Supporting Information

Acceptorless Dehydrogenation of Alcohols to Carboxylic Acids by Palladium Nanoparticles Supported on NiO: Delving into Metal-Support Cooperation in Catalysis

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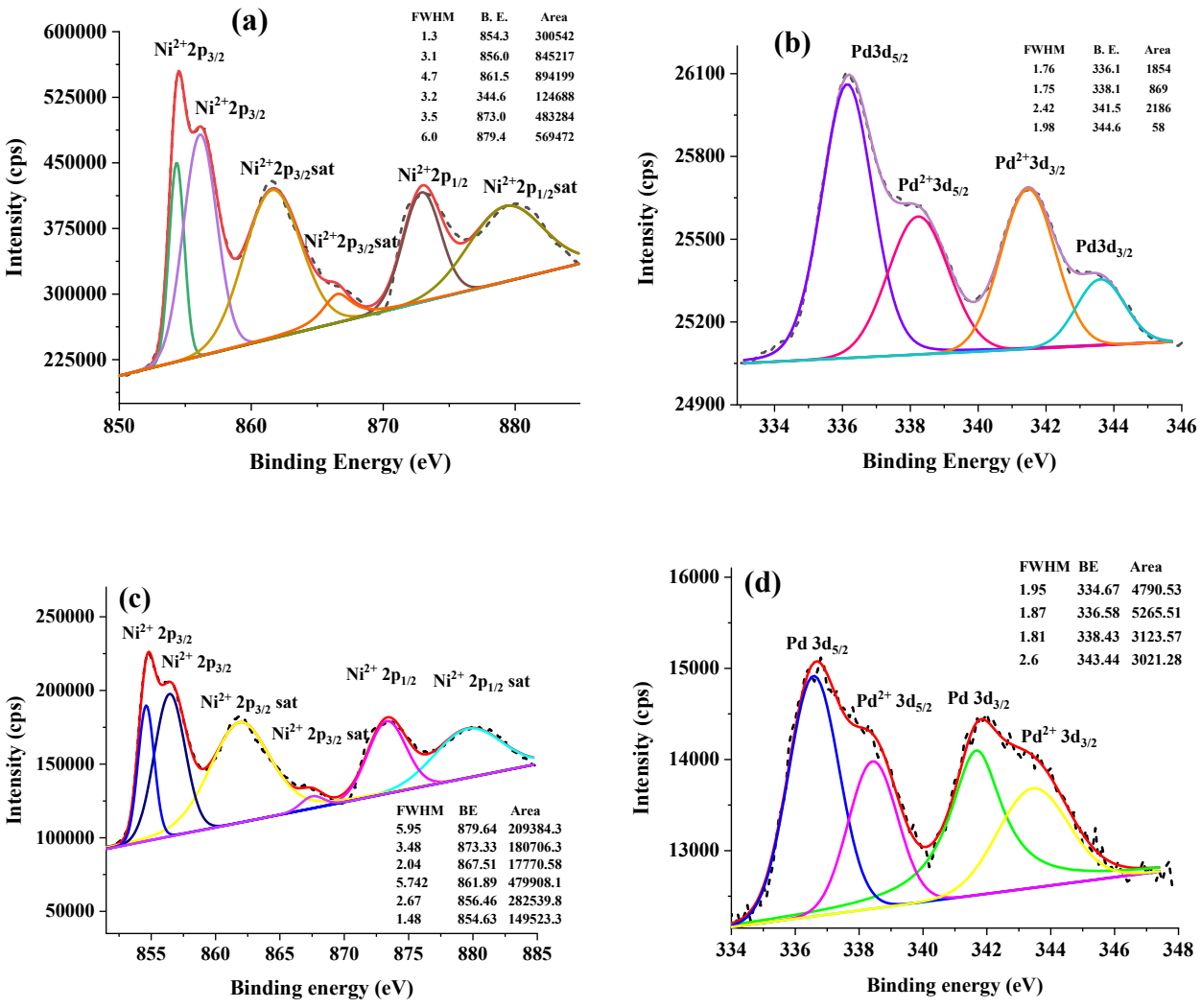


Figure S1 XPS spectra of as prepared $Pd_{0.05}$@NiO [(a), (b)] and $Pd_{0.01}$@NiO [(c), (d)] (FWHM = full width at half maximum, BE = binding energy)

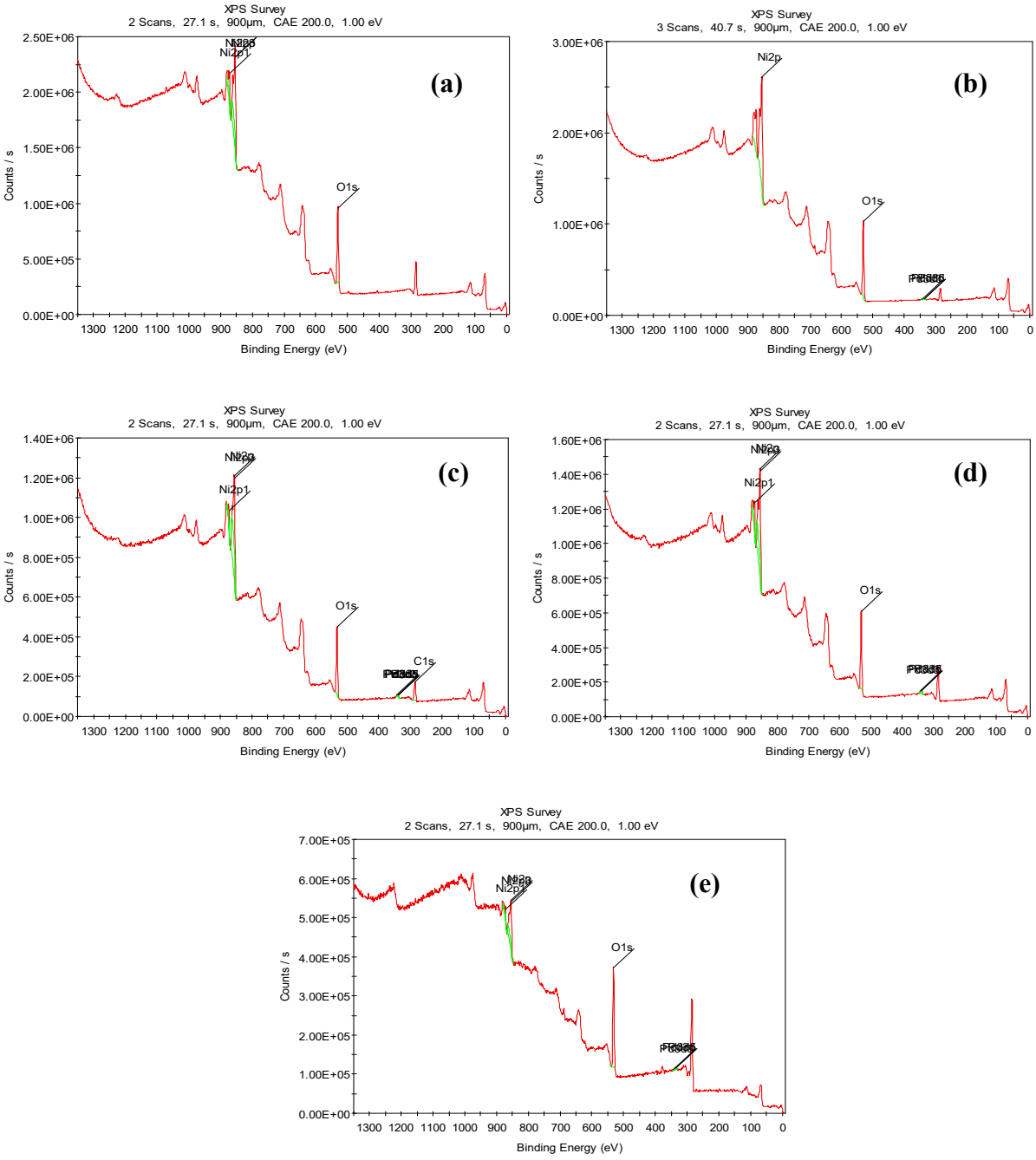


Figure S2 XPS survey spectrum of the as prepared (a) NiO, (b) $Pd_{0.05}$@NiO, (c) $Pd_{0.1}$@NiO, (d) $Pd_{0.2}$@NiO, (e) recycled $Pd_{0.2}$@NiO materials

NiO (**S1**)

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHERMO1	TXFN	Backgnd	PP Height CPS	PP Hgt (N)	PP At. %
Ni2p1	881	872.14	864	243482	4.06	1321885.33	0.35	10.53	Standard	1	6.588	13417.63	Smart	418109.34	0	16.75
Ni2p	882	854.77	846	927664.7	5.76	9442341.04	0.77	23.45	Standard	1	20.765	13378.5	Smart	1122588.45	0	14.03
Ni2p3	864	854.56	848	810894.9	5.13	5343397.19	0.64	19.43	Standard	1	14.176	13378.02	Smart	1110265.36	0	20.31
O1s	540	530.18	526	670641.9	4.77	3366868.43	1.53	46.59	Standard	1	2.881	12735.86	Smart	702469.08	0.01	48.91

$Pd_{0.05}$@NiO (**S2**)

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHER	TXFN	Backgnd	PP Height CPS	PP Hgt (N)	PP At. %
Ni2p	884	855.09	842	1155681	5.47	13928467.45	1.14	38.81	Standard	1	20.765	13379	Smart	1407150.07	0	22.29
O1s	537.5	529.94	523	816098.9	4.56	3935094.59	1.79	61.07	Standard	1	2.881	12735	Smart	877104.95	0.01	77.37
Pd3d3	345	341.71	338	1967.01	2	4757.24	0	0.02	Standard	1	7.943	12418	Smart	3861.78	0	0.2
Pd3d	345	335	331	7137.5	0.08	41403.48	0	0.09	Standard	1	19.353	12407	Smart	7440.16	0	0.01
Pd3d5	338	334.89	332	3929.96	0.77	4010.93	0	0.01	Standard	1	11.455	12407	Smart	7440.16	0	0.14

$Pd_{0.1}$@NiO (**S3**)

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHERMO1	TXFN	Backgnd	PP Height CPS	PP Hgt (N)	PP At. %
O1s	540	531.35	526	345649.1	4.61	1697983.06	0.77	38.65	Standard	1	2.881	12738	Smart	364555.32	0	36.89
C1s	296	285.46	281	91461.52	4.55	463196.4	0.53	26.35	Standard	1	1	12328	Smart	95005.52	0	24.03
Ni2p1	881	873.18	864	76370.71	2.27	165288.07	0.04	2.17	Standard	1	6.588	13420	Smart	187544.28	0	10.92
Ni2p	882	856.31	846	528859.7	6.24	4811567.63	0.39	19.67	Standard	1	20.765	13382	Smart	619619.28	0	11.26
Ni2p3	864	855.91	848	395146.4	4.71	2153749.65	0.26	12.89	Standard	1	14.176	13381	Smart	619619.28	0	16.49
Pd3d3	345	342.67	338	2997.46	0.94	8039.32	0	0.06	Standard	1	7.943	12419	Smart	4075.3	0	0.13
Pd3d	345	338.01	331	11654.68	4.77	71230.71	0	0.22	Standard	1	19.353	12412	Smart	19655.62	0	0.26

$Pd_{0.2}$@NiO (**S4**)

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHERMO1	TXFN	Backgnd	PP Height CPS	PP Hgt (N)	PP At. %
O1s	540	530.43	526	453004.8	4.52	2175311.36	0.99	48.66	Standard	1	2.881	12736	Smart	472447.29	0	49.66
Pd3d3	345	342.75	338	6750.64	1.07	14894.48	0	0.11	Standard	1	7.943	12419	Smart	10841.77	0	0.37
Pd3d	345	336.33	331	20572.15	4.35	147048.09	0.01	0.44	Standard	1	19.353	12409	Smart	25438.25	0	0.35
Pd3d5	338	335.96	332	8695.75	1.99	25152.39	0	0.13	Standard	1	11.455	12408	Smart	25329.82	0	0.6
Ni2p1	881	872.28	864	139143.9	3.56	599441.91	0.16	7.72	Standard	1	6.588	13418	Smart	252771.69	0	15.29
Ni2p	882	855.09	846	615650.5	5.79	6000207.71	0.49	24.09	Standard	1	20.765	13379	Smart	730926.31	0	13.79
Ni2p3	864	854.86	848	522470.4	4.84	3206977.74	0.38	18.86	Standard	1	14.176	13379	Smart	722067.57	0	19.95

$Pd_{0.2}$@NiO recovered after 6th cycle (**S5**)

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %	Peak Type	Q	SF ALTHER	TXFN	Backgnd	PP Height CPS	PP Hgt (N)	PP At. %
Ni2p	884	855.09	842	1155681	5.47	13928467.45	1.14	38.81	Standard	1	20.765	13379	Smart	1407150.07	0	22.29
O1s	537.5	529.94	523	816098.9	4.56	3935094.59	1.79	61.07	Standard	1	2.881	12735	Smart	877104.95	0.01	77.37
Pd3d3	345	341.71	338	1967.01	2	4757.24	0	0.02	Standard	1	7.943	12418	Smart	3861.78	0	0.2
Pd3d	345	335	331	7137.5	0.08	41403.48	0	0.09	Standard	1	19.353	12407	Smart	7440.16	0	0.01
Pd3d5	338	334.89	332	3929.96	0.77	4010.93	0	0.01	Standard	1	11.455	12407	Smart	7440.16	0	0.14

Table S1-S5 XPS survey peak analyses for the as prepared (a) NiO (**S1**), (b) $Pd_{0.05}$@NiO (**S2**), (c) $Pd_{0.1}$@NiO (**S3**), (d) $Pd_{0.2}$@NiO (**S4**), (e) recycled $Pd_{0.2}$@NiO (**S5**) materials

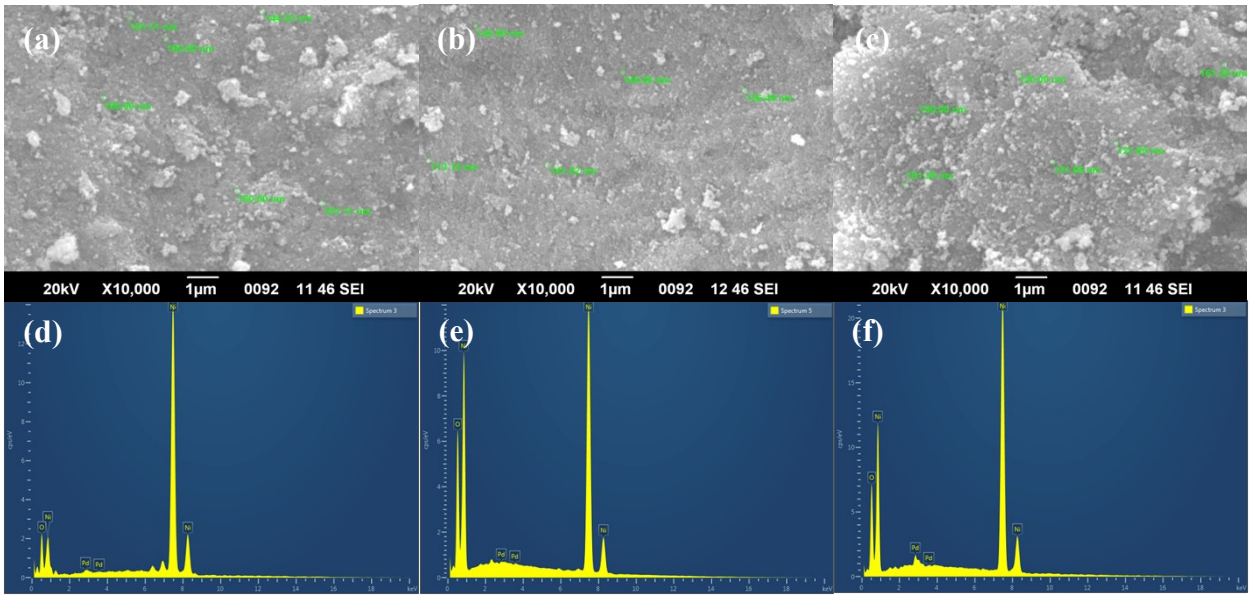


Fig S3 SEM images of (a) $Pd_{0.05}$@NiO, (b) $Pd_{0.1}$@NiO, and (c) $Pd_{0.2}$@NiO; EDAX spectra of (d) $Pd_{0.05}$@NiO, (e) $Pd_{0.1}$@NiO, and (f) $Pd_{0.2}$@NiO

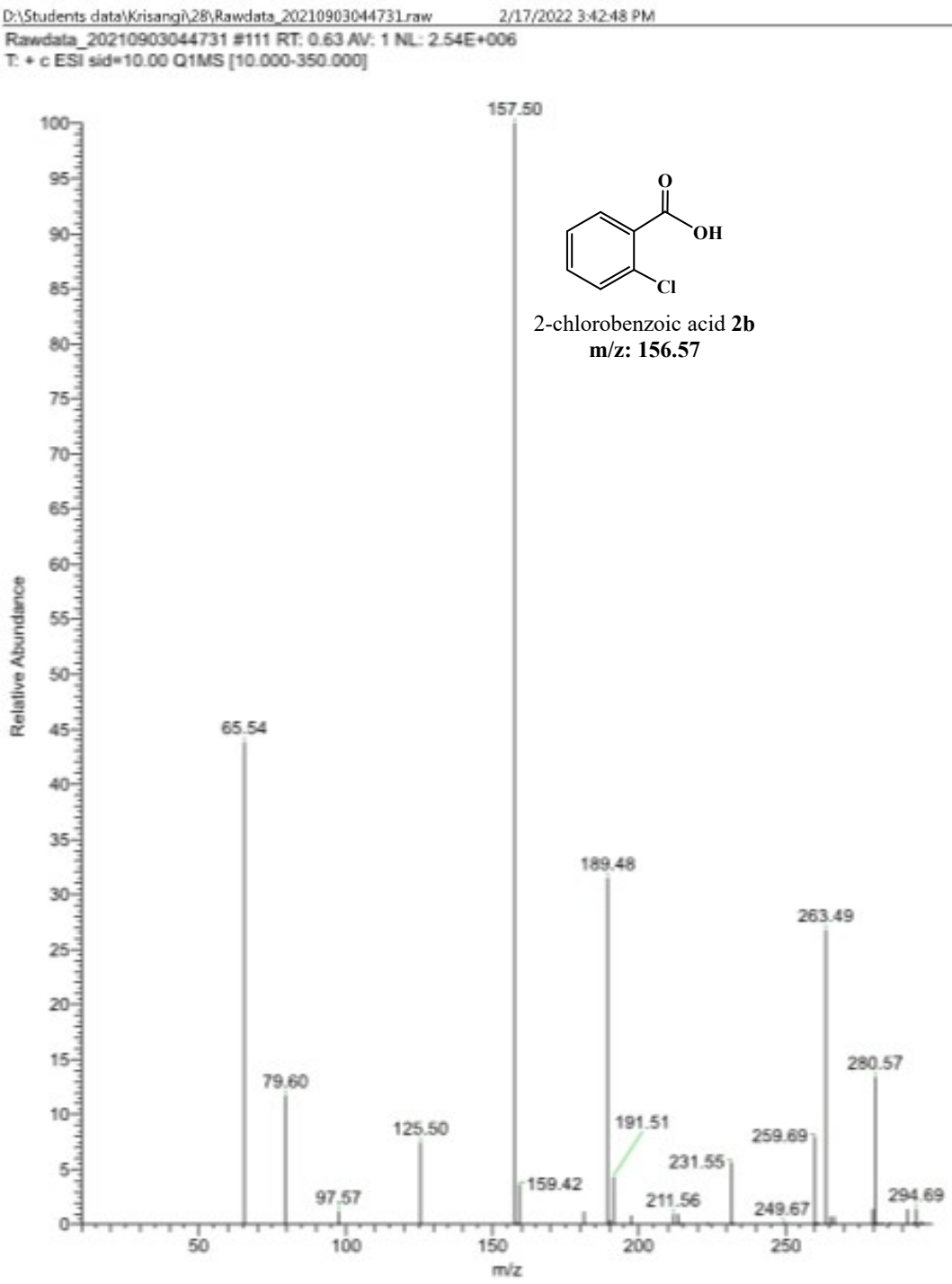


Fig S4 LC-MS spectrum of 2-chlorobenzoic acid (Table 2, Entry **2b**)

