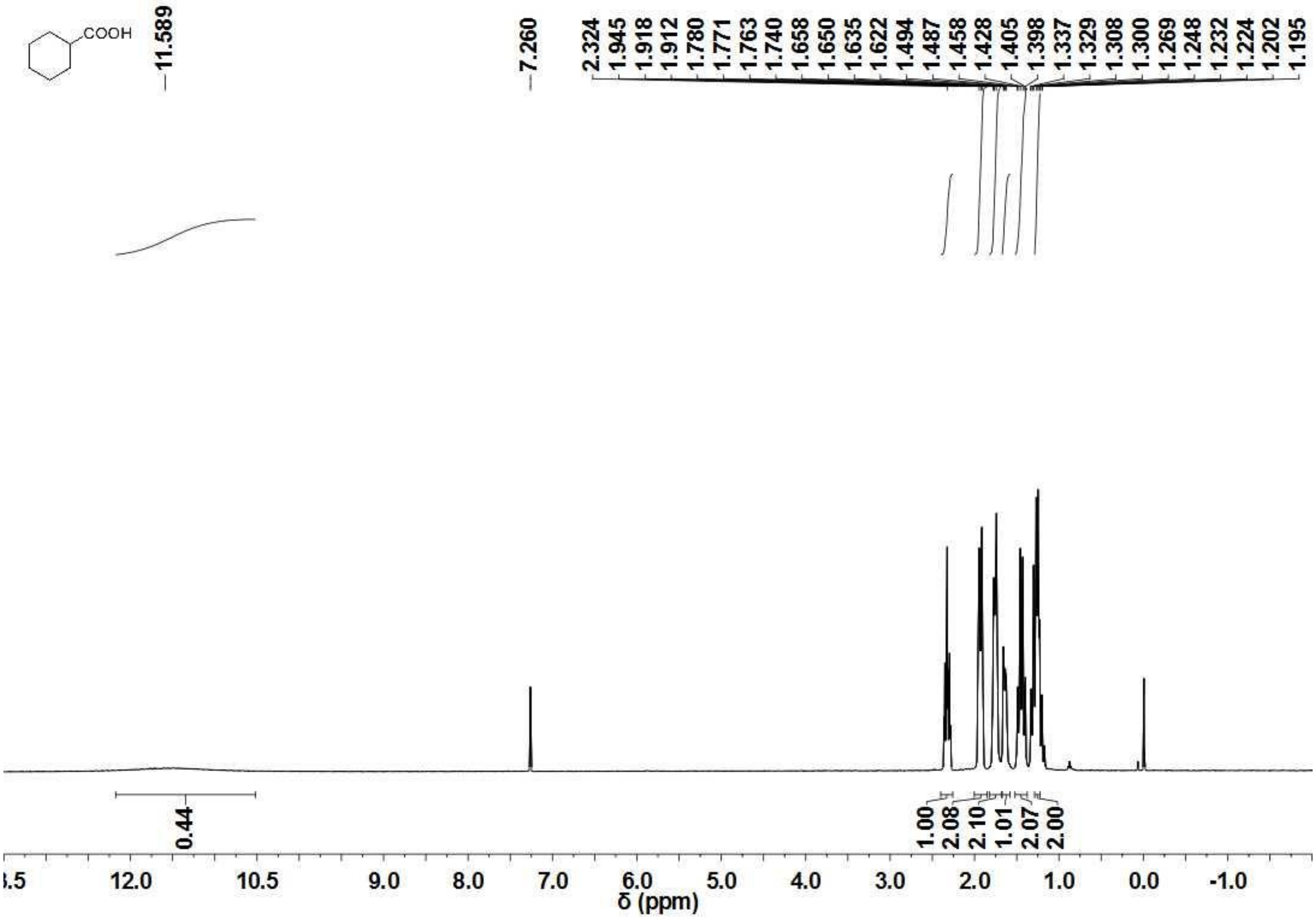
MS Spectrum

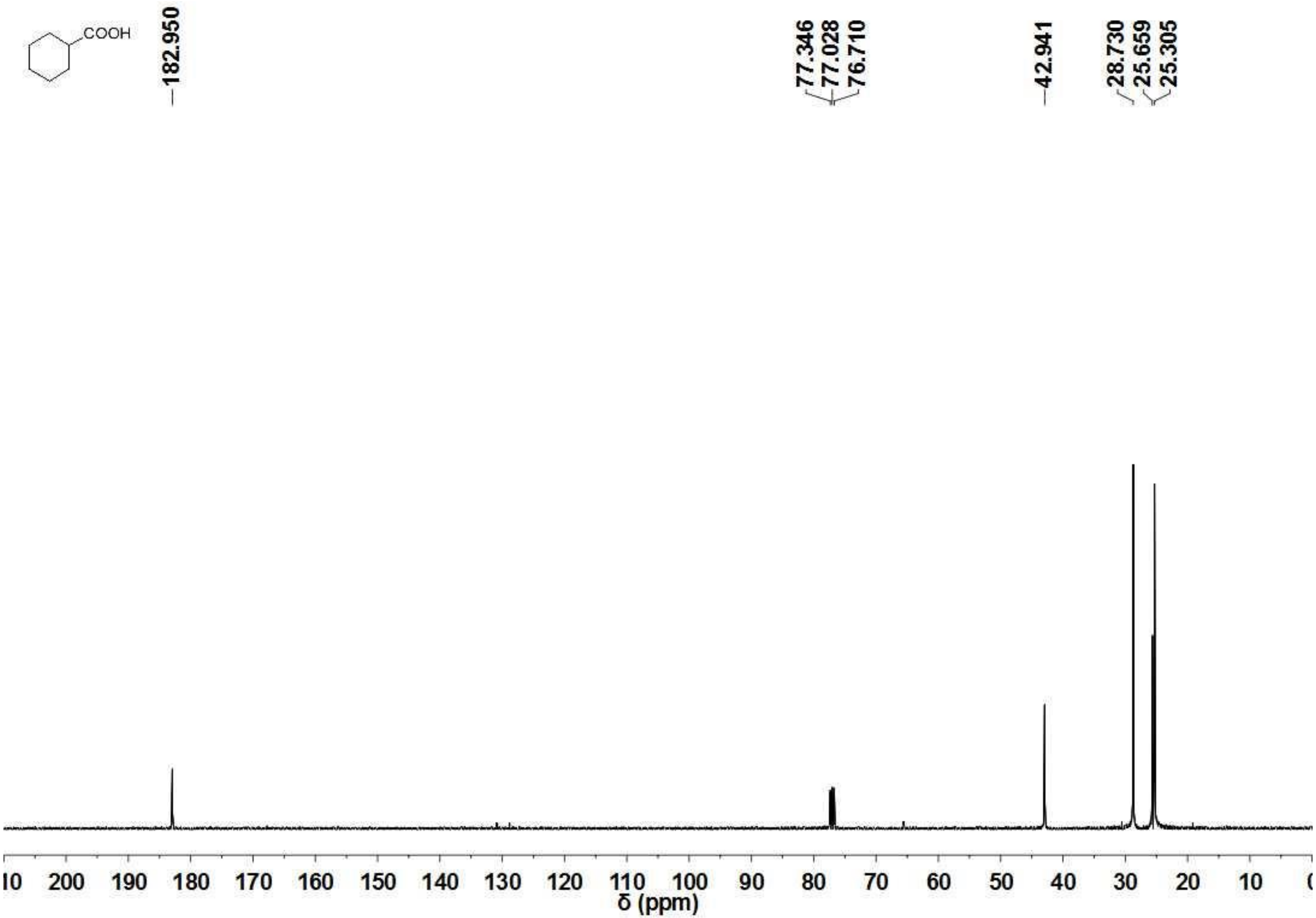


MS Zoomed Spectrum

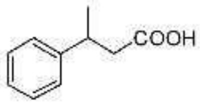


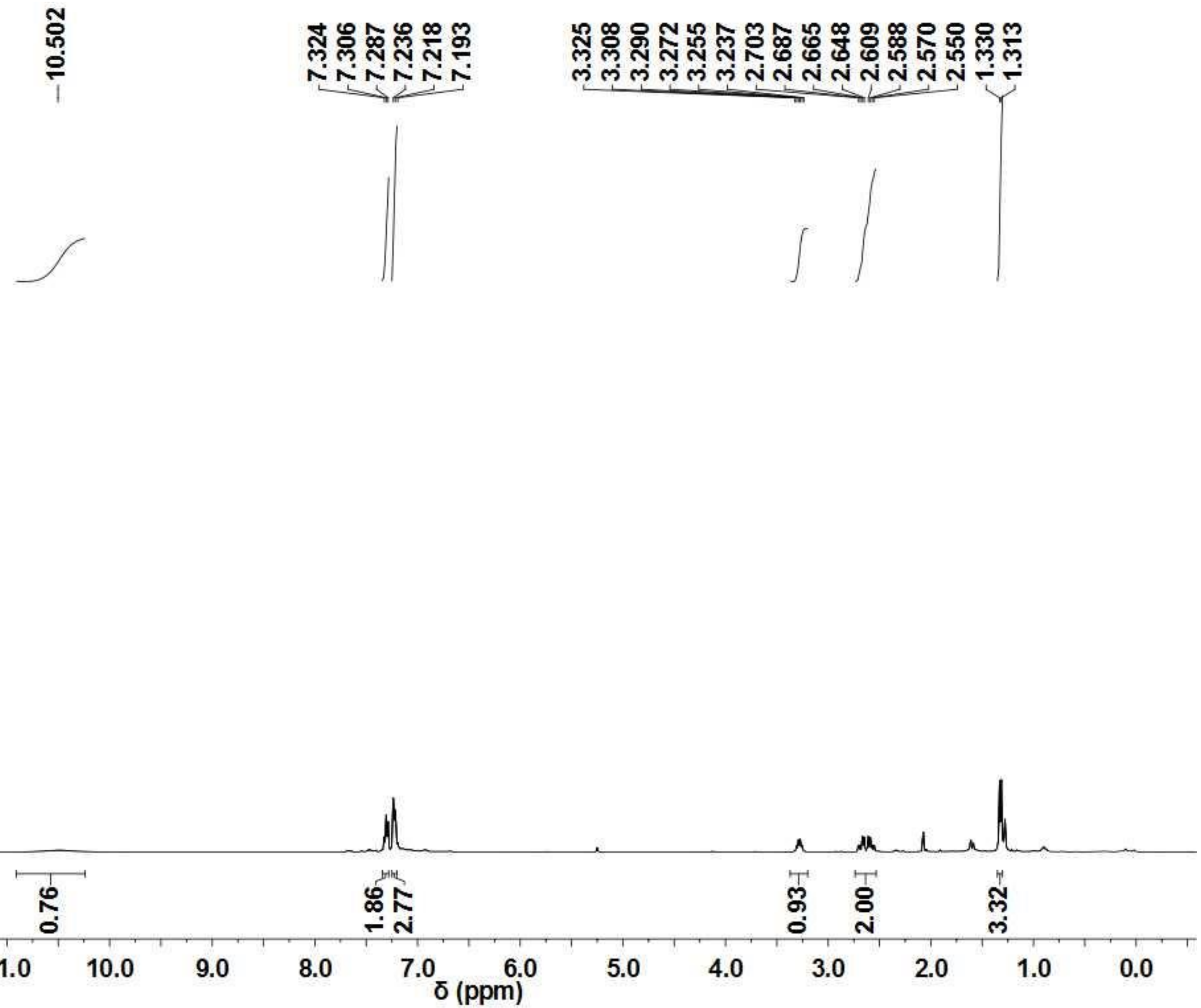
Cyclohexanecarboxylic acid, **2u**
400 MHz, $CDCl_3$

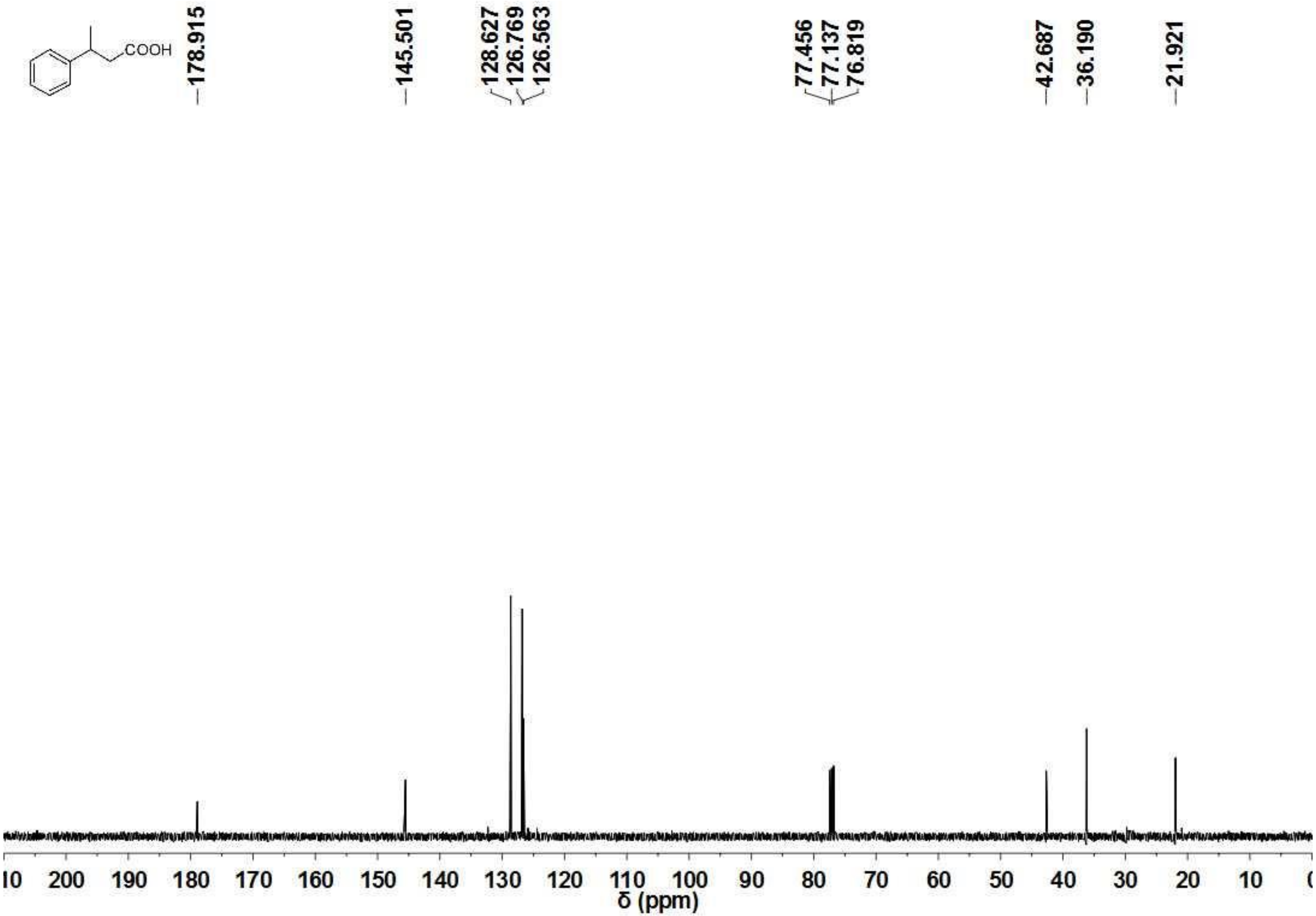



COOH
182.950
77.346
77.028
76.710
42.941
28.730
25.659
25.305
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)

