

Sustainable Access to Sulfonic Acids from Halides and Thiourea Dioxide with Air

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Supporting Information

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I. General Information

^1H and ^{13}C NMR spectra were recorded on 400 MHz NMR spectrometers (Bruker AVANCE), using D_2O , Chemical shifts are reported in parts per million (ppm), Chemical shifts for protons are reported in part per million relative to chloroform (D_2O & 4.79), Data are represented as follows: Chemical shift, multiplicity (br = broad, s = singlet, d = triplet, q = quartet, m = multiple), coupling constants in Hertz (Hz), integration, Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra. IR spectra were recorded on TENSOR (27) Series FT-IR 241. Spectrometers.

II. General procedure for synthesis of aryl sulfonic acid

Under air atmosphere, aromatic iodine **1** (0.5 mmol, 1.0 equiv.), thiourea dioxide (1.5 mmol, 3.0 equiv.), $\text{PdCl}_2(\text{dppf})$ (0.0125 mmol, 2.5 mol %), Cs_2CO_3 (1.0 mmol, 2.0 equiv.), and DMSO (5 mL) were added to a Schlenk tube. The mixture was stirred at $100\text{ }^\circ\text{C}$ for 14 h, and the solvent was removed under vacuum. Water was added to dilute the residue, and the mixture was acidified with aq. HCl. Some insoluble impurities were filtered through a medium filter paper. The filtrate was extracted with DCM, and the aqueous layer was concentrated to remove the solvent under vacuum. Subsequently, 20 mL MeOH/DCM (1:1) was added to the residue solid. The mixture was filtered through a medium filter paper once again, and the filter cake was washed with MeOH/DCM (1:1) several times. The organic layers were combined and evaporated under vacuum. Purification by HPLC afforded aryl sulfonic acid **2** (0.1% CH_3COOH aq / trituration). The method is shown as follow:

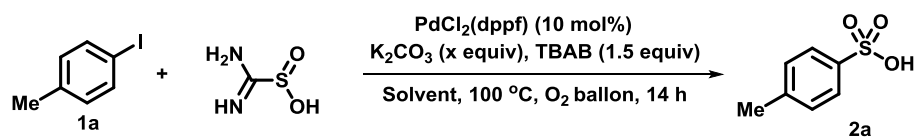
	Time(min)	A%(0.1% CH ₃ COOH aq)	B% (CH ₃ CN)	Speed(mL/min)
1	0.00	95.0	5.0	3.0 mL/min
2	5.00	95.0	5.0	
3	8.00	45.0	55.0	
4	16.00	30.0	70.0	
5	20.00	30.0	70.0	
6	25.00	5.0	95.0	
7	29.00	5.0	95.0	
8	31.00	95.0	5.0	
9	35.00	95.0	5.0	

III. General procedure for synthesis of alkyl sulfonic acid

Under air atmosphere, alkyl bromide (0.5 mmol, 1.0 equiv.), thiourea dioxide (1.5 mmol, 3.0 equiv.), Cs₂CO₃ (1.0 mmol, 2.0 equiv.), KI (1.0 mmol, 2.0 equiv.) and DMSO (5 mL) were added to a Schlenk tube. The mixture was stirred at 100 °C for 14 h, and the solvent was removed under vacuum. Water was added to dilute the residue, and the mixture was acidified with aq. HCl. Some insoluble impurities were filtered through a medium filter paper. The filtrate was extracted with DCM, and the aqueous layer was concentrated to remove the solvent under vacuum. Subsequently, 20 mL MeOH/DCM (1:1) was added to the residue solid. The mixture was filtered through a medium filter paper once again, and the filter cake was washed with MeOH/DCM (1:1) several times. The organic layers were combined and evaporated under vacuum. Purification by HPLC afforded alkyl sulfonic acid **3**. The method reference the preparation of aryl sulfonic acid.

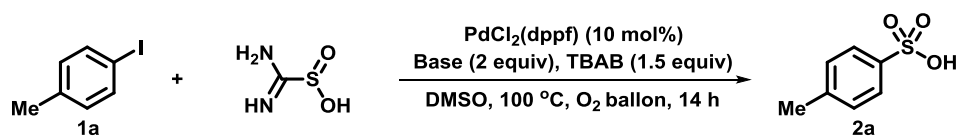
IV. The optimization of reaction conditions

Table S1: Solvent optimization



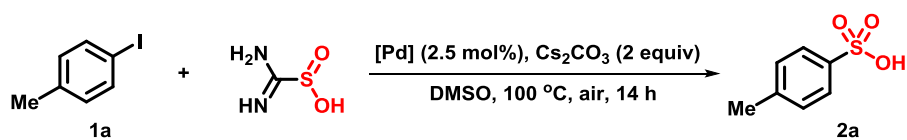
Entry	Base	Solvent	Yield ^[a]
1	K_2CO_3 (3 eq)	MeCN	Trace
2	K_2CO_3 (3 eq)	CCl_3H	Trace
3	K_2CO_3 (3 eq)	Dioxane	5%
4	K_2CO_3 (3 eq)	DCE	Trace
5	K_2CO_3 (3 eq)	H_2O	Trace
6	K_2CO_3 (3 eq)	Toluene	Trace
7	K_2CO_3 (3 eq)	DMF	62 %
8	K_2CO_3 (3 eq)	DMSO	49 %
9	K_2CO_3 (2 eq)	DMF	35 %
10	K_2CO_3 (2 eq)	DMSO	79 %
11	K_2CO_3 (1.5 eq)	DMF	6 %
12	K_2CO_3 (1.5 eq)	DMSO	66 %

[a]Yield is determined by LC-MS using 4-chlorobenzenesulfonic acid as an internal standard.

Table S2 Base optimization

Entry	Base	Yield ^[a]
1	KOH	67%
2	Cs_2CO_3	>95%
3	K_3PO_4	88%
4	NaHCO_3	85%
5	DBU	85%
6	DIPEA	85%
7	DABCO	75%

[a] Yield is determined by LC-MS using 4-chlorobenzenesulfonic acid as an internal standard

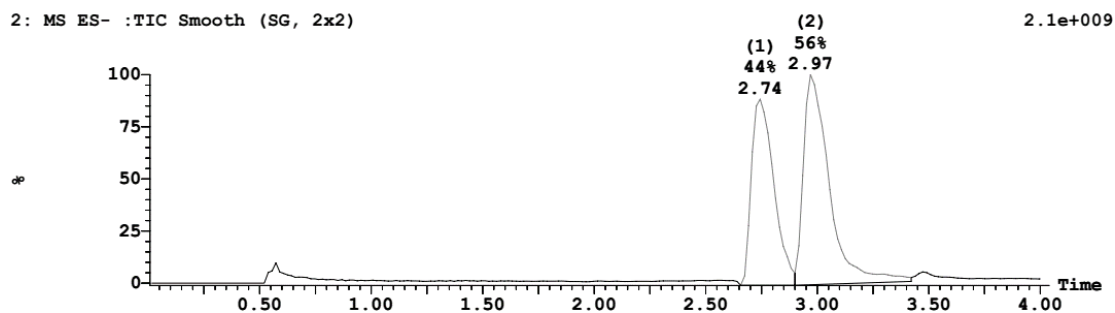
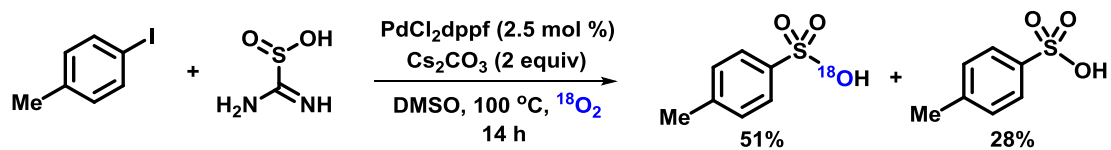
Table S3 Pd catalyst optimization

Entry	[Pd]	Yield ^[a]
1	PdCl_2	6%
2	$\text{Pd}(\text{OAc})_2$	6%
3	$\text{Pd}(\text{dba})_2$	5%
4	$\text{Pd}(\text{acac})_2$	10%
5	$\text{PdCl}_2(\text{dppm})$	10%
6	$\text{PdCl}_2(\text{dppp})$	54%
7	$\text{PdCl}_2(\text{dppf})$	87%

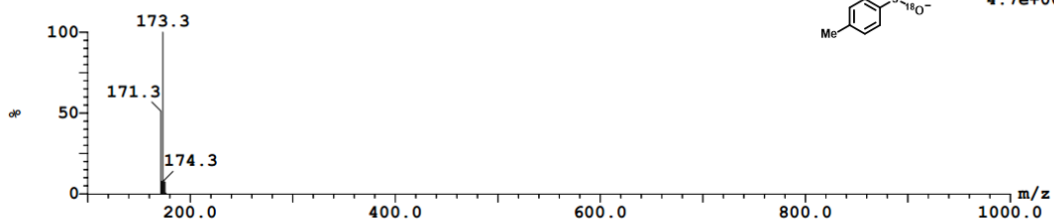
[a] Yield is determined by LC-MS using 4-chlorobenzenesulfonic acid as an internal standard

V. Mechanistic study

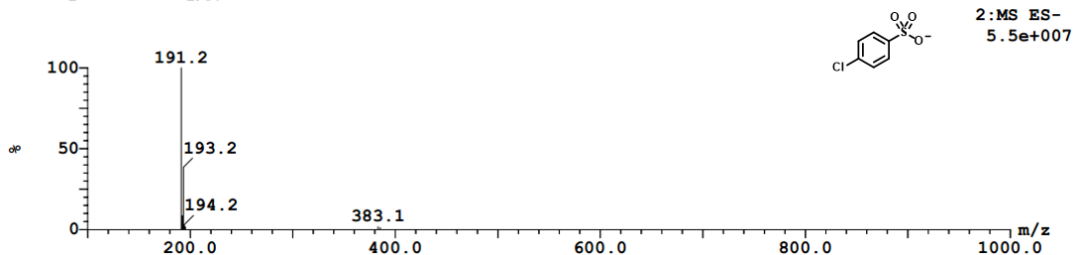
(1)

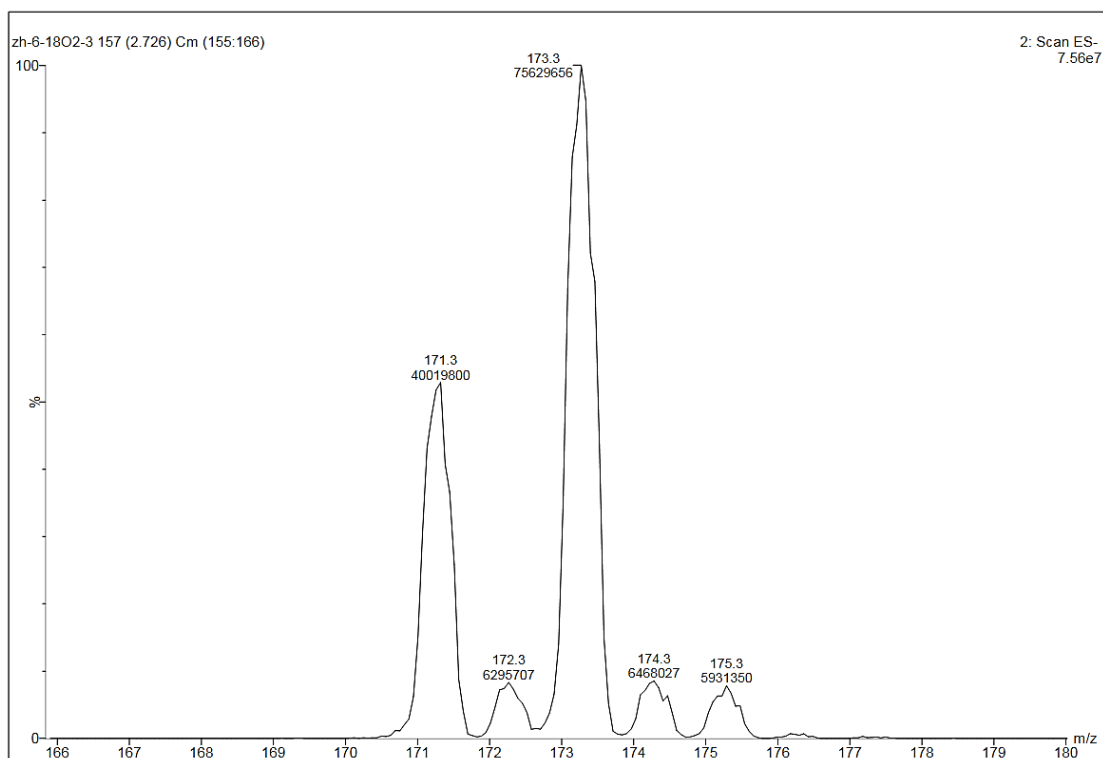


Peak ID	Compound	Time	Mass Found
1		2.74	

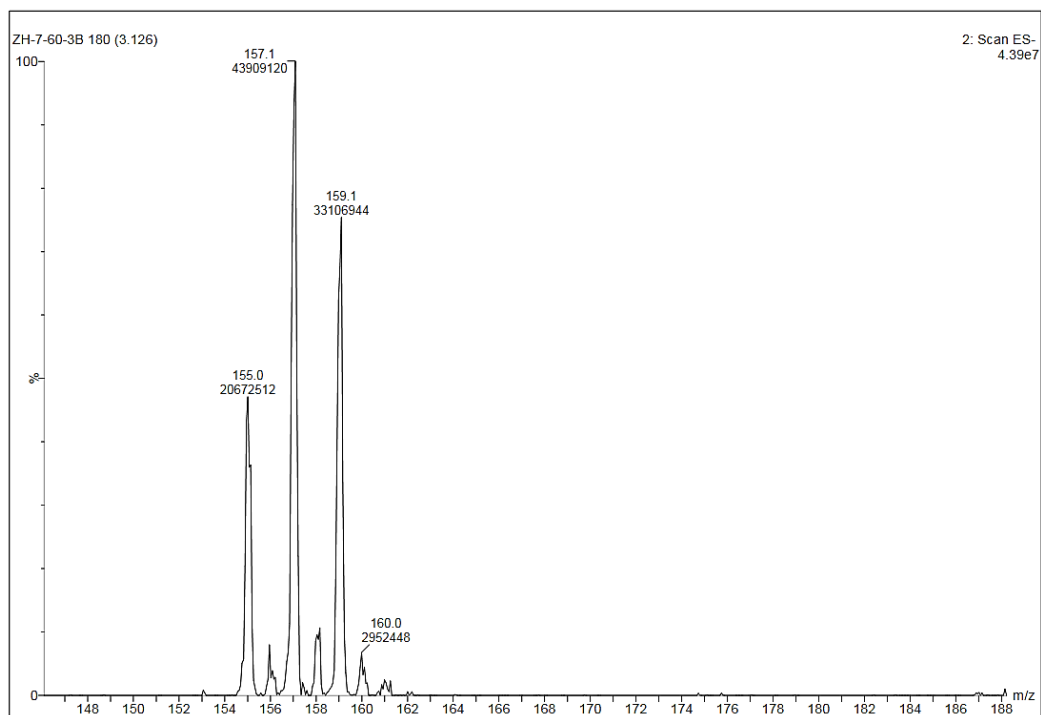
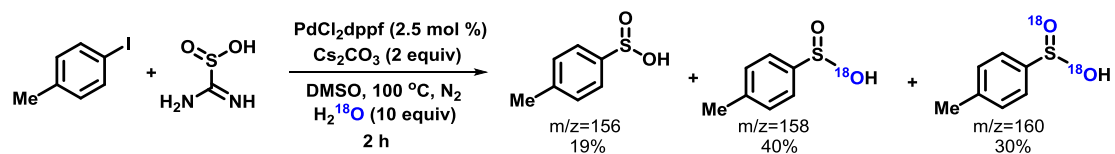


Peak ID	Compound	Time	Mass Found
2		2.97	

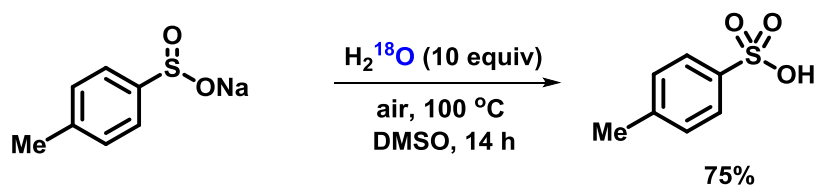




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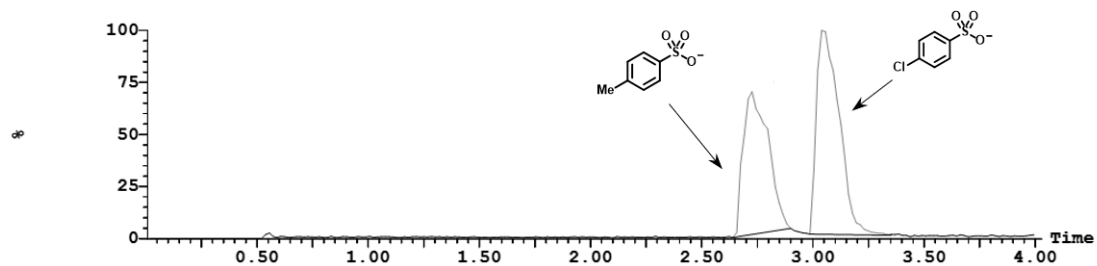


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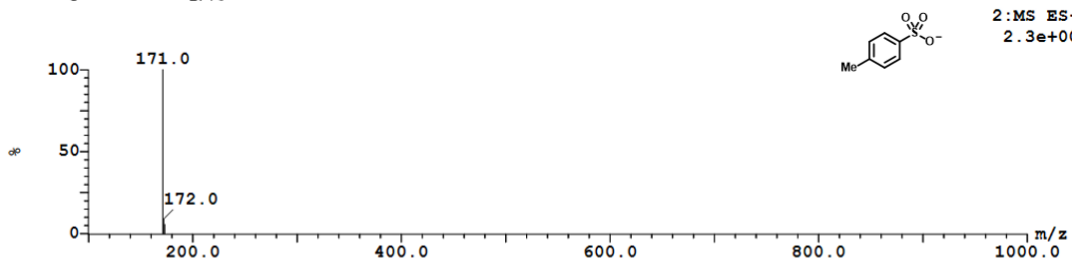