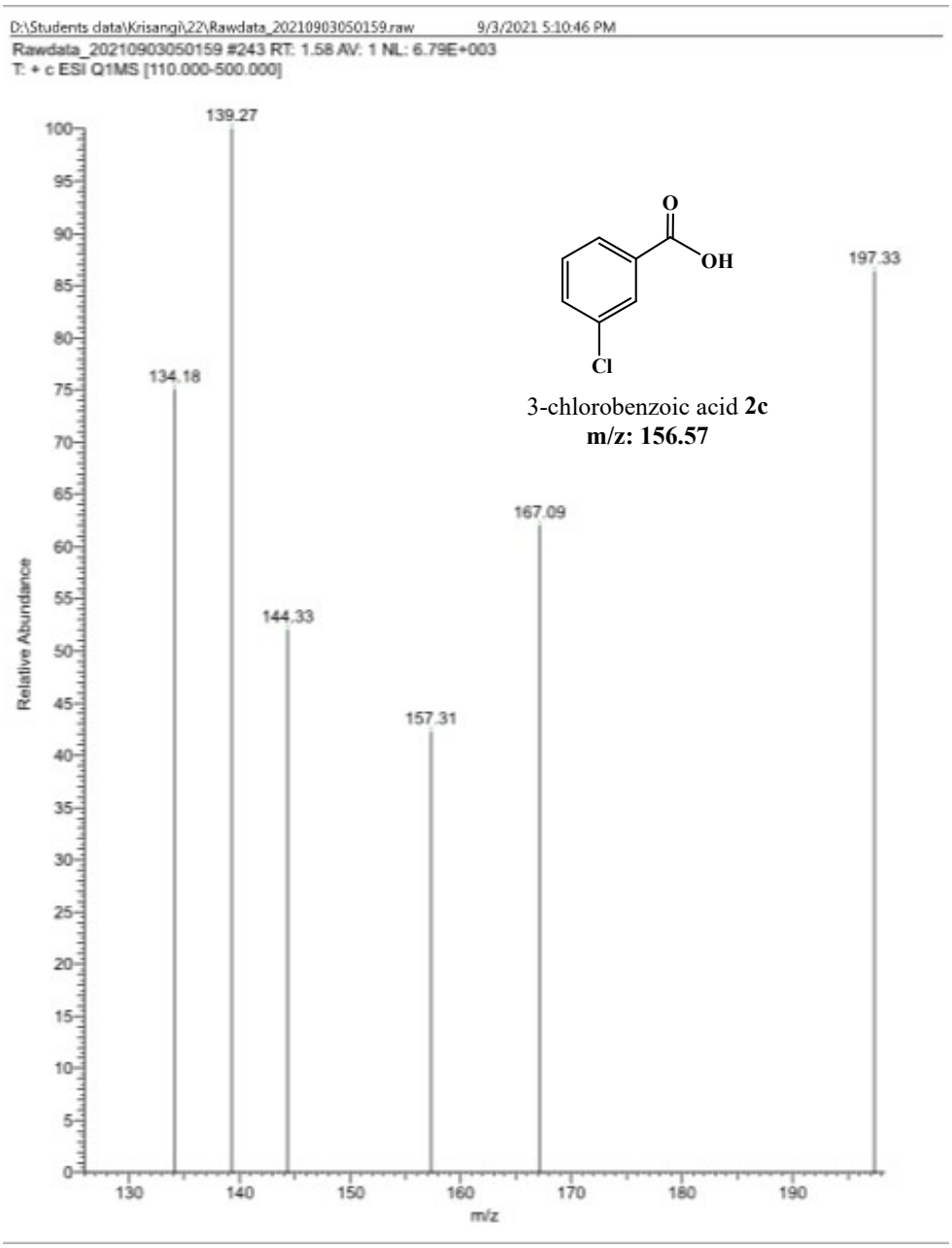


Fig S5 LC-MS spectrum of 3-chlorobenzoic acid (Table 2, Entry **2c**)

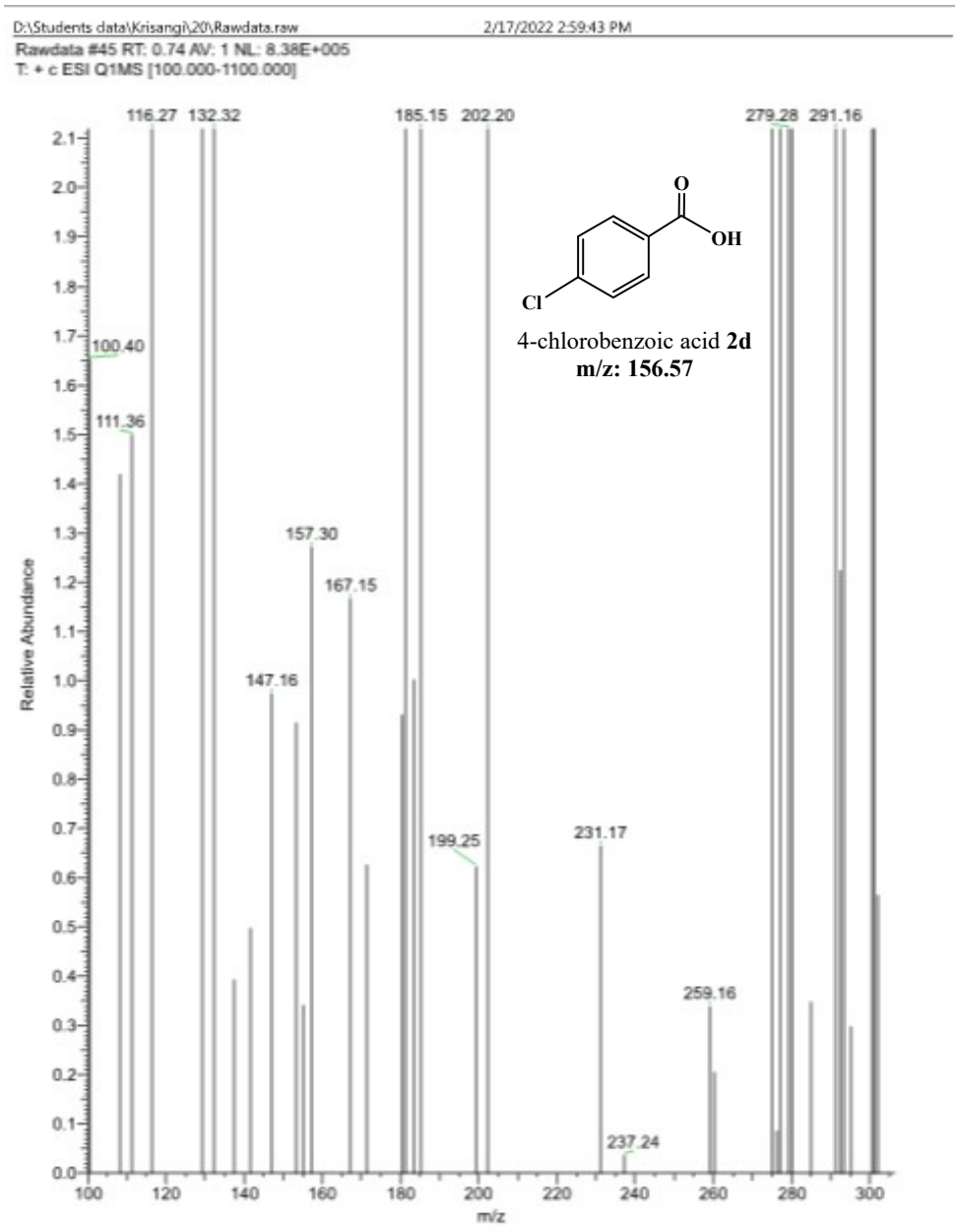


Fig S6 LC-MS spectrum of 4-chlorobenzoic acid (Table 2, Entry **2d**)

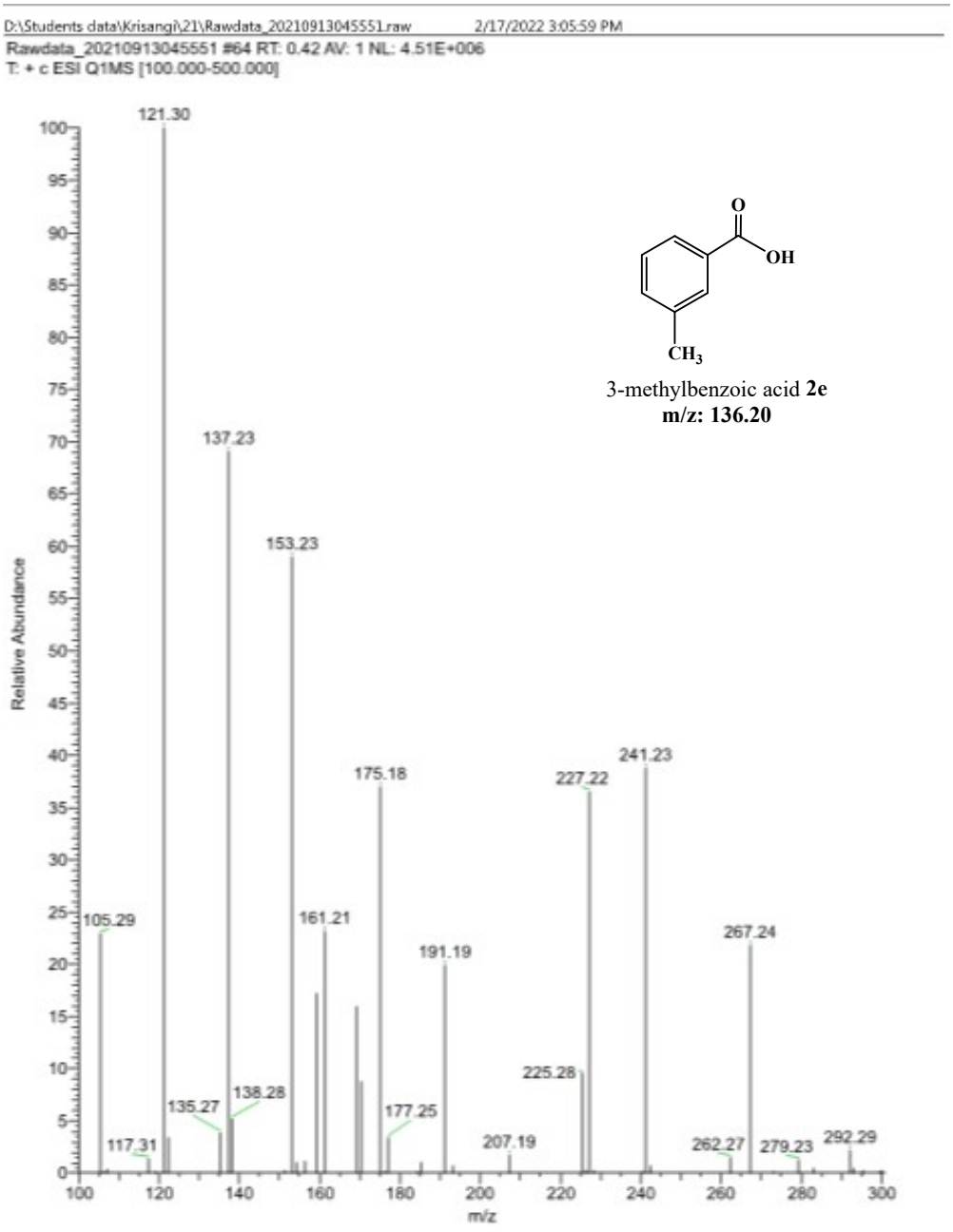


Fig S7 LC-MS spectrum of 3-methylbenzoic acid (Table 2, Entry **2e**)

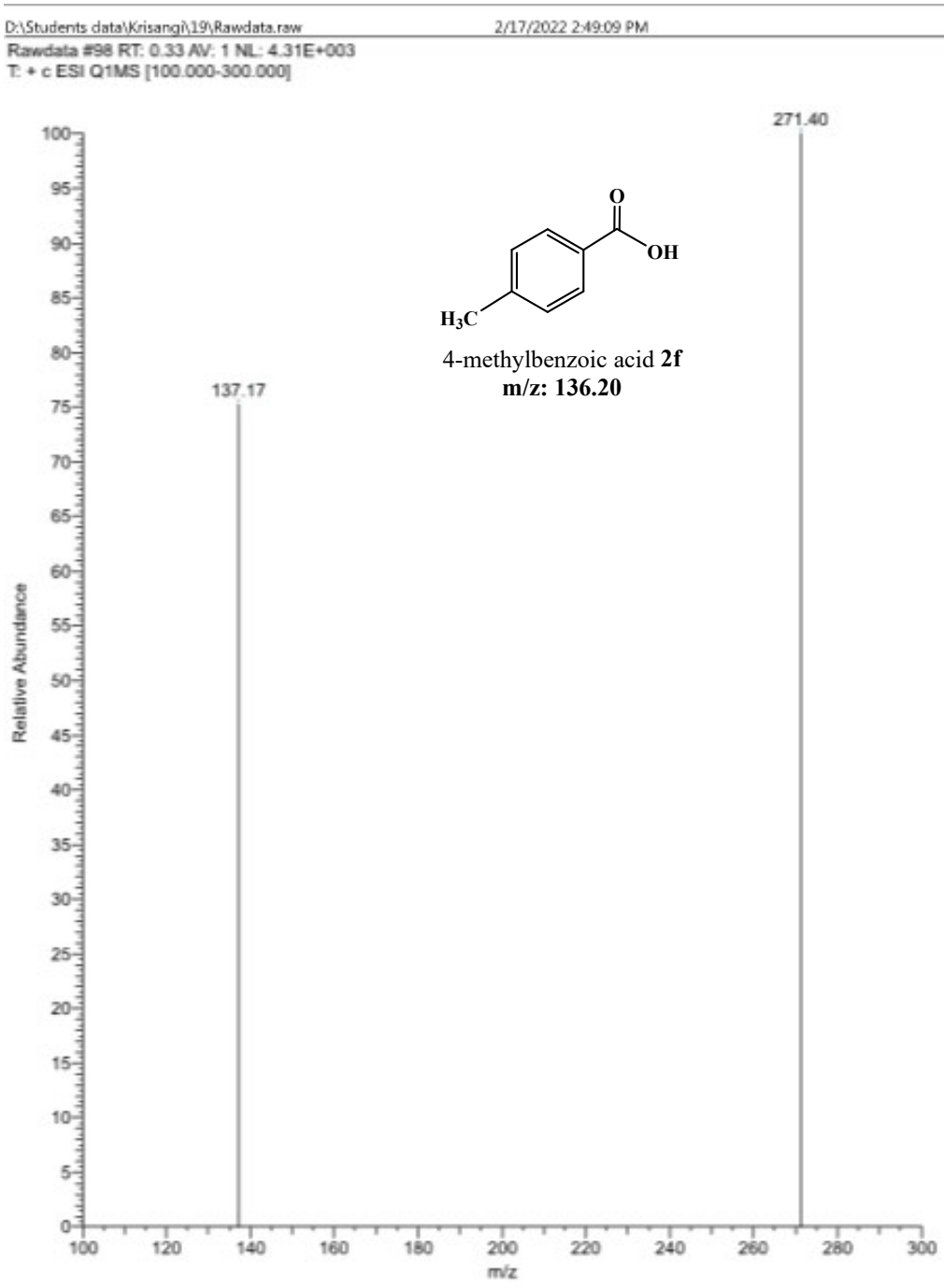


Fig S8 LC-MS spectrum of 4-methylbenzoic acid (Table 2, Entry **2f**)