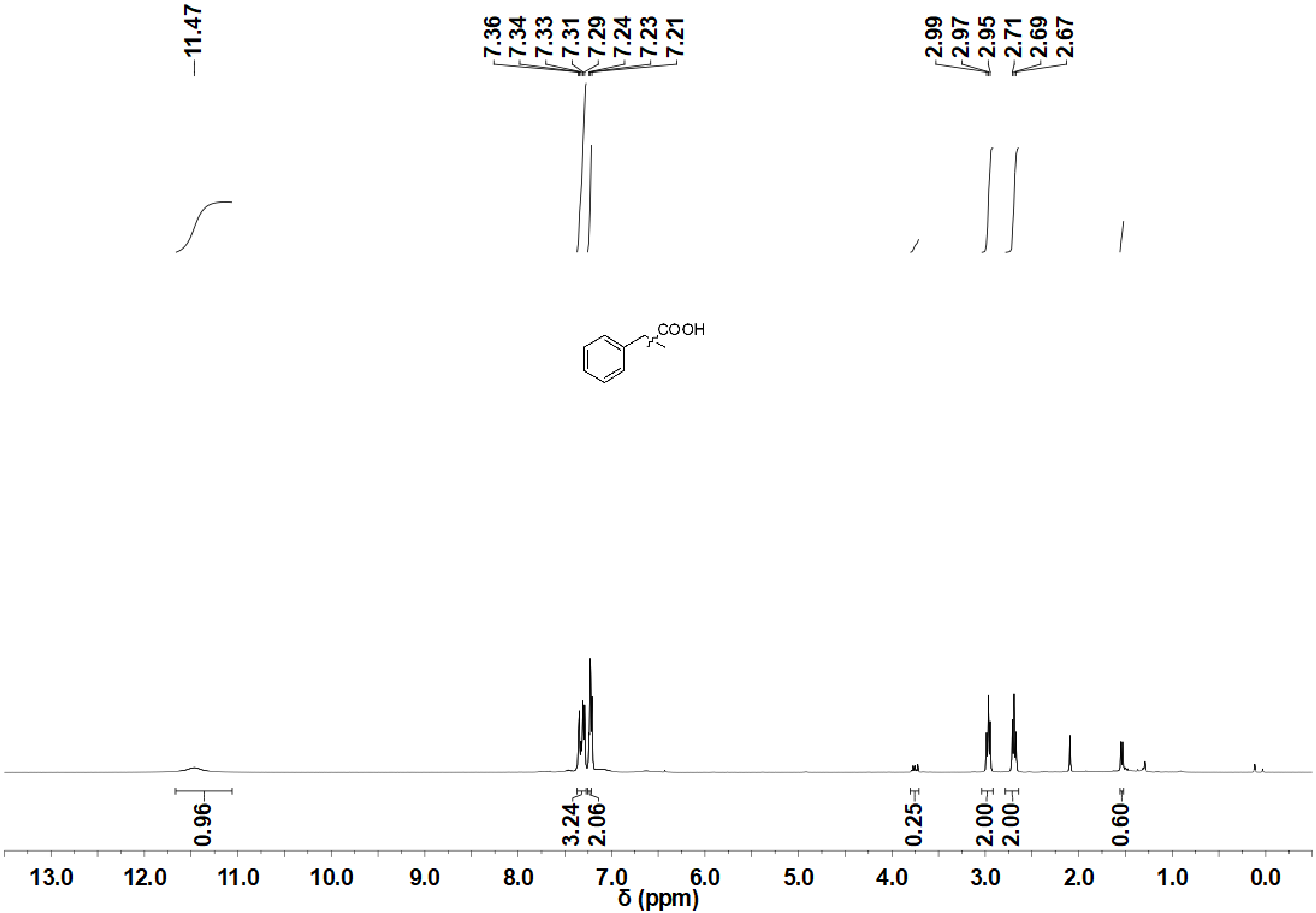
3-phenylbutyric acid, **2x**
400 MHz, $CDCl_3$

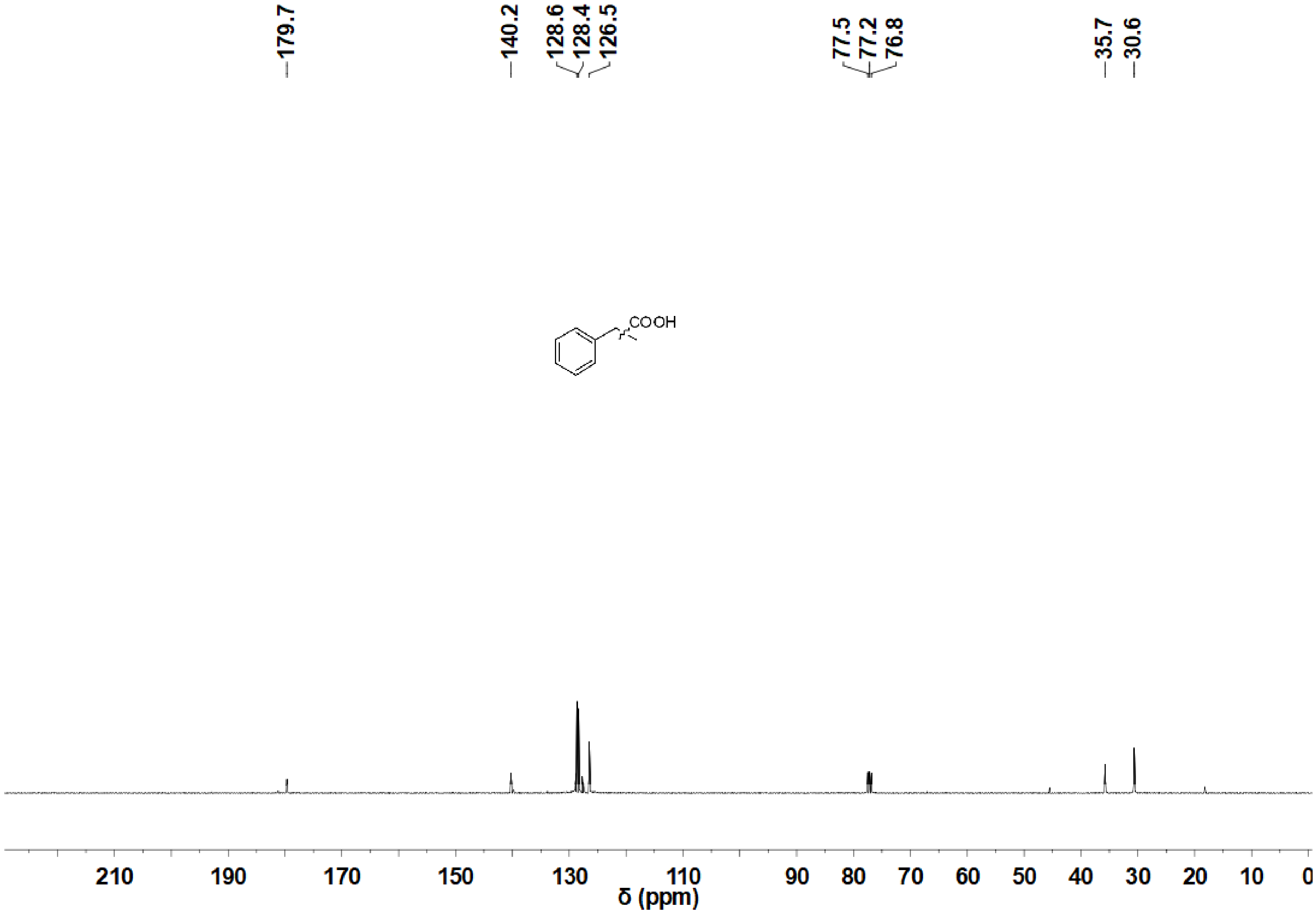




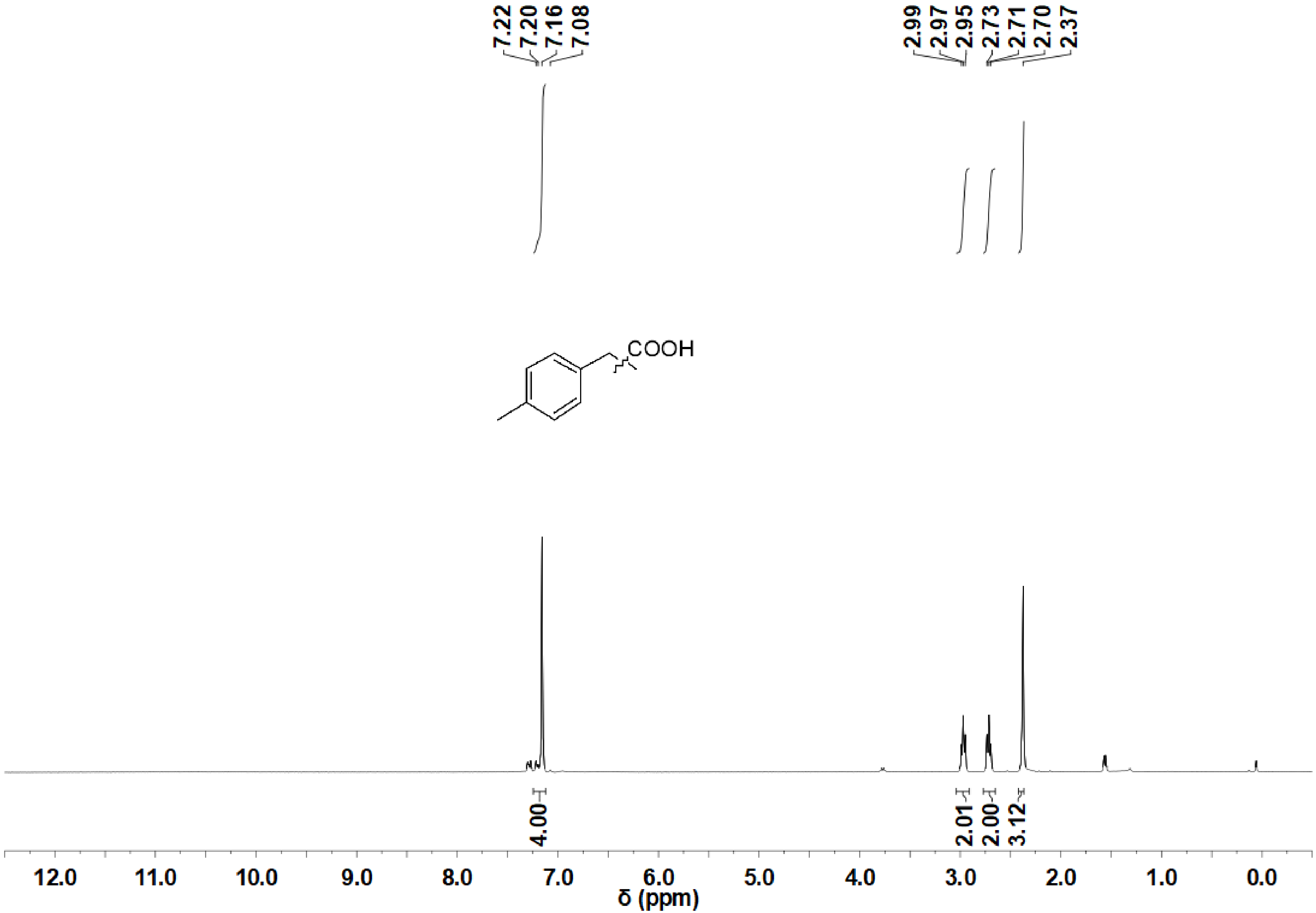

COOH
178.915
145.501
128.627
126.769
126.563
77.456
77.137
76.819
42.687
36.190
21.921
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)

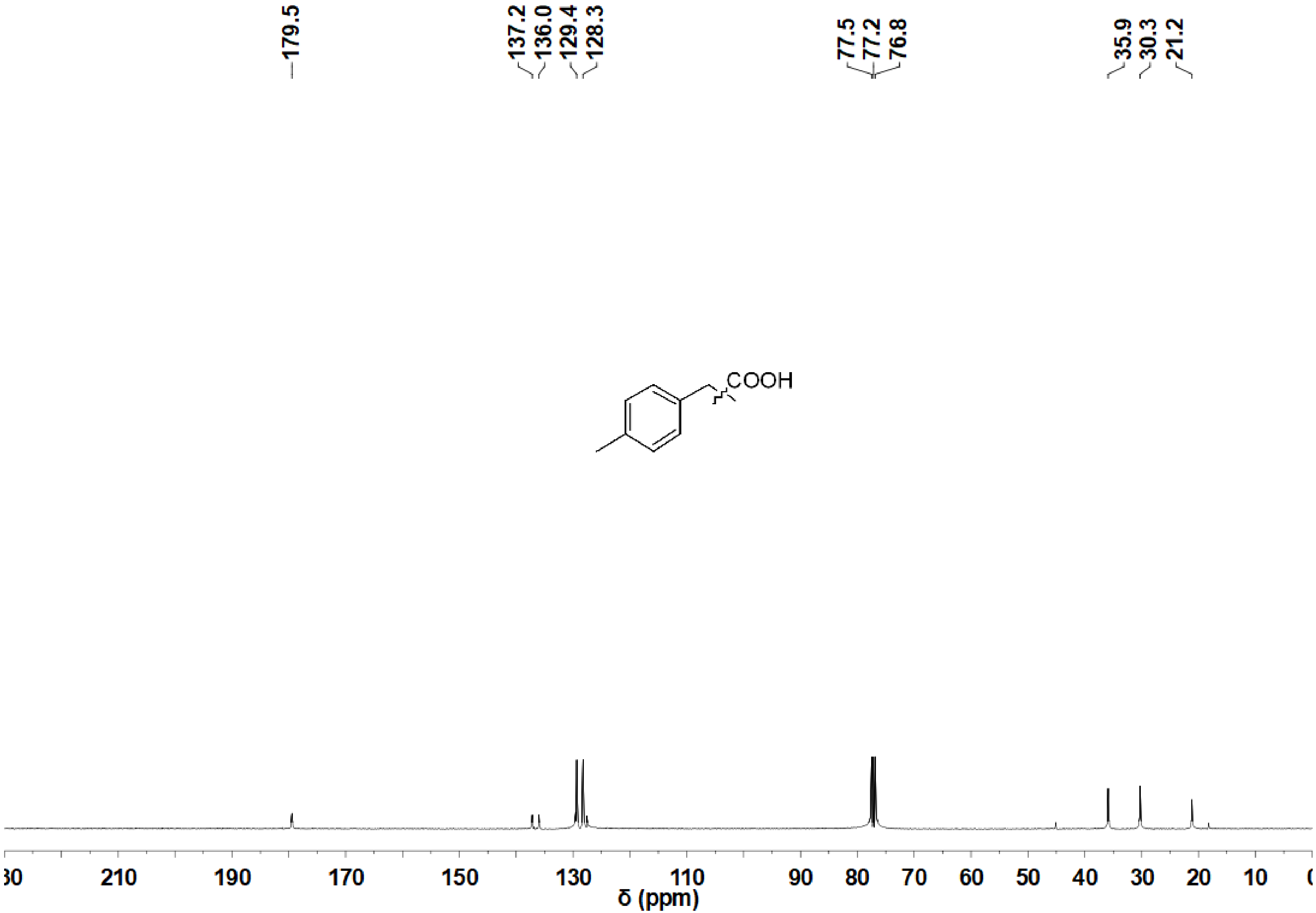
3-phenylpropionic acid, **3a**
400 MHz, $CDCl_3$



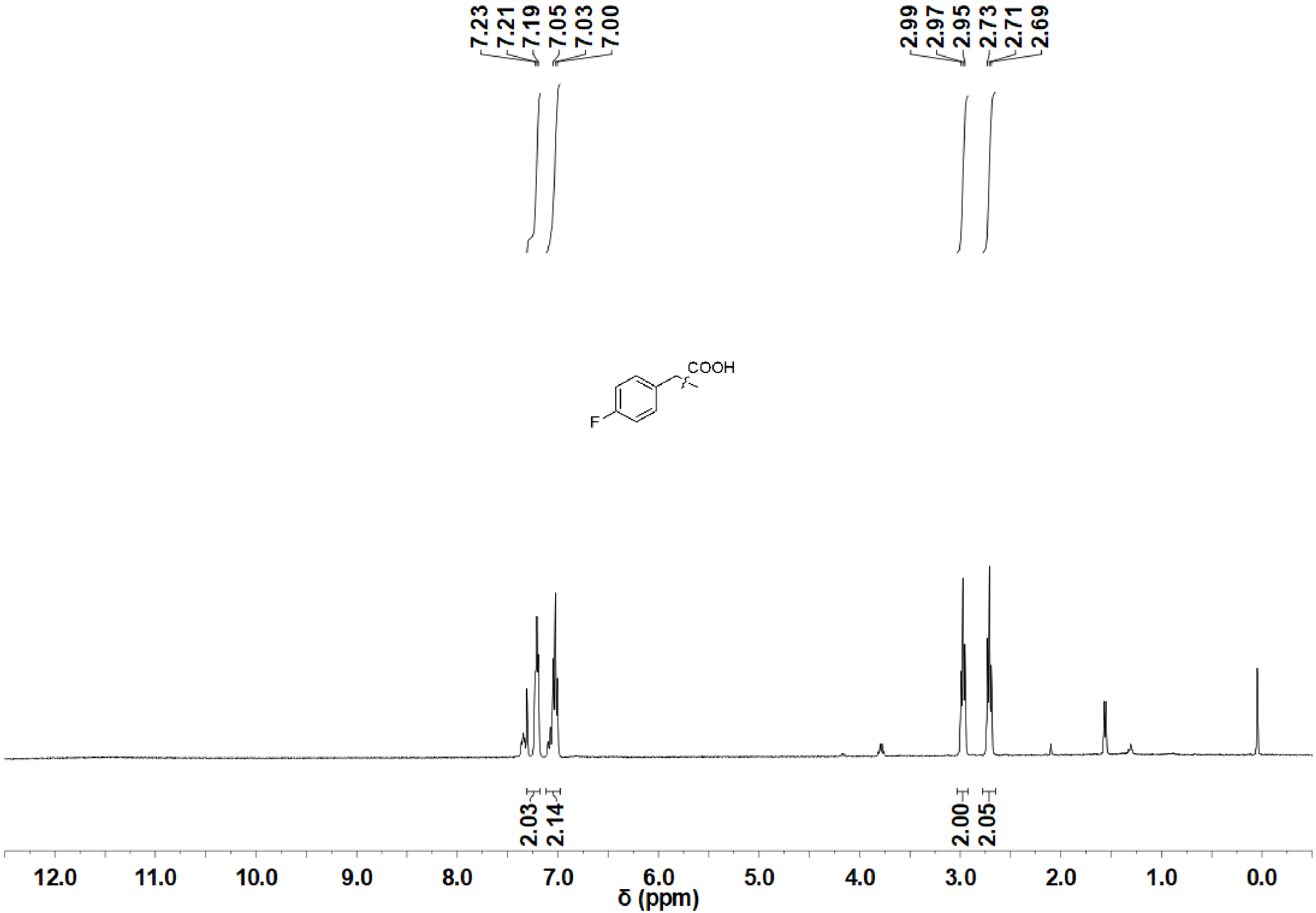

179.7
140.2
128.6
128.4
126.5
77.5
77.2
76.8
35.7
30.6
COOH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