2: MS ES- :TIC

7.8e+008

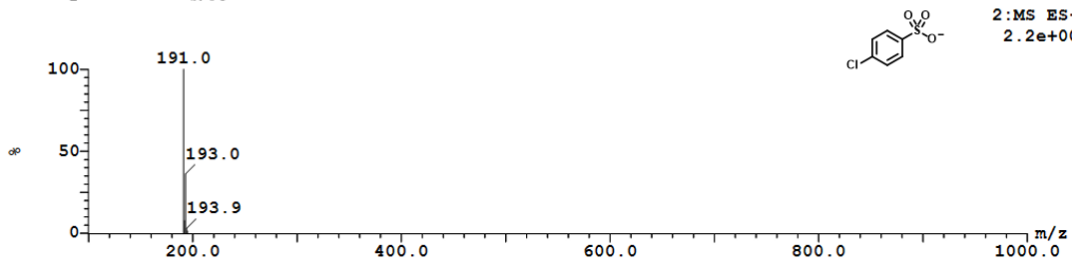


Peak ID	Compound	Time	Mass Found
1		2.73	



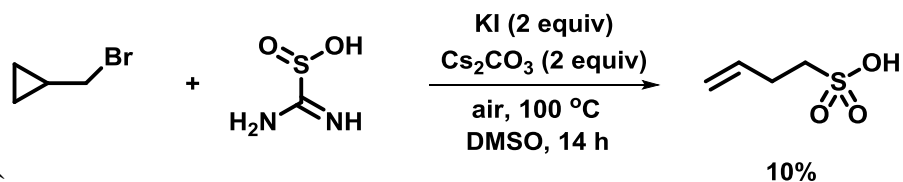
2:MS ES-
2.3e+007

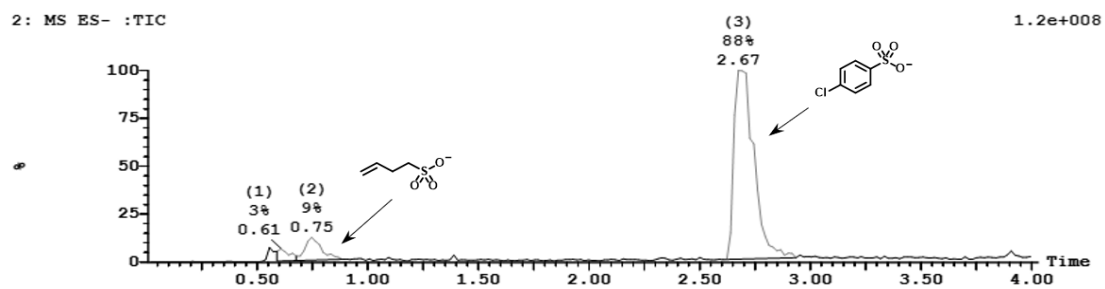
Peak ID	Compound	Time	Mass Found
2		3.04	



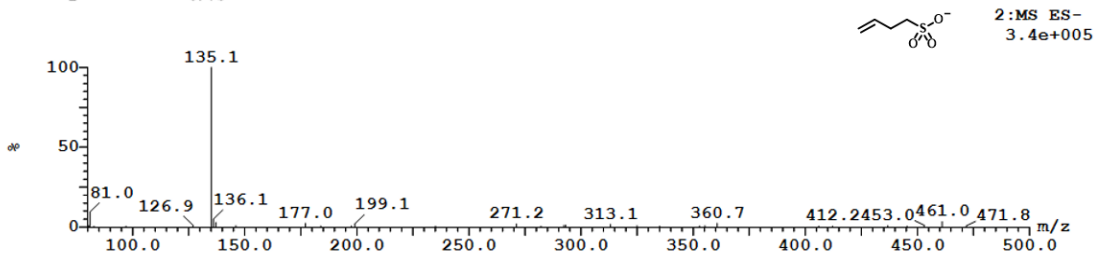
2:MS ES-
2.2e+007

(4)

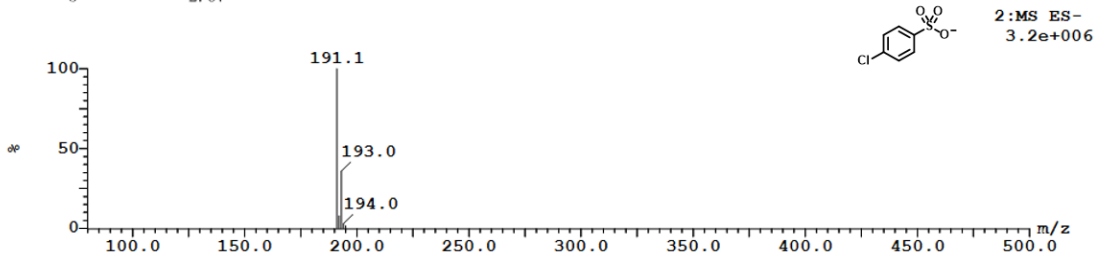




Peak ID Compound Time Mass Found

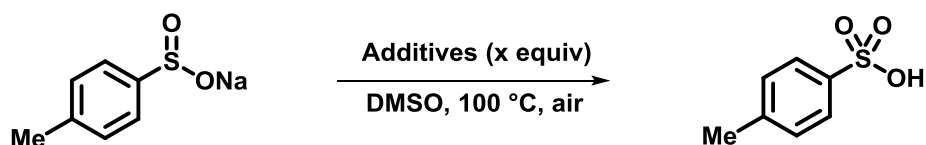


Peak ID Compound Time Mass Found



(5) Control Experiments

All the reactions were conducted under standard conditions with certain amounts of additives.¹ The corresponding yields were determined by LC-MS using 4-chlorobenzenesulfonic acid as an internal standard.

Table S3: Control Experiments

Entry	Additives (x equiv)	Funcations	Yields
1	-	-	84%
2	1,3-diphenylisobenefuran (1 equiv)	O ₂ ⁻ inhibitor	75%
3	9,10-dimethylanthr (1 equiv)	O ₂ ⁻ inhibitor	86%
4	NaN ₃ (1 equiv)	HO [•] inhibitor	72%
5	Co(acac) ₂ (0.06 equiv)	¹ O ₂ inhibitor	89%
6	^t BuOH (1 equiv)	HO [•] inhibitor	72%

(6) Studies on Hydrogen Peroxide

The amount of H₂O₂ was determined by titration with iodide ion, as described previously in the literature^{2,3} in which the reflux procedures was instead by stirring at room temperature. In an iodometric titration, the formation of I₃⁻ and the consumption of H₂O₂ follows a one-to-one ratio as eqs S1-3. The concentration H₂O₂ can be derived from the concentration of I₃⁻ (Abs@361 nm = εb[I₃⁻]). All iodometric titrations are conducted anaerobically to avoid the oxidation of I⁻ to I₃⁻ by O₂.

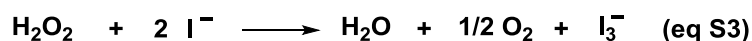
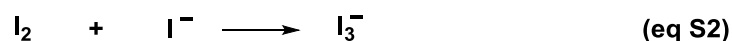
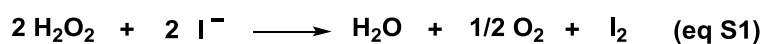
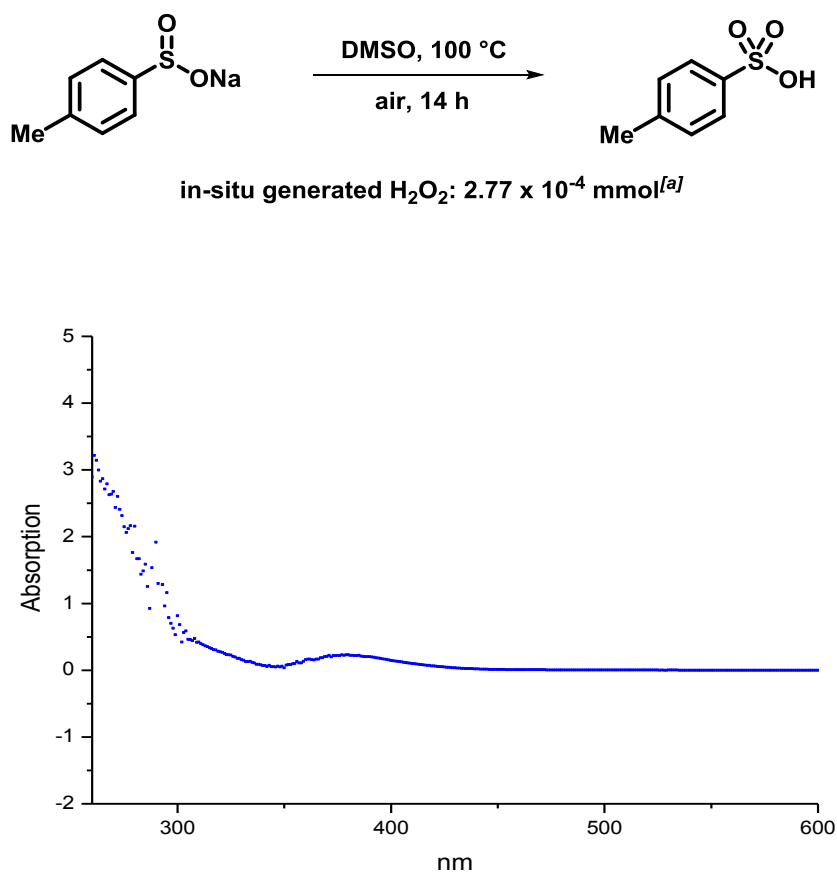


Figure S2: Ultraviolet-visible Absorption of Reaction Systems

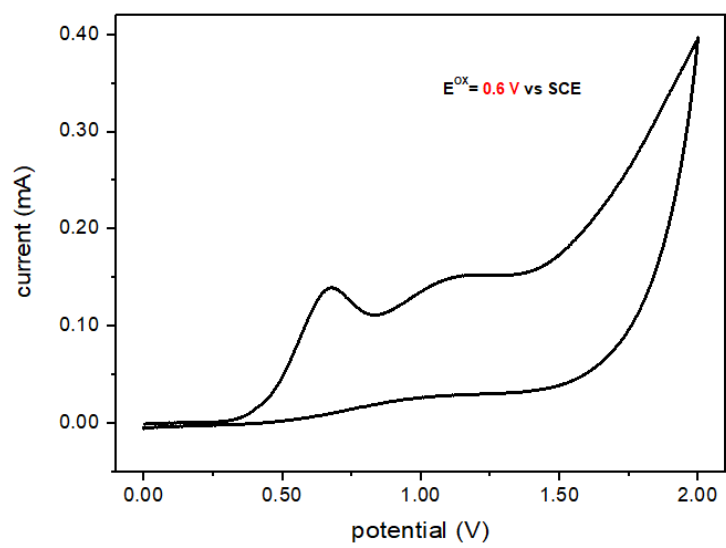


[a] Experiments data based on the UV-Vis Absorption of I^{3-} Generated by different concentration of H_2O_2 and standard curve of the amount of I^{3-} for its quantitative studies.

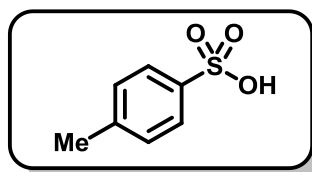
(7) Electrochemical Measurements

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. Samples were prepared with 0.4 mmol of substrate in 10 mL of 0.1 M tetra-n-butylammonium hexafluorophosphate in dry, degassed N, N-Dimethylformamide. Measurements employed a platinum plate working electrode, platinum wire counter electrode, saturated calomel electrode as reference electrode, and a scan rate of 100 mV/s, ranging from 0 V to 3.0 V. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction; the platinum plate working electrode was polished between each scan.

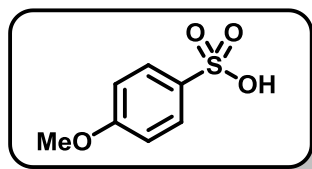
Figure S3: Cyclic Voltammogram of Sodium *p*-Toluenesulfinate



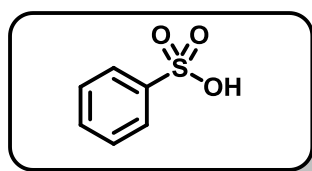
VI. Characterization of sulfonic acid product



(4-methylbenzenesulfonic acid) 2a. Prepared following general procedure using aryl iodine **1a** (109.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2a** in 78% yield. ¹H NMR (400 MHz, D₂O) δ 7.56 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.24 (s, 3H). ¹³C NMR (100 MHz, D₂O) δ 142.4, 139.4, 129.3, 125.3, 20.4. IR ν 1477, 1161, 1033, 816, 686, 565 cm⁻¹. HRMS (ESI) for C₇H₇O₃S: Calculated: 171.0121, [M-H]⁻ found: 171.0112.

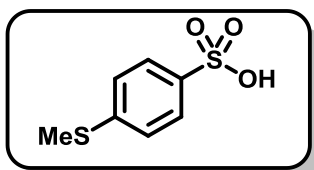


(4-methoxybenzenesulfonic acid) 2b. Prepared following general procedure using aryl iodine **1b** (117.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2b** in 71% yield. ¹H NMR (400 MHz, D₂O) δ 7.66 – 7.64 (m, 2H), 6.92 (dd, J = 6.8, 2.0 Hz, 2H), 3.73 (s, 3H). ¹³C NMR (100 MHz, D₂O) δ 161.1, 134.9, 127.3, 114.0, 55.5. IR ν 1598, 1226, 1091, 1024, 835, 698 cm⁻¹. HRMS (ESI) for C₇H₇O₄S: Calculated: 187.0071, [M-H]⁻ found: 187.0061.

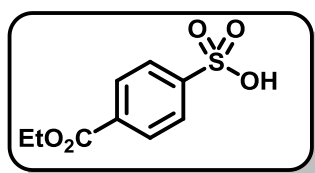


(benzenesulfonic acid) 2c. Prepared following general procedure using aryl iodine **1c** (102.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2c** in 86% yield. ¹H NMR (400 MHz, D₂O) δ 7.85 (dd, J = 8.0, 1.6 Hz, 2H), 7.63 – 7.52 (m, 3H). ¹³C NMR (100 MHz, D₂O) δ 142.3, 131.7, 129.1, 125.4. IR ν 1658, 1446, 1178, 1126, 1018, 733 cm⁻¹. HRMS (ESI) for C₆H₅O₃S: Calculated: 156.9965,

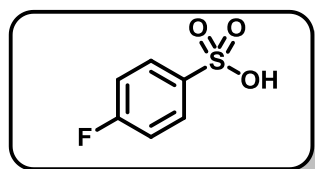
[M-H]⁻ found: 156.9955.



(4-(methylthio)benzenesulfonic acid) 2d. Prepared following general procedure using aryl iodide **1d** (125.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2d** in 53% yield. ¹H NMR (400 MHz, D₂O) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.53 (s, 3H). ¹³C NMR (100 MHz, D₂O) δ 142.8, 138.7, 126.0, 125.8, 14.1. IR ν 1653, 1508, 1084, 1020, 833, 675 cm⁻¹. HRMS (ESI) for C₇H₇O₃S₂: Calculated: 202.9842, [M-H]⁻ found: 202.9834.

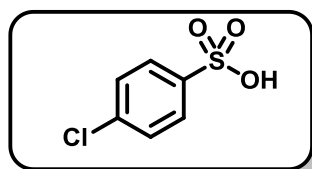


(4-(ethoxycarbonyl)benzenesulfonic acid) 2e. Prepared following general procedure using aryl iodide **1e** (138.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2e** in 60% yield. ¹H NMR (400 MHz, D₂O) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, D₂O) δ 167.9, 146.6, 132.4, 130.0, 125.7, 62.6, 13.4. IR ν 1716, 1458, 1398, 1184, 1101, 630 cm⁻¹. HRMS (ESI) for C₉H₉O₅S: Calculated: 229.0176, [M-H]⁻ found: 229.0170.

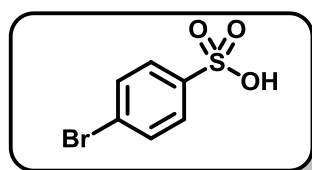


(4-fluorobenzenesulfonic acid) 2f. Prepared following general procedure using aryl iodide **1f** (111.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2f** in 41% yield. ¹H NMR (400 MHz, D₂O) δ 7.93 – 7.85 (m, 2H), 7.36 – 7.27 (m, 2H). ¹³C NMR (100 MHz, D₂O) δ 164.1 (*J* = 249.9 Hz), 138.6, 128.1 (*J* = 9.3 Hz), 115.9 (*J* = 22.6 Hz). ¹⁹F NMR (376 MHz, D₂O) δ -109.05. IR ν 1662,

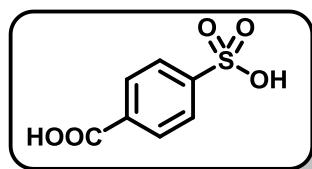
1467, 1020, 829, 613 cm^{-1} . **HRMS (ESI)** for $\text{C}_6\text{H}_4\text{O}_3\text{FS}$: Calculated: 174.9871, $[\text{M}-\text{H}]^-$ found: 174.9861.



(4-chlorobenzenesulfonic acid) 2g. Prepared following general procedure using aryl iodine **1g** (119.2 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $\text{PdCl}_2(\text{dppf})$ (9.2 mg, 0.0125 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2g** in 74% yield. **^1H NMR (400 MHz, D_2O)** δ 7.31 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H). **^{13}C NMR (100 MHz, D_2O)** δ 140.7, 136.7, 128.8, 126.8. **IR** ν 1724, 1479, 1089, 829, 760, 563 cm^{-1} . **HRMS (ESI)** for $\text{C}_6\text{H}_4\text{O}_3\text{ClS}$: Calculated: 190.9575, $[\text{M}-\text{H}]^-$ found: 190.9567.