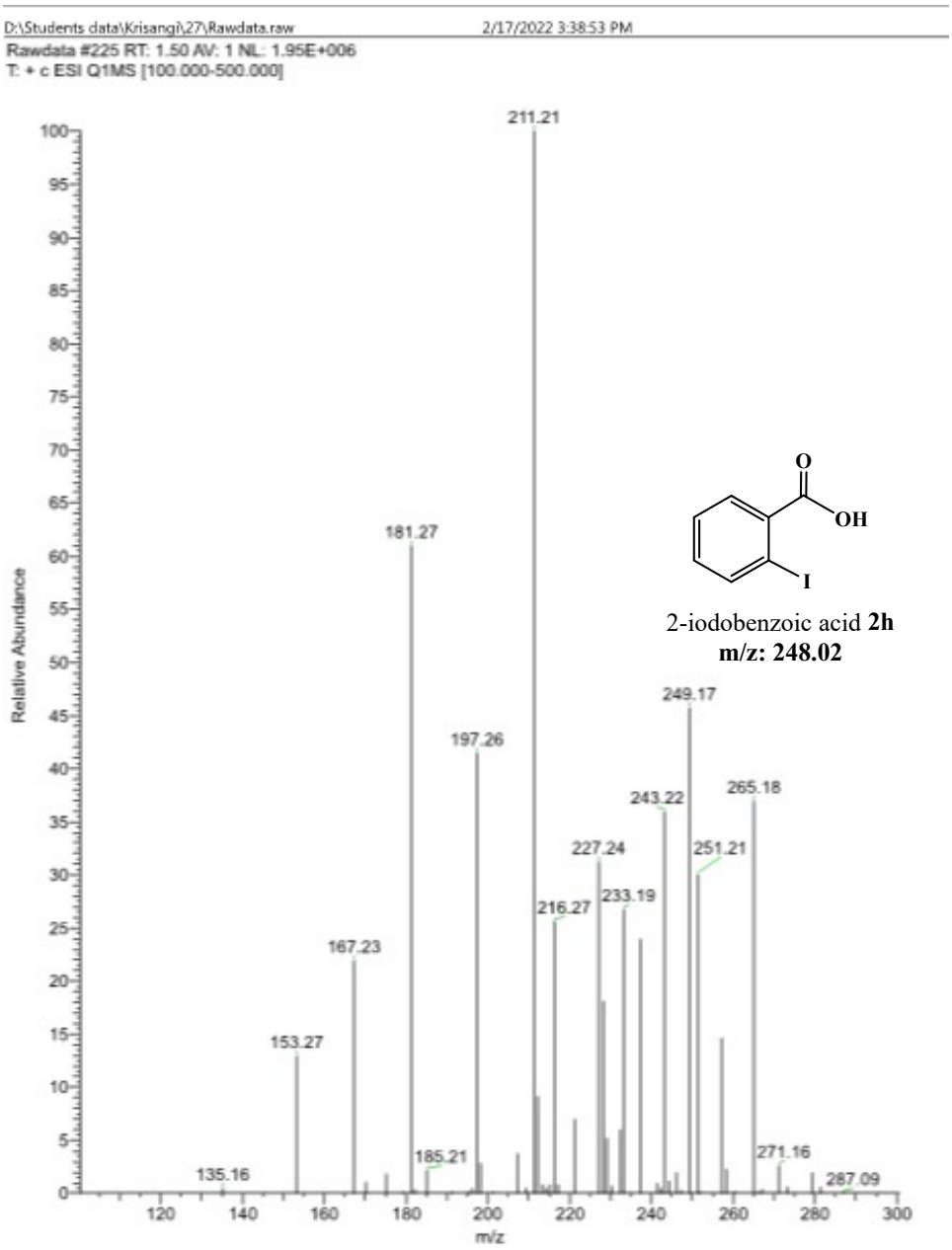


Fig S9 LC-MS spectrum of 2-iodobenzoic acid (Table 2, Entry **2h**)

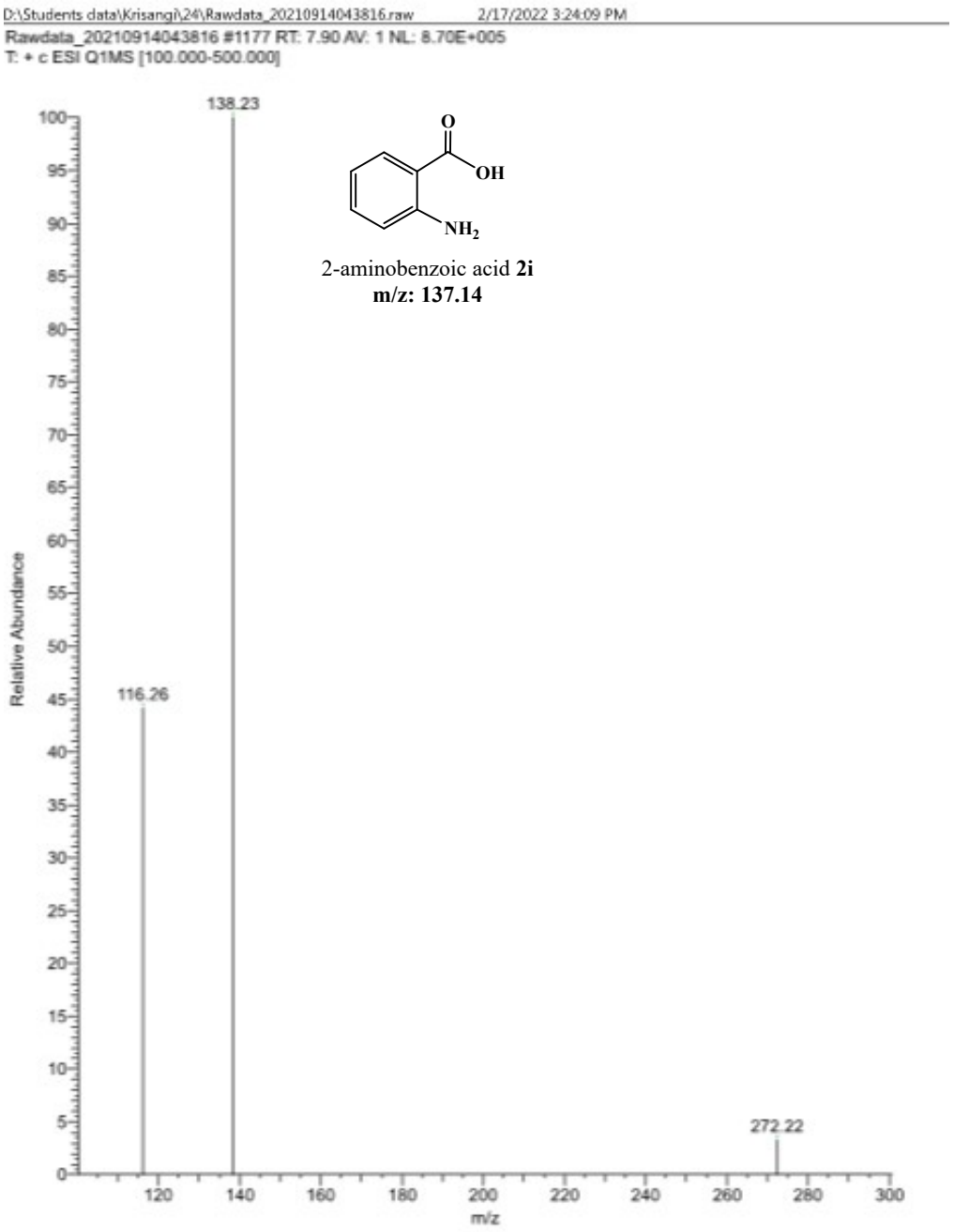


Fig S10 LC-MS spectrum of 2-aminobenzoic acid (Table 2, Entry **2i**)

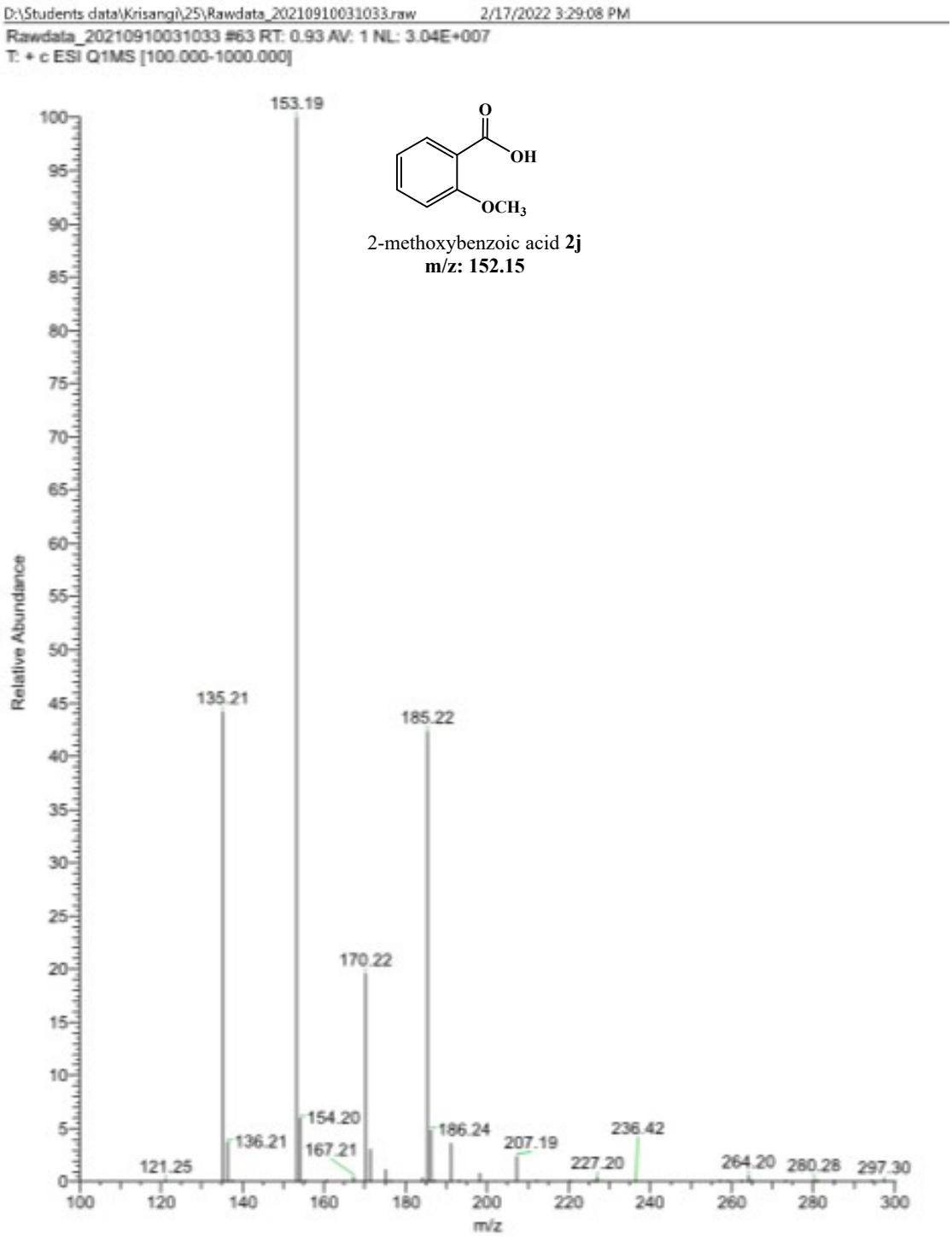


Fig S11 LC-MS spectrum of 2-methoxybenzoic acid (Table 2, Entry **2j**)

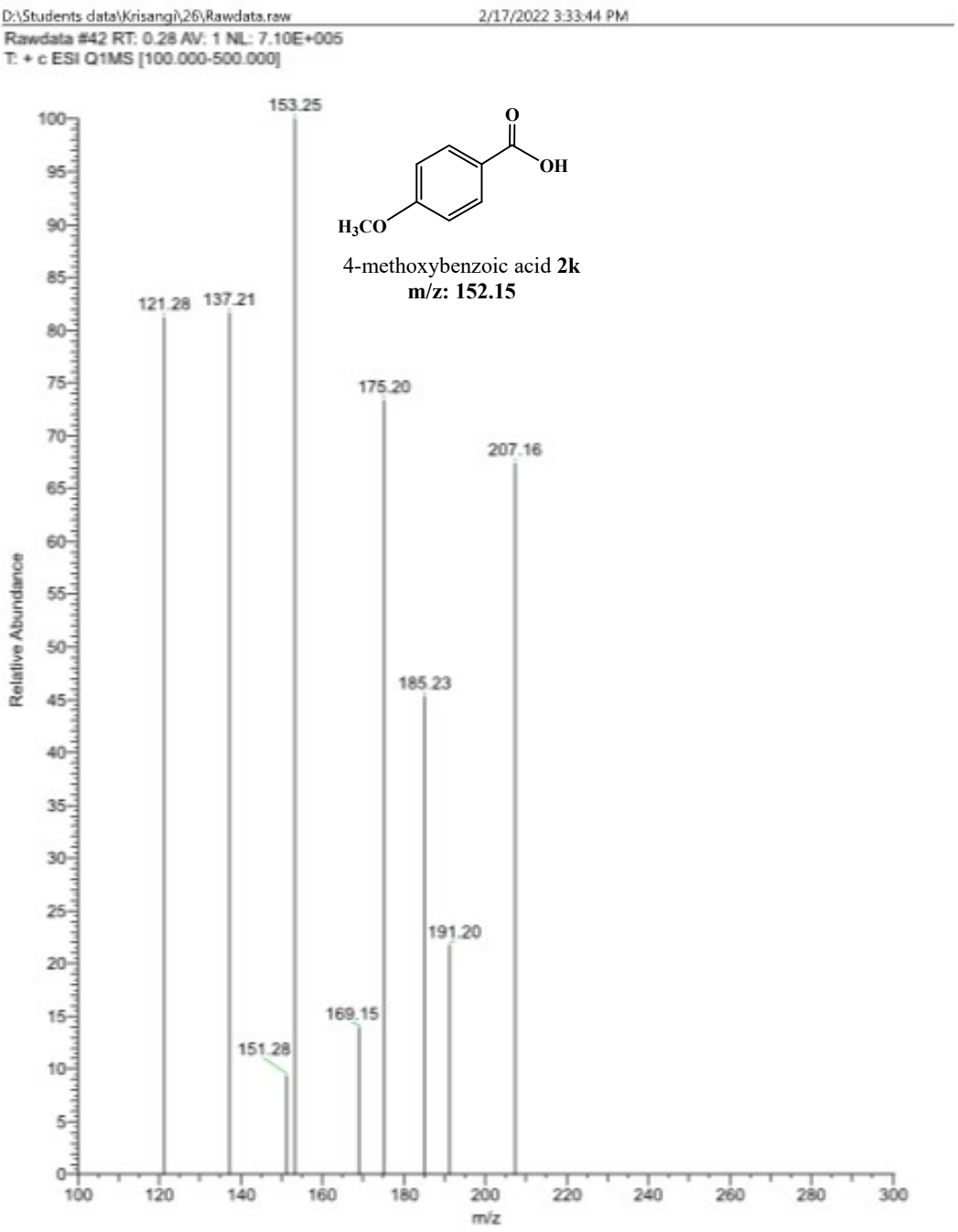


Fig S12 LC-MS spectrum of 4-methoxybenzoic acid (Table 2, Entry **2k**)

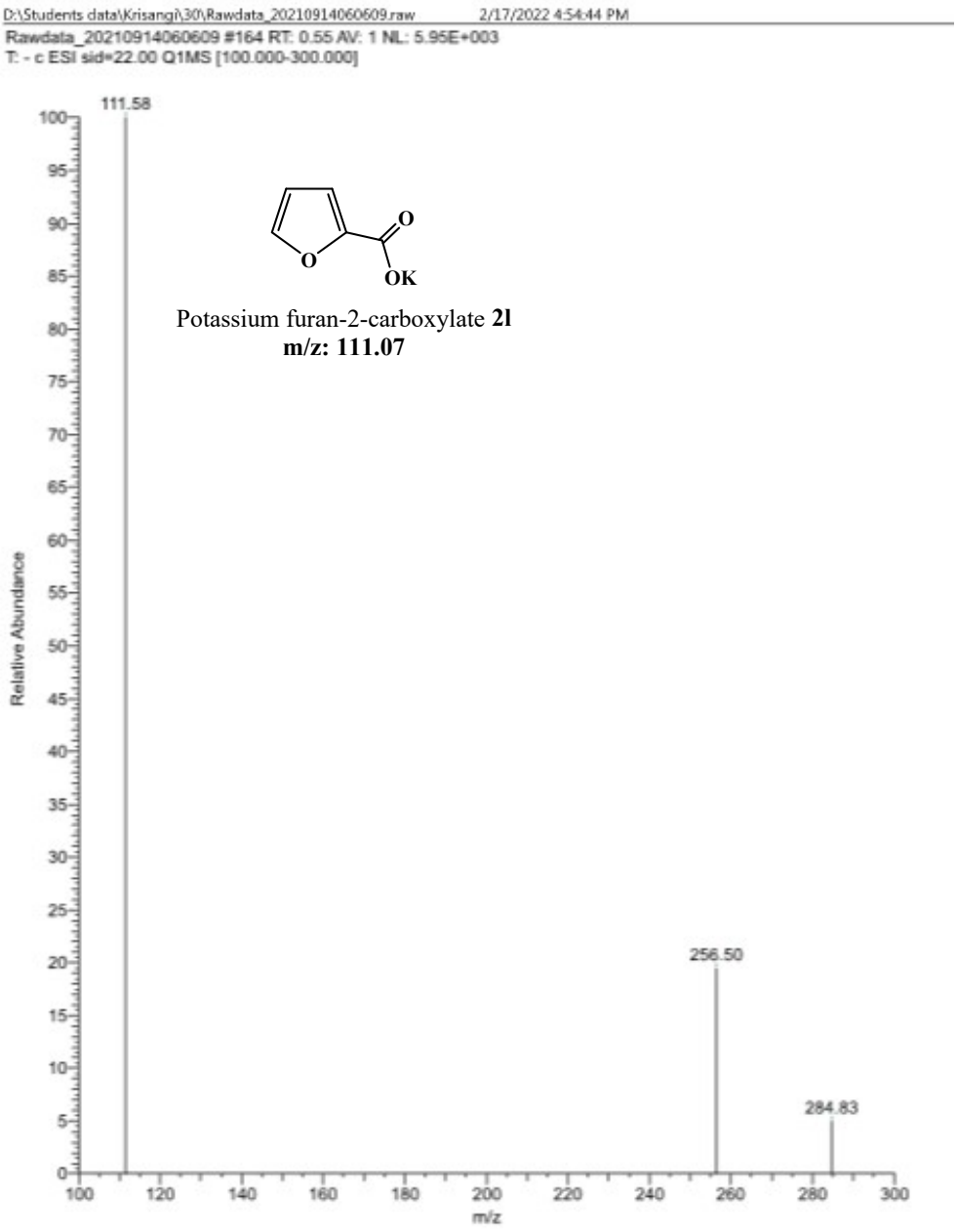


Fig S13 LC-MS spectrum of Potassium furan-2-carboxylate (Table 2, Entry **2l**)