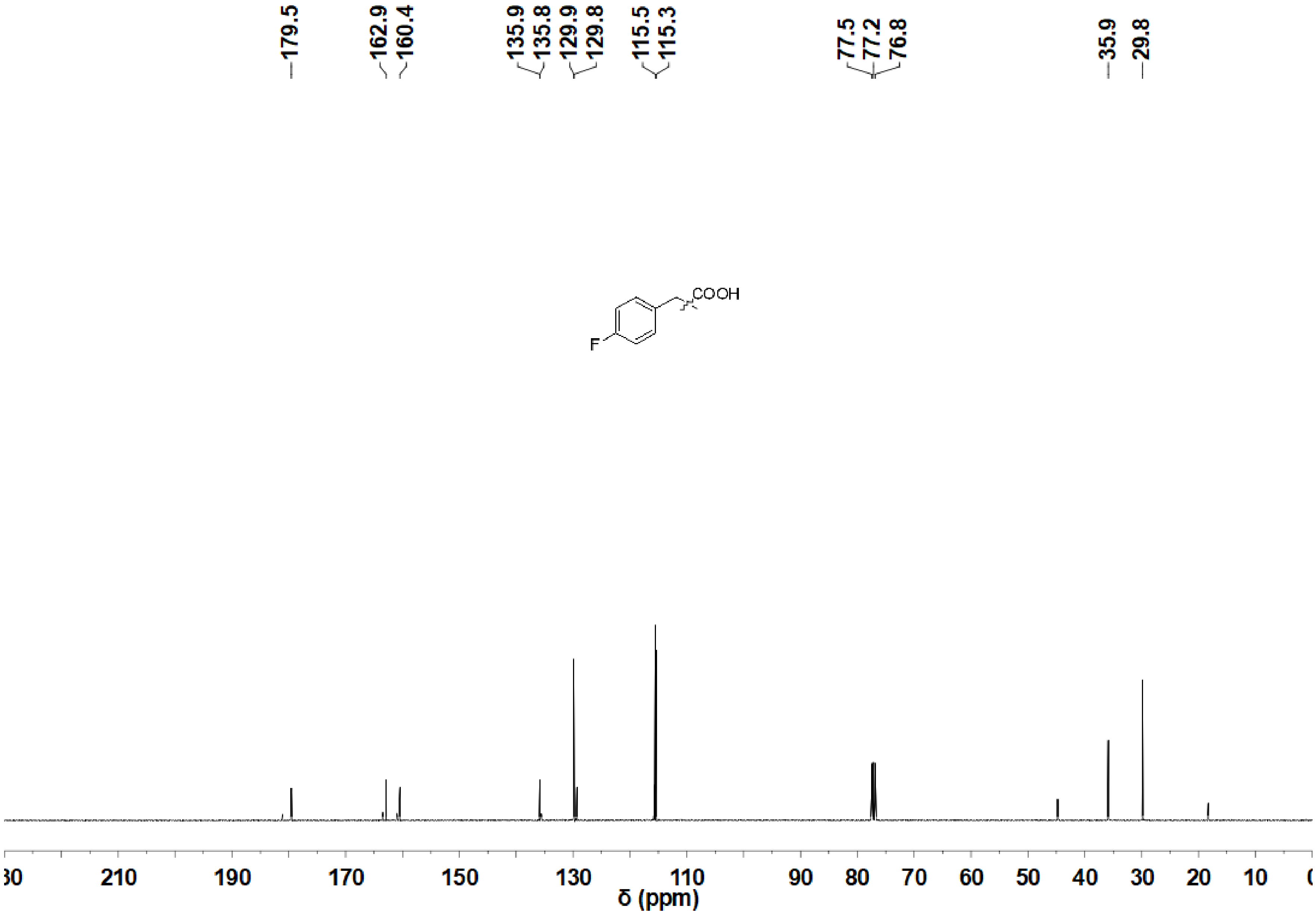
3-(4-methylphenyl) propanoic acid, **3b**
400 MHz, $CDCl_3$




179.5
137.2
136.0
129.4
128.3
77.5
77.2
76.8
35.9
30.3
21.2
COOH
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

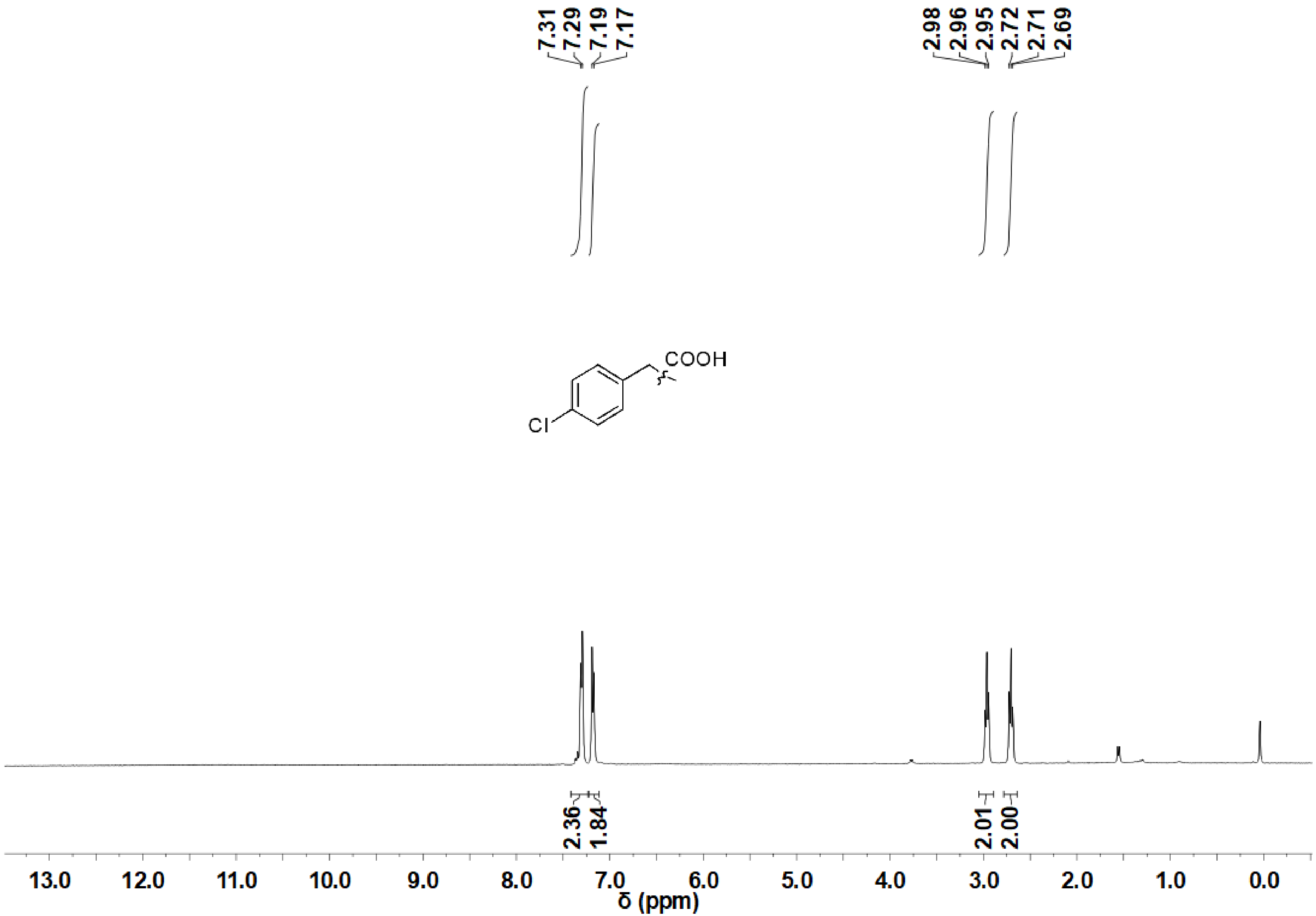
3-(4-fluorophenyl) propionic acid, **3e**
400 MHz, $CDCl_3$

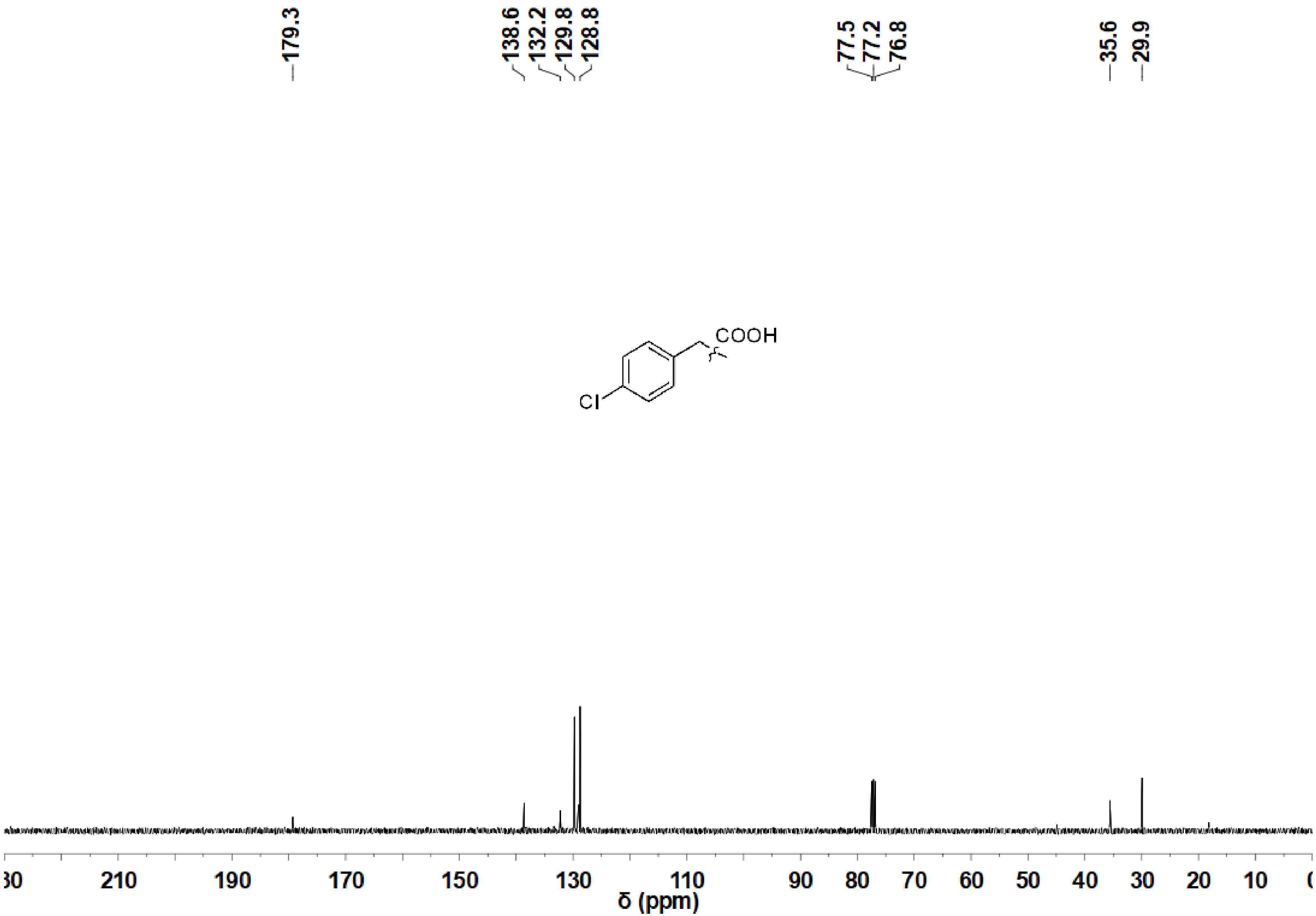




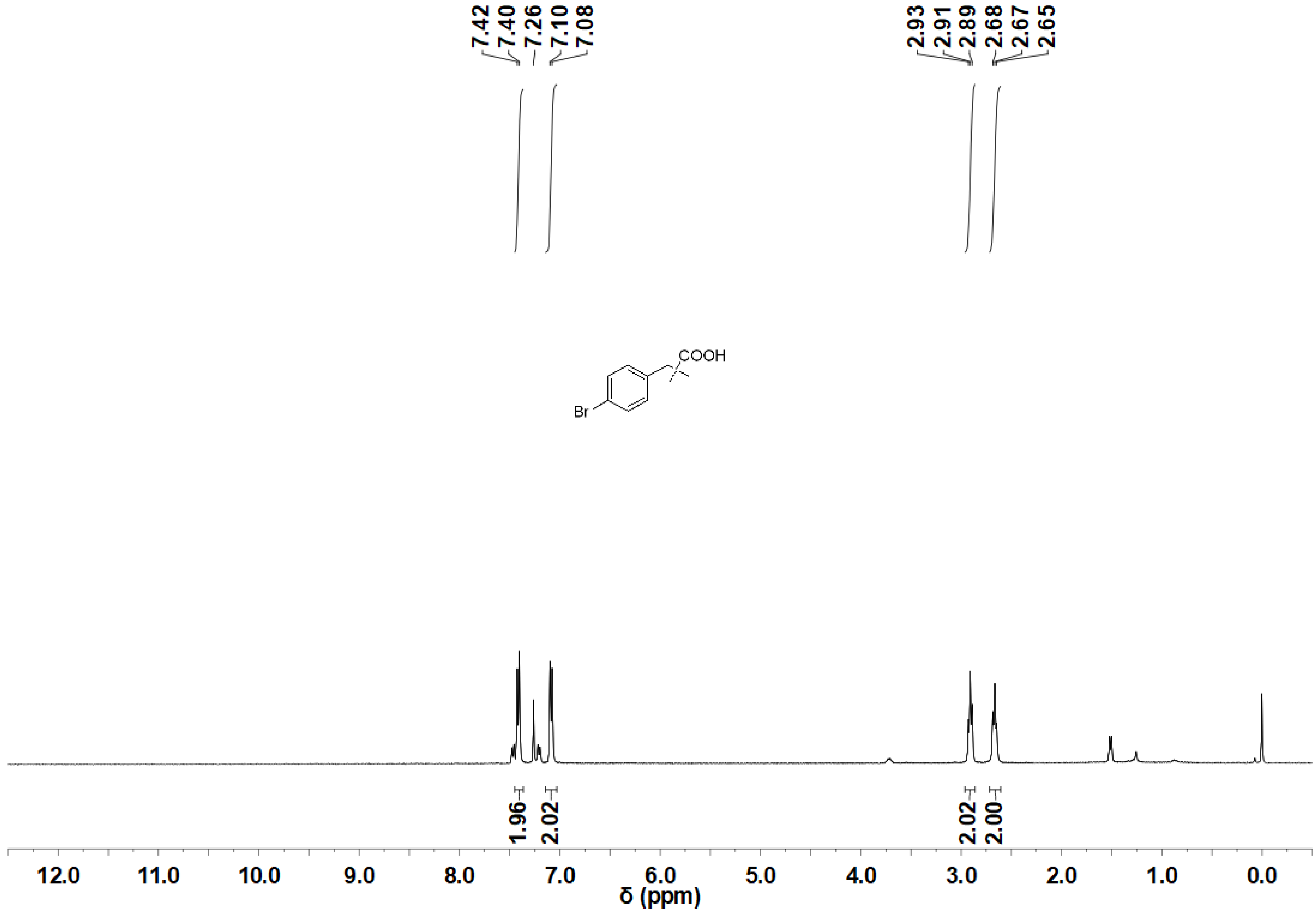
179.5
162.9
160.4
135.9
135.8
129.9
129.8
115.5
115.3
77.5
77.2
76.8
35.9
29.8
COOH
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