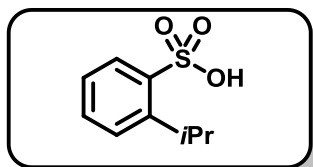


(4-bromobenzenesulfonic acid) 2h. Prepared following general procedure using aryl iodine **1h** (141.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $\text{PdCl}_2(\text{dppf})$ (9.2 mg, 0.0125 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2h** in 75% yield. **^1H NMR (400 MHz, D_2O)** δ 7.56 – 7.51 (m, 2H), 7.51 – 7.46 (m, 2H). **^{13}C NMR (100 MHz, D_2O)** δ 141.4, 131.9, 127.1, 125.3. **IR** ν 1751, 1577, 1473, 1070, 821, 632 cm^{-1} . **HRMS (ESI)** for $\text{C}_6\text{H}_4\text{O}_3^{\text{81}}\text{BrS}$: Calculated: 234.9050, $[\text{M}-\text{H}]^-$ found: 234.9044.

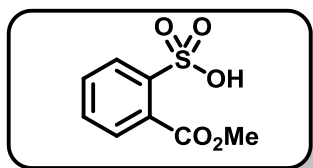


(4-sulfobenzoic acid) 2i. Prepared following general procedure using aryl iodine **1i** (124.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $\text{PdCl}_2(\text{dppf})$ (9.2 mg, 0.0125 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2i** in 67% yield. **^1H NMR (400 MHz, D_2O)** δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.87 (d, $J = 8.4$ Hz, 2H). **^{13}C NMR (100 MHz, D_2O)** δ 170.9, 145.9, 134.4, 130.0, 125.6. **IR** ν 1728, 1516, 1452, 1200, 835, 630 cm^{-1} . **HRMS (ESI)** for $\text{C}_7\text{H}_5\text{O}_5\text{S}$: Calculated: 200.9863,

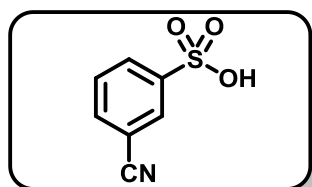
[M-H]⁻ found: 200.9856.



(2-isopropylbenzenesulfonic acid) 2j. Prepared following general procedure using aryl iodine **1j** (123.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2j** in 66% yield. **¹H NMR (400 MHz, D₂O)** δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.55(m, 2H), 7.39 – 7.32 (m, 1H), 3.95 – 3.82 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 6H). **¹³C NMR (100 MHz, D₂O)** δ 147.8, 139.7, 132.1, 127.7, 126.8, 125.8, 29.3, 23.4. **IR** ν 2960, 2870, 1176, 1082, 763, 613 cm⁻¹ **HRMS (ESI)** for C₉H₁₁O₃S: Calculated: 199.0434, [M-H]⁻ found: 199.0427.

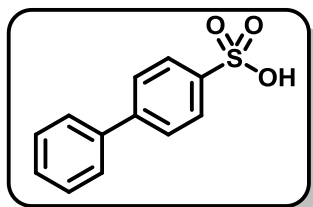


(2-(methoxycarbonyl)benzenesulfonic acid) 2k. Prepared following general procedure using aryl iodine **1k** (131.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2k** in 62% yield. **¹H NMR (400 MHz, D₂O)** δ 8.03 – 7.98 (m, 1H), 7.76 – 7.68 (m, 2H), 7.68 – 7.63 (m, 1H), 4.01 (s, 3H). **¹³C NMR (100 MHz, D₂O)** δ 171.4, 139.9, 131.6, 131.2, 130.6, 128.1, 127.4, 53.6. **IR** ν 1736, 1456, 1082, 754, 621 cm⁻¹. **HRMS (ESI)** for C₈H₇O₅S: Calculated: 215.0020, [M-H]⁻ found: 215.0013.

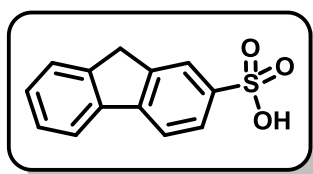


(3-cyanobenzenesulfonic acid) 2l. Prepared following general procedure using aryl iodine **1l** (114.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2l** in 83% yield. **¹H NMR (400 MHz, D₂O)** δ 8.10 (t, *J* = 1.5 Hz, 1H), 8.02 – 7.98 (m, 1H), 7.86 – 7.81 (m, 1H), 7.61 (t, *J* = 7.9 Hz, 1H). **¹³C NMR (100**

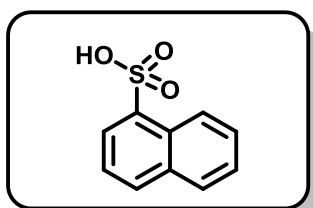
MHz, D₂O) δ 143.6, 135.1, 130.2, 130.0, 129.4, 118.6, 111.9. **IR** ν 2236, 1510, 1473, 847, 800, 619 cm^{-1} . **HRMS (ESI)** for $\text{C}_7\text{H}_4\text{O}_3\text{NS}$: Calculated: 181.9917, $[\text{M}-\text{H}]^-$ found: 181.9908.



(Biphenyl-4-sulfonic acid) 2m. Prepared following general procedure using aryl iodine **1m** (140.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $\text{PdCl}_2(\text{dppf})$ (9.2 mg, 0.0125 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2m** in 81% yield. **¹H NMR (400 MHz, D₂O)** δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 6.8$ Hz, 2H), 7.32 – 7.22 (m, 3H). **¹³C NMR (100 MHz, D₂O)** δ 143.3, 141.2, 139.0, 129.0, 128.2, 127.2, 127.0, 126.0. **IR** ν 1724, 1658, 1456, 1184, 841, 760, 619 cm^{-1} . **HRMS (ESI)** for $\text{C}_{12}\text{H}_9\text{O}_3\text{S}$: Calculated: 233.0278, $[\text{M}-\text{H}]^-$ found: 233.0272.

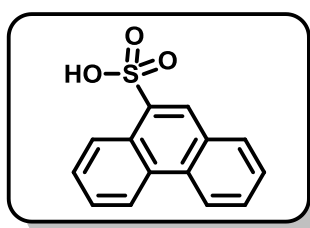


(9H-fluorene-2-sulfonic acid) 2n. Prepared following general procedure using aryl iodine **1n** (146.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), $\text{PdCl}_2(\text{dppf})$ (9.2 mg, 0.0125 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2n** in 72% yield. **¹H NMR (400 MHz, D₂O)** δ 7.85 (s, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.69 – 7.62 (m, 2H), 7.50 – 7.45 (m, 1H), 7.33 (dd, $J = 5.5, 2.9$ Hz, 2H), 3.66 (s, 2H). **¹³C NMR (101 MHz, D₂O)** δ 144.3, 143.9, 143.8, 140.5, 139.7, 127.8, 126.9, 125.1, 124.2, 122.0, 120.5, 119.9, 36.3. **IR** ν 1452, 1223, 1184, 1090, 835, 731, 619 cm^{-1} . **HRMS (ESI)** for $\text{C}_{13}\text{H}_9\text{O}_3\text{S}$: Calculated: 245.0278, $[\text{M}-\text{H}]^-$ found: 245.0273.

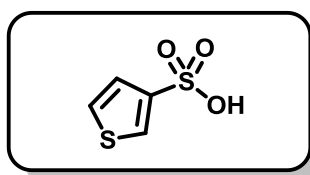


(naphthalene-1-sulfonic acid) 2o. Prepared following general procedure using aryl iodine **1o** (127.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol),

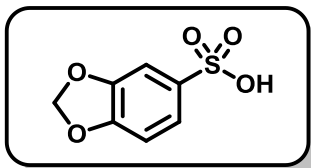
PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2o** in 71% yield. **¹H NMR (400 MHz, D₂O)** δ 8.60 (d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H). **¹³C NMR (100 MHz, D₂O)** δ 137.7, 133.9, 132.7, 128.9, 127.9, 127.7, 126.7, 126.1, 124.9, 124.6. **IR** ν 1745, 1180, 1070, 800, 768, 746, 613 cm⁻¹. **HRMS (ESI)** for C₁₀H₇O₃S: Calculated: 207.0121, [M-H]⁻ found: 207.0113.



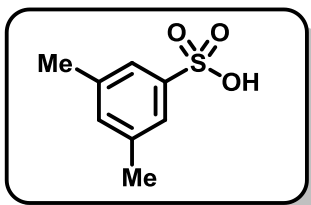
(phenanthrene-9-sulfonic acid) 2p. Prepared following general procedure using aryl iodine **1p** (152.1 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2p** in 64% yield. **¹H NMR (400 MHz, D₂O)** δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 7.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H). **¹³C NMR (100 MHz, D₂O)** δ 136.2, 130.6, 130.4, 129.5, 128.9, 128.5, 127.8, 127.1, 127.0, 127.0, 126.0, 125.8, 122.9, 121.9. **IR** ν 1726, 1163, 1043, 754, 734, 648 cm⁻¹. **HRMS (ESI)** for C₁₄H₉O₃S: Calculated: 257.0278, [M-H]⁻ found: 257.0274.



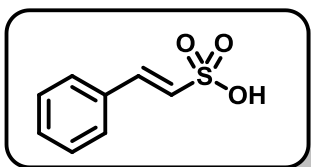
(thiophene-3-sulfonic acid) 2q. Prepared following general procedure using aryl iodine **1q** (105.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2q** in 77% yield. **¹H NMR (400 MHz, D₂O)** δ 7.96 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.60 (dd, *J* = 5.2, 3.2 Hz, 1H), 7.40 (dd, *J* = 5.2, 1.6 Hz, 1H). **¹³C NMR (100 MHz, D₂O)** δ 142.3, 128.4, 127.4, 124.9. **IR** ν 1508, 1178, 1082, 1020, 611 cm⁻¹. **HRMS (ESI)** for C₄H₃O₃S₂: Calculated: 162.9529, [M-H]⁻ found: 162.9519.



(benzo[d][1,3]dioxole-5-sulfonic acid) 2r. Prepared following general procedure using aryl iodine **1r** (124.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2r** in 82% yield. **¹H NMR (400 MHz, D₂O)** δ 7.35 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 2H). **¹³C NMR (100 MHz, D₂O)** δ 149.7, 147.5, 136.1, 120.4, 108.2, 106.0, 102.1. **IR** ν 2831, 1163, 1118, 1072, 808, 708, 629 cm⁻¹. **HRMS (ESI)** for C₇H₅O₅S: Calculated: 200.9863, [M-H]⁻ found: 200.9856.

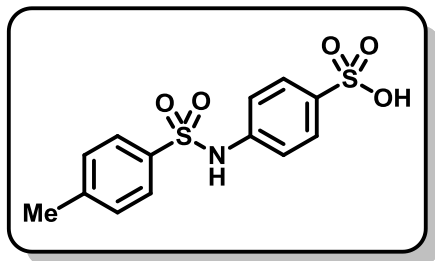


(3,5-dimethylbenzenesulfonic acid) 2s. Prepared following general procedure using aryl iodine **1s** (116.0 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2s** in 65% yield. **¹H NMR (400 MHz, D₂O)** δ 7.40 (s, 2H), 7.22 (s, 1H), 2.32 (s, 6H). **¹³C NMR (100 MHz, D₂O)** δ 142.1, 139.3, 132.8, 122.7, 20.3. **IR** ν 1452, 1205, 1086, 1020, 706 cm⁻¹. **HRMS (ESI)** for C₈H₉O₃S: Calculated: 185.0278, [M-H]⁻ found: 185.0269.



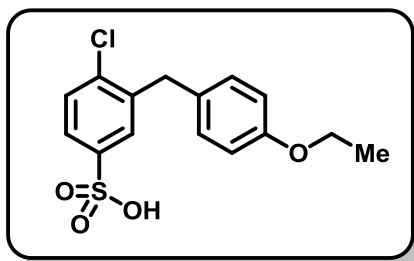
((E)-2-phenylethene-1-sulfonic acid) 2t. Prepared following general procedure using beta-bromostyrene **1t** (91.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2t** in 57% yield. **¹H NMR (400 MHz, D₂O)** δ 7.60 (dt, *J* = 5.6, 3.5 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.35 (d, *J* = 15.7 Hz, 1H), 7.03 (d, *J* = 15.7 Hz, 1H). **¹³C NMR (100 MHz, D₂O)** δ 136.9, 133.5, 130.2, 129.1, 127.9, 127.7. **IR** ν 1744, 1579, 1186, 1035, 746 cm⁻¹. **HRMS (ESI)** for C₈H₇O₃S: Calculated: 183.0121,

[M-H]⁻ found: 183.0113.



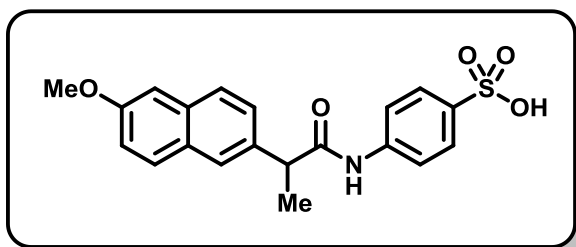
(4-((4-methylphenyl)sulfonamido)benzenesulfonic acid) 2u. Prepared following general procedure using aryl iodine **1u** (186.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃

(325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2u** in 83% yield. **¹H NMR (400 MHz, D₂O)** δ 7.65 – 7.60 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 2.10 (s, 3H). **¹³C NMR (100 MHz, D₂O)** δ 145.3, 139.3, 138.8, 134.1, 129.9, 126.9, 126.9, 120.2, 20.6. **IR** ν 1329, 1157, 1090, 839, 914, 613 cm⁻¹. **HRMS (ESI)** for C₁₃H₁₂O₅NS₂: Calculated: 326.0162, [M-H]⁻ found: 326.0160.



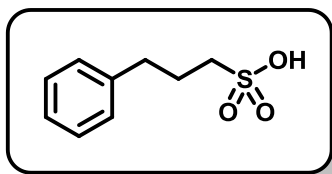
(4-chloro-3-(4-ethoxybenzyl)benzenesulfonic acid) 2v. Prepared following general procedure using aryl iodine **1v** (186.3 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃

(325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2v** in 52% yield. **¹H NMR (400 MHz, D₂O)** δ 7.52 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 3.60 (s, 2H), 3.47 (q, *J* = 6.8 Hz, 2H), 0.97 (t, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, D₂O)** δ 156.6, 141.6, 139.6, 136.6, 131.0, 129.8, 129.7, 127.9, 124.9, 114.4, 63.6, 37.9, 14.1. **IR** ν 1510, 1232, 1163, 1026, 736, 648 cm⁻¹. **HRMS (ESI)** for C₁₅H₁₄O₄ClS: Calculated: 325.0307, [M-H]⁻ found: 325.0303.



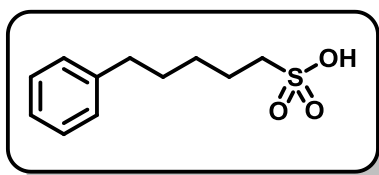
(4-(2-(6-methoxynaphthalen-2-yl)propanamido)benzenesulfonic acid) 2w.

Prepared following general procedure using aryl iodide **1w** (215.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), PdCl₂(dppf) (9.2 mg, 0.0125 mmol), Cs₂CO₃ (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **2w** in 56% yield. ¹H NMR (400 MHz, D₂O) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.16 (m, 3H), 7.03-7.01 (m, 3H), 6.51 (d, *J* = 7.9 Hz, 1H), 6.34 (s, 1H), 3.51 (d, *J* = 5.7 Hz, 1H), 3.10 (s, 3H), 1.15 (d, *J* = 5.6 Hz, 3H). ¹³C NMR (100 MHz, D₂O) δ 174.9, 156.7, 139.8, 138.5, 135.7, 133.2, 128.9, 128.4, 127.0, 126.3, 125.5, 120.2, 118.2, 105.4, 54.5, 46.5, 17.7. IR ν 1508, 1233, 1163, 1091, 1031, 835 cm⁻¹. HRMS (ESI) for C₂₀H₁₈O₅NS: Calculated: 384.0911, [M-H]⁻ found: 384.0907.



(3-phenylpropane-1-sulfonic acid) 3a. Prepared following general procedure using alkyl bromide **2a'** (99.50 mg, 0.5 mmol), thiourea dioxide (99.6 mg, 1.5 mmol), KI (166.00 mg, 1.0 mmol), Cs₂CO₃ (325.8 mg,

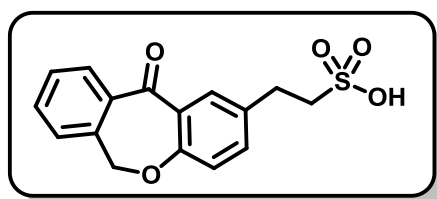
1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **3a** in 57% yield. ¹H NMR (400 MHz, D₂O) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.22-7.18 (m, 3H), 2.83 (dd, *J* = 9.0, 6.7 Hz, 2H), 2.67 (dd, *J* = 14.1, 6.5 Hz, 2H), 2.03 – 1.93 (m, 2H). ¹³C NMR (100 MHz, D₂O) δ 141.5, 128.6, 128.5, 126.2, 50.4, 33.6, 25.8. IR ν 2830, 1452, 1169, 1032, 750, 629 cm⁻¹. HRMS (ESI) for C₉H₁₁O₃S: Calculated: 199.0434, [M-H]⁻ found: 199.0426.



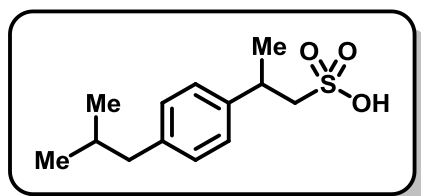
(5-phenylpentane-1-sulfonic acid) 3b. Prepared following general procedure using alkyl bromide **2b'** (113.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), KI (166.00 mg, 1.0 mmol), Cs₂CO₃

(325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for

14 h to afford product **3b** in 43% yield. $^1\text{H NMR}$ (400 MHz, D_2O) δ 7.15 (t, $J = 7.1$ Hz, 2H), 7.07-7.02 (m, 3H), 2.80 – 2.72 (m, 2H), 2.44 (t, $J = 7.1$ Hz, 2H), 1.72 – 1.60 (m, 2H), 1.51 – 1.39 (m, 2H), 1.29 – 1.19 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, D_2O) δ 142.7, 128.4, 128.3, 125.6, 51.1, 35.1, 30.5, 27.6, 24.0. **IR** ν 1594, 1454, 1167, 1016, 765, 613 cm^{-1} . **HRMS** (ESI) for $\text{C}_{11}\text{H}_{15}\text{O}_3\text{S}$: Calculated: 227.0747, $[\text{M-H}]^-$ found: 227.0742.