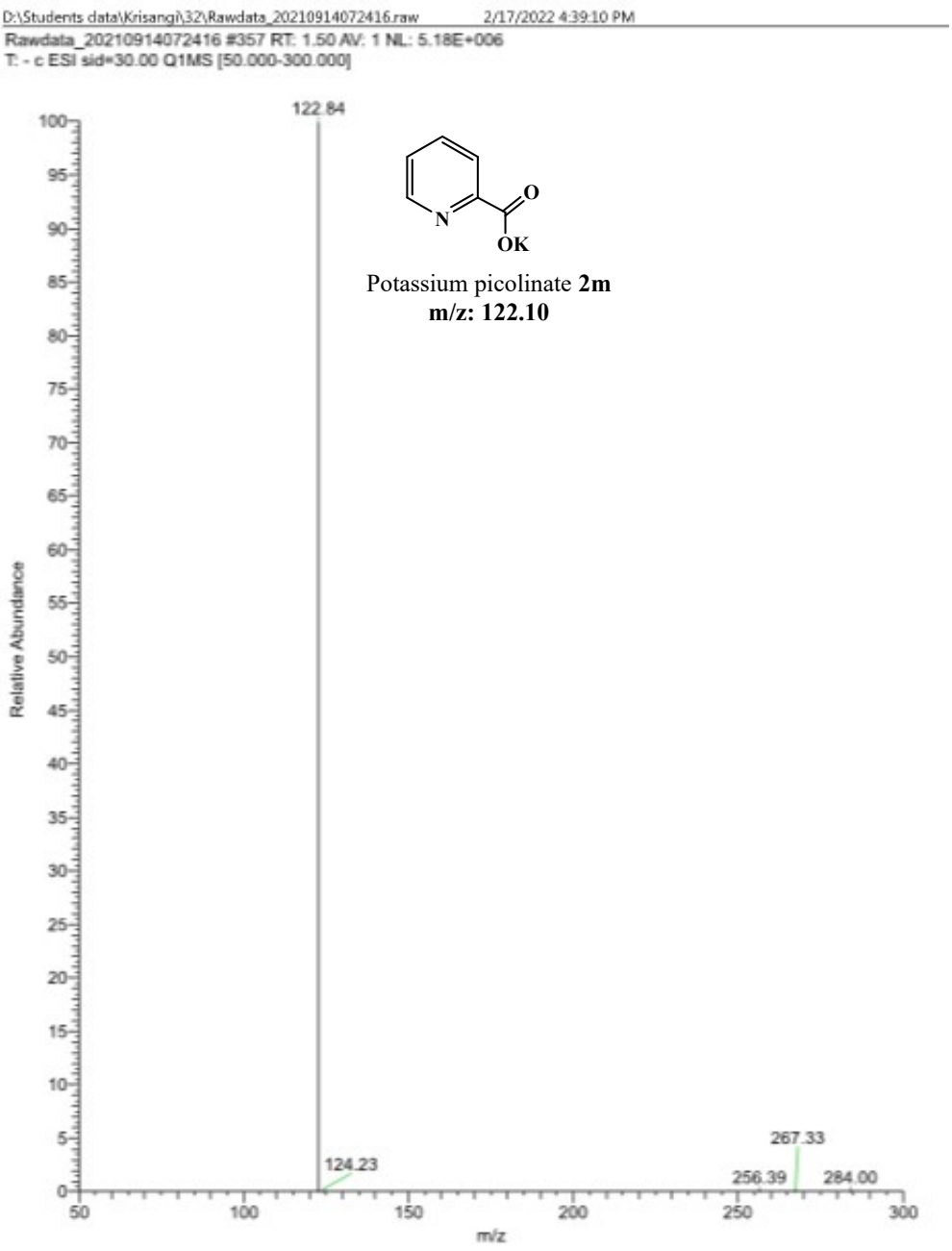


Fig S14 LC-MS spectrum of Potassium picolinate (Table 2, Entry **2m**)

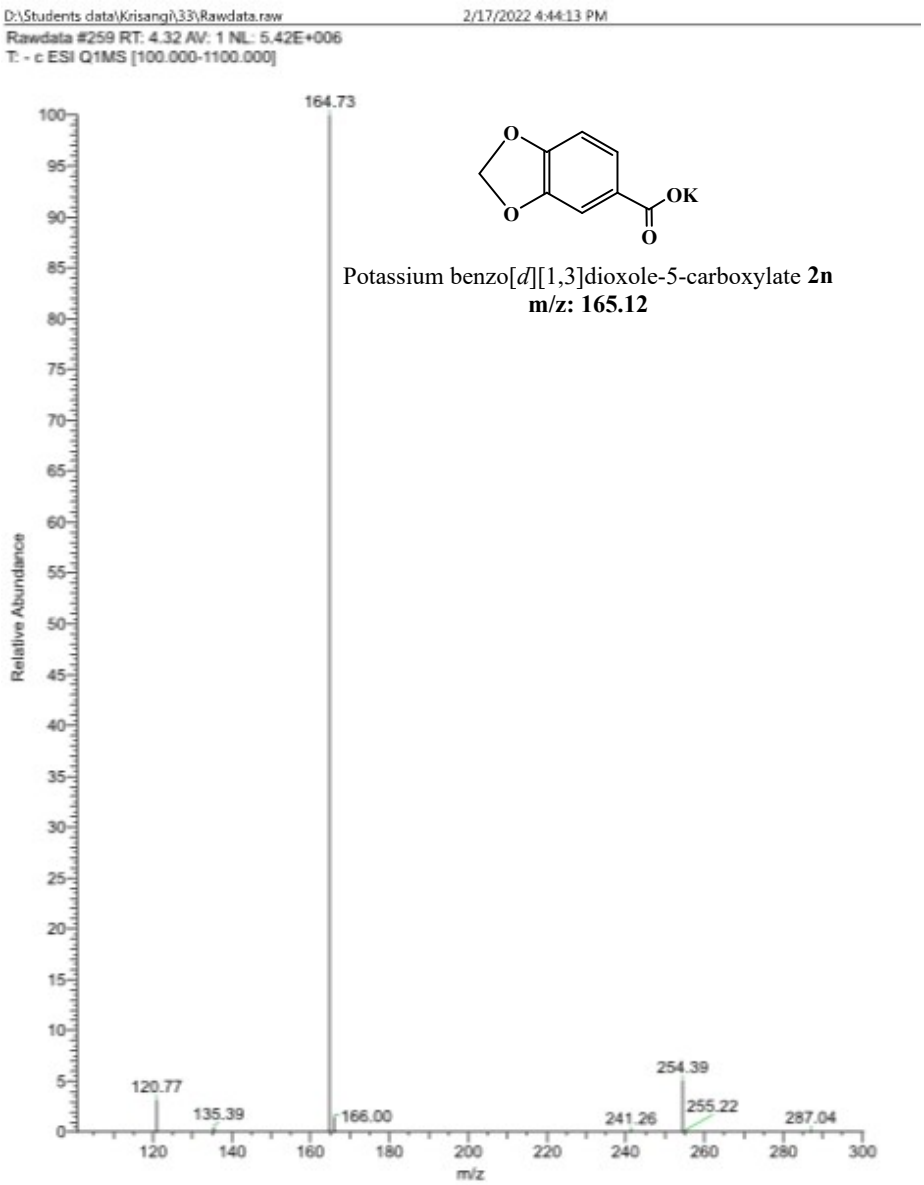


Fig S15 LC-MS spectrum of Potassium benzo[d] [1,3] dioxole-5-carboxylate (Table 2, Entry **2n**)

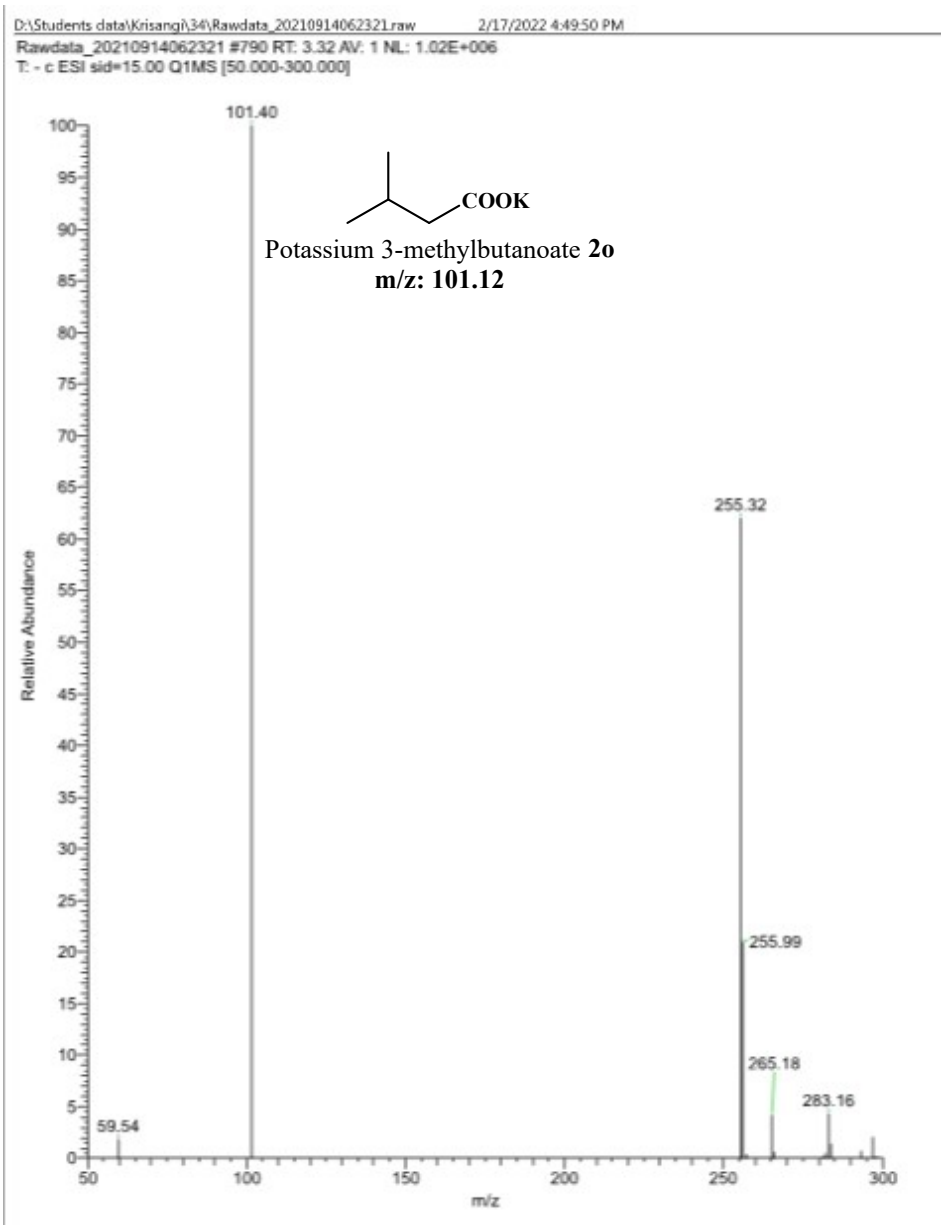


Fig S16 LC-MS spectrum of Potassium 3-methylbutanoate (Table 2, Entry **2o**)

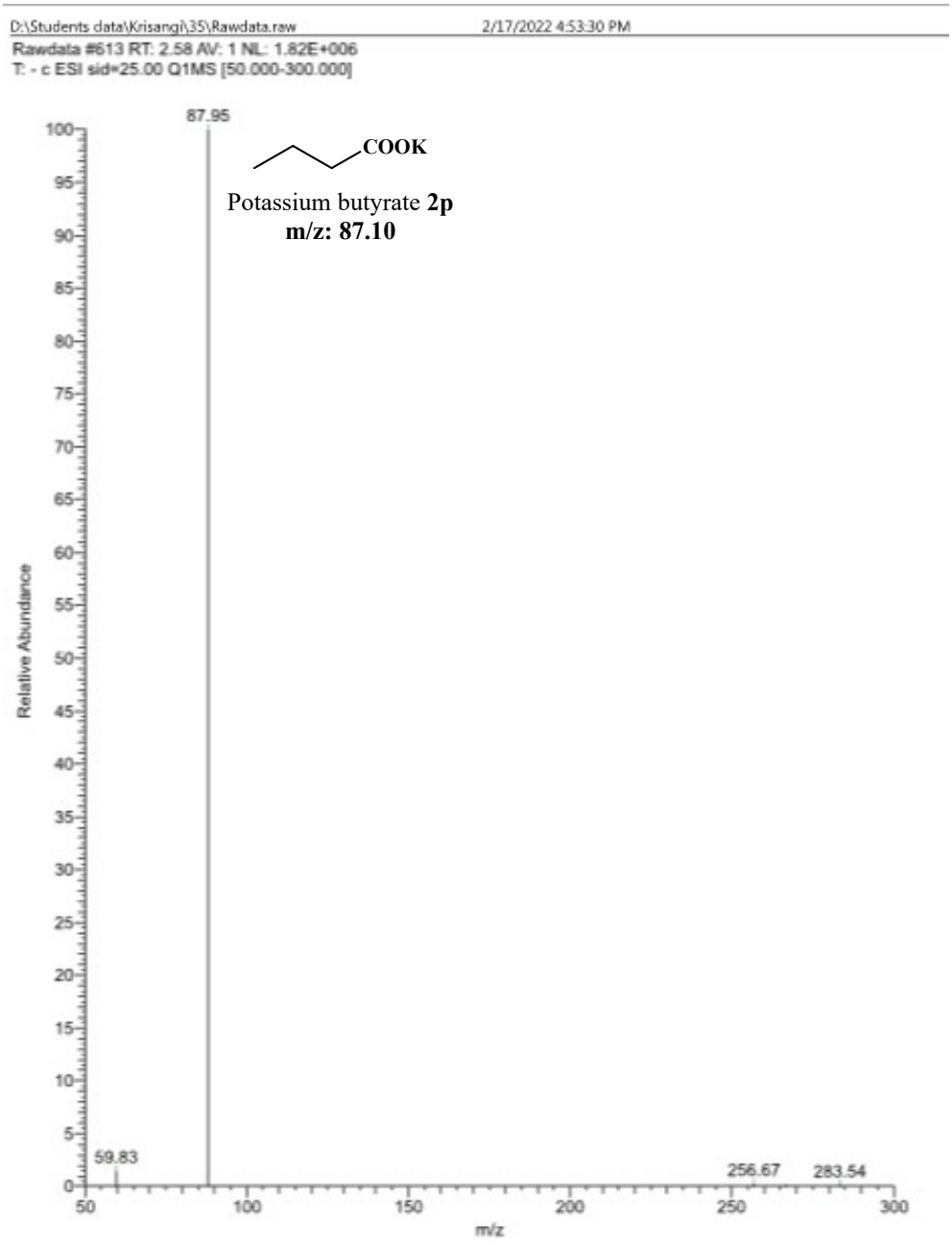


Fig S17 LC-MS spectrum of Potassium butyrate (Table 2, Entry **2p**)

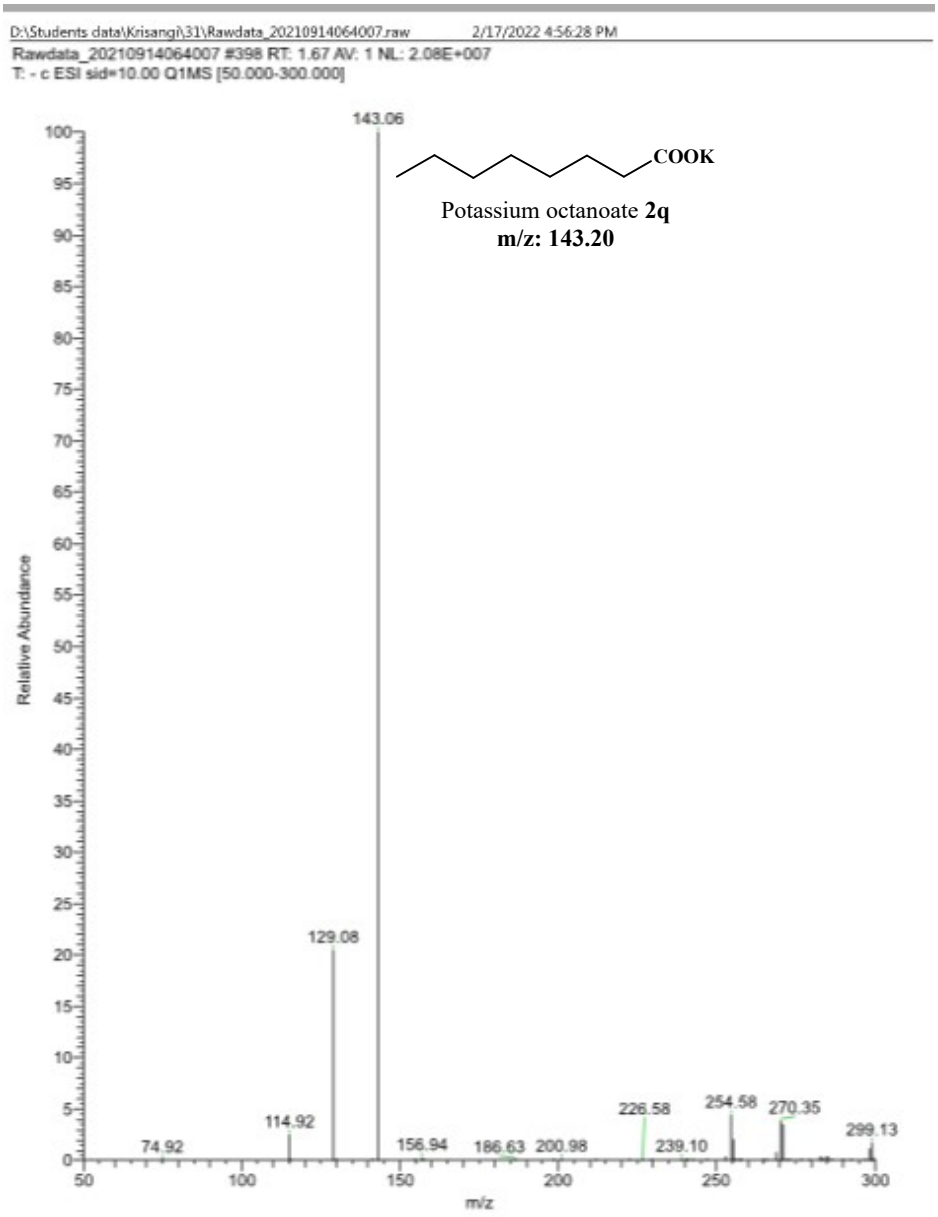


Fig S18 LC-MS spectrum of Potassium octanoate (Table 2, Entry **2q**)