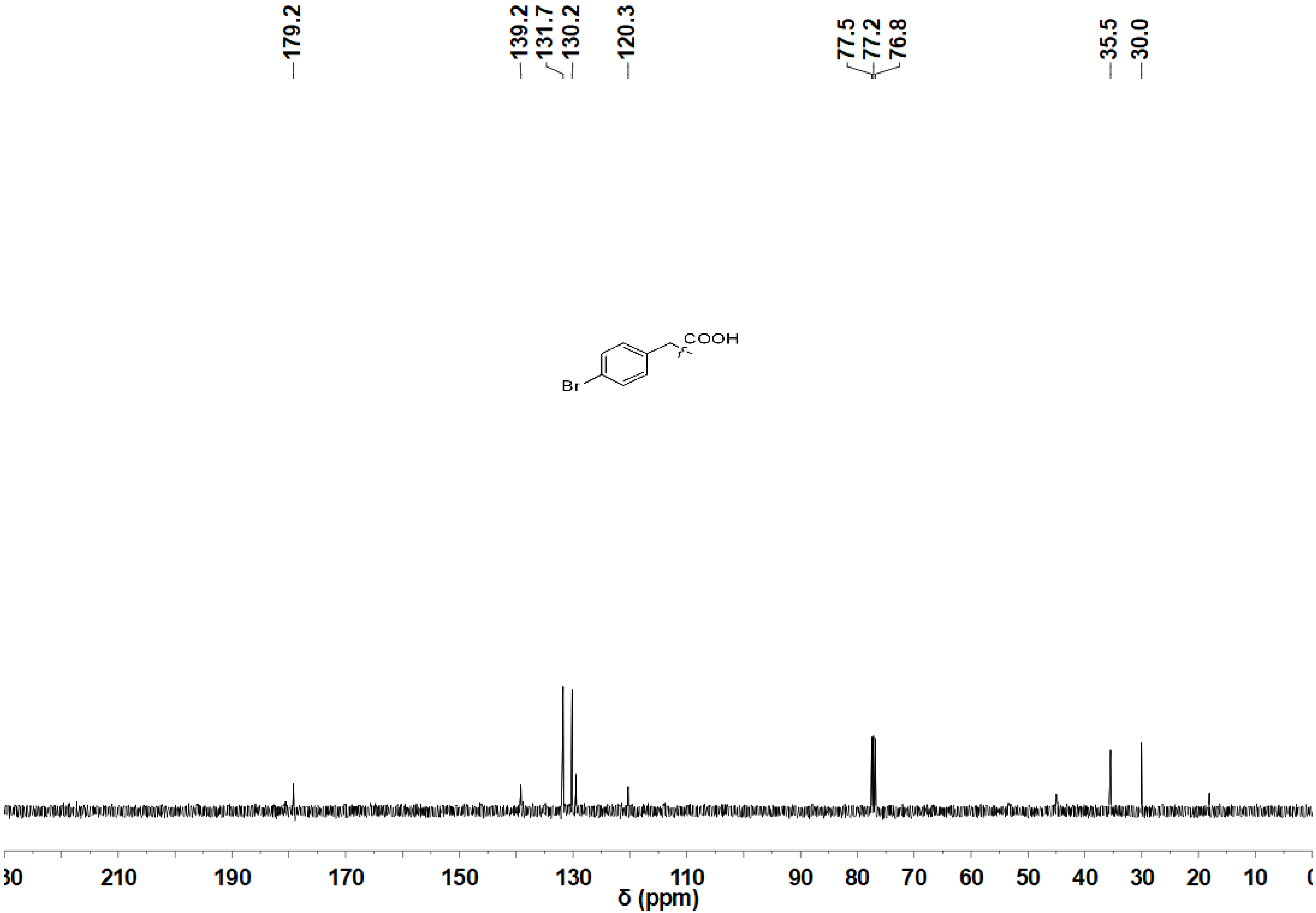
3-(4-chlorophenyl) propionic acid, **3f**
400 MHz, $CDCl_3$



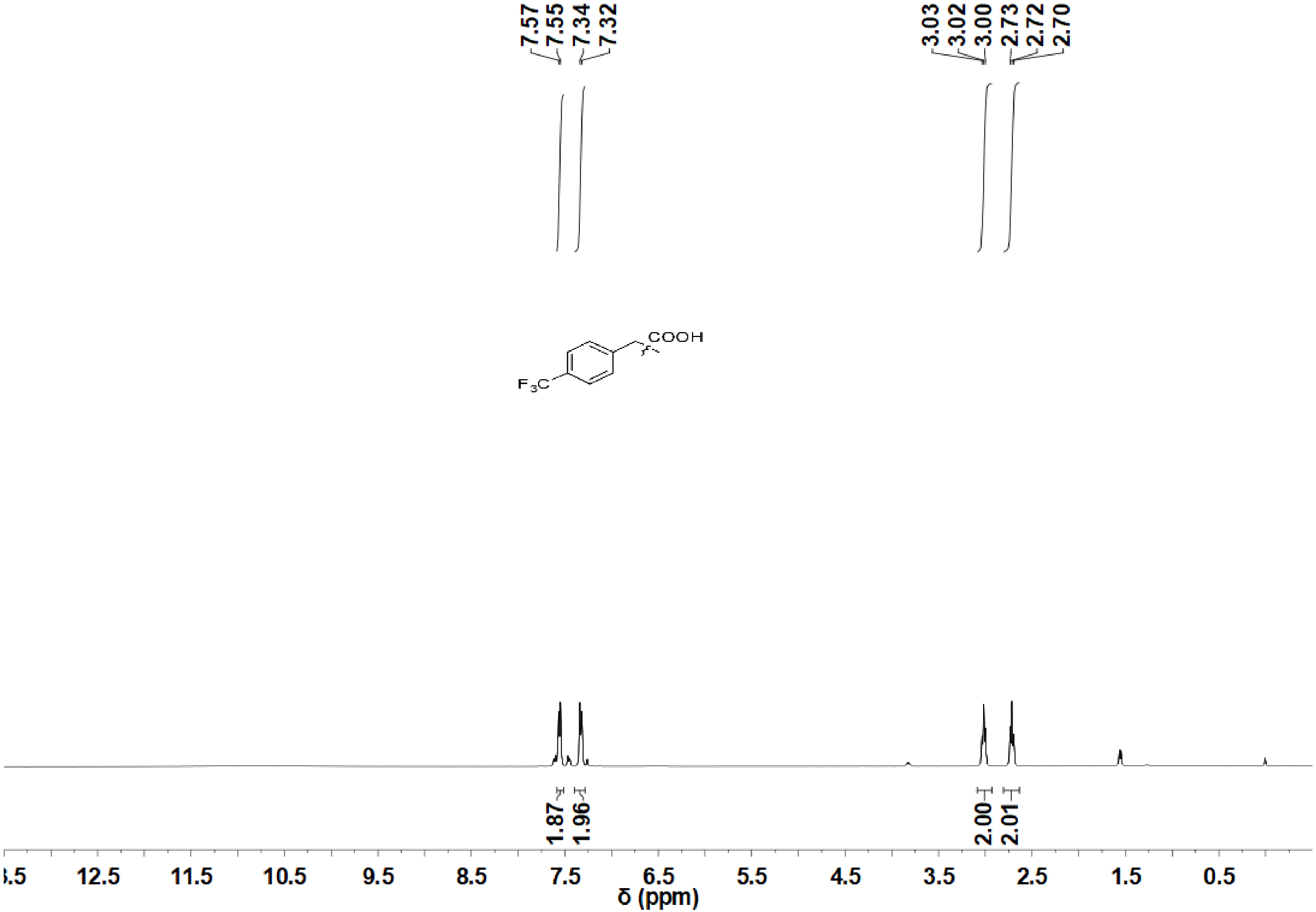

179.3
138.6
132.2
129.8
128.8
77.5
77.2
76.8
35.6
29.9
COOH
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

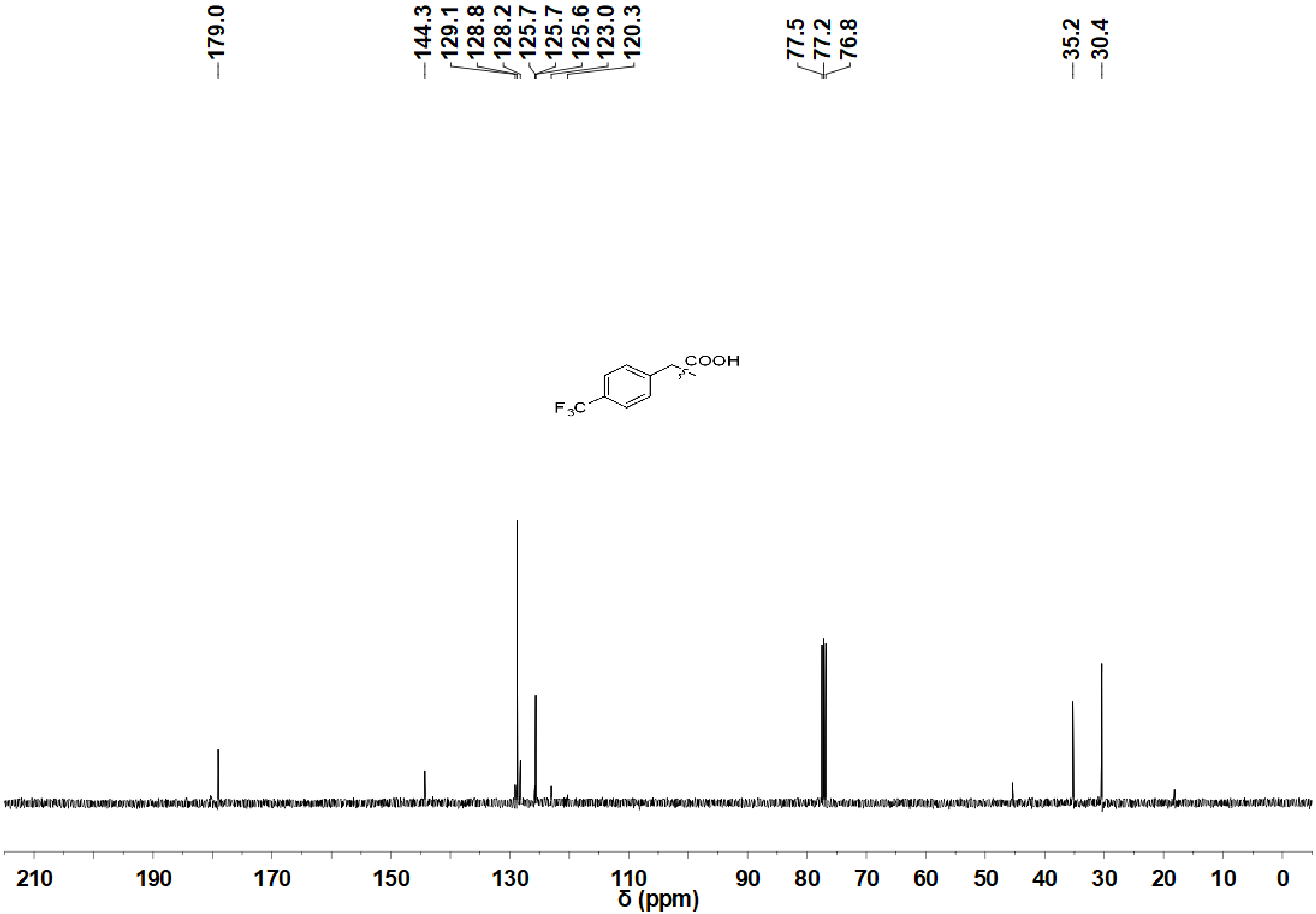
3-(4-bromophenyl) propanoic acid, **3g**
400 MHz, $CDCl_3$



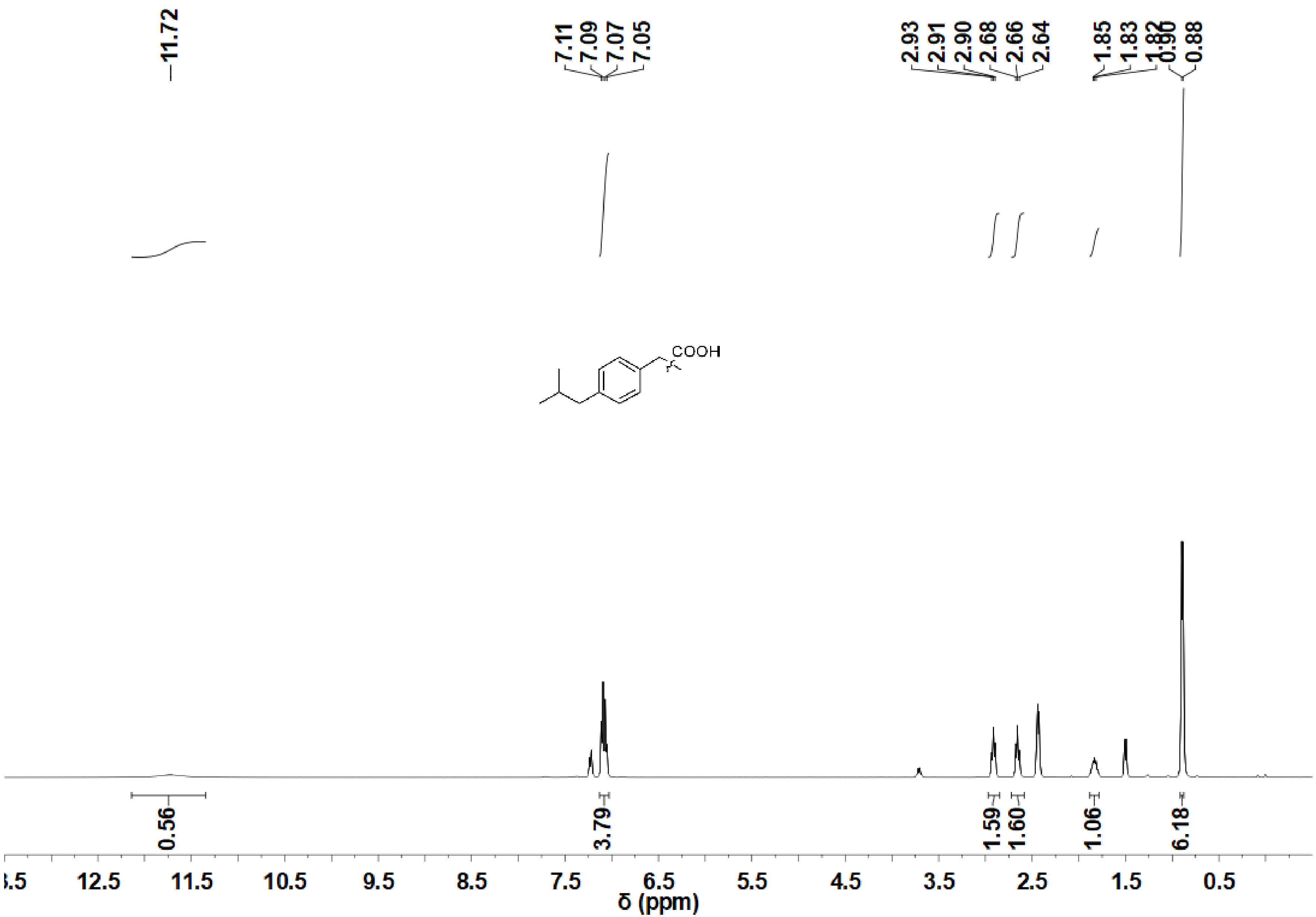

179.2
139.2
131.7
130.2
120.3
77.5
77.2
76.8
35.5
30.0
COOH
Br
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