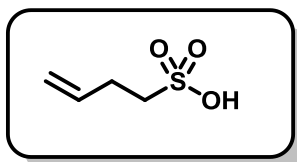


(2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)ethane-1-sulfonic acid) **3c**. Prepared following general procedure using alkyl bromide **2c'** (158.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), KI (166.00 mg, 1.0 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 $^\circ\text{C}$ for 14 h to afford product **3c** in 53% yield. $^1\text{H NMR}$ (400 MHz, D_2O) δ 7.73 (d, $J = 2.3$ Hz, 1H), 7.64 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.59 (td, $J = 7.2, 1.2$ Hz, 1H), 7.46 (td, $J = 7.6, 0.8$ Hz, 1H), 7.32 (dd, $J = 13.0, 4.7$ Hz, 2H), 6.80 (t, $J = 6.7$ Hz, 1H), 4.97 (s, 2H), 3.12 – 3.04 (m, 2H), 2.99 – 2.90 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, D_2O) δ 193.7, 159.6, 139.2, 136.6, 135.6, 133.7, 133.2, 130.4, 129.3, 128.8, 128.1, 124.3, 120.8, 73.1, 52.0, 29.4. **IR** ν 1489, 1163, 1035, 758, 835, 609 cm^{-1} . **HRMS** (ESI) for $\text{C}_{16}\text{H}_{13}\text{O}_5\text{S}$: Calculated: 317.0489, $[\text{M-H}]^-$ found: 317.0486.



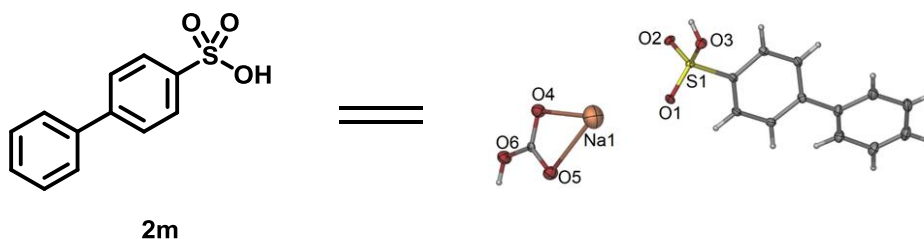
(2-(4-isobutylphenyl)propane-1-sulfonic acid) **3d**. Prepared following general procedure using alkyl bromide **2d'** (127.6 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), KI (166.00 mg, 1.0 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 $^\circ\text{C}$ for 14 h to afford product **3d** in 61% yield. $^1\text{H NMR}$ (400 MHz, D_2O) δ 7.19 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 3.32 – 3.21 (m, 1H), 3.21 – 3.07 (m, 2H), 2.40 (d, $J = 7.1$ Hz, 2H), 1.84 – 1.71 (m, $J = 13.3, 6.6$ Hz, 1H), 1.36 (d,

$J = 6.8$ Hz, 3H), 0.84 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, D_2O) δ 143.4, 140.1, 129.4, 126.7, 58.3, 44.4, 35.8, 29.7, 21.8, 21.4. IR ν 2960, 2913, 1151, 1020, 847, 629 cm^{-1} . HRMS (ESI) for $\text{C}_{13}\text{H}_{19}\text{O}_3\text{S}$: Calculated: 255.1060, $[\text{M}-\text{H}]^-$ found: 255.1059.



(3-Butene-1-sulfonic acid) 5. Prepared following general procedure using alkyl bromide **4** (67.5 mg, 0.5 mmol), thiourea dioxide (162.2 mg, 1.5 mmol), KI (166.00 mg, 1.0 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol), DMSO (5 mL), the reaction mixture was stirred at 100 °C for 14 h to afford product **5** in 10% yield. ^1H NMR (400 MHz, D_2O) δ 6.30 – 6.14 (m, 1H), 5.51 – 5.34 (m, 2H), 3.34 – 3.22 (m, 2H), 2.81 – 2.70 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 136.4, 116.5, 50.6, 28.7. IR ν 1653, 1204, 1174, 1045, 594 cm^{-1} . HRMS (ESI) for $\text{C}_4\text{H}_7\text{O}_3\text{S}$: Calculated: 135.0121, $[\text{M}-\text{H}]^-$ found: 135.0111.

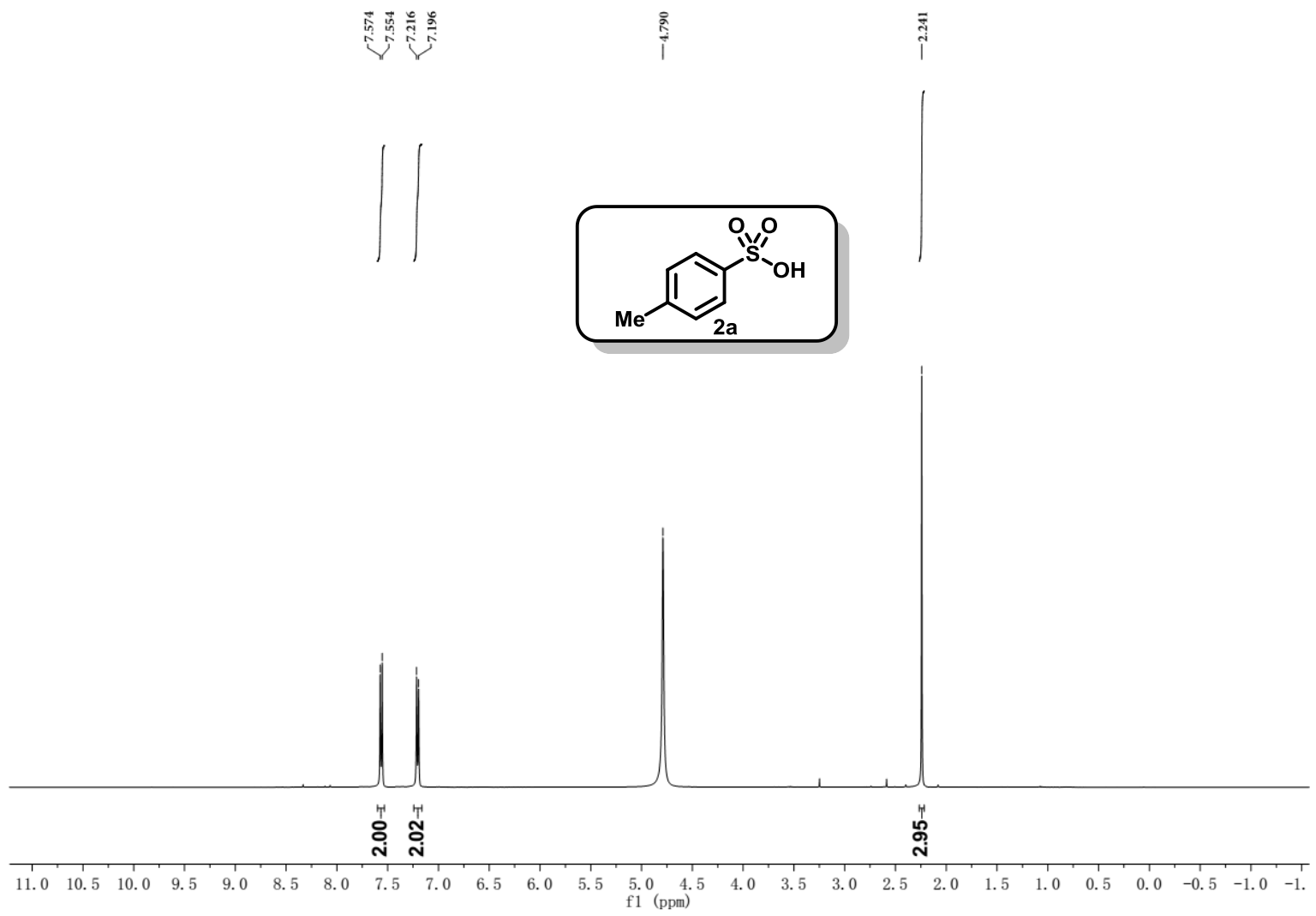
VII. X-Ray crystal structure

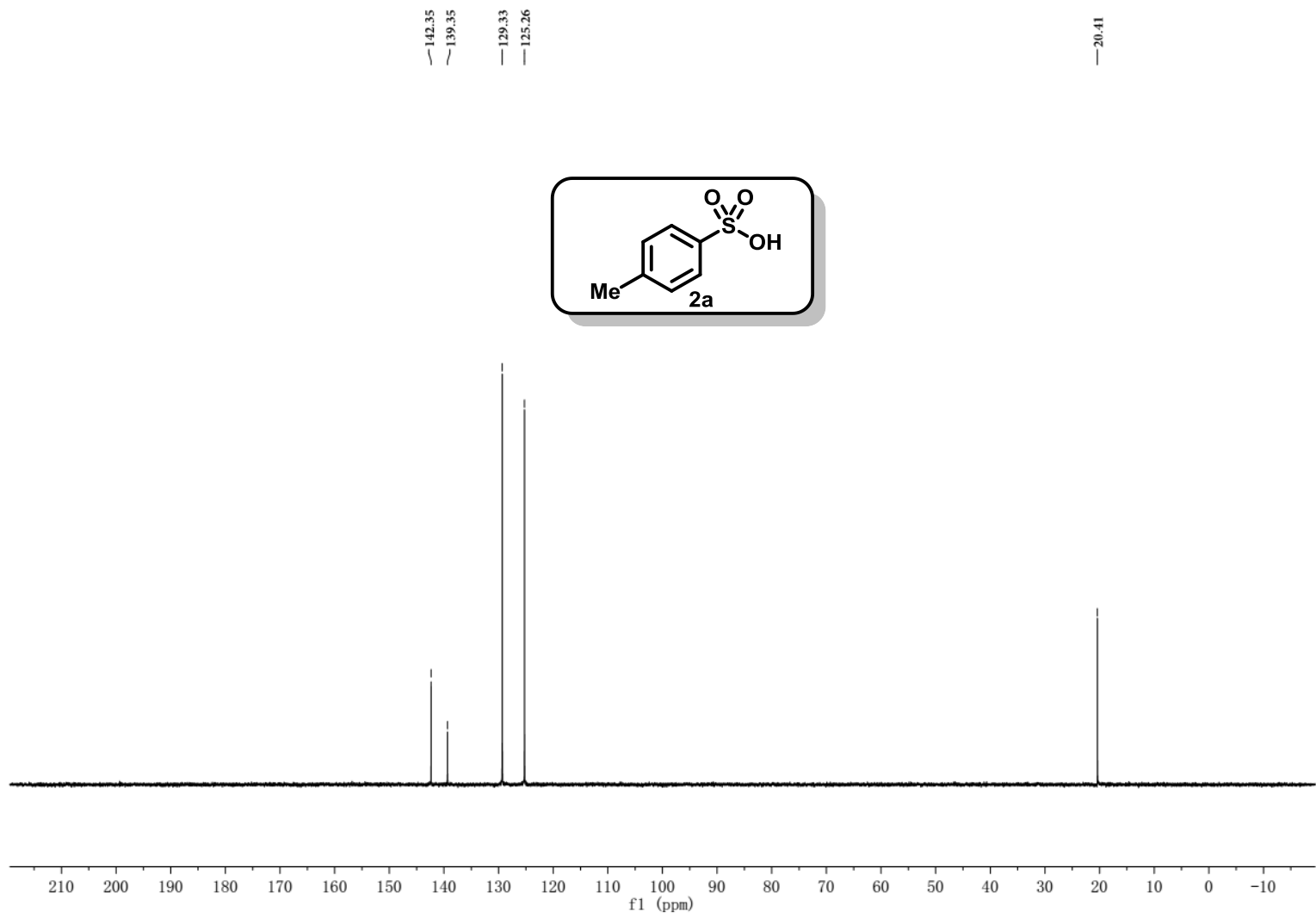


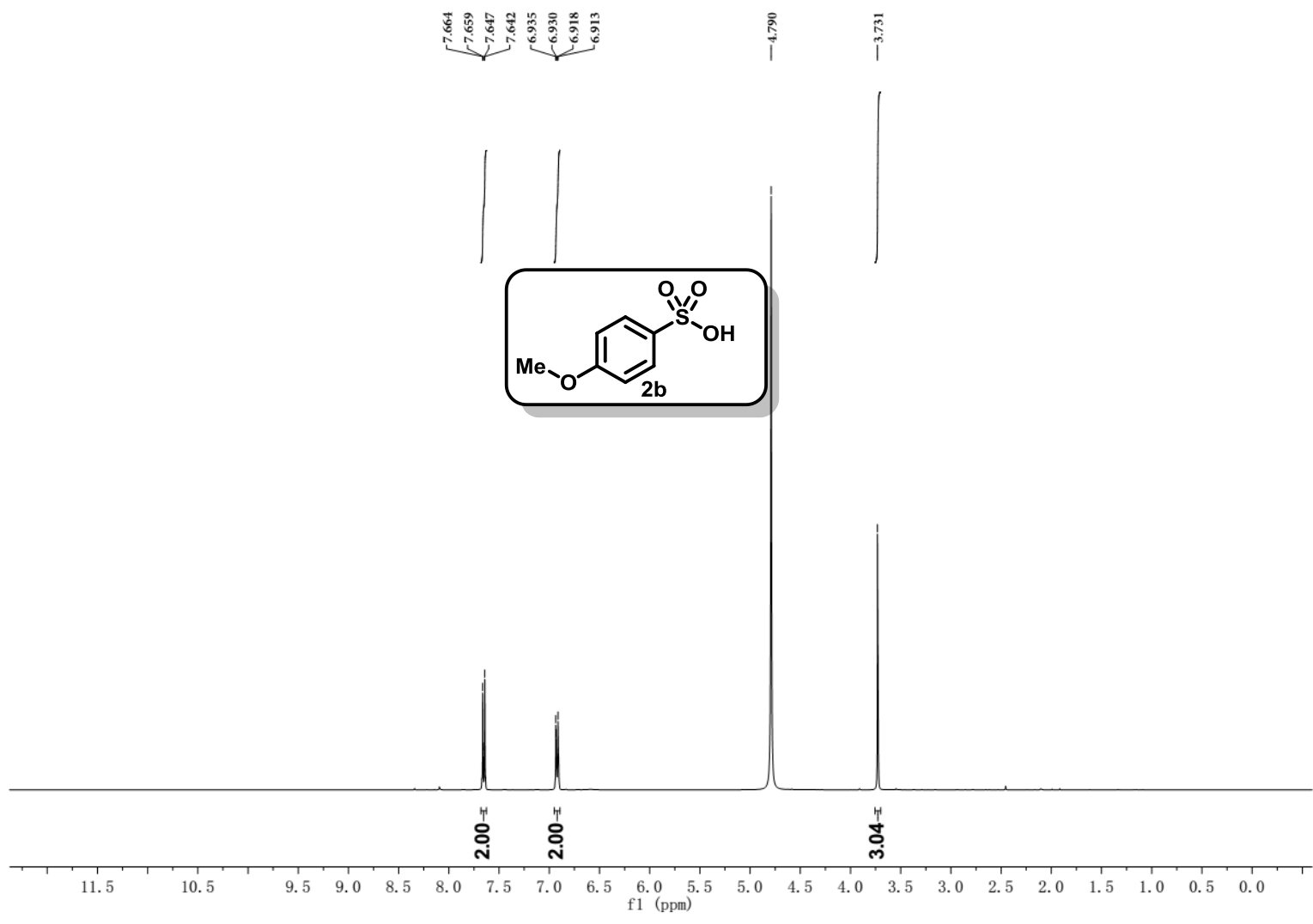
Bond precision:	O-C 0.0030
Cell:	Wavelength = 1.54184
	a = 16.2484(1) $\alpha = 90$
	b = 11.3597(1) $\beta = 100.148(1)$
	c = 8.2456(1) $\gamma = 90$
Temperature:	100 K
Volume:	1498.14(2)
Space group:	P 1 21/c 1
Sum formula	C13 H11 Na O6 S
Mr	318.27
Dx, g cm ⁻³	1.411
Z	4
Mu (mm ⁻¹)	2.432
F000	656.0
h,k,lmax	19,13,9
Nref	2563
Tmin, Tmax	0.382, 1.000
Correction method= # Reported T	Tmin = 0.382 Tmax = 1.000
Limits	
AbsCorr = MULTI-SCAN	
Data completeness	0.960
Theta(max)	67.074
R(reflections)	0.0725(2515)
wR2(reflections)	0.1609(2563)
S	1.166
Npar	302