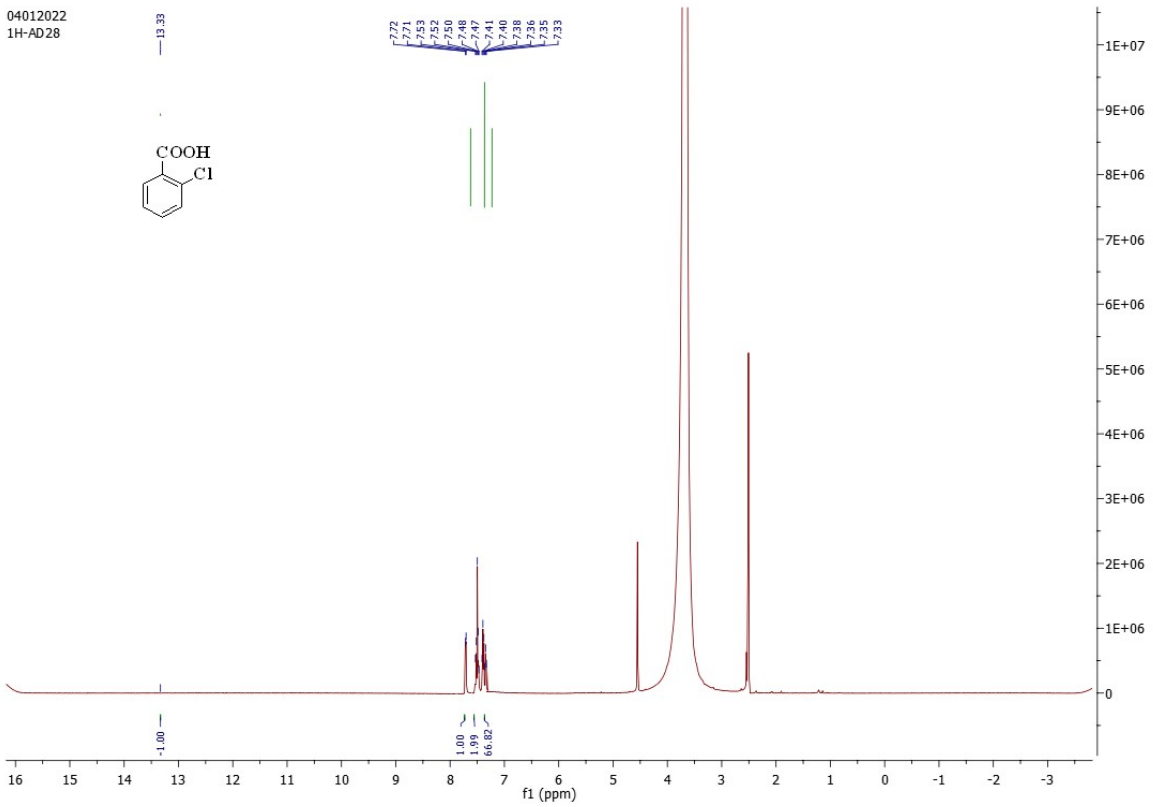


Fig S19 ^{1}H NMR of acid **2b** in DMSO-D_6 (Table 2, Entry 2b)

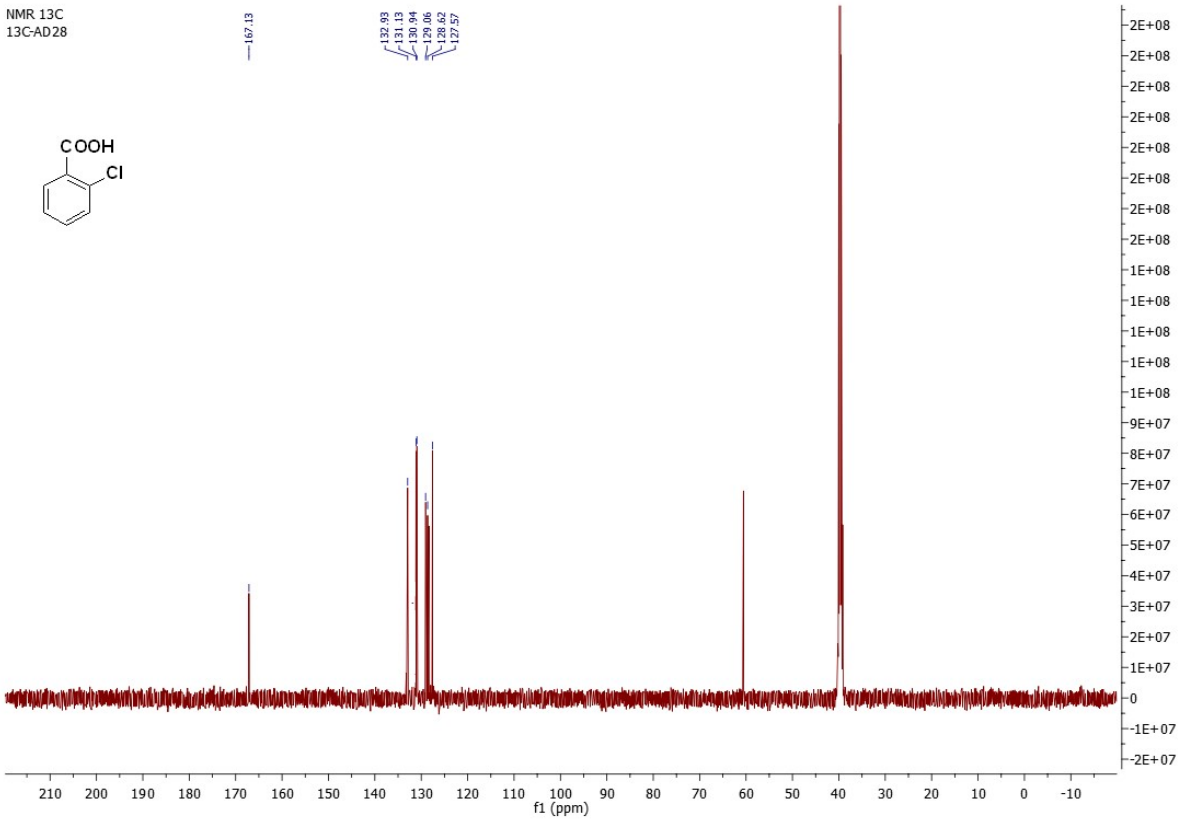


Fig S20 ^{13}C NMR of acid **2b** in DMSO-D_6 (Table 2, Entry 2b)

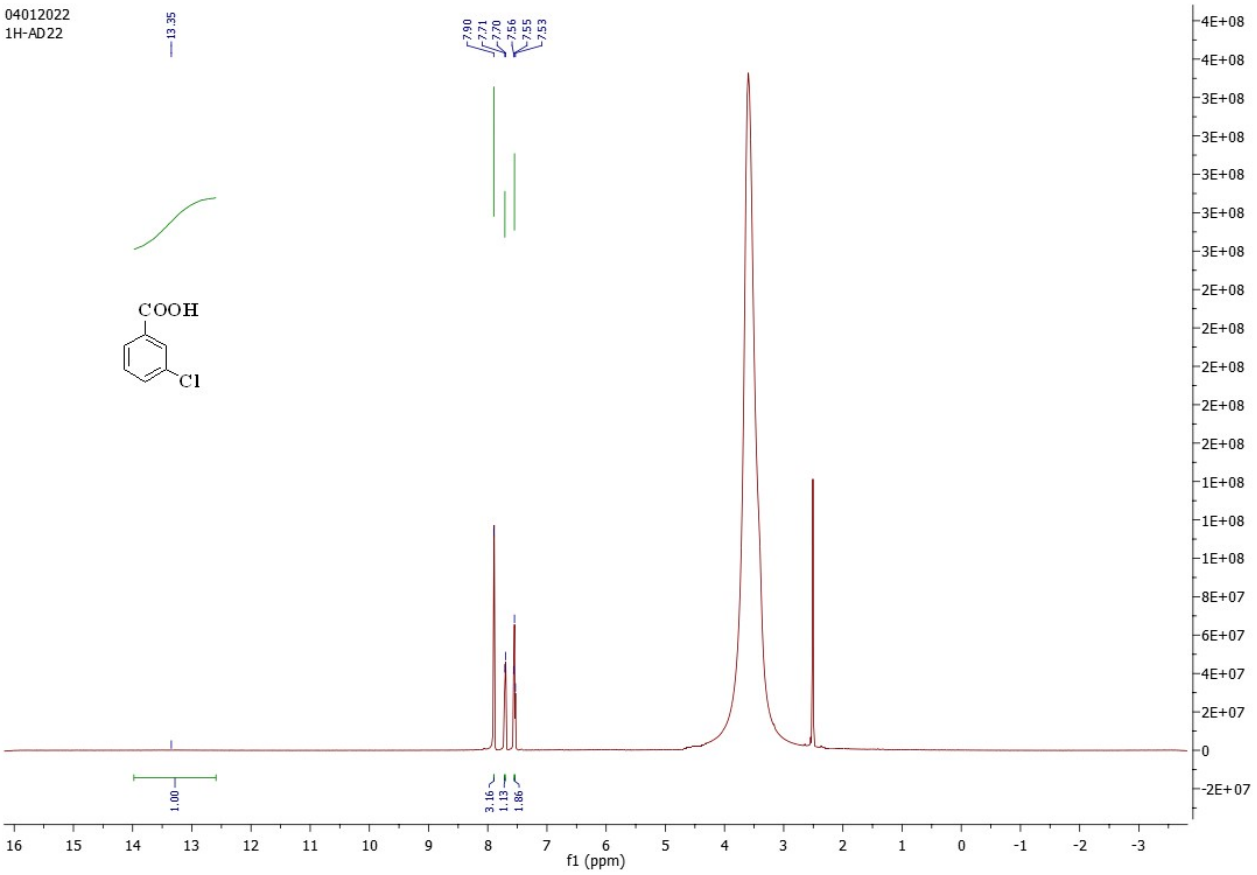


Fig S21 ^{1}H NMR of acid **2c** in DMSO-D_6 (Table 2, Entry 2c)

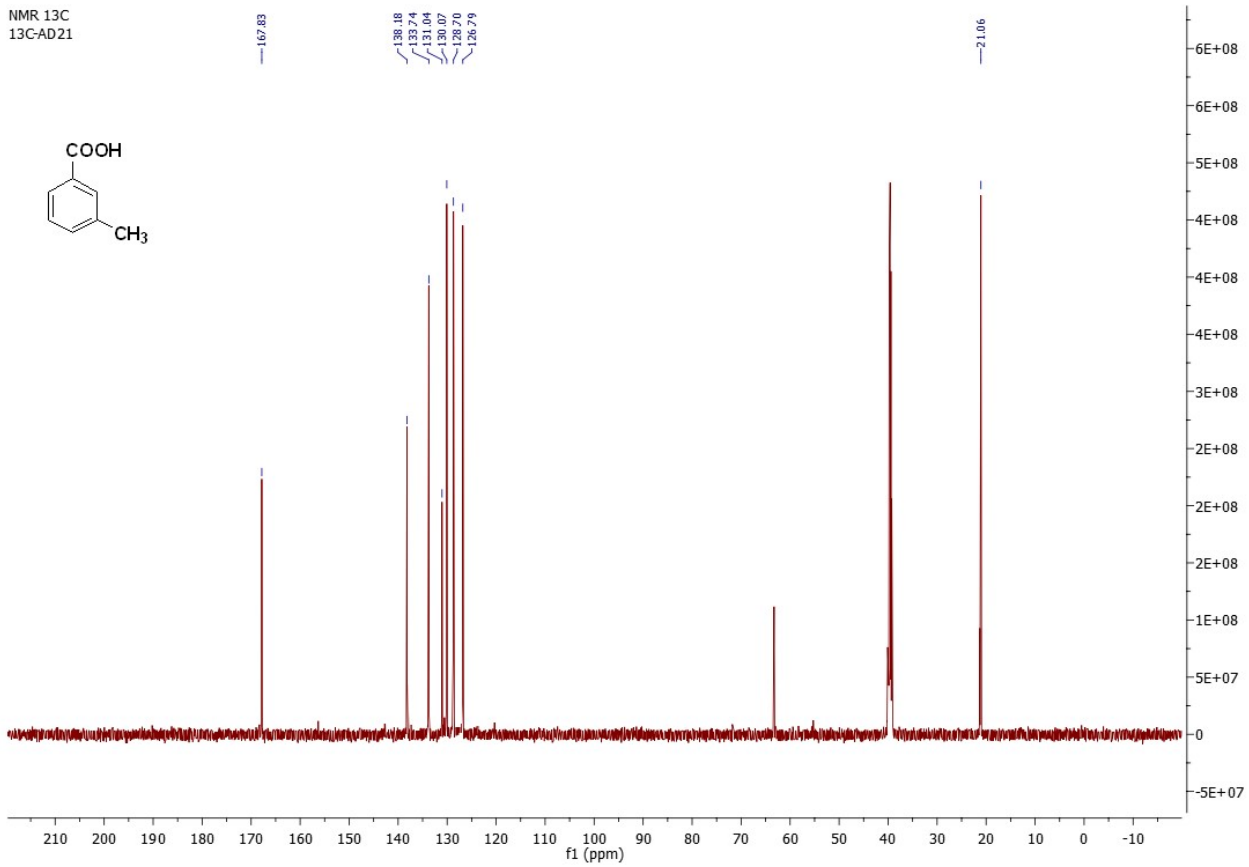


Fig S22 ^{13}C NMR of acid **2c** in DMSO-D_6 (Table 2, Entry 2c)

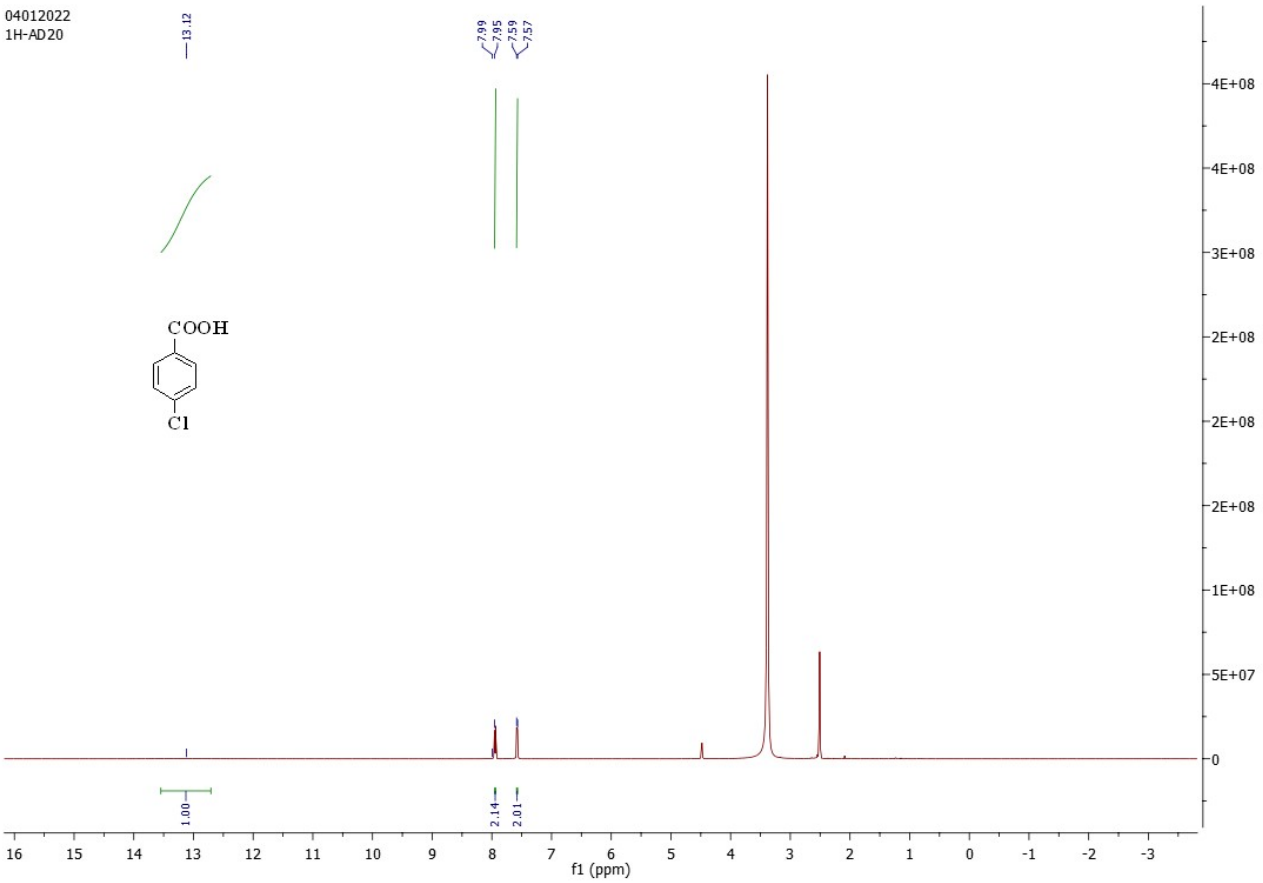


Fig S23 ^{1}H NMR of acid **2d** in DMSO-D_6 (Table 2, Entry 2d)