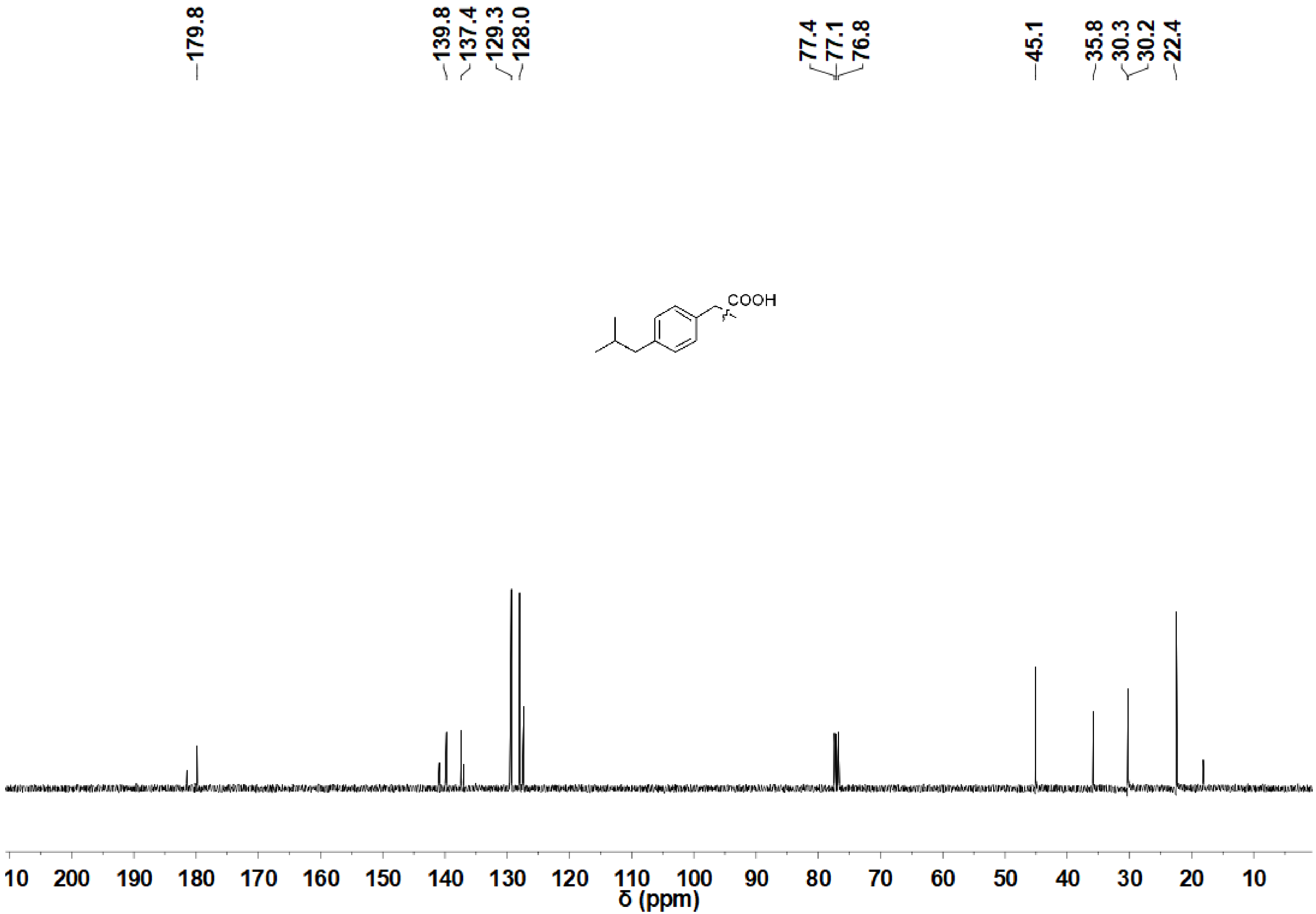
3-(4-trifluromethylphenyl) propanoic acid, **3i**
400 MHz, $CDCl_3$



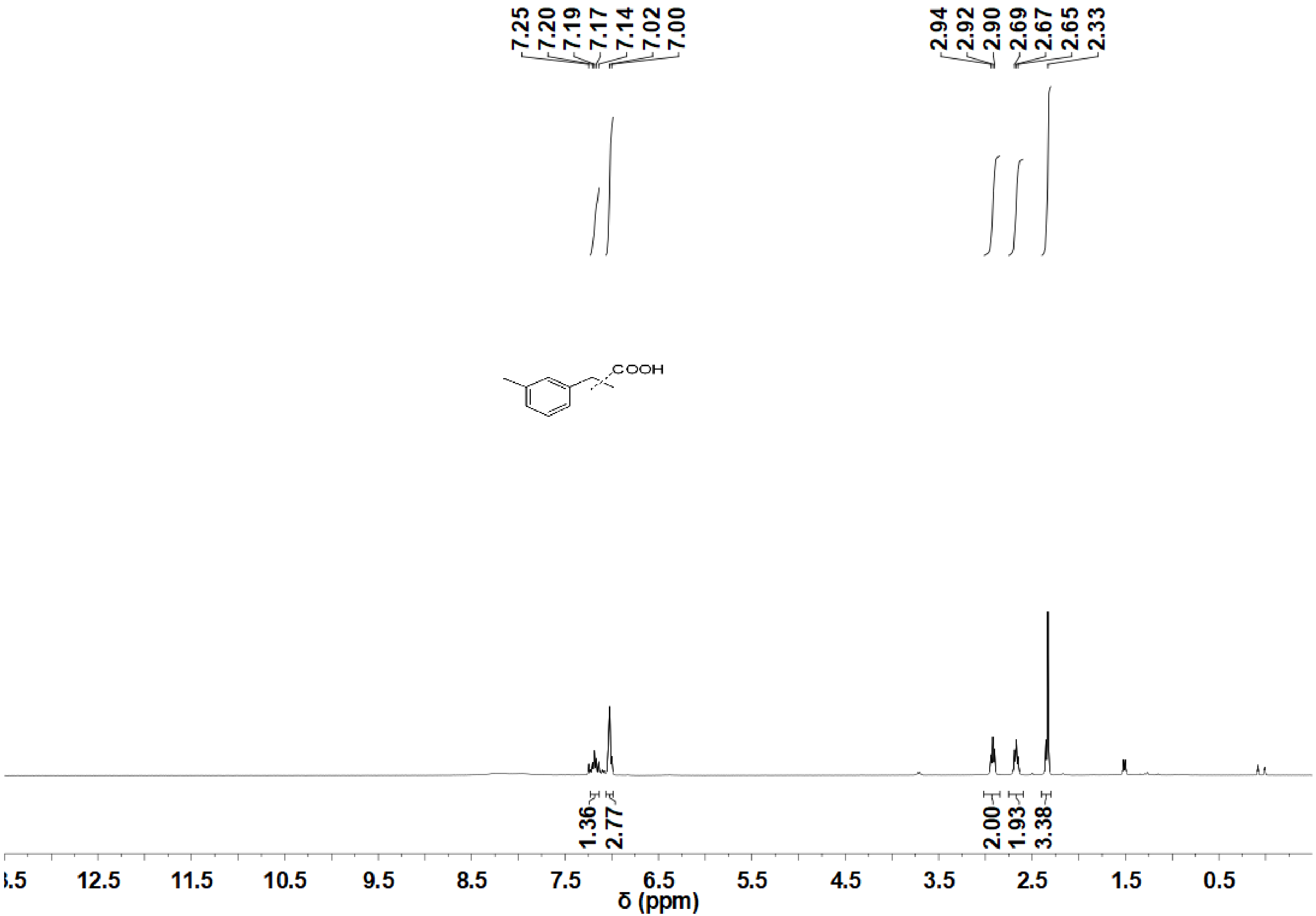

179.0
144.3
129.1
128.8
128.2
125.7
125.7
125.6
123.0
120.3
77.5
77.2
76.8
35.2
30.4
COOH
F3C
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

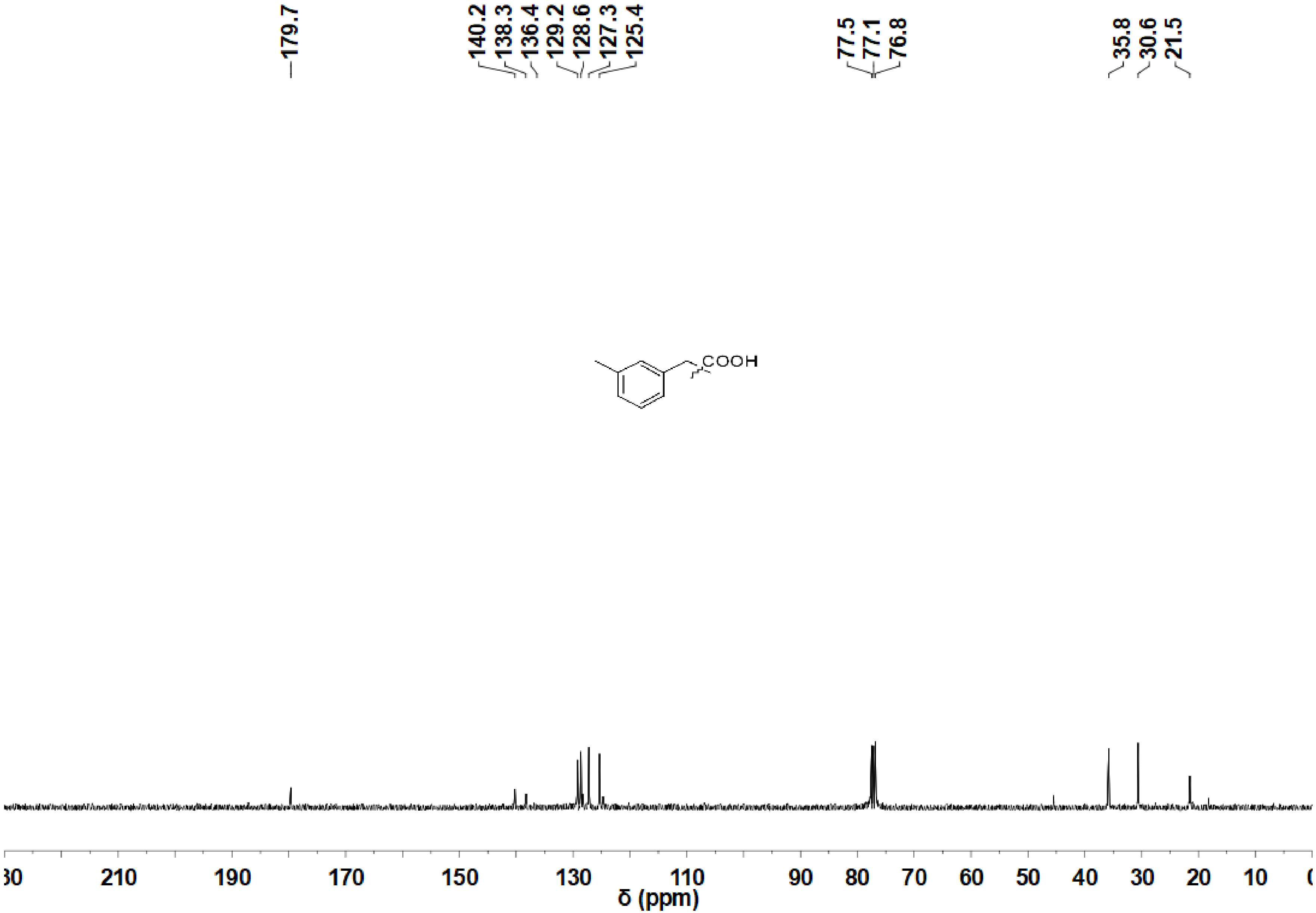
3-(4-isobutylphenyl) propionic acid, **3l**
400 MHz, $CDCl_3$



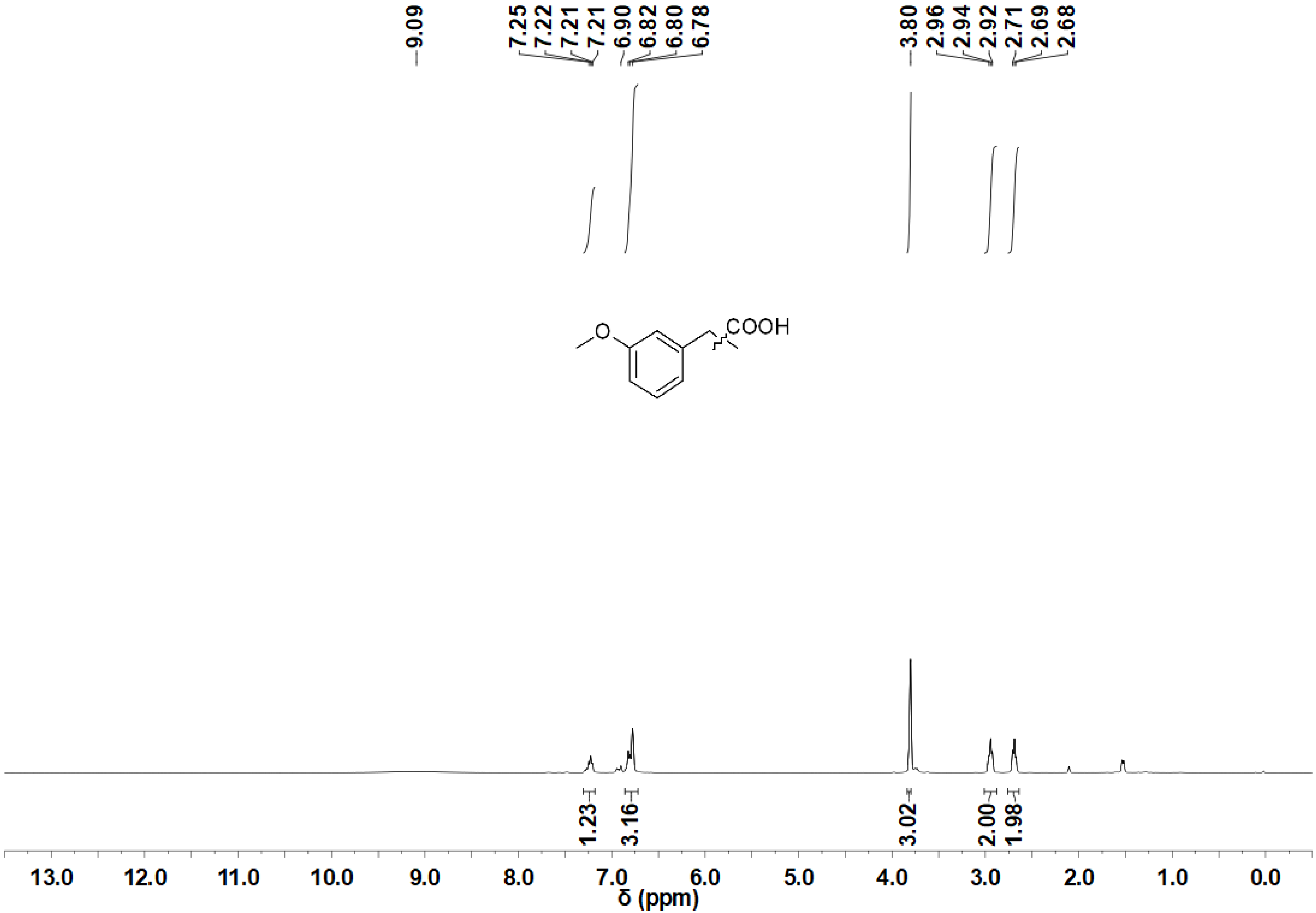

179.8
139.8
137.4
129.3
128.0
77.4
77.1
76.8
45.1
35.8
30.3
30.2
22.4
COOH
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)