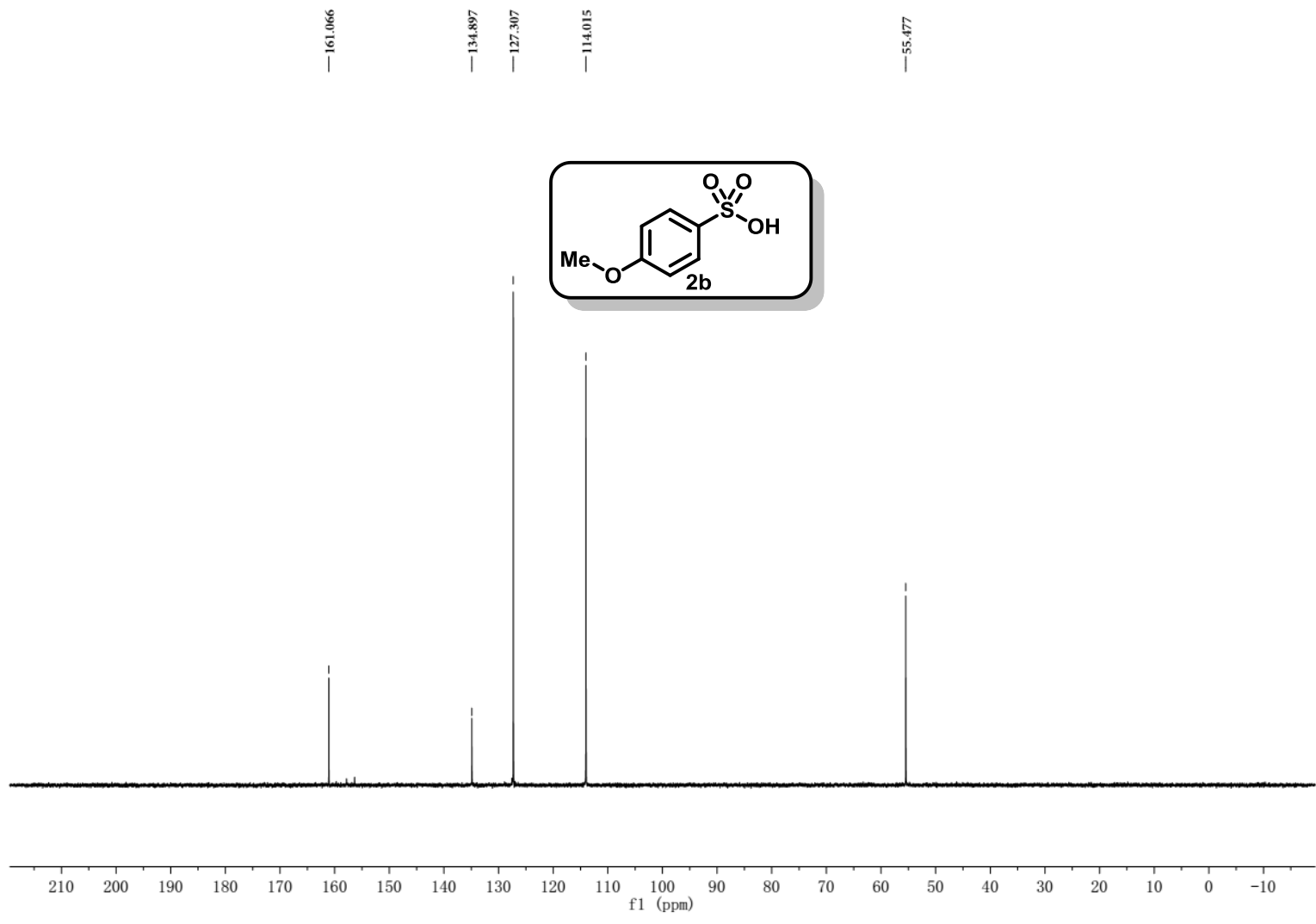
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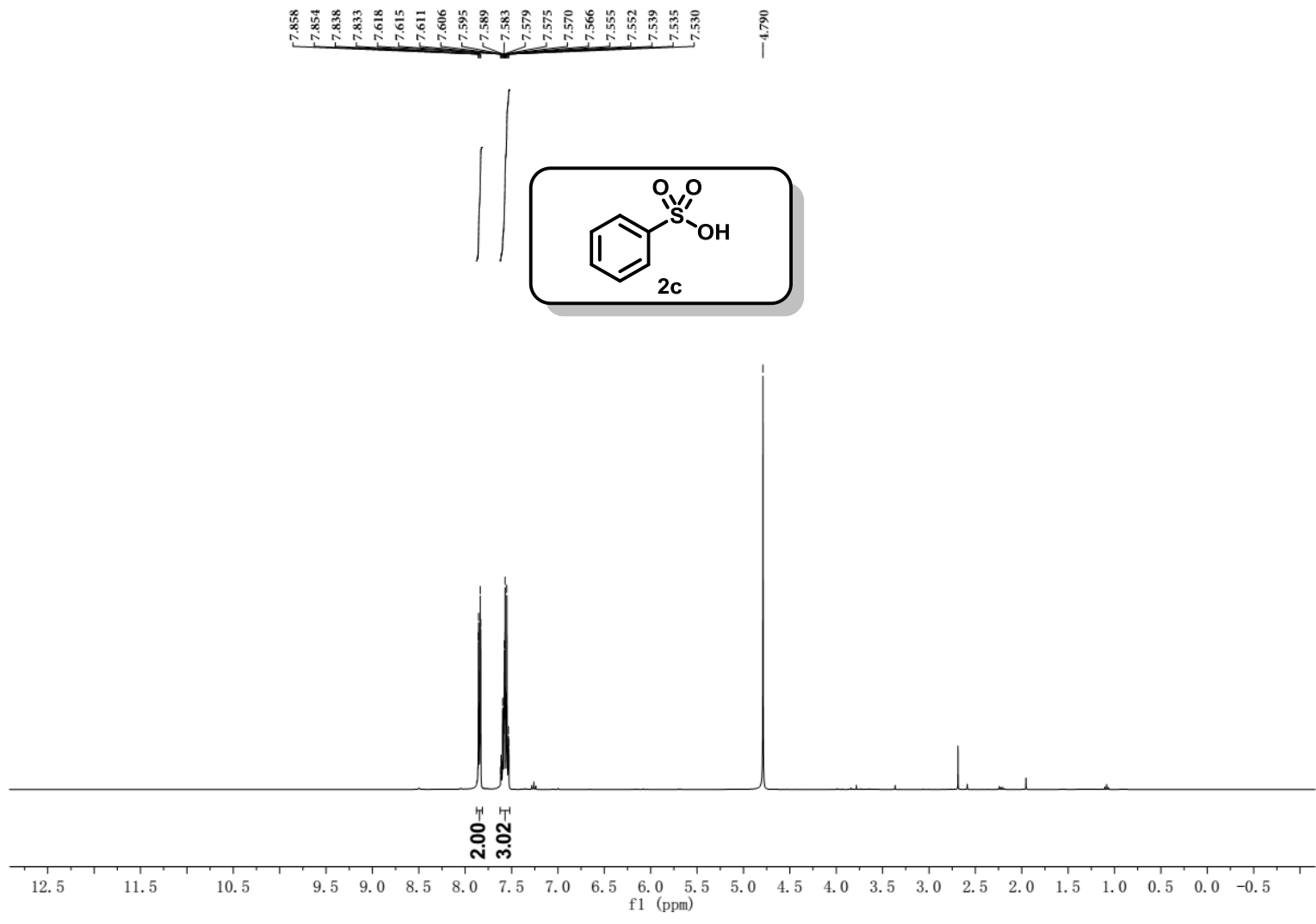
1. Y. Nosaka and A. Y. Nosaka, *Chem. Rev.* 2017, **117**, 11302.
2. R. D. Mair and A. J. Graupner. *Anal. Chem.* 1964, **36**, 194.
3. Y. Li, S. A. Rizvi, D. Hu, D. Sun, A. Gao, Y. Zhou, J. Li and X. Jiang. *Angew. Chem., Int. Ed.*, 2019, **58**, 13499.