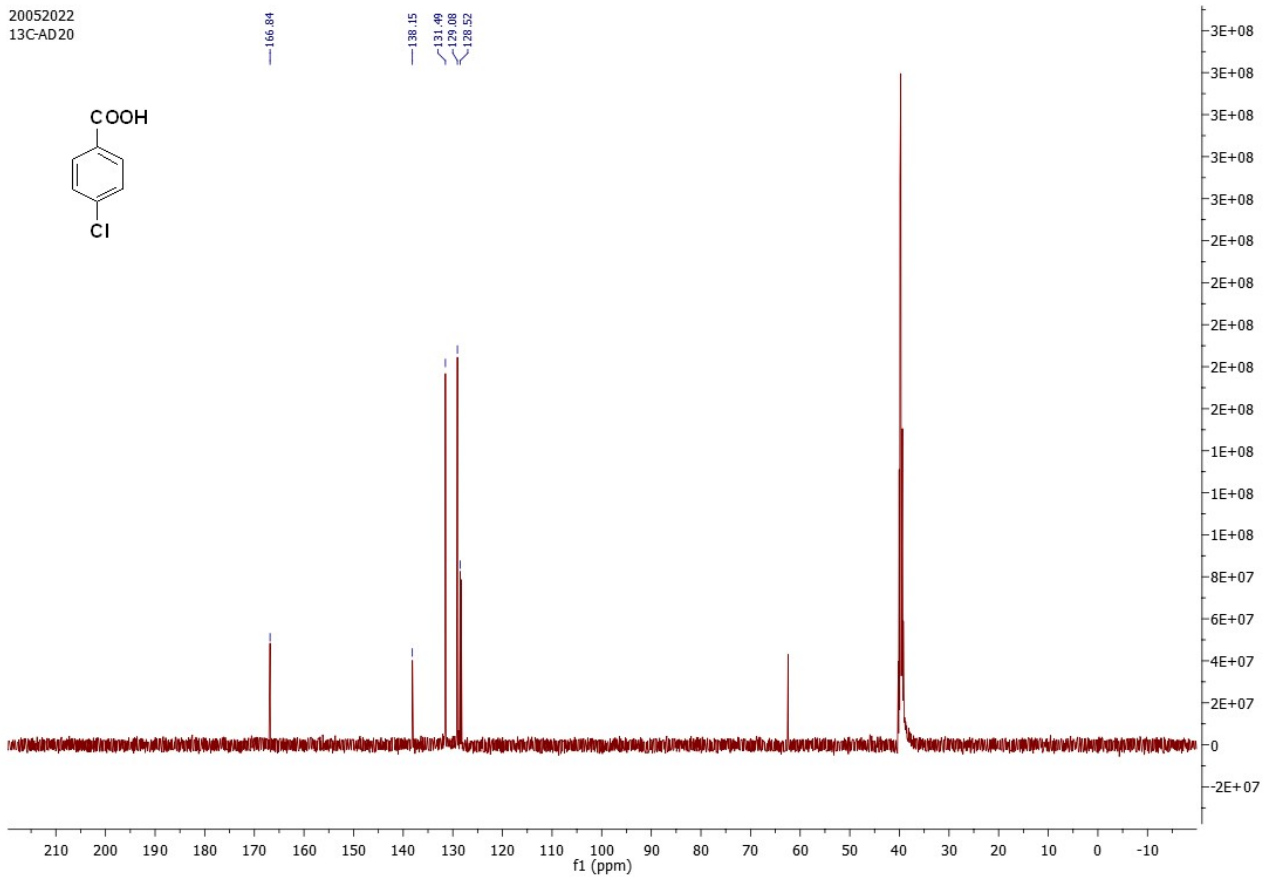


Fig S24 ^{13}C NMR of acid **2d** in DMSO-D_6 (Table 2, Entry 2d)

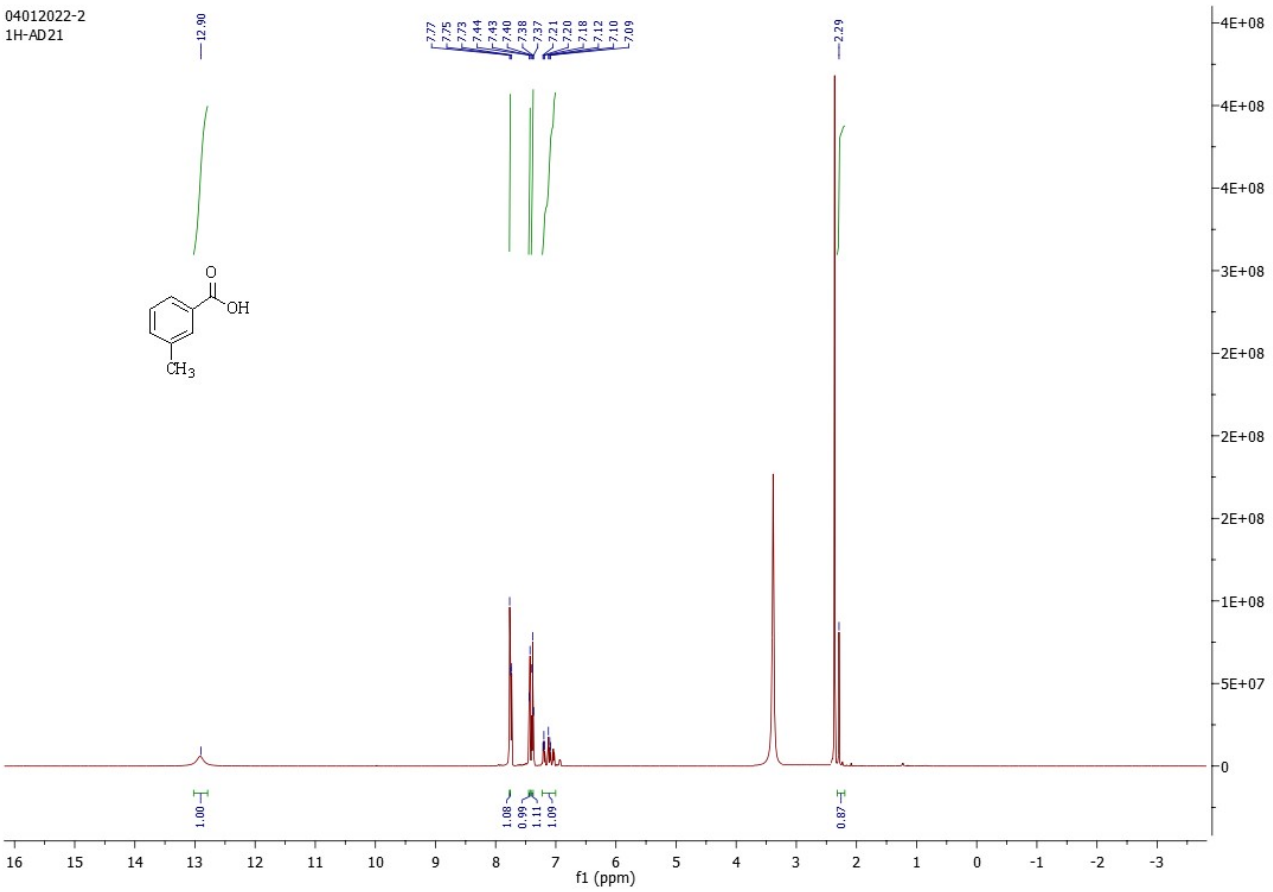


Fig S25 ^{1}H NMR of acid **2e** in DMSO-D_6 (Table 2, Entry 2e)

Fig S26 ^{13}C NMR of acid **2e** in DMSO-D_6 (Table 2, Entry 2e)

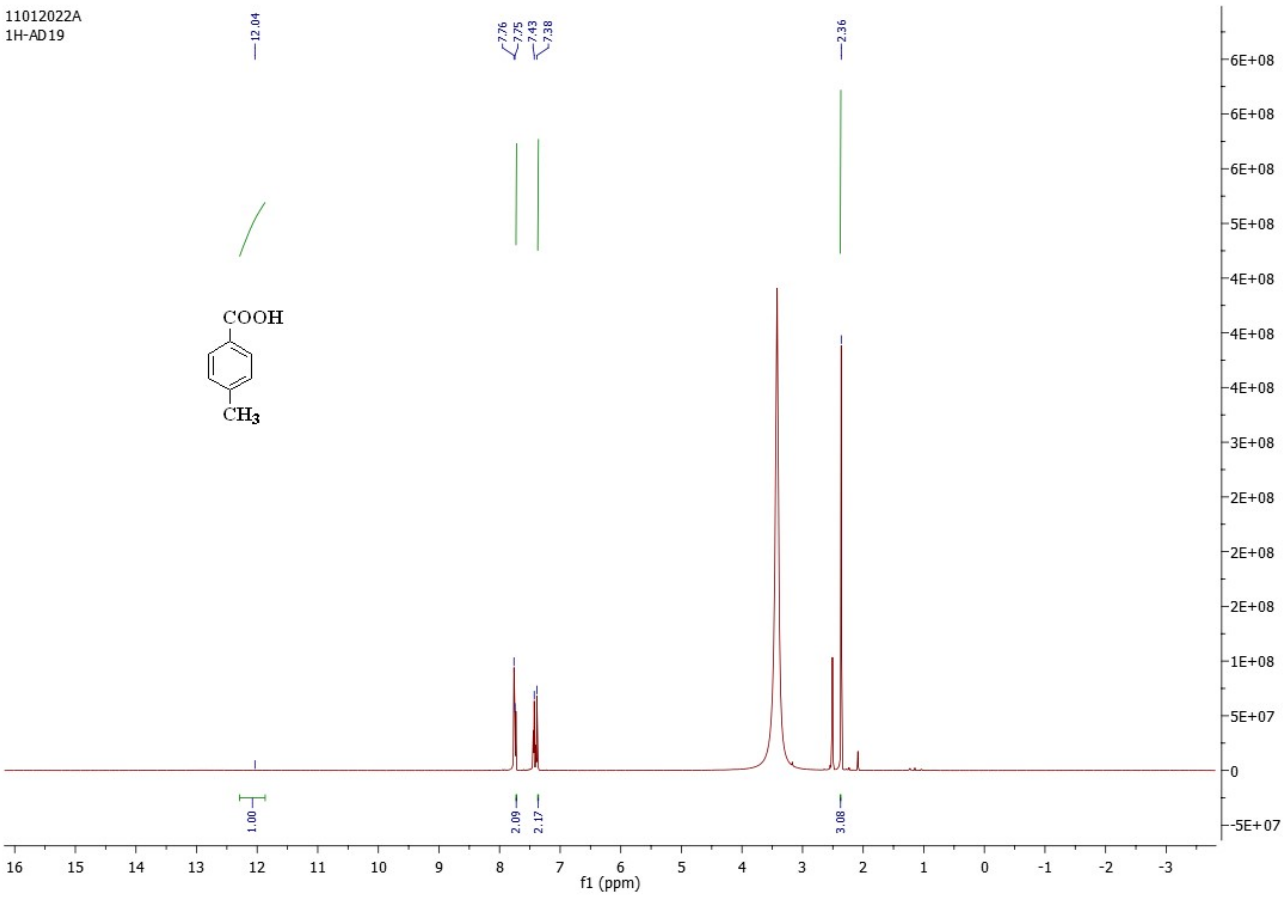


Fig S27 ^{1}H NMR of acid **2f** in DMSO-D_6 (Table 2, Entry 2f)

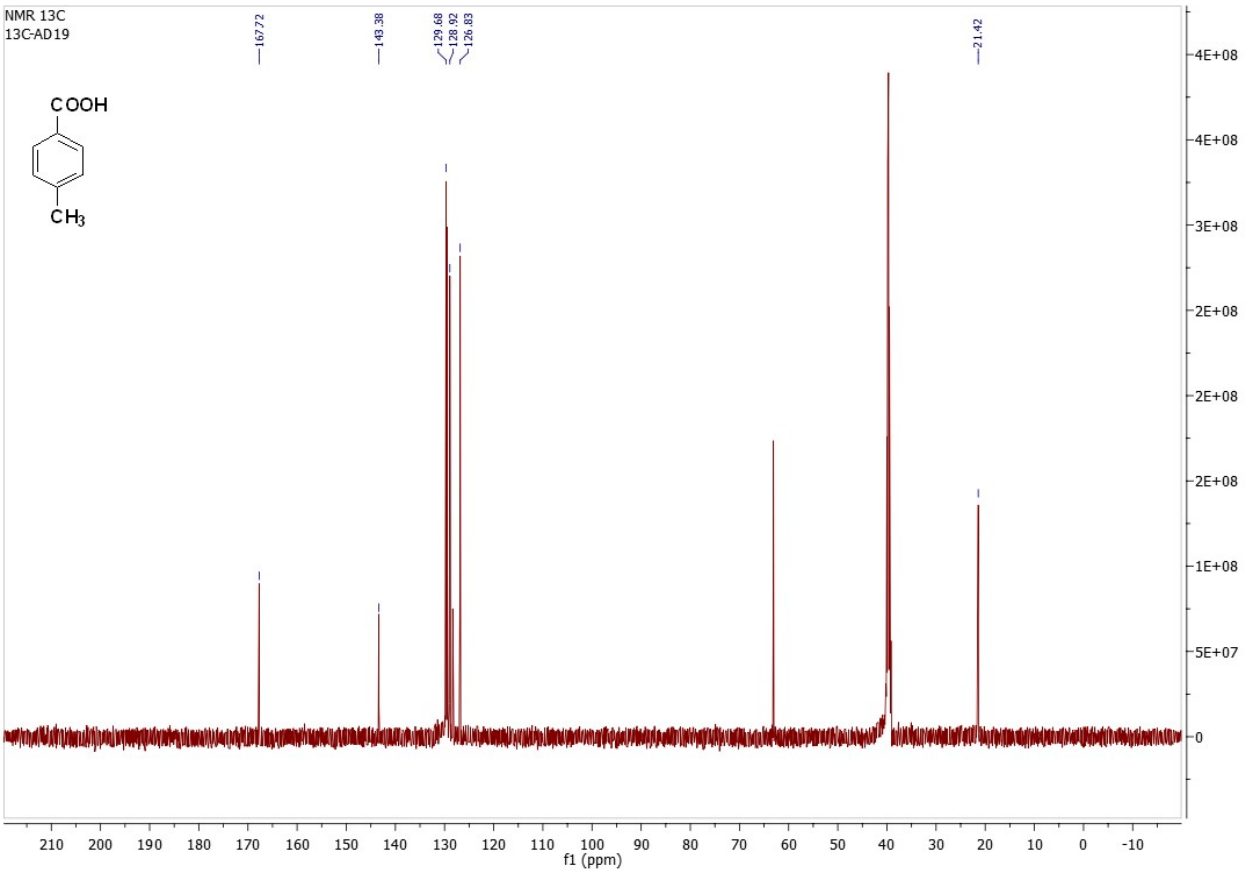


Fig S28 ^{13}C NMR of acid **2f** in DMSO-D_6 (Table 2, Entry 2f)

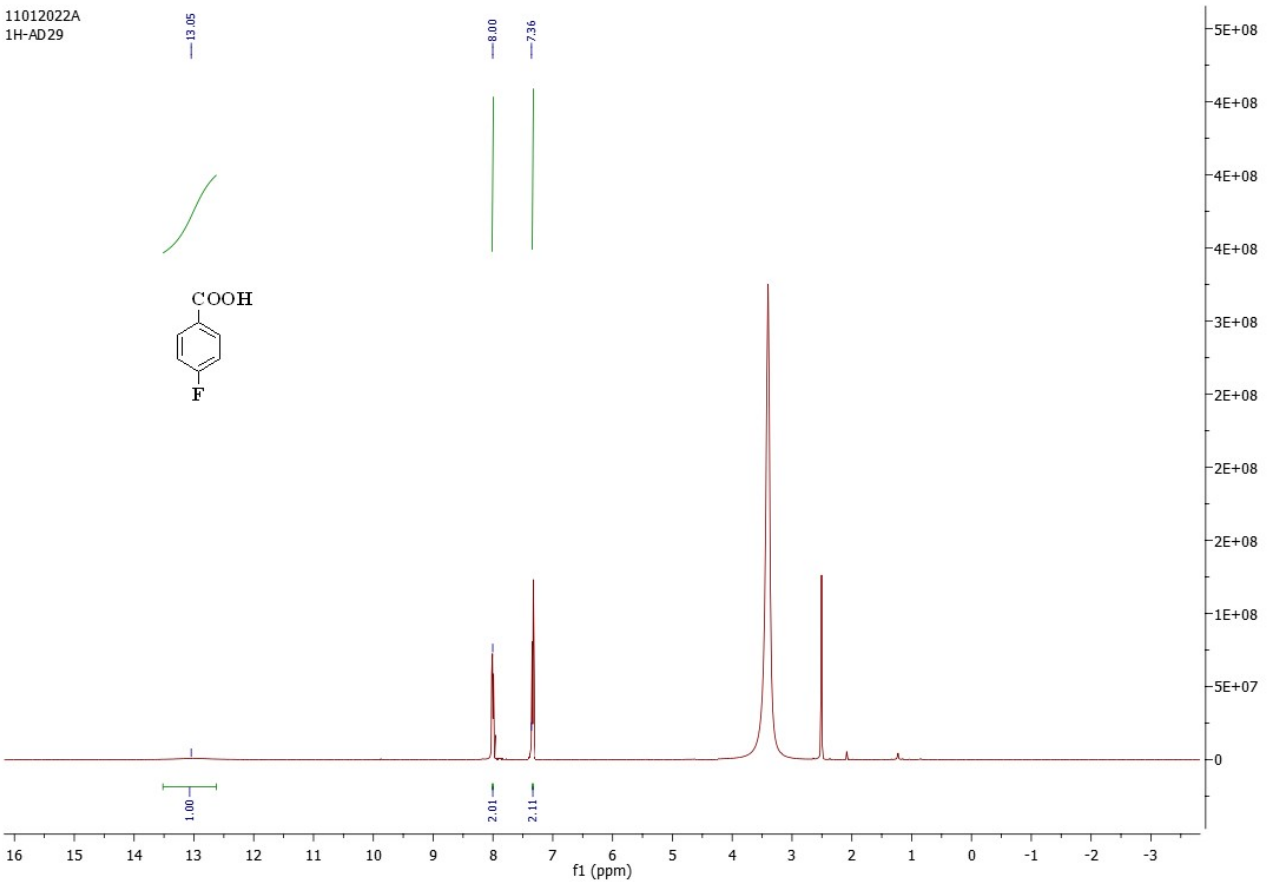


Fig S29 ^{1}H NMR of acid **2g** in DMSO-D_6 (Table 2, Entry 2g)