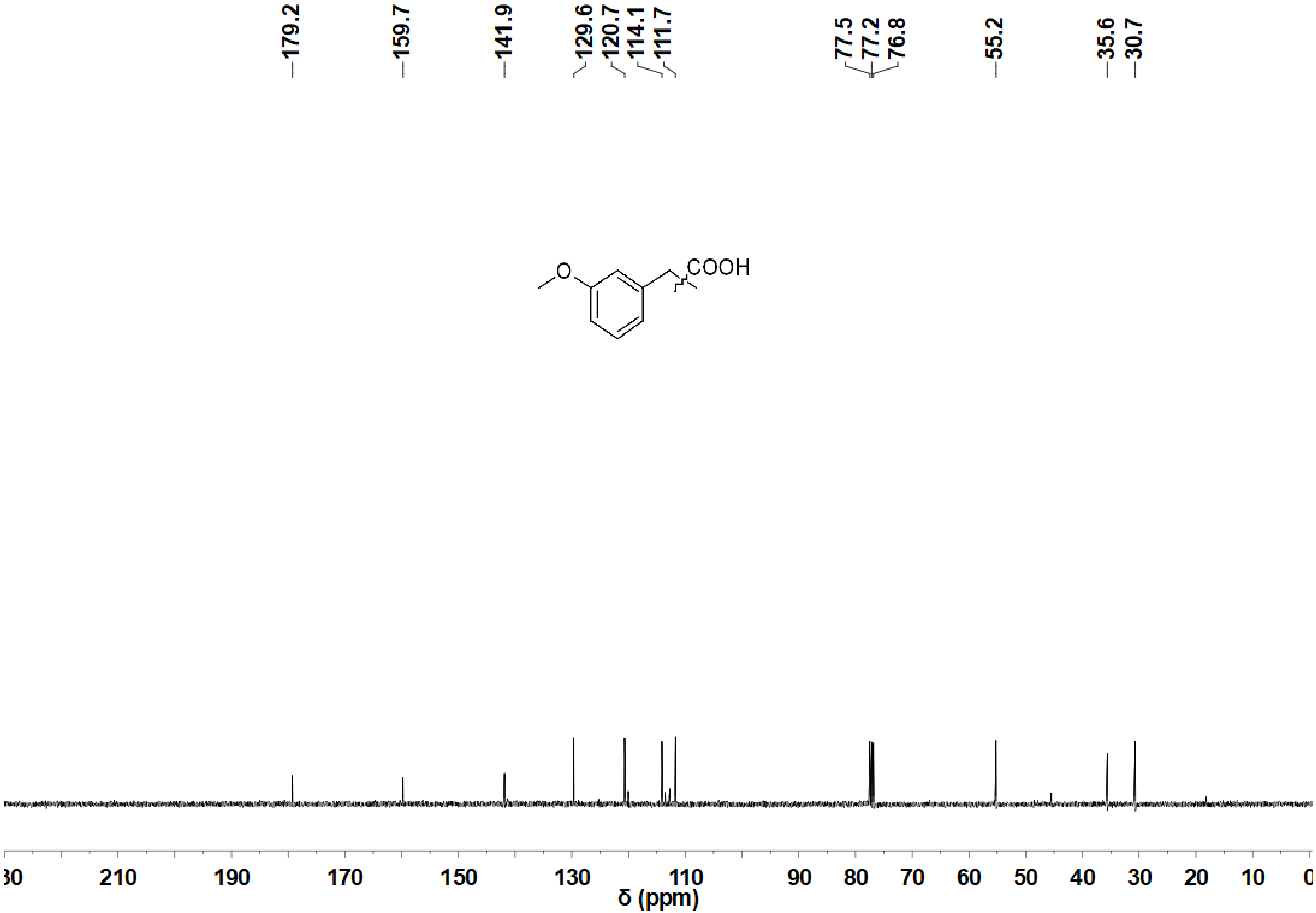
3-(3-methylphenyl) propanoic acid, **3m**
400 MHz, $CDCl_3$



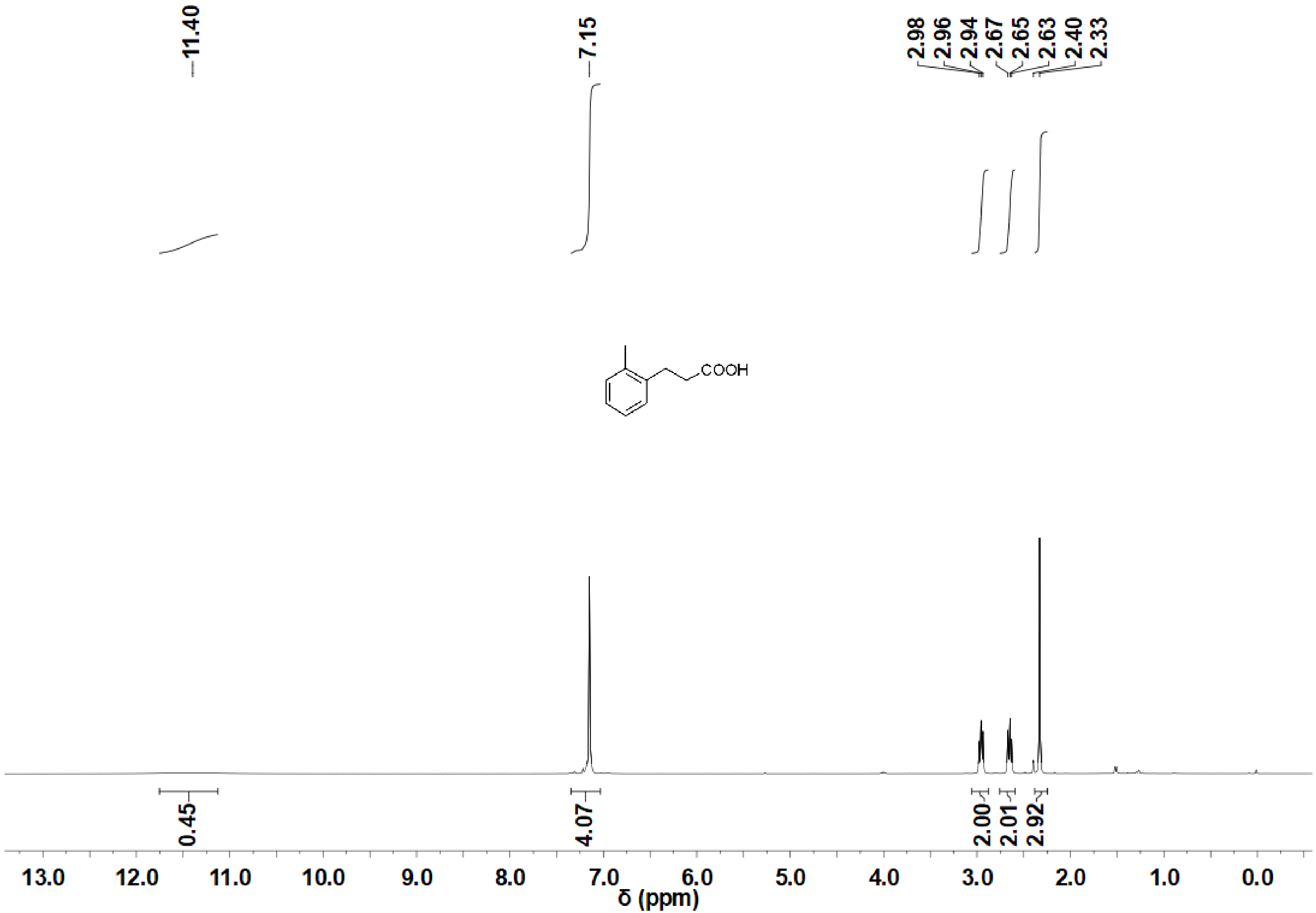

179.7
140.2
138.3
136.4
129.2
128.6
127.3
125.4
77.5
77.1
76.8
35.8
30.6
21.5
COOH
δ (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10

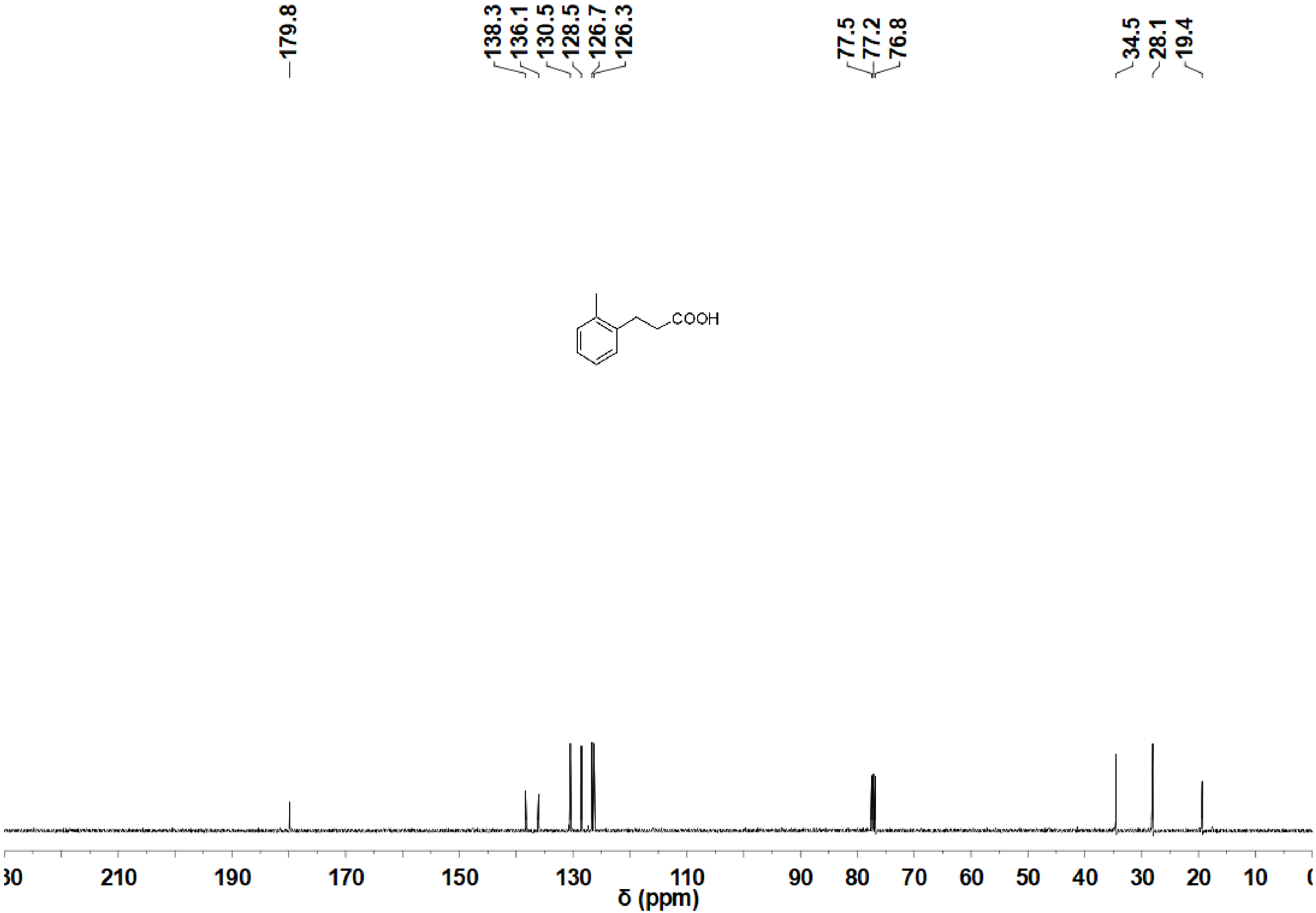
3-(3-methoxyphenyl) propanoic acid, **3n**
400 MHz, $CDCl_3$



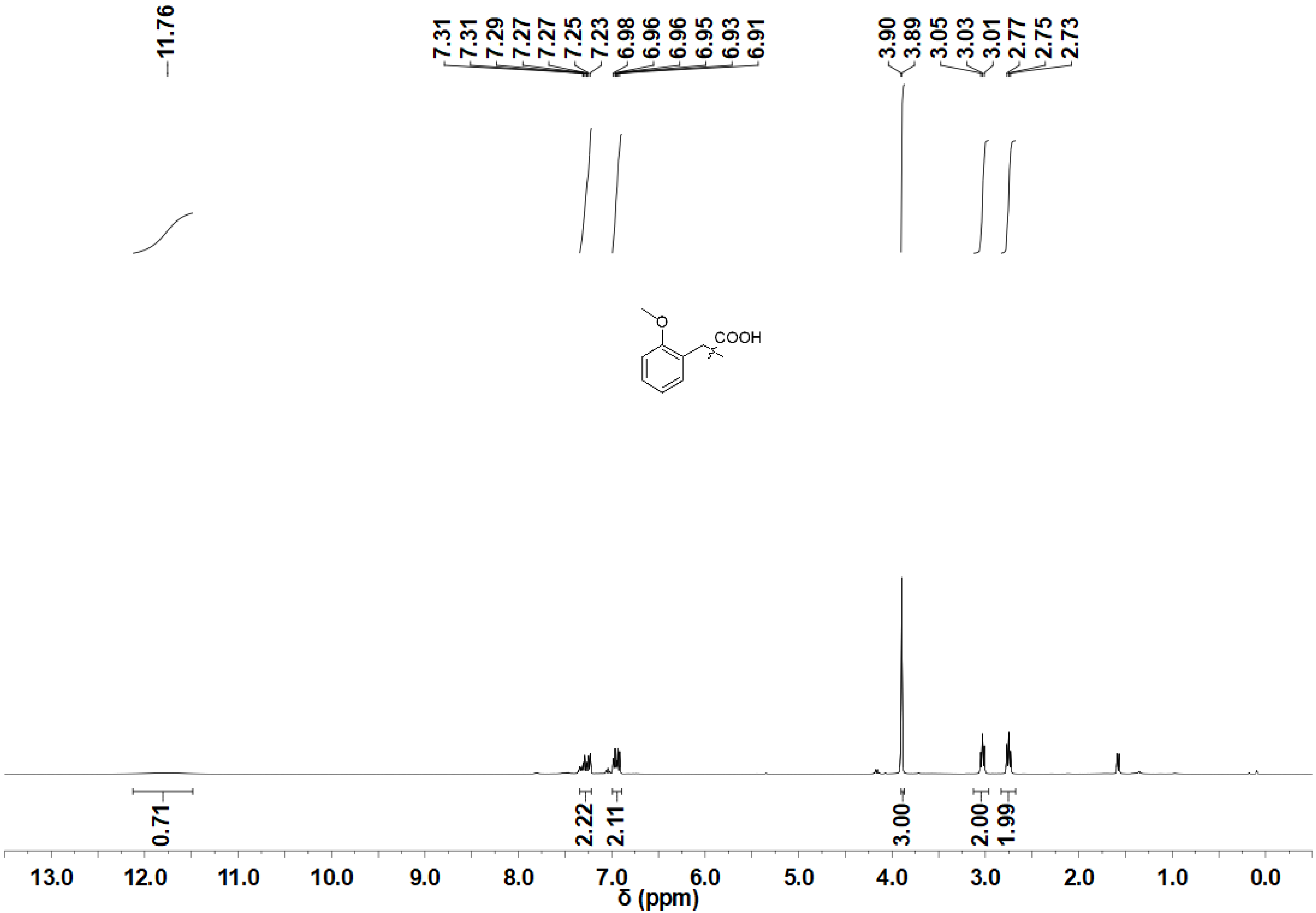

179.2
159.7
141.9
129.6
120.7
114.1
111.7
77.5
77.2
76.8
55.2
35.6
30.7
COOH
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

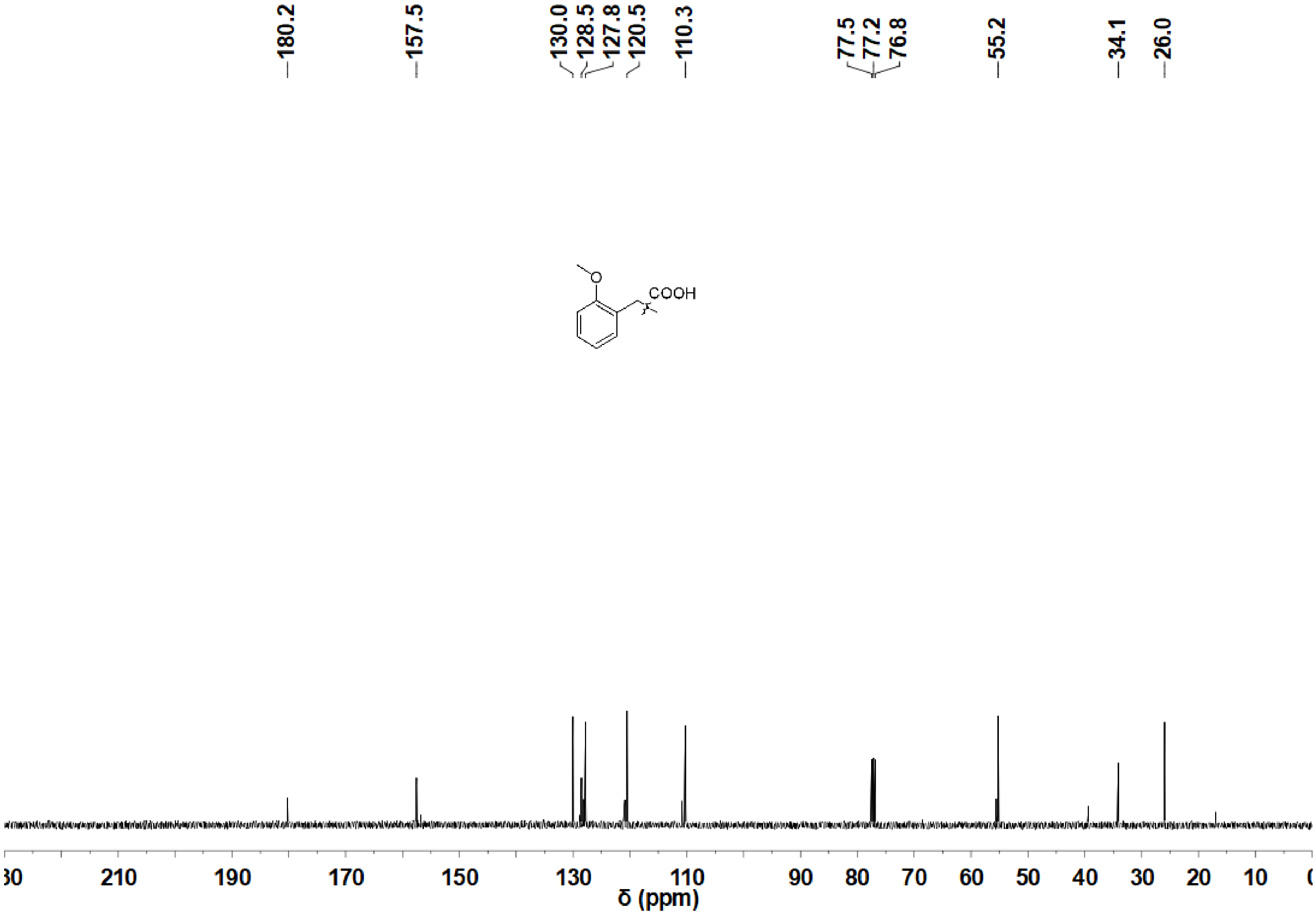
3-(2-methylphenyl) propanoic acid, **3p**
400 MHz, $CDCl_3$