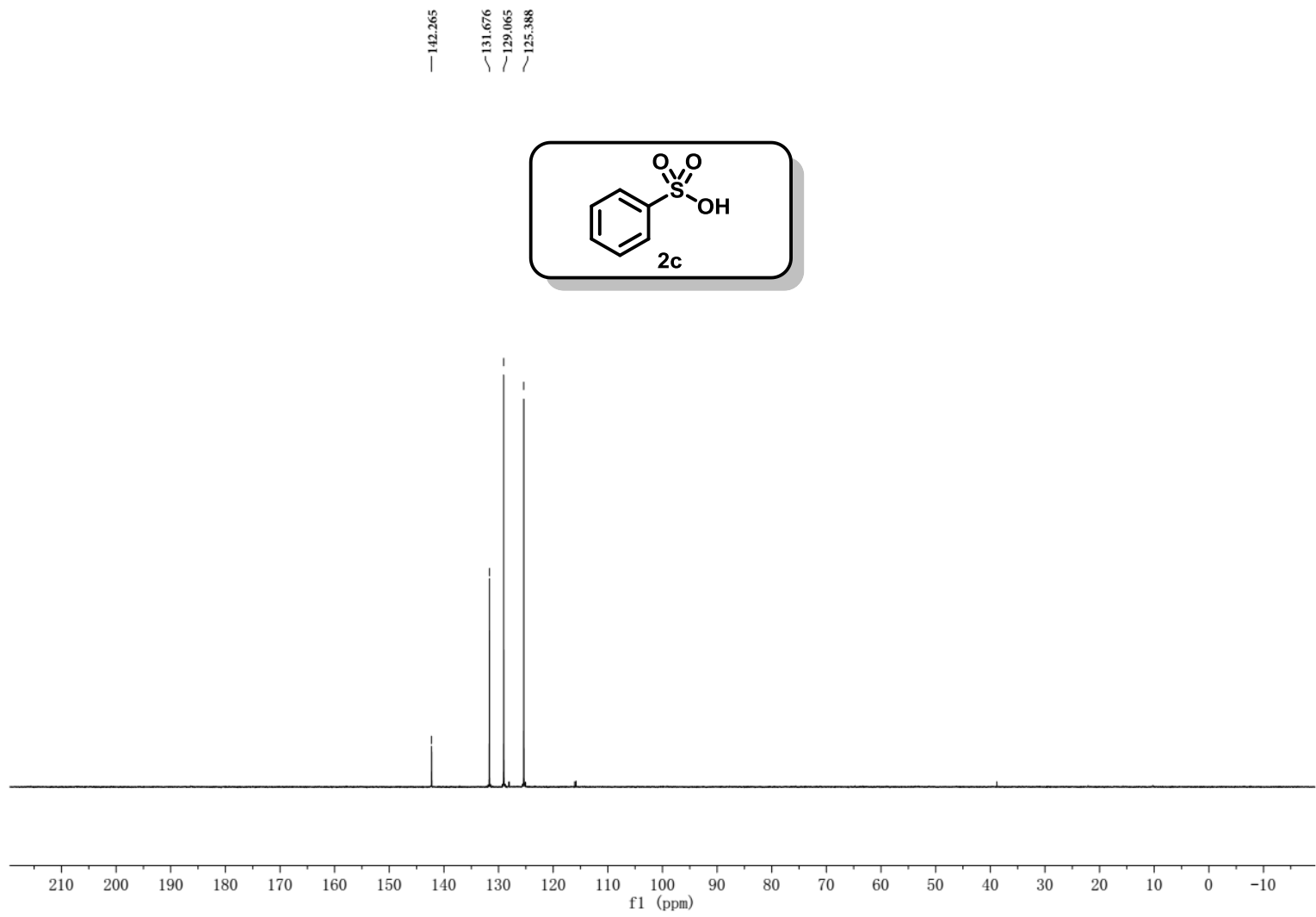


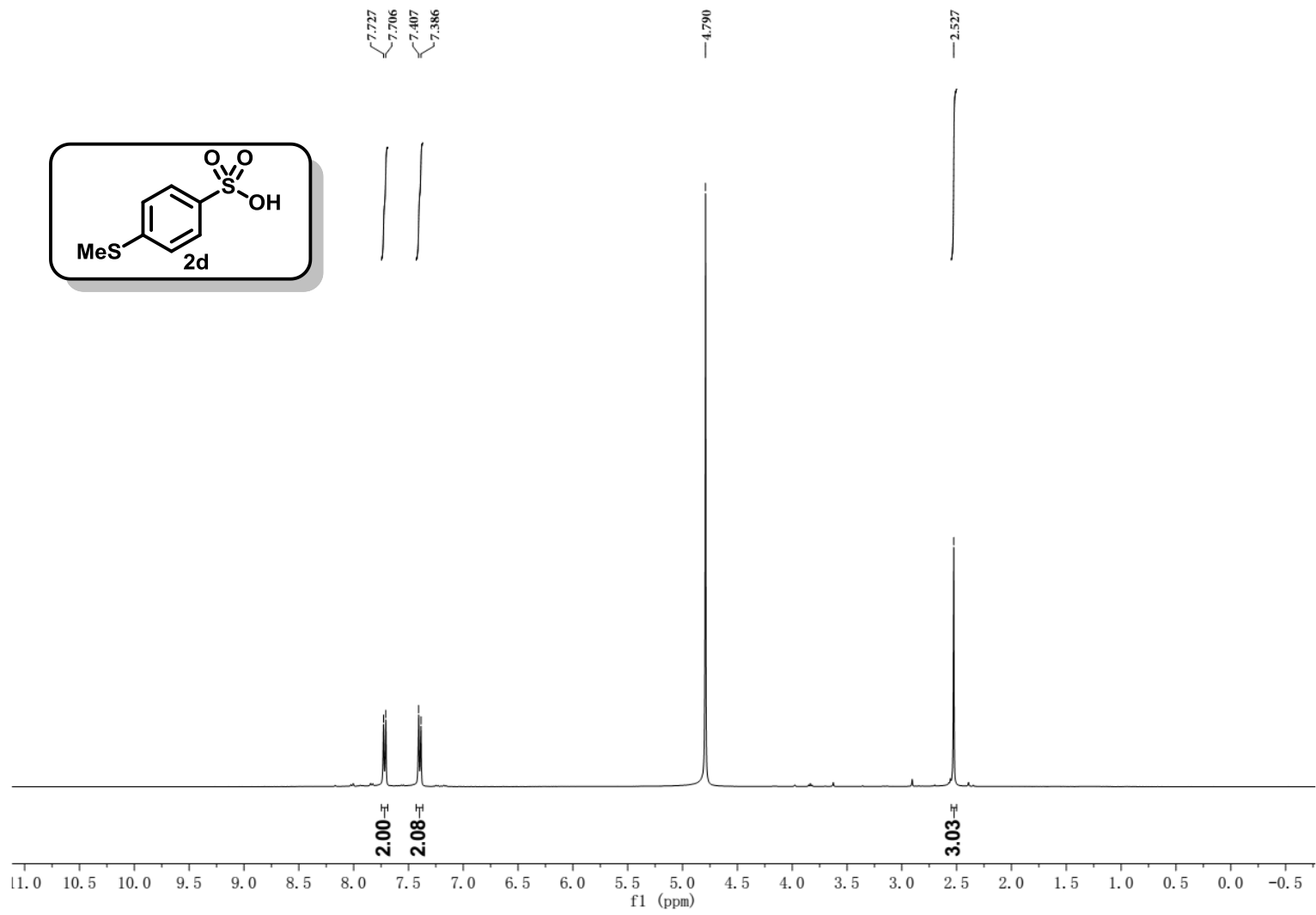


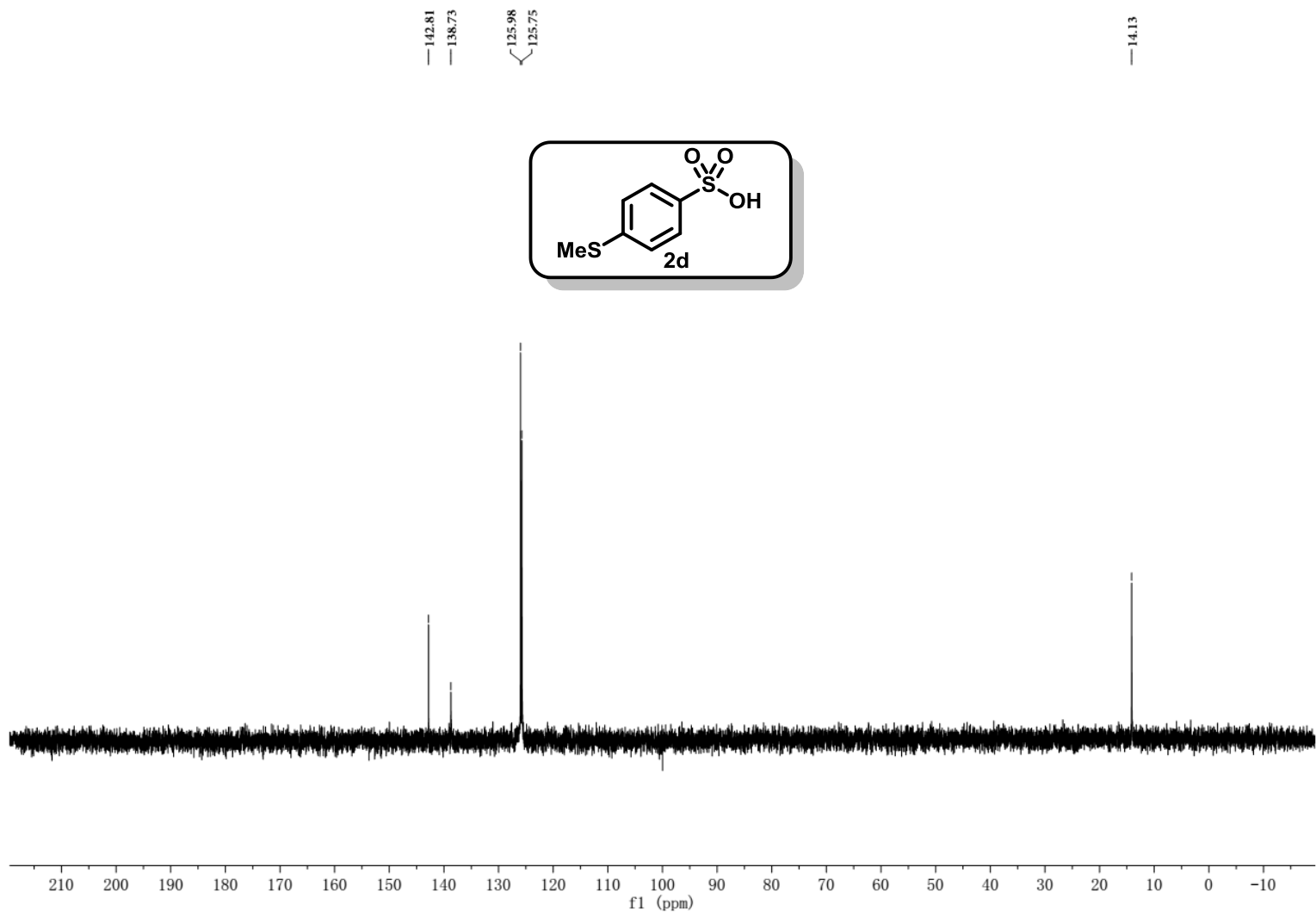


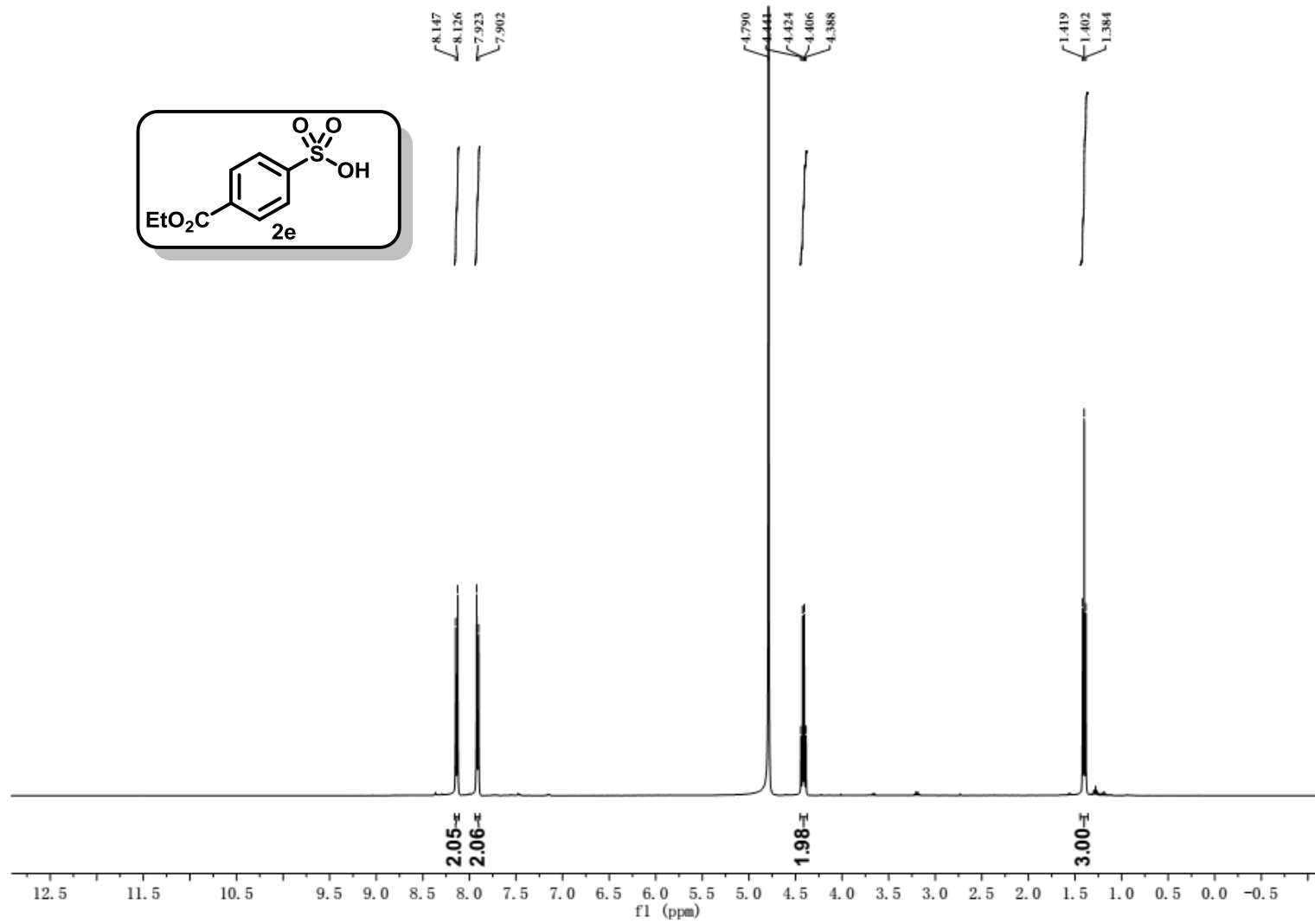


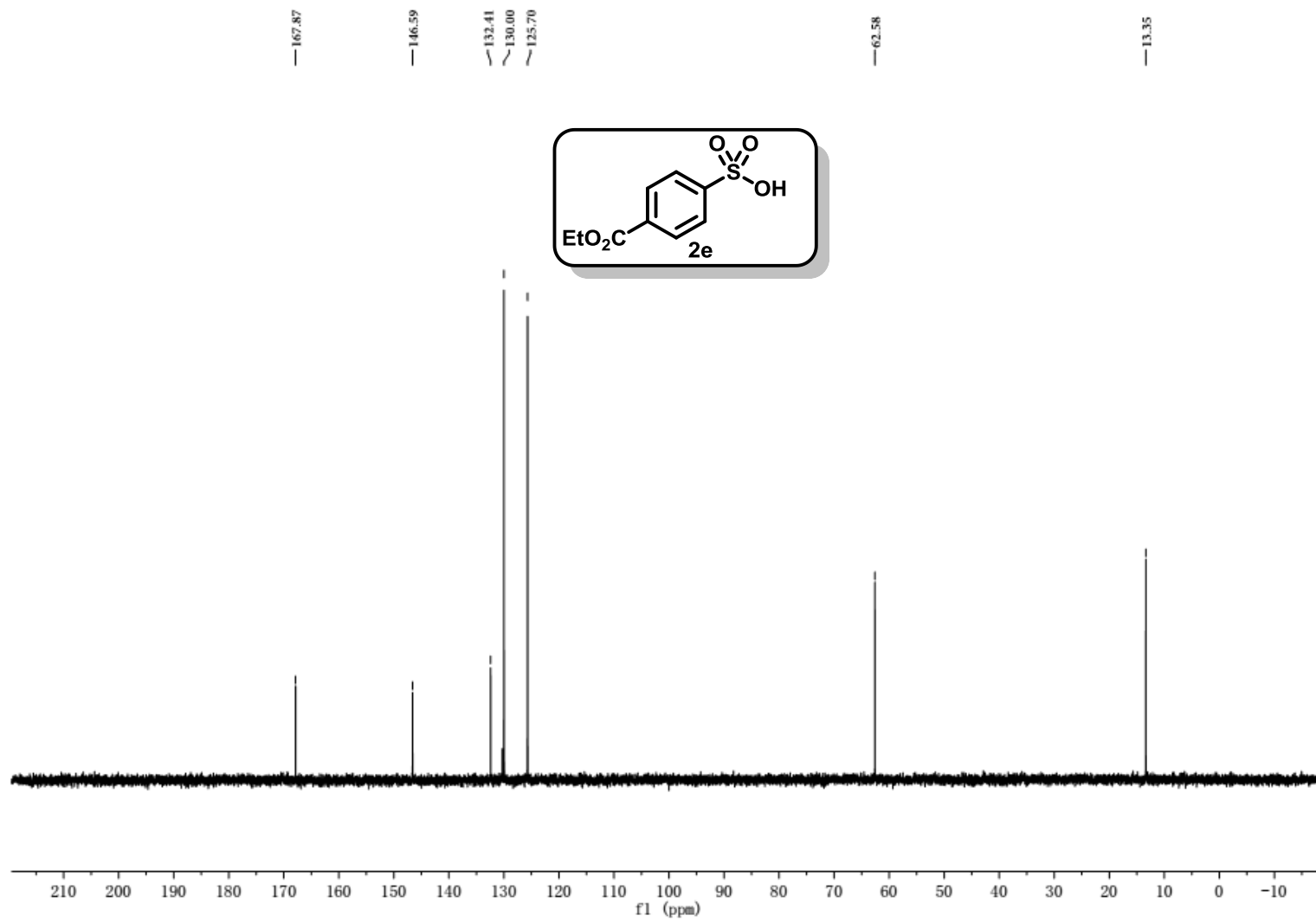


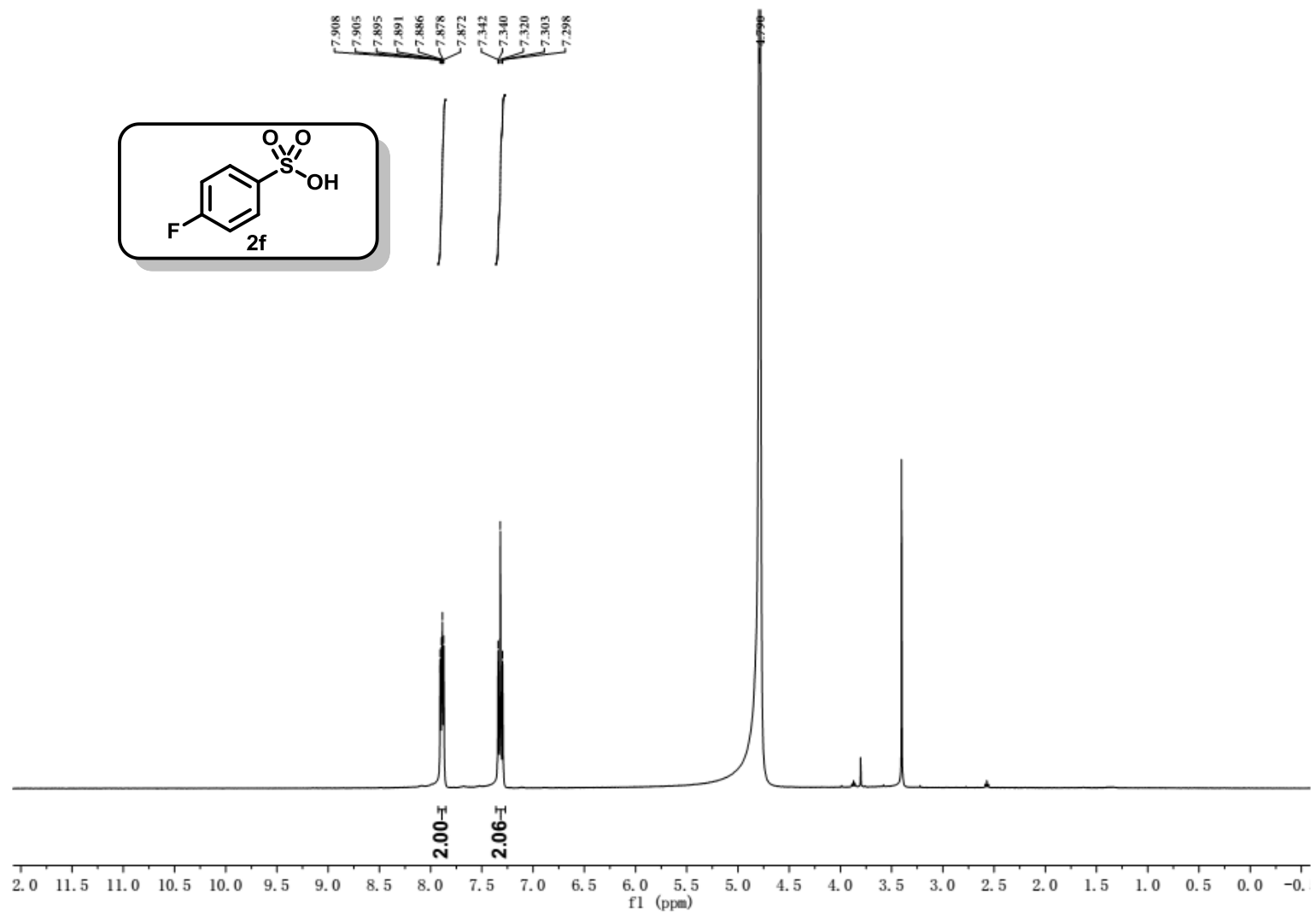










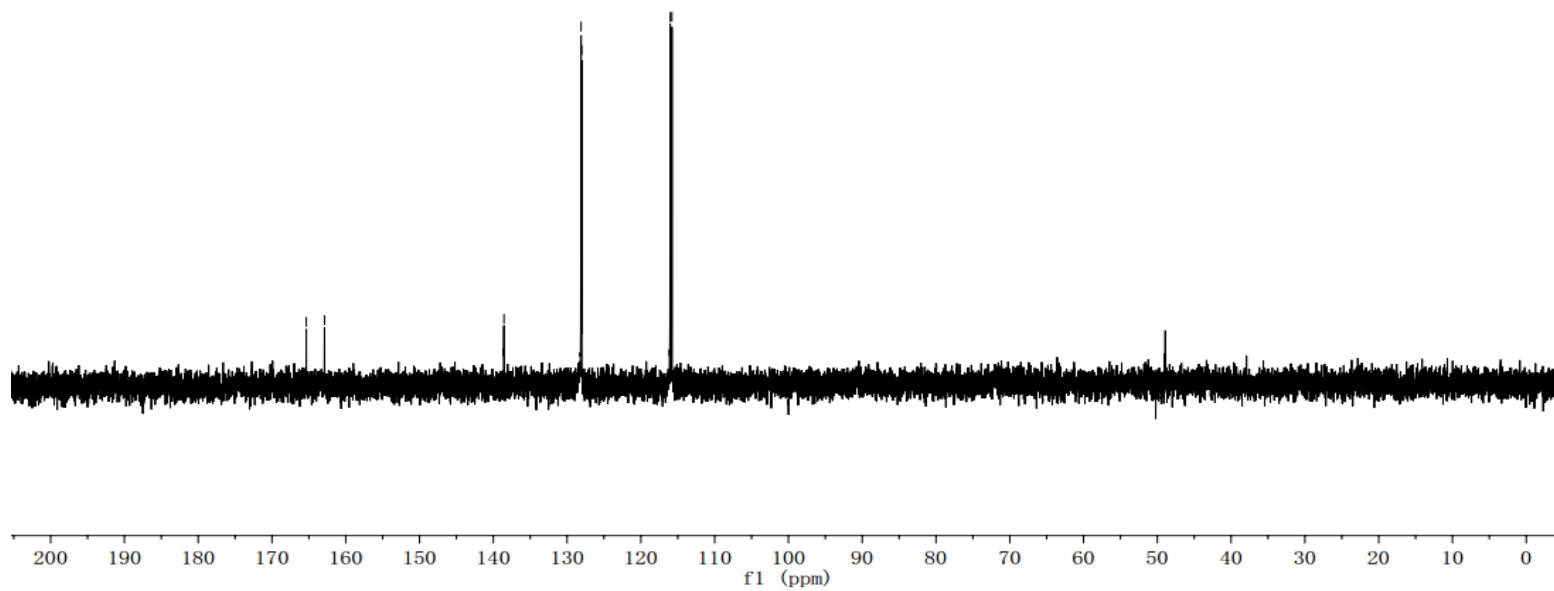
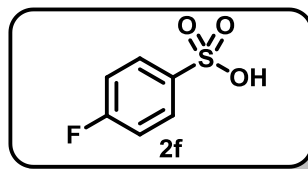


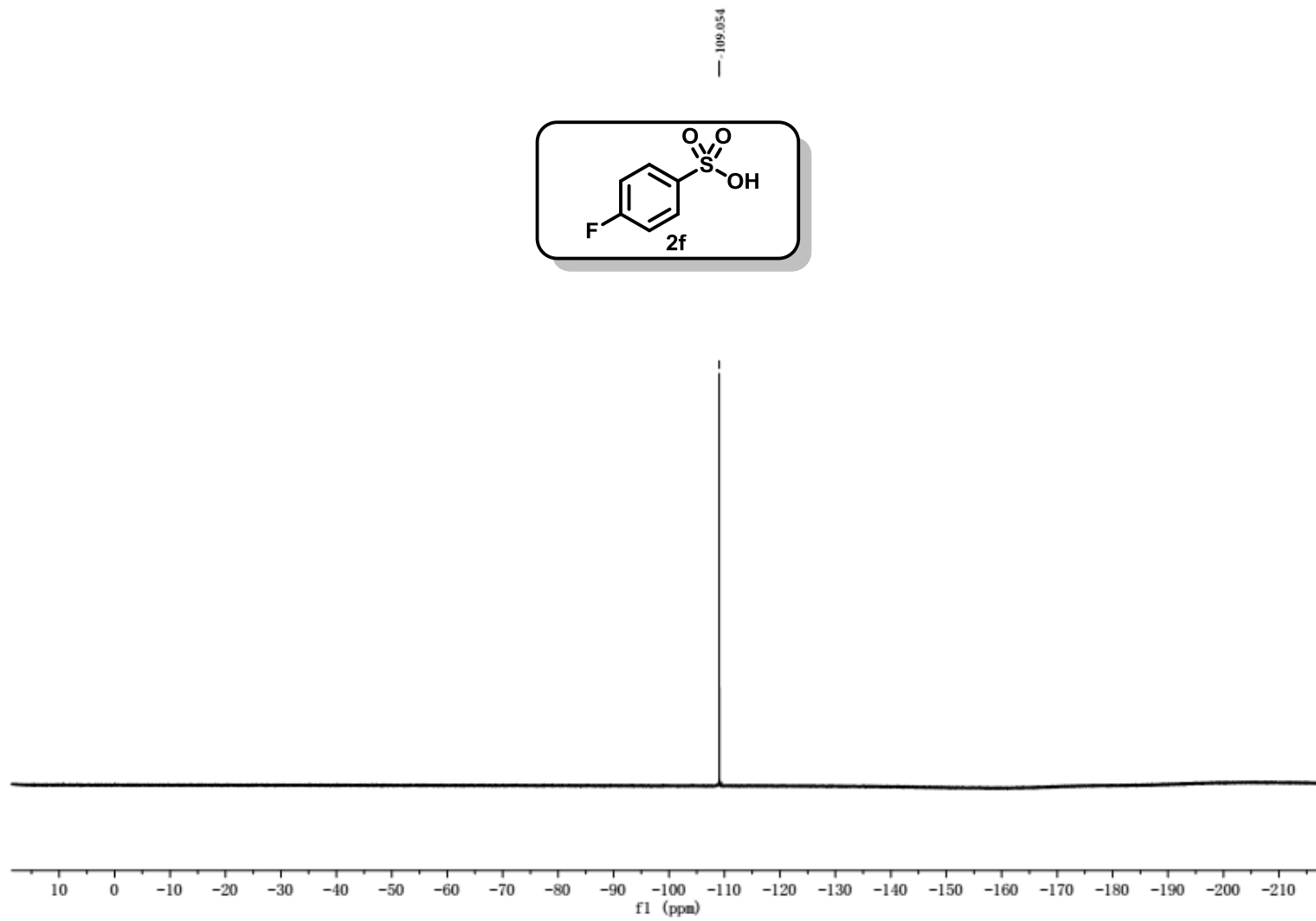
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162.873