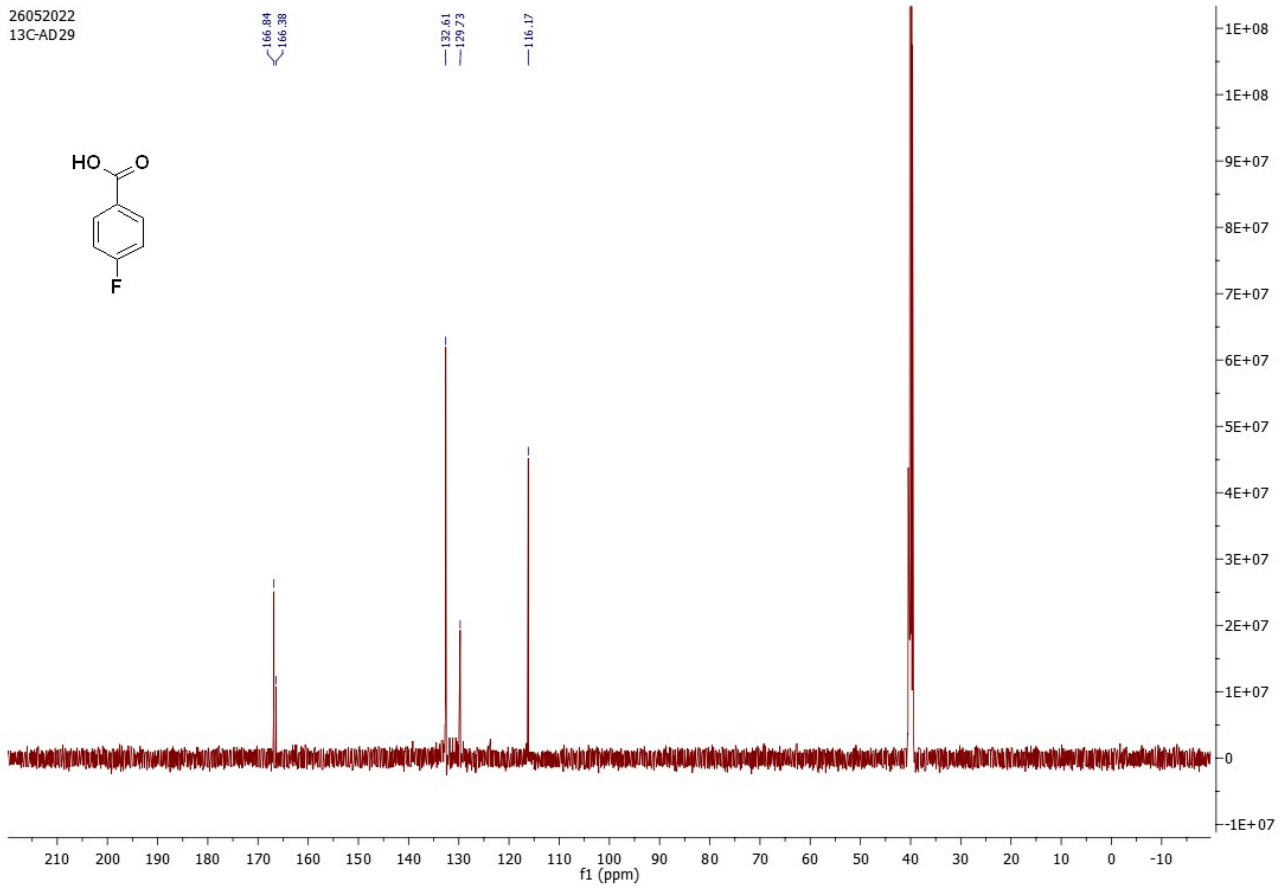


Fig S30 ^{13}C NMR of acid **2g** in DMSO-D_6 (Table 2, Entry 2g)

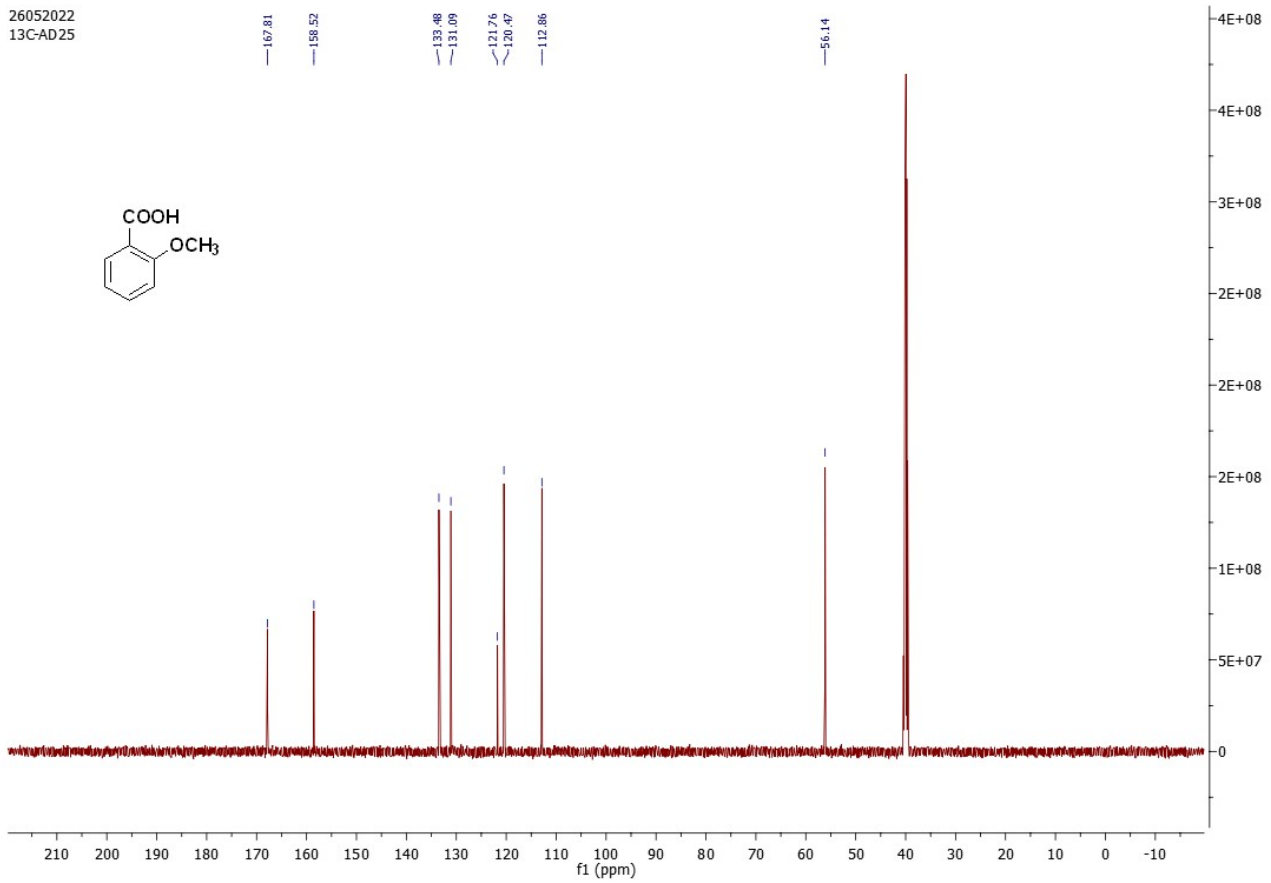


Fig S31 ^{13}C NMR of acid **2j** in DMSO-D_6 (Table 2, Entry 2j)

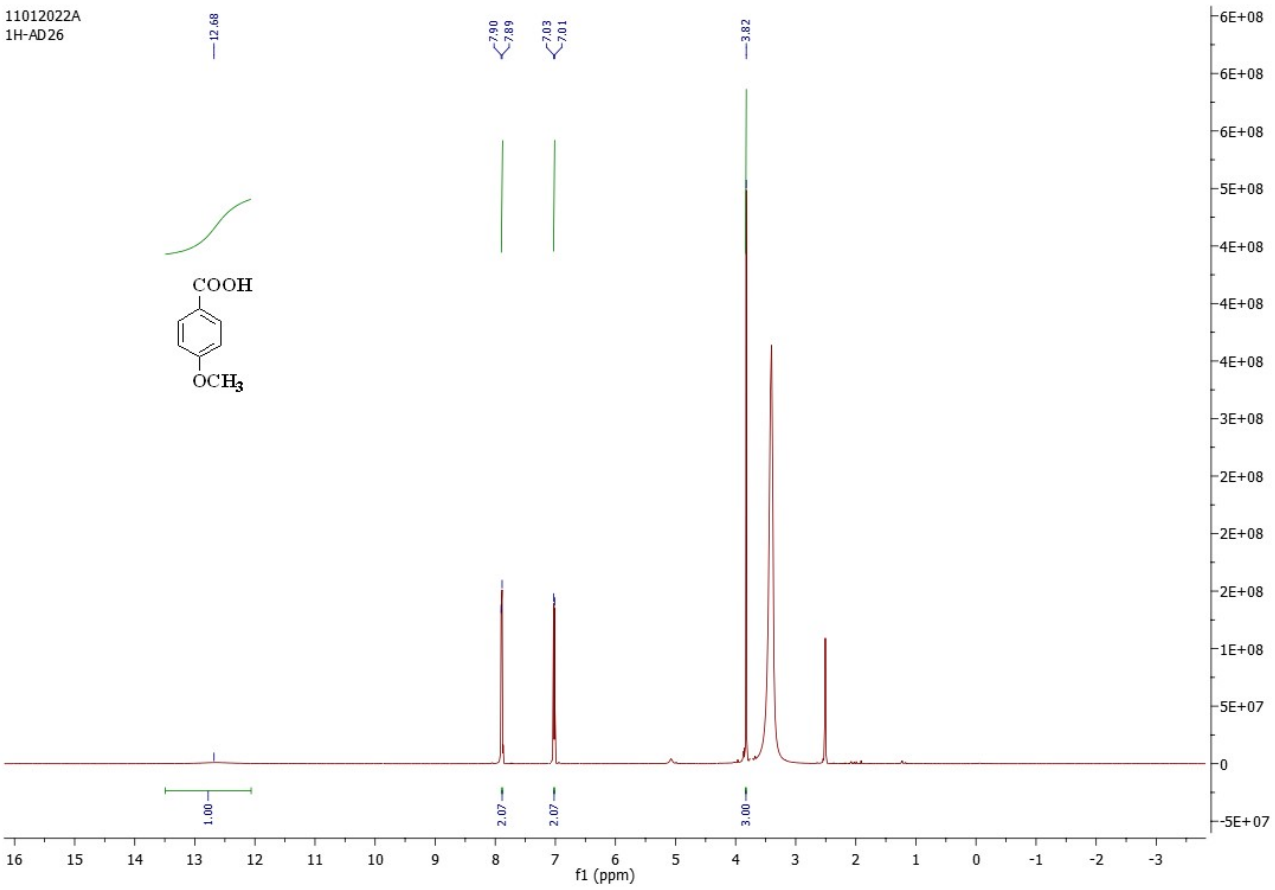


Fig S32 ^{1}H NMR of acid **2k** in DMSO-D_6 (Table 2, Entry 2k)

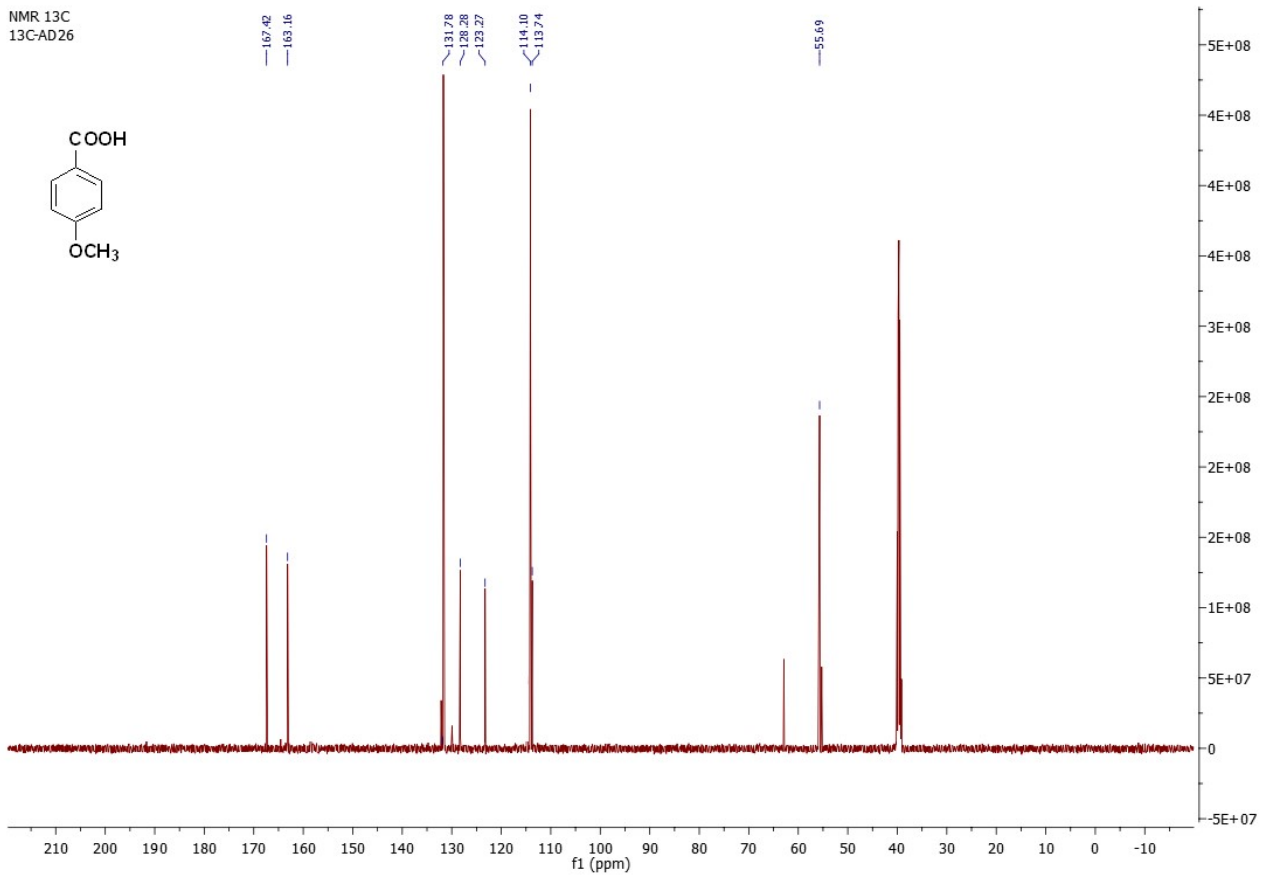


Fig S33 ^{13}C NMR of acid **2k** in DMSO-D_6 (Table 2, Entry 2k)

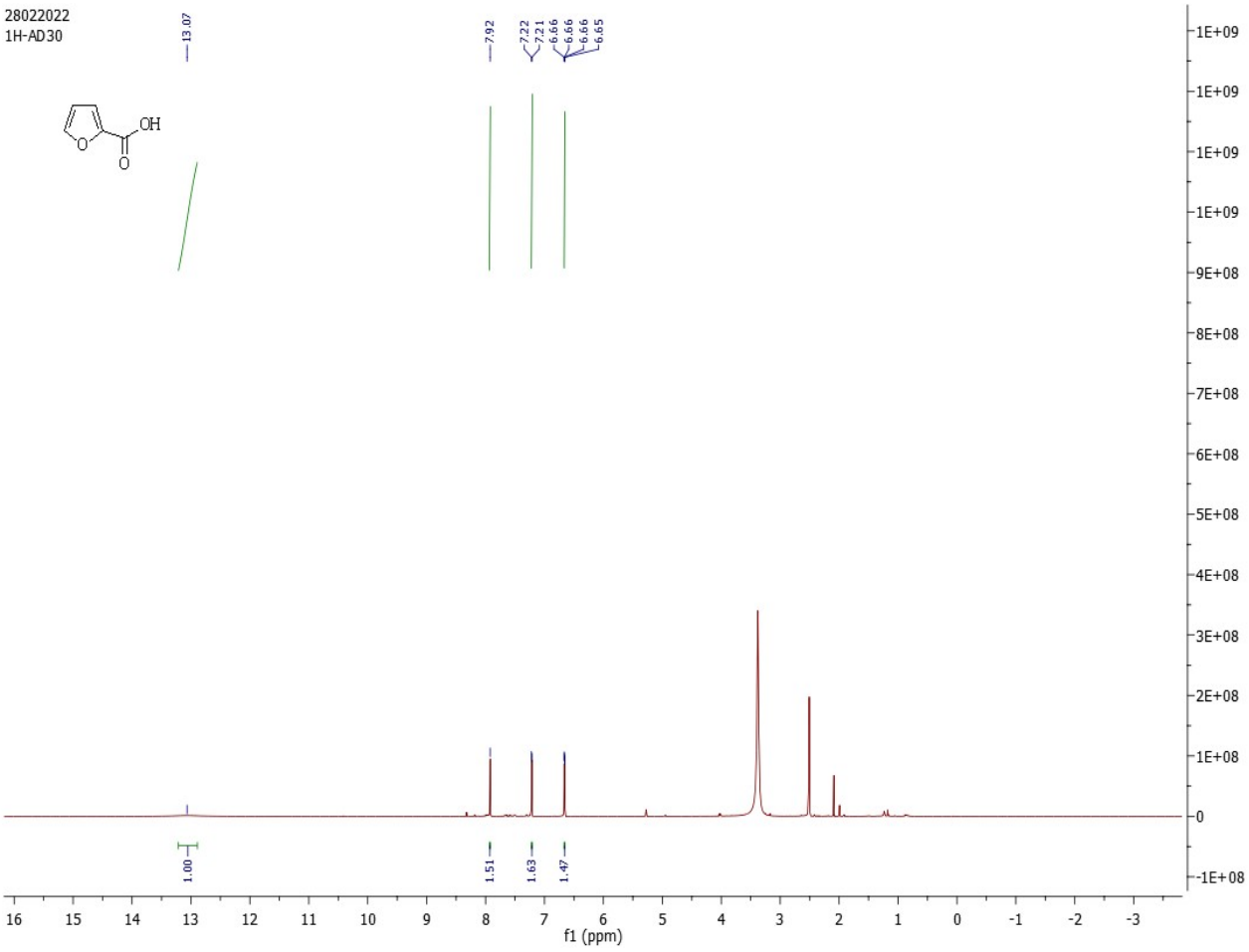


Fig S34 ^{1}H NMR of acid **2l** in DMSO-D_6 (Table 2, Entry 2l)

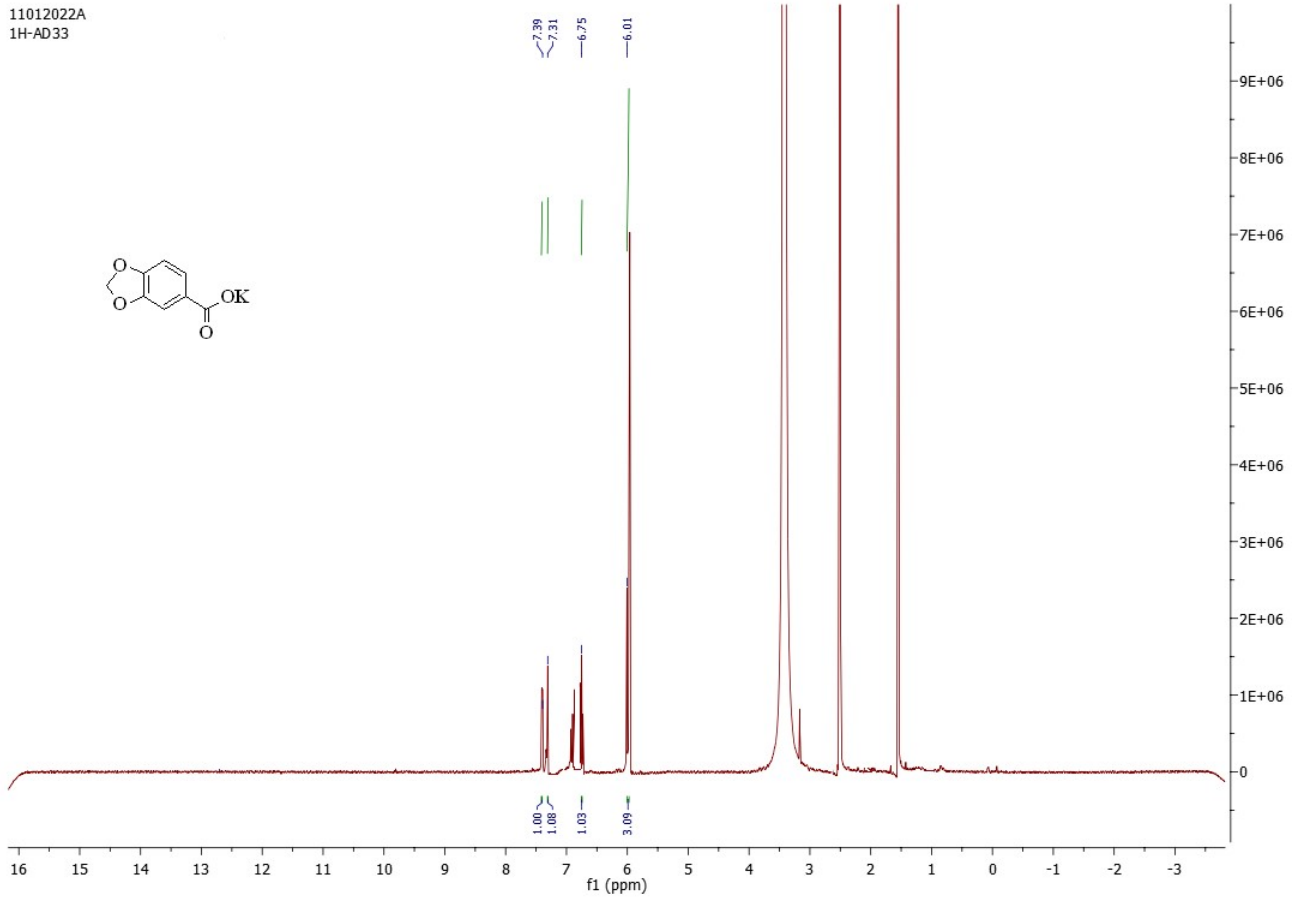


Fig S35 ^{1}H NMR of acid salt **2n** in DMSO-D_6 (Table 2, Entry 2n)

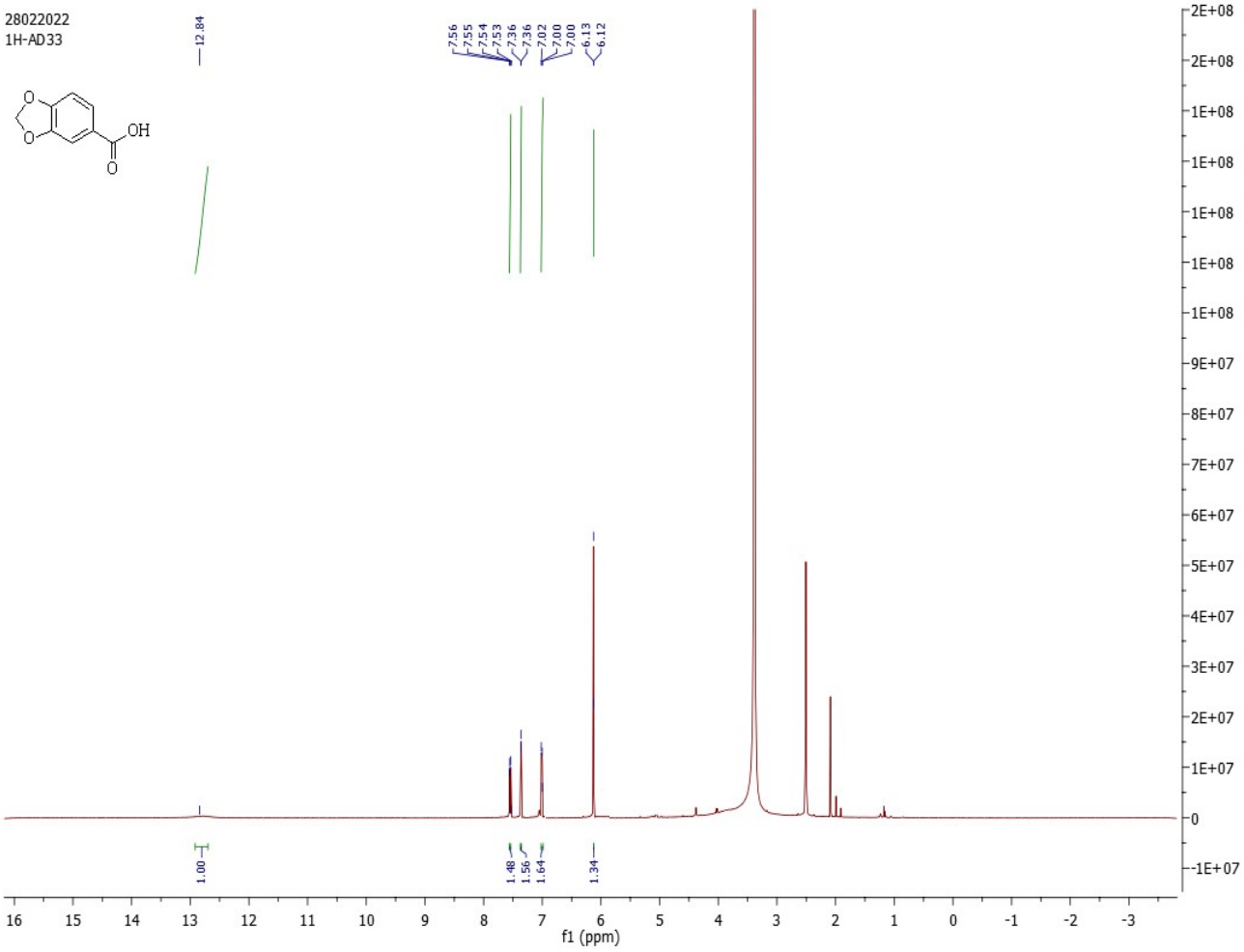


Fig S36 ^{1}H NMR of acid **2n** in DMSO-D_6 (Table 2, Entry 2n)

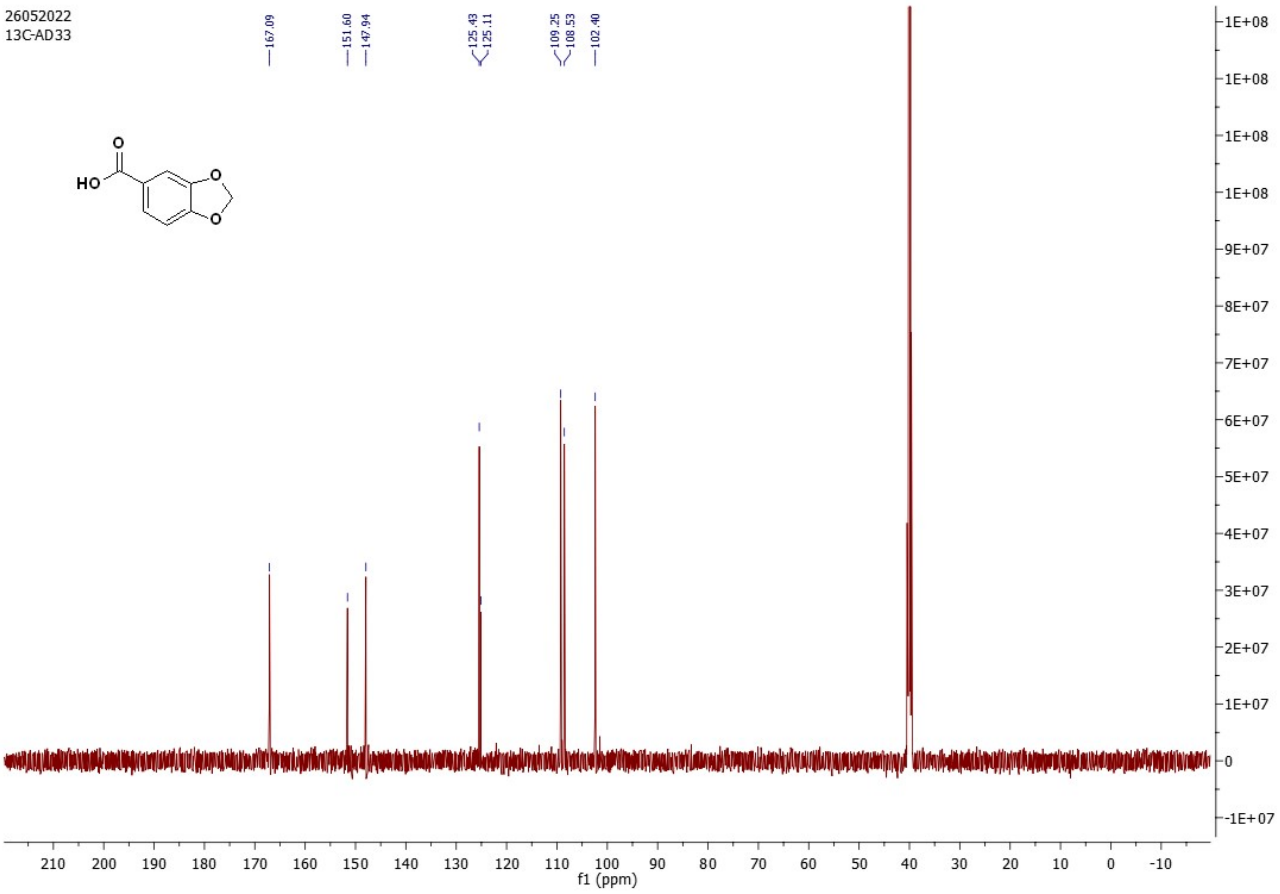


Fig S37 ^{13}C NMR of acid **2n** in DMSO-D_6 (Table 2, Entry 2n)

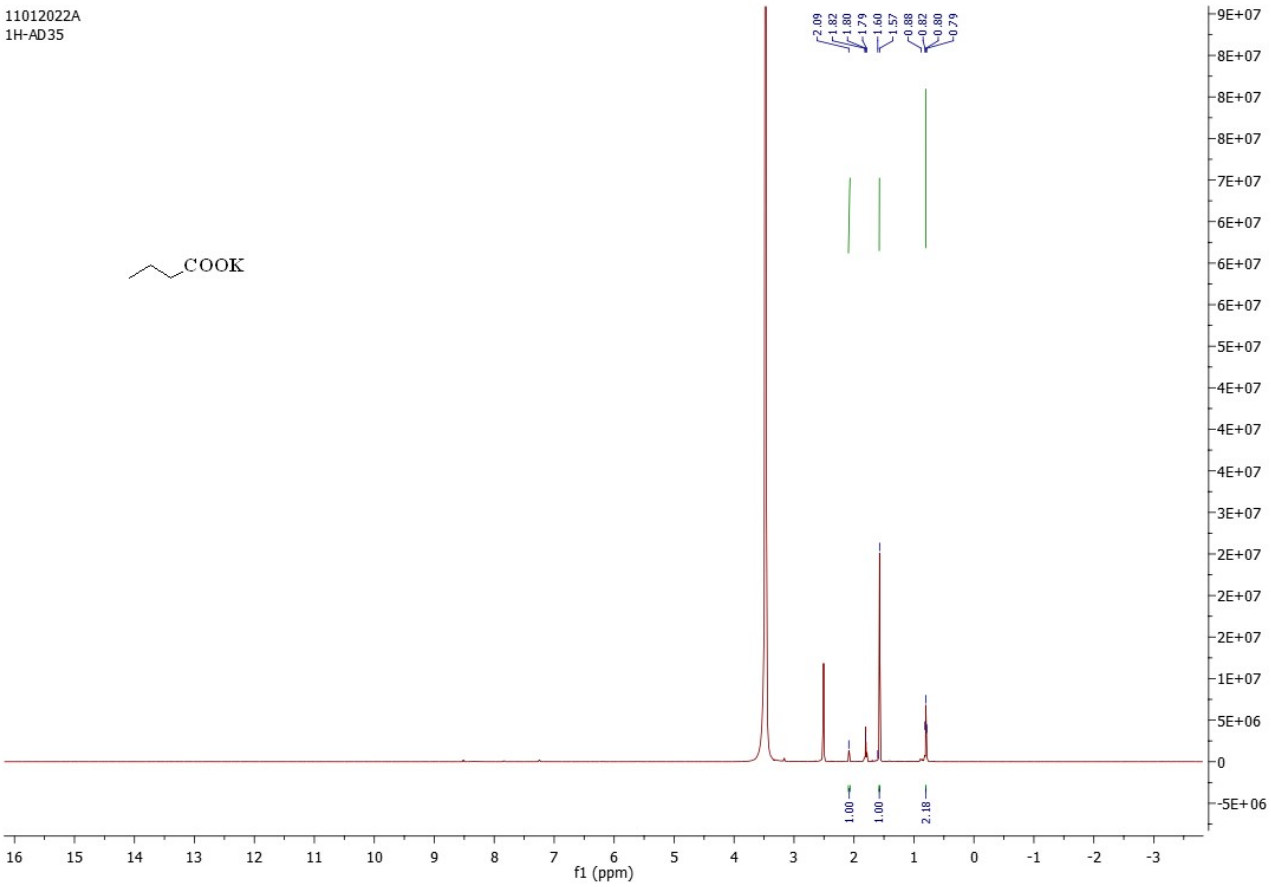
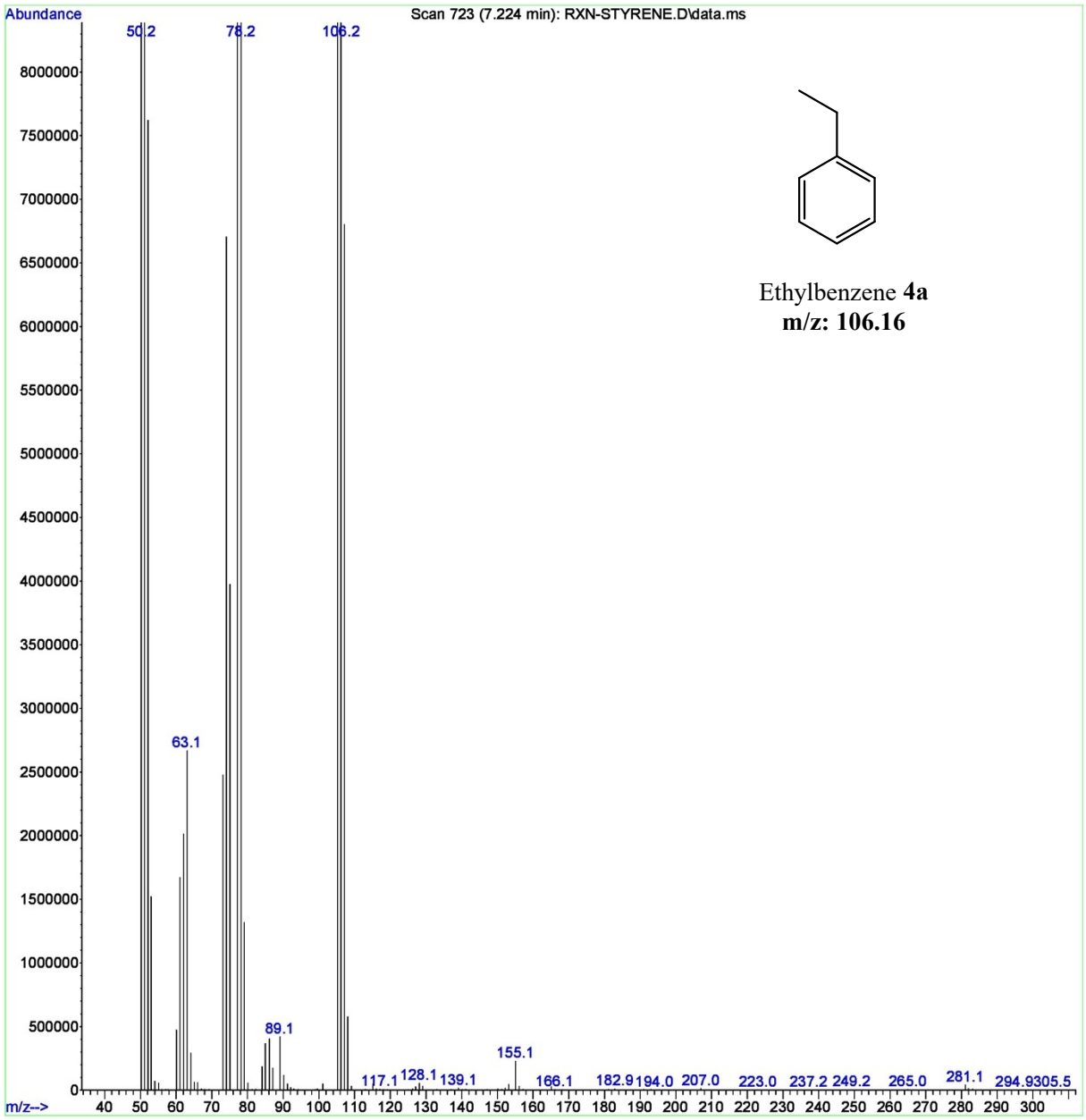


Fig S38 ^{1}H NMR of acid salt **2p** in DMSO-D_6 (Table 2, Entry 2p)

Hydrogenation of Styrene

Instrument : GCMSD
Sample Name: RXN-styrene
Misc Info :
Vial Number: 1



Ethylbenzene **4a**
m/z: 106.16

Fig S39 GC-MS spectrum for one-pot hydrogenation of styrene, **3a** to ethylbenzene, **4a** using benzyl alcohol as hydrogen source and $Pd_{0.2}$@NiO as catalyst under optimized conditions