179.8
138.3
136.1
130.5
128.5
126.7
126.3
77.5
77.2
76.8
34.5
28.1
19.4
COOH
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

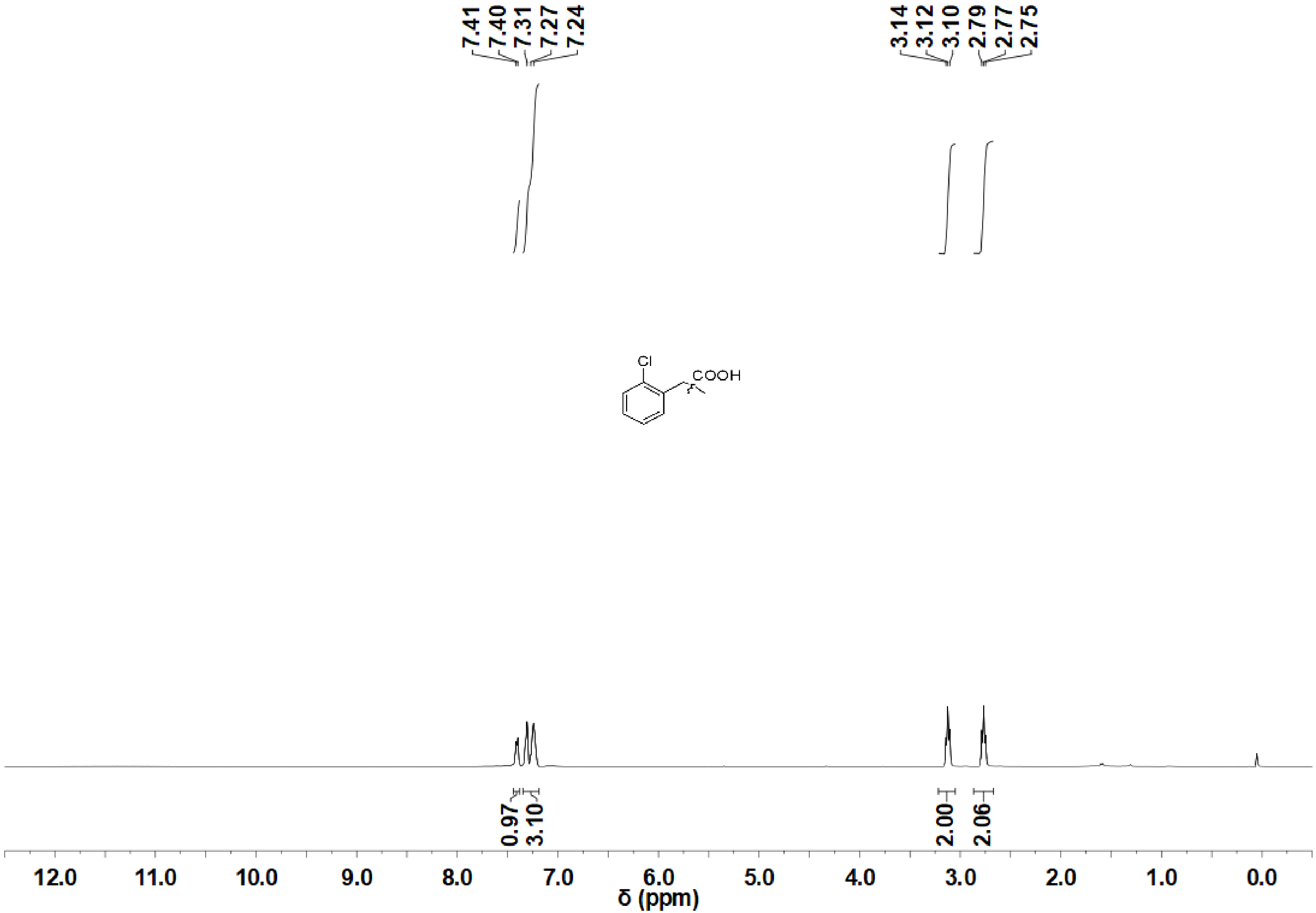
3-(2-methoxyphenyl) propanoic acid, **3q**
400 MHz, $CDCl_3$

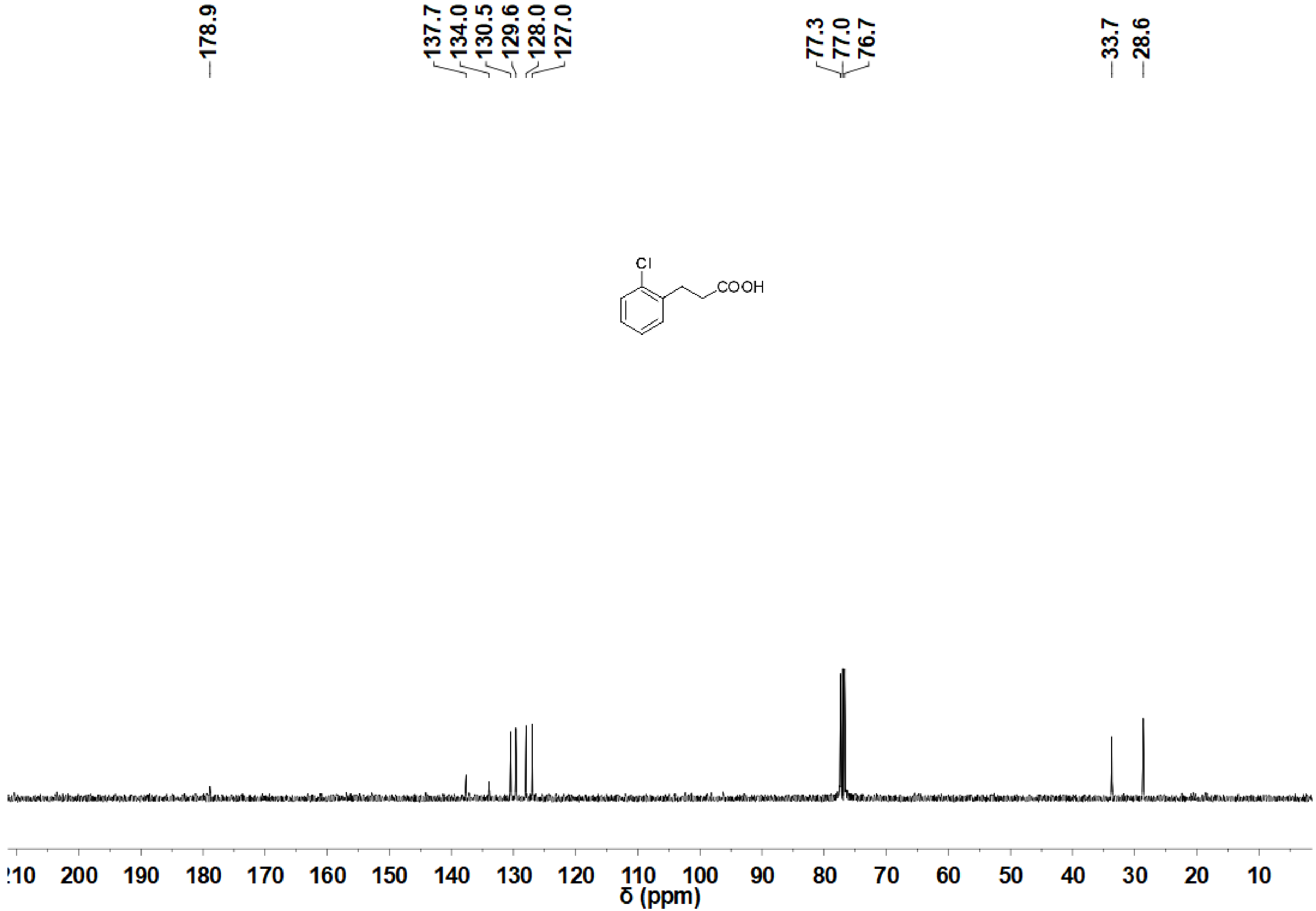




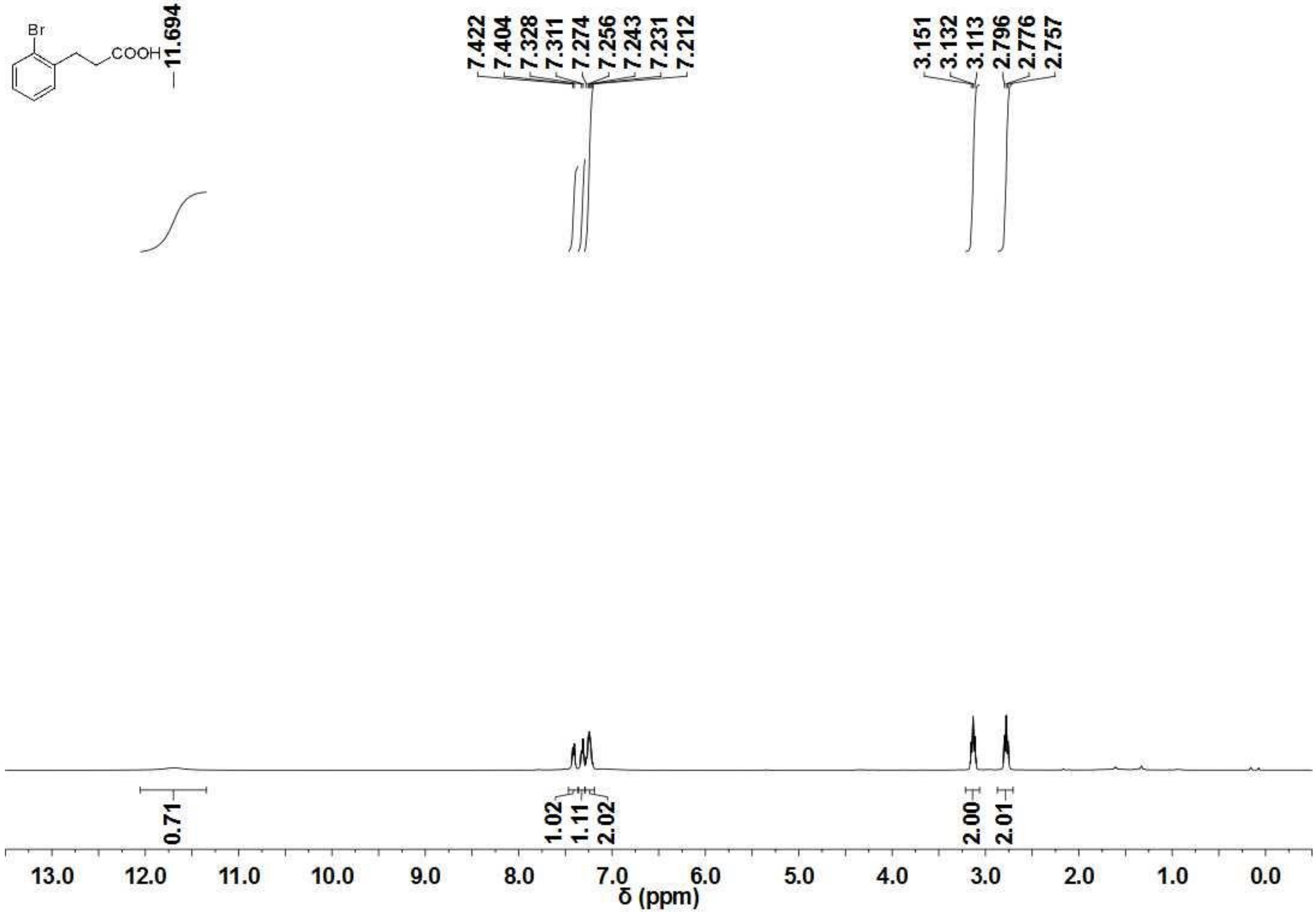
180.2
157.5
130.0
128.5
127.8
120.5
110.3
77.5
77.2
76.8
55.2
34.1
26.0
COOH
O
δ (ppm)

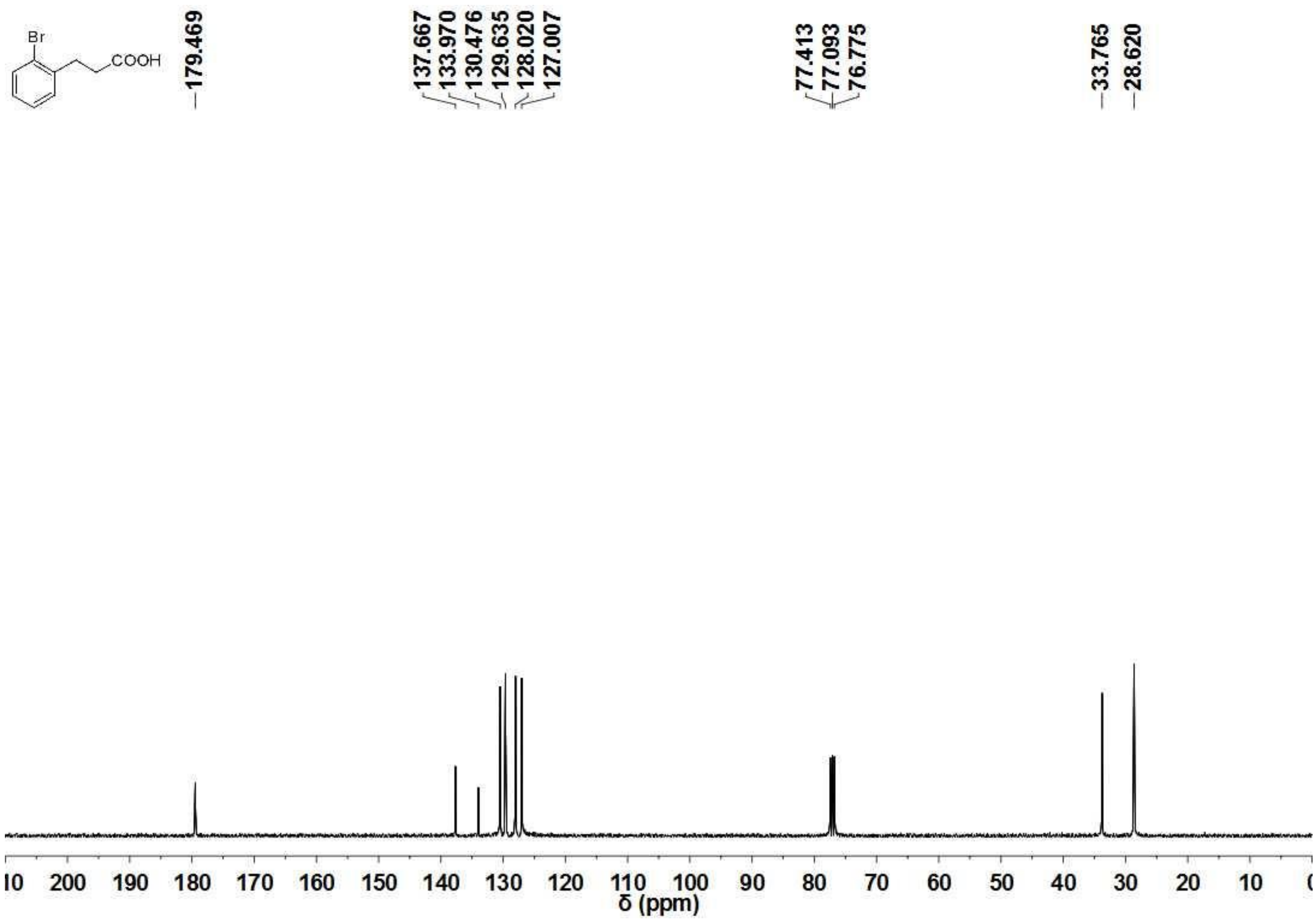
3-(2-chlorophenyl) propionic acid, **3s**
400 MHz, $CDCl_3$