138.559

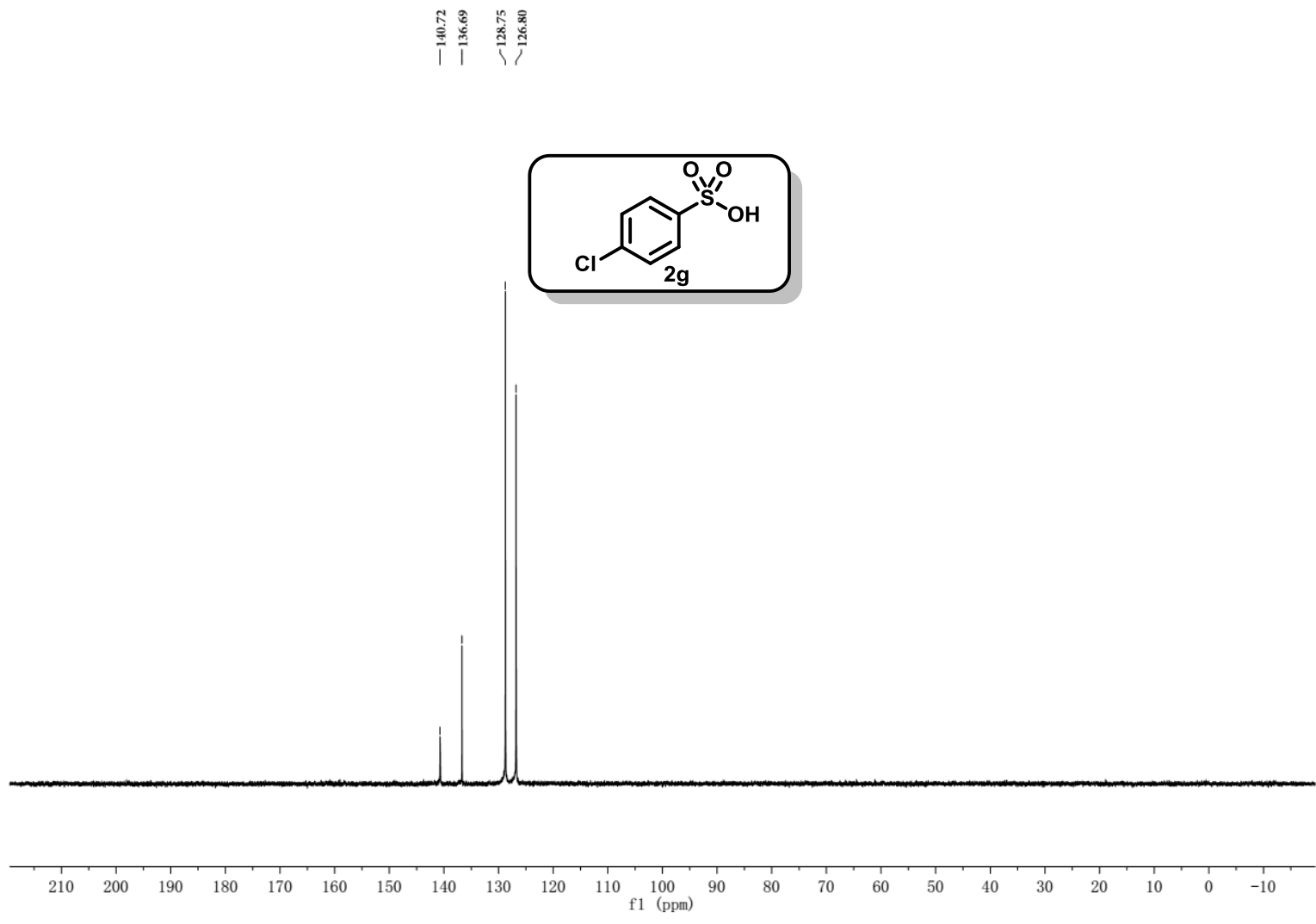
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128.017

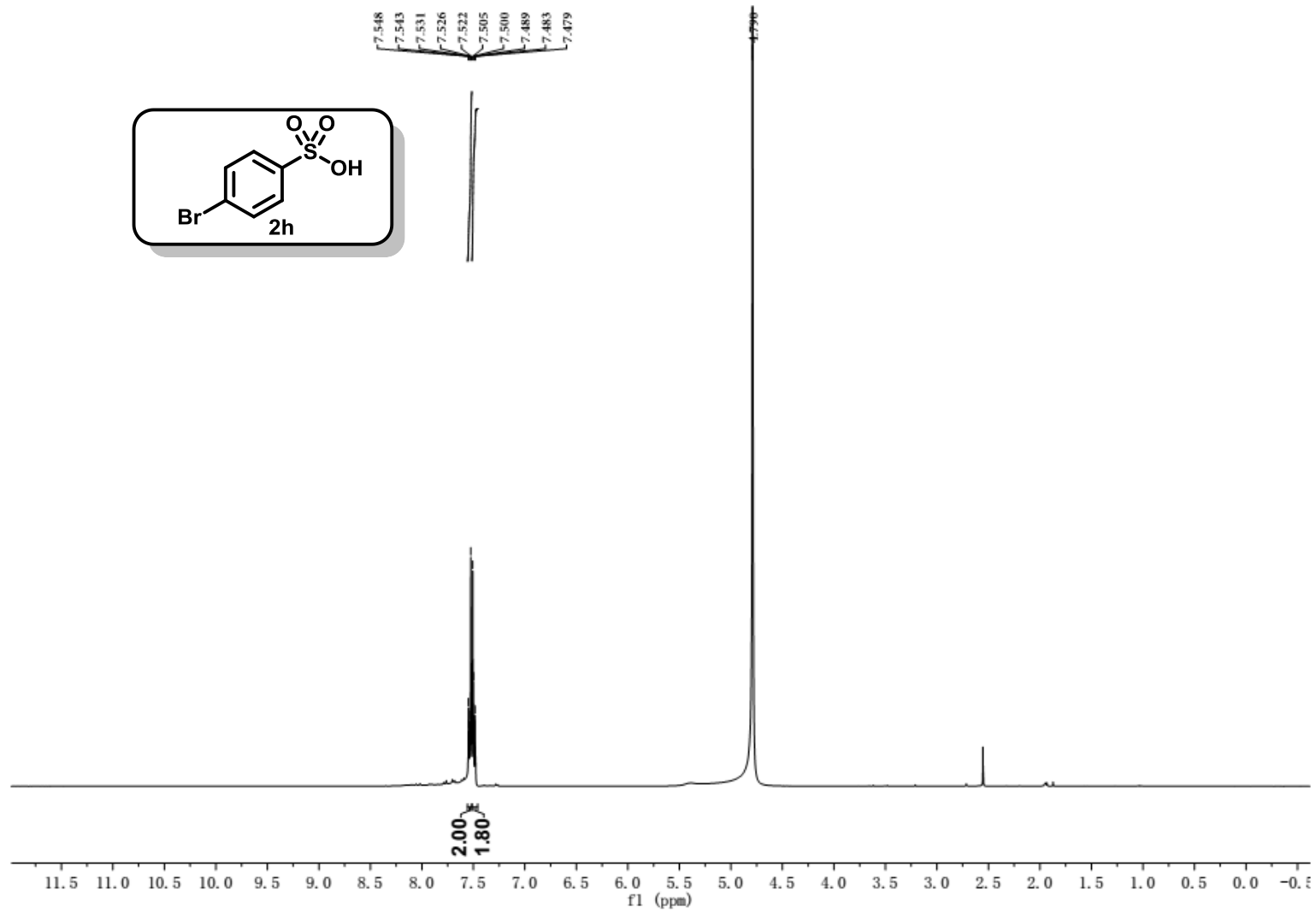
116.021
115.797



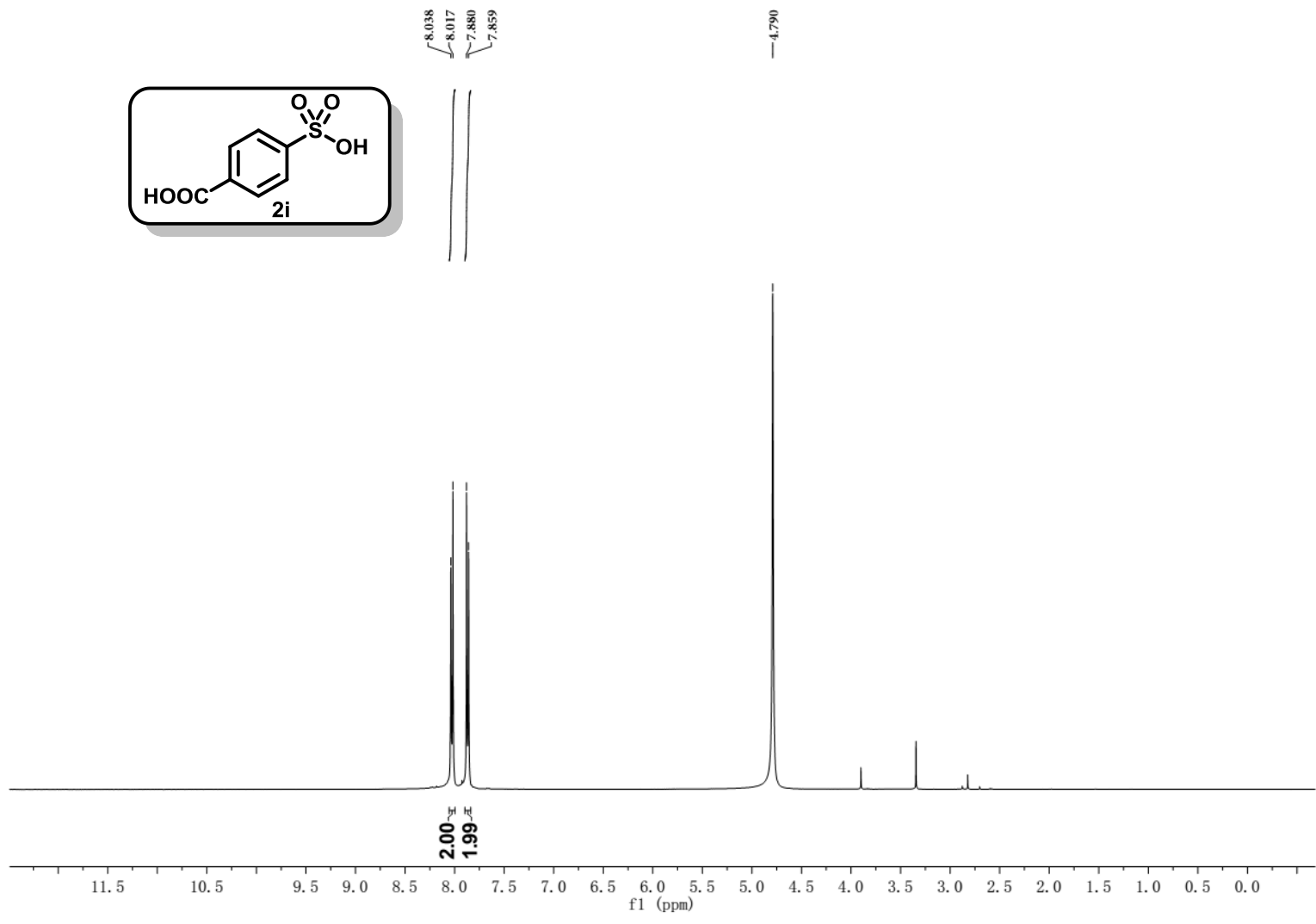


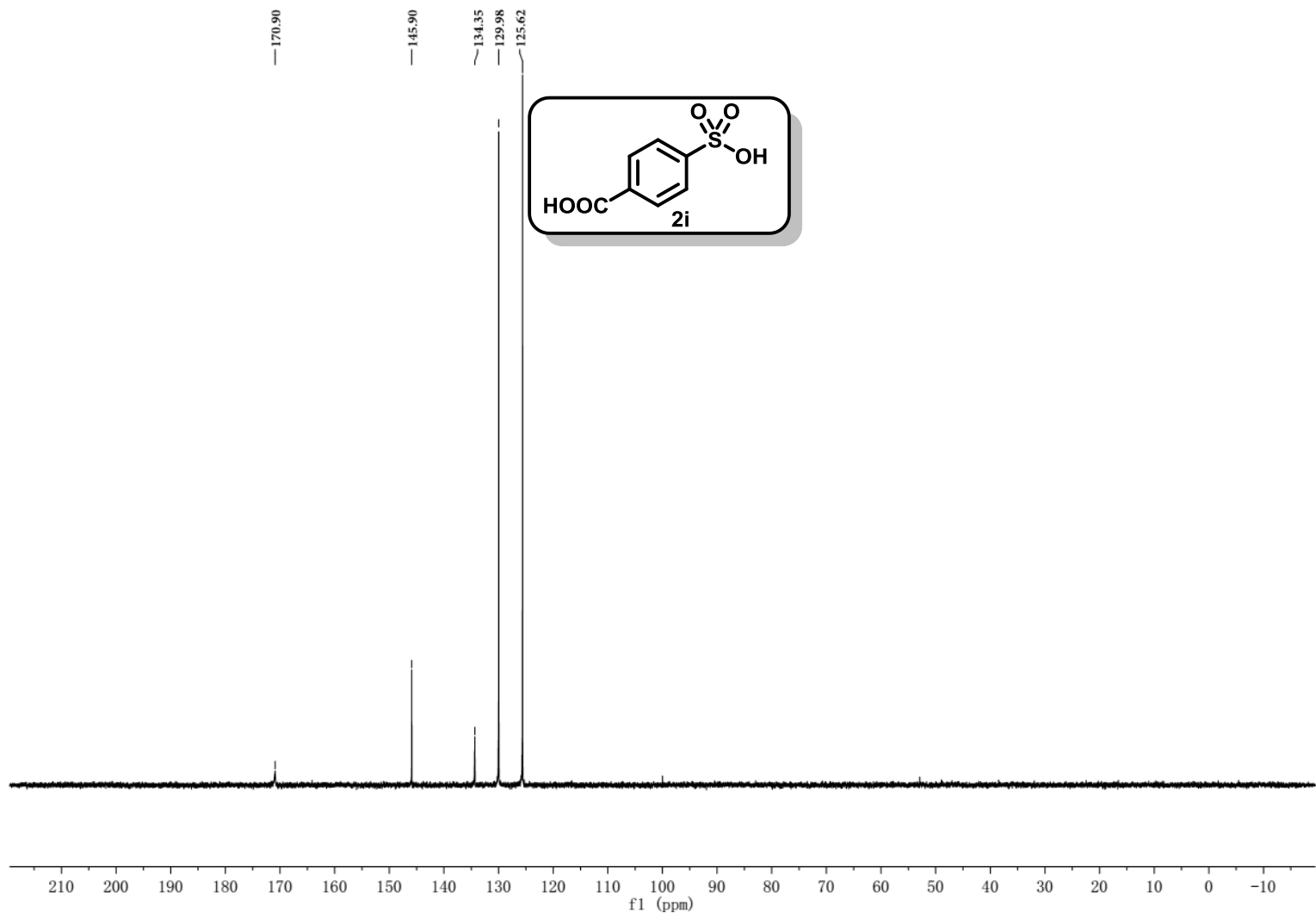


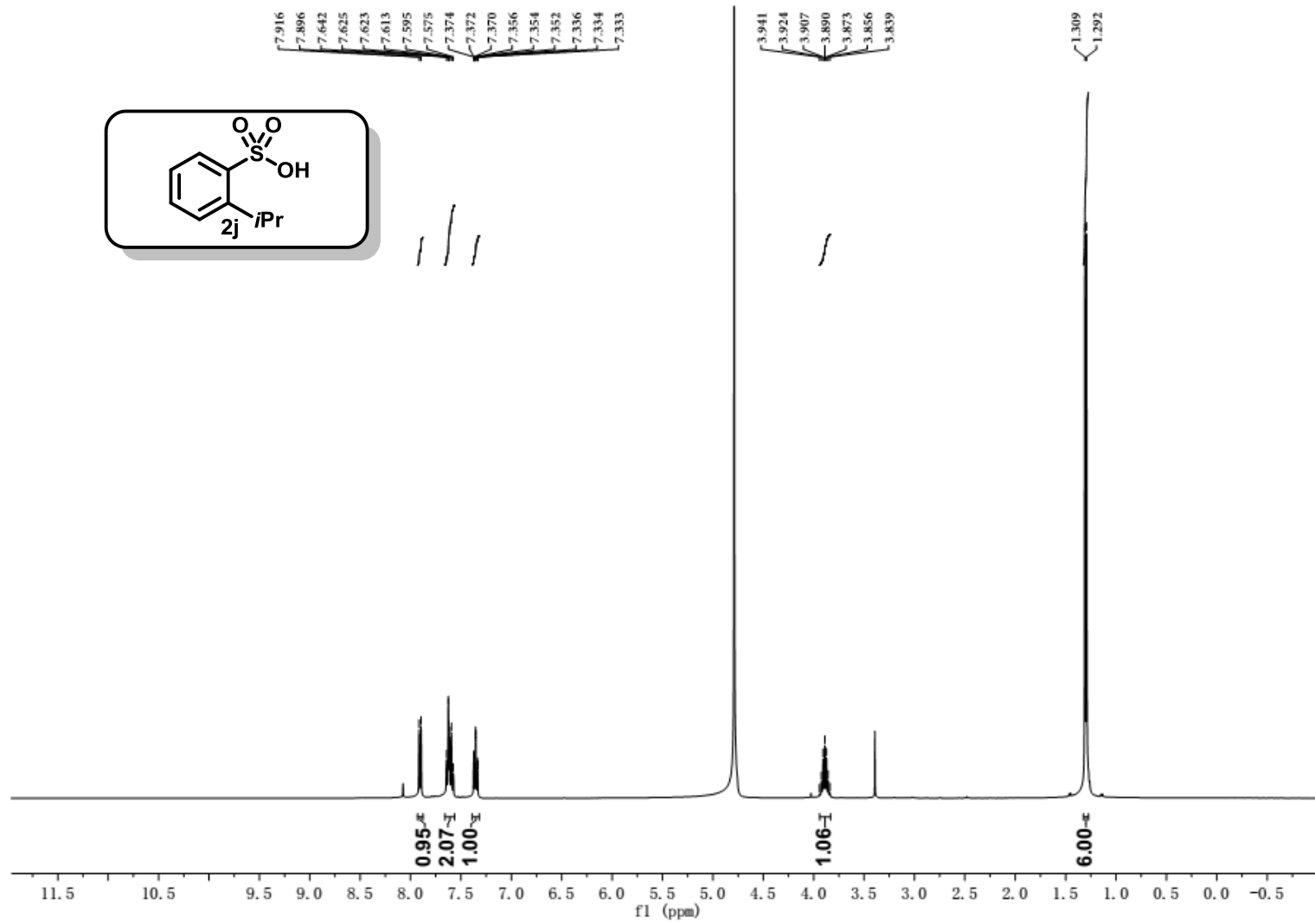


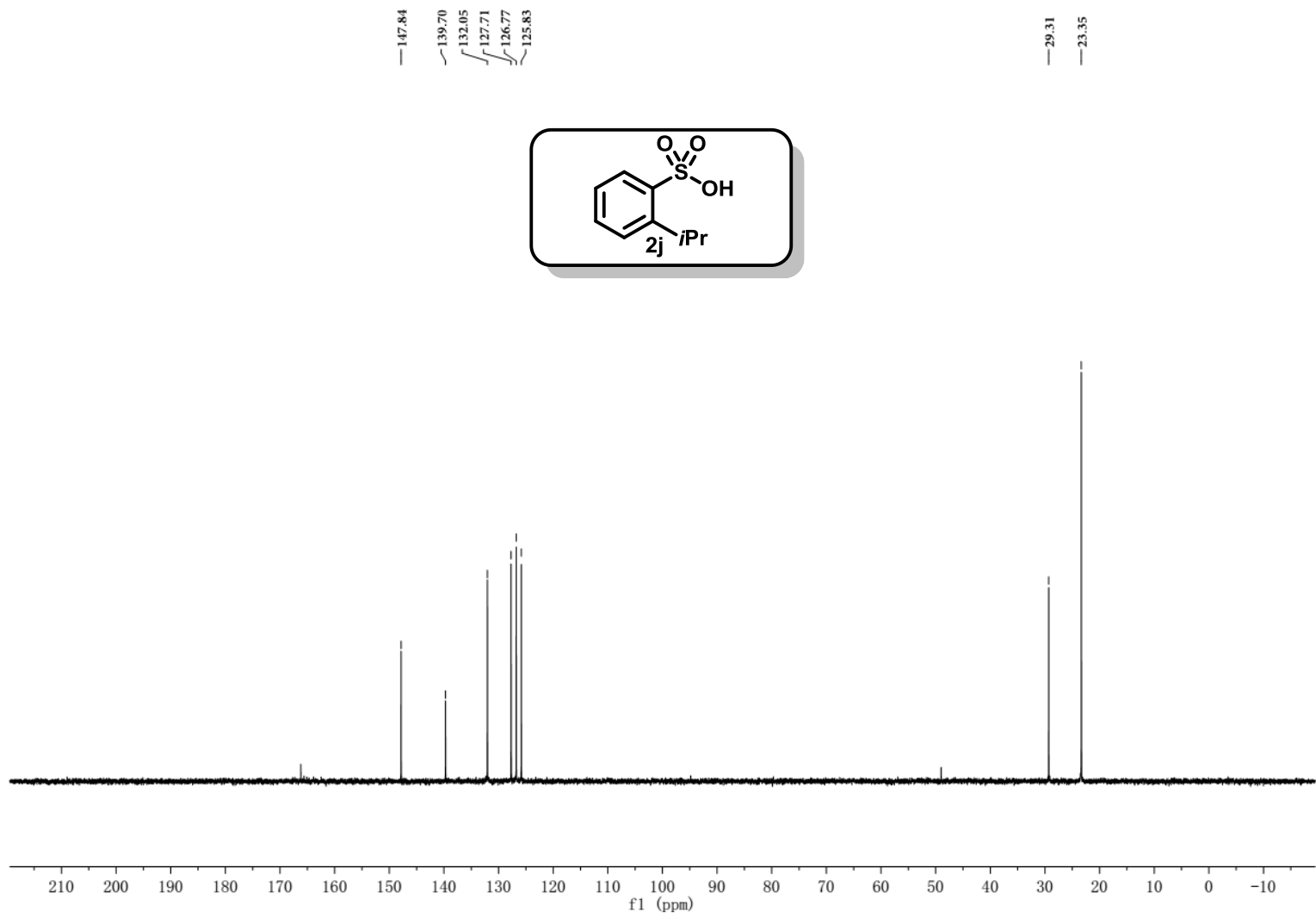


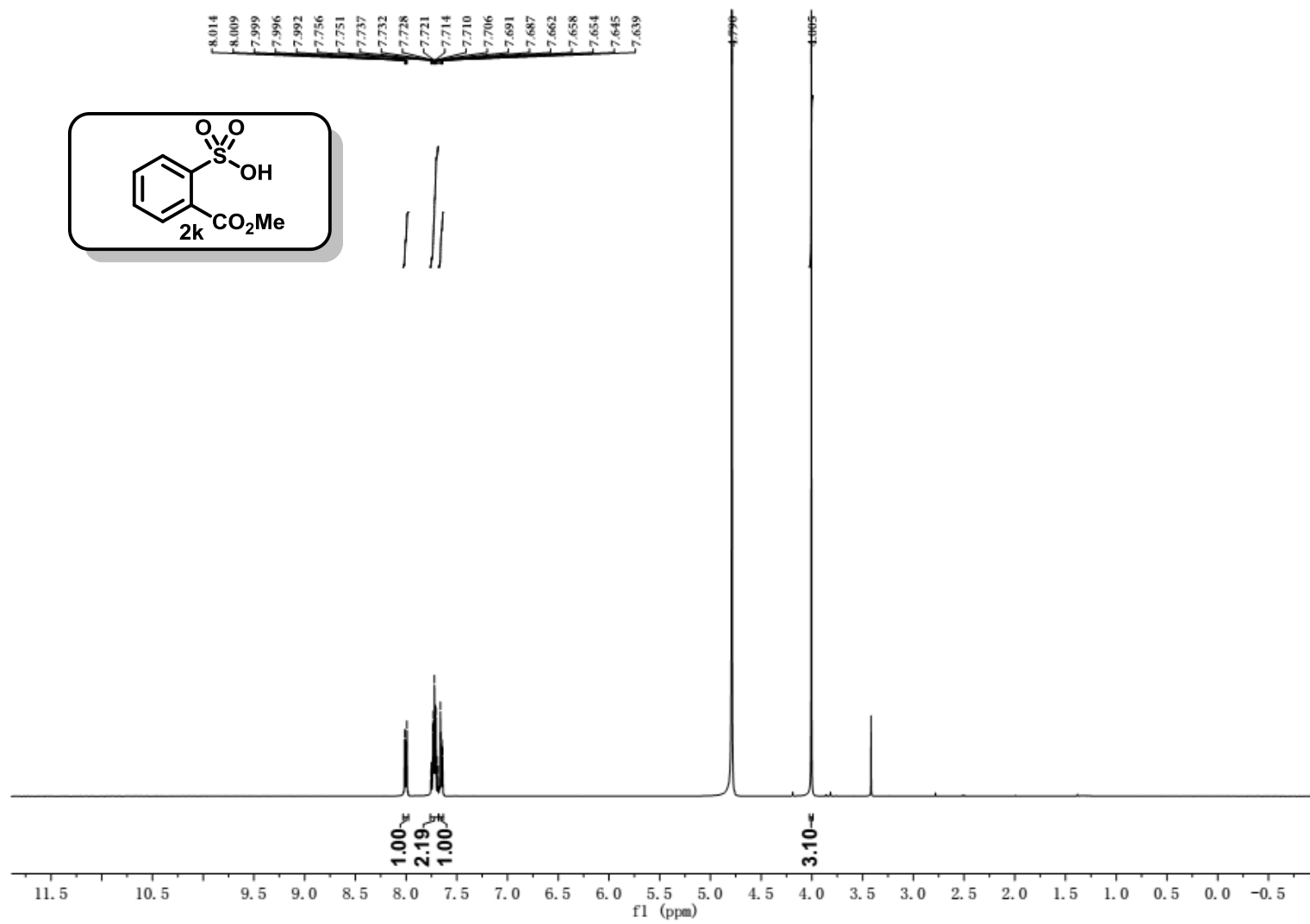


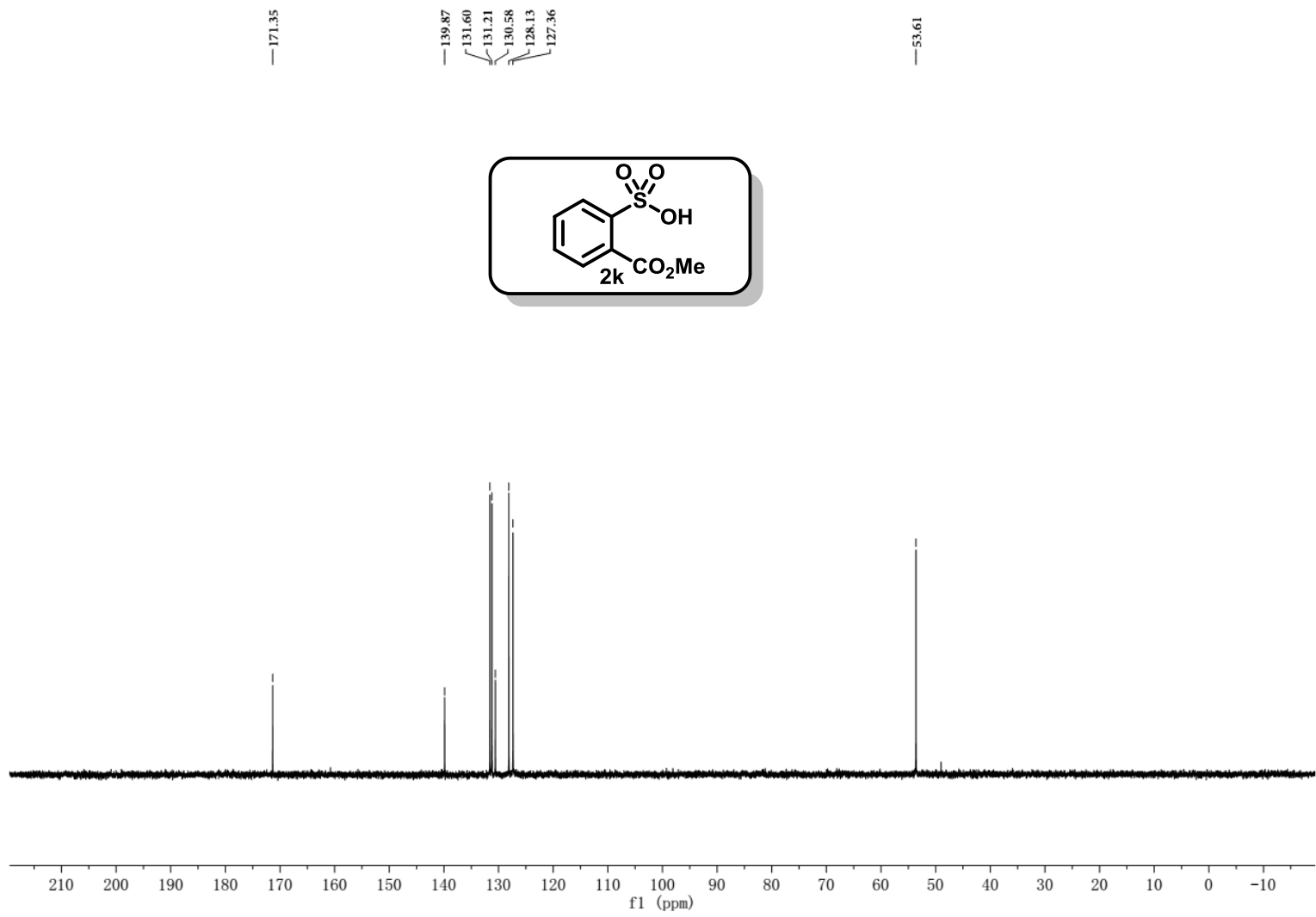


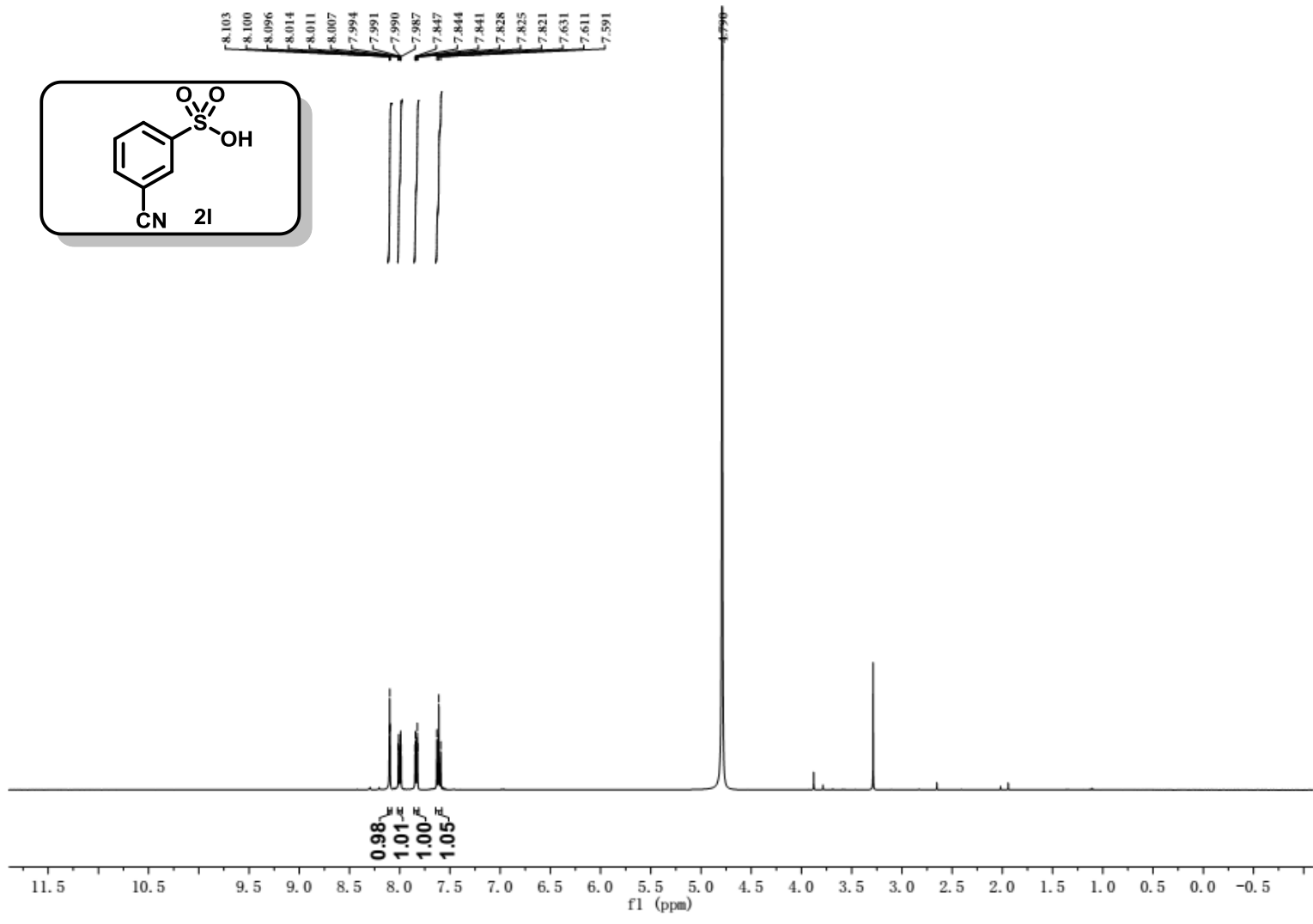




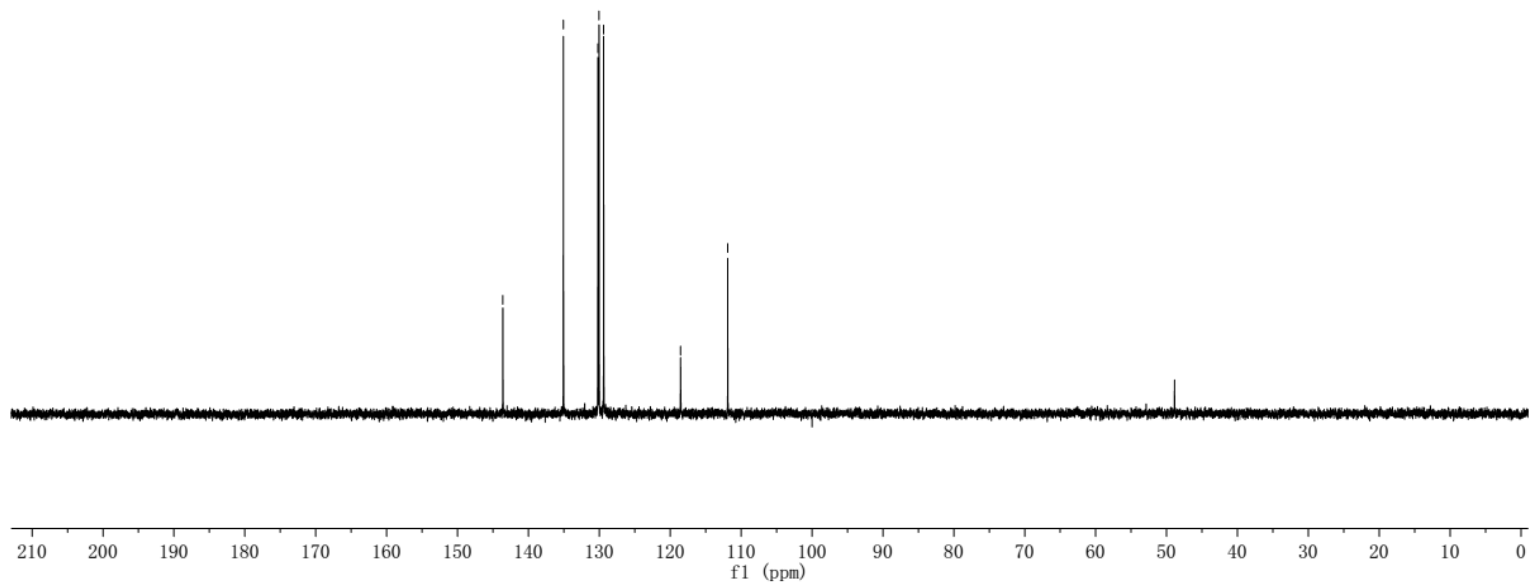
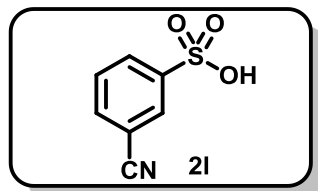