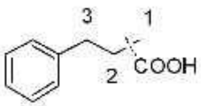

178.9
137.7
134.0
130.5
129.6
128.0
127.0
77.3
77.0
76.7
33.7
28.6
Cl
COOH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)

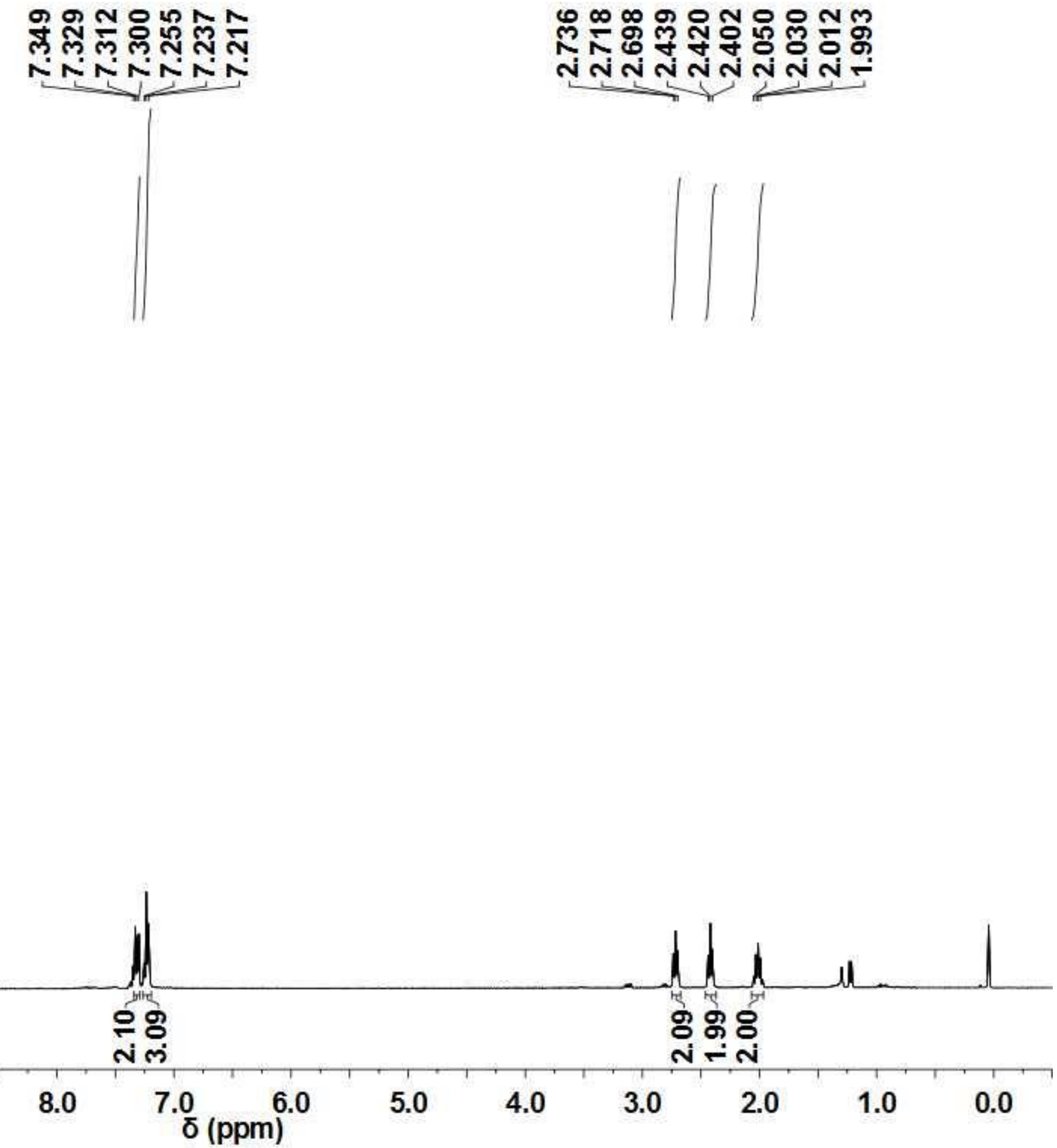
3-(2-bromophenyl) propanoic acid, **3x**
400 MHz, $CDCl_3$

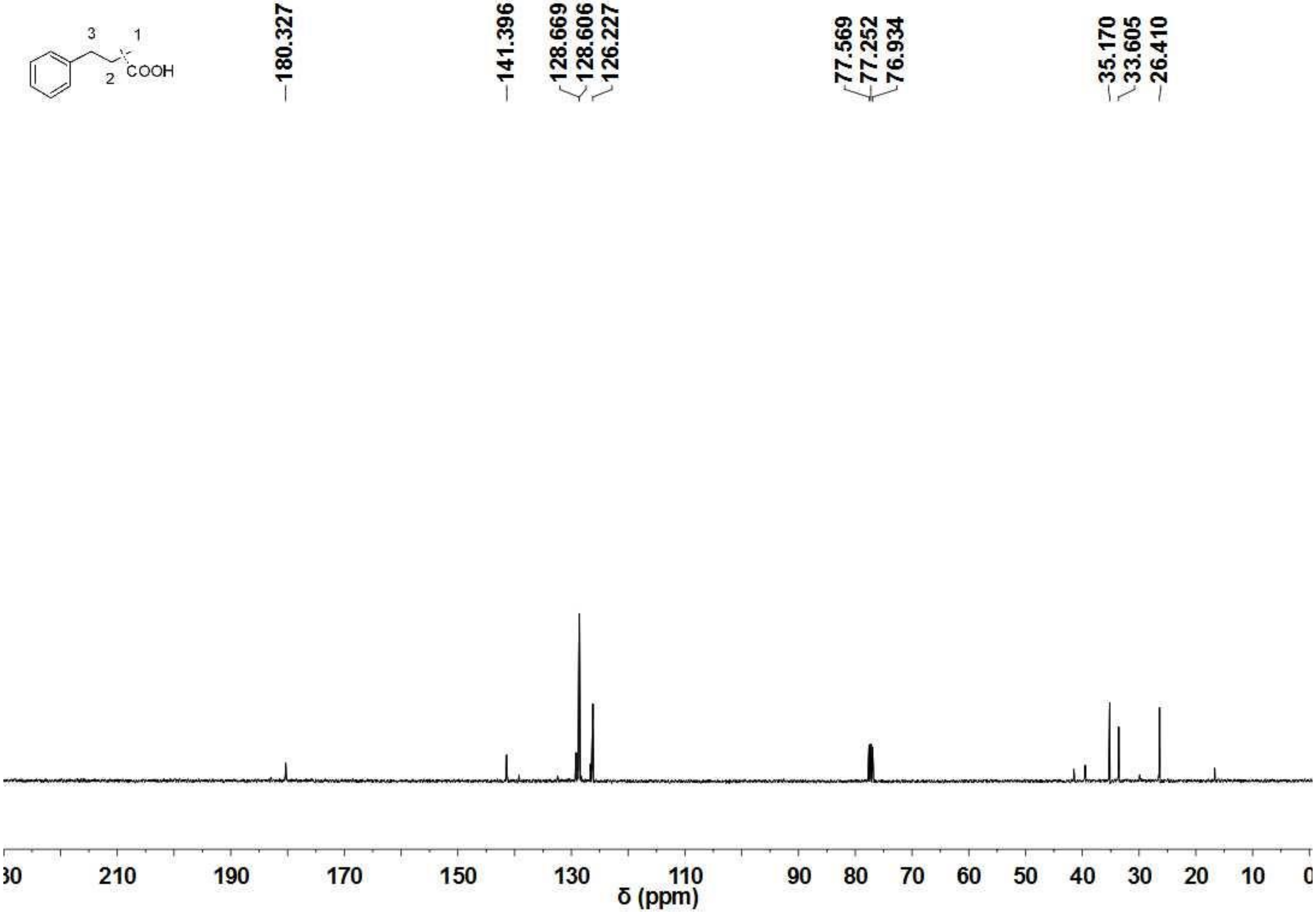



Br
COOH
179.469
137.667
133.970
130.476
129.635
128.020
127.007
77.413
77.093
76.775
33.765
28.620
δ (ppm)

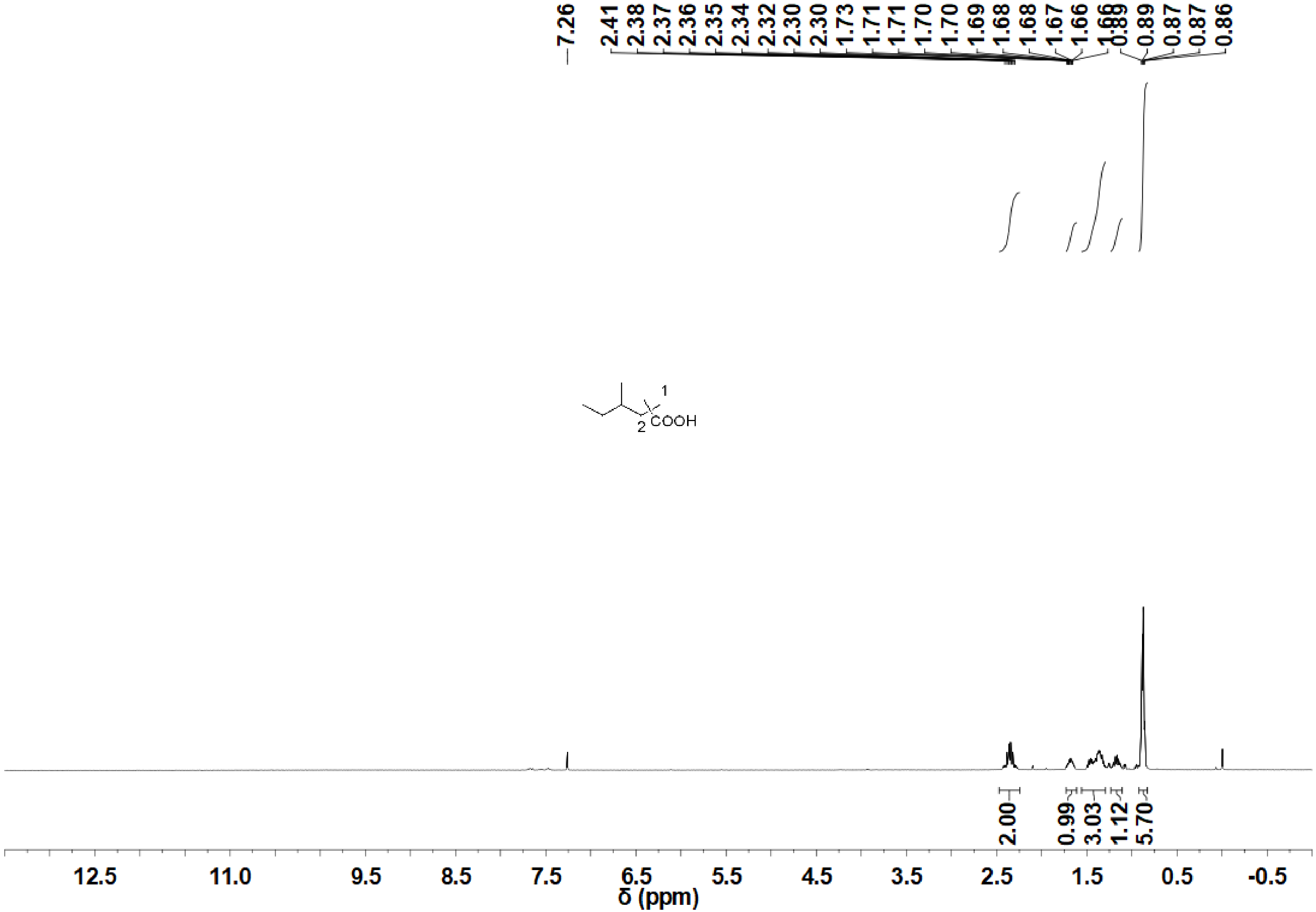
4-phenylbutanoic acid, **3z**
400 MHz, $CDCl_3$

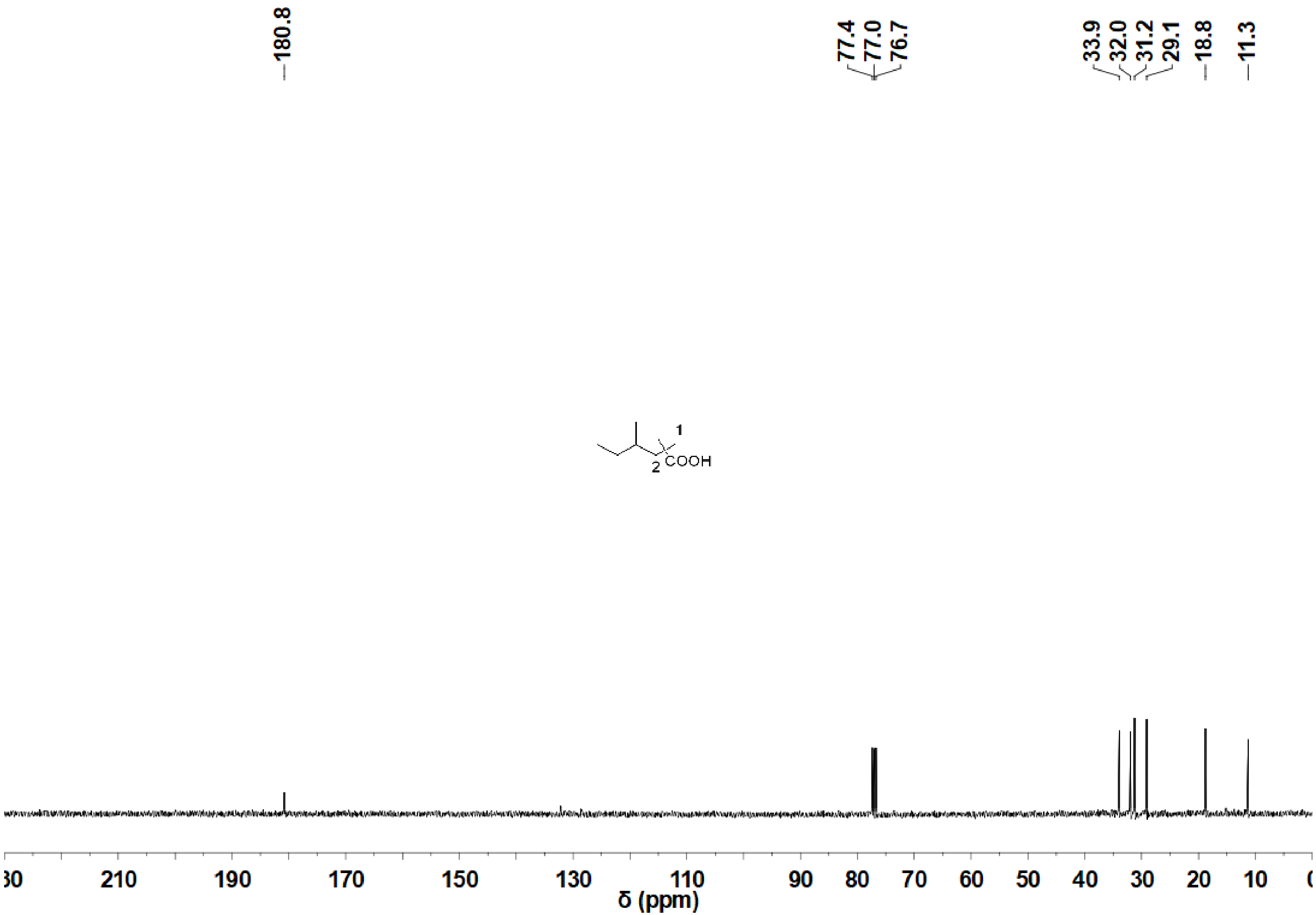





3
1
2
COOH
180.327
141.396
128.669
128.606
126.227
77.569
77.252
76.934
35.170
33.605
26.410
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)

4-methylhexanoic acid, **3aa**
400 MHz, $CDCl_3$




180.8
77.4
77.0
76.7
33.9
32.0
31.2
29.1
18.8
11.3
1
2
COOH
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
δ (ppm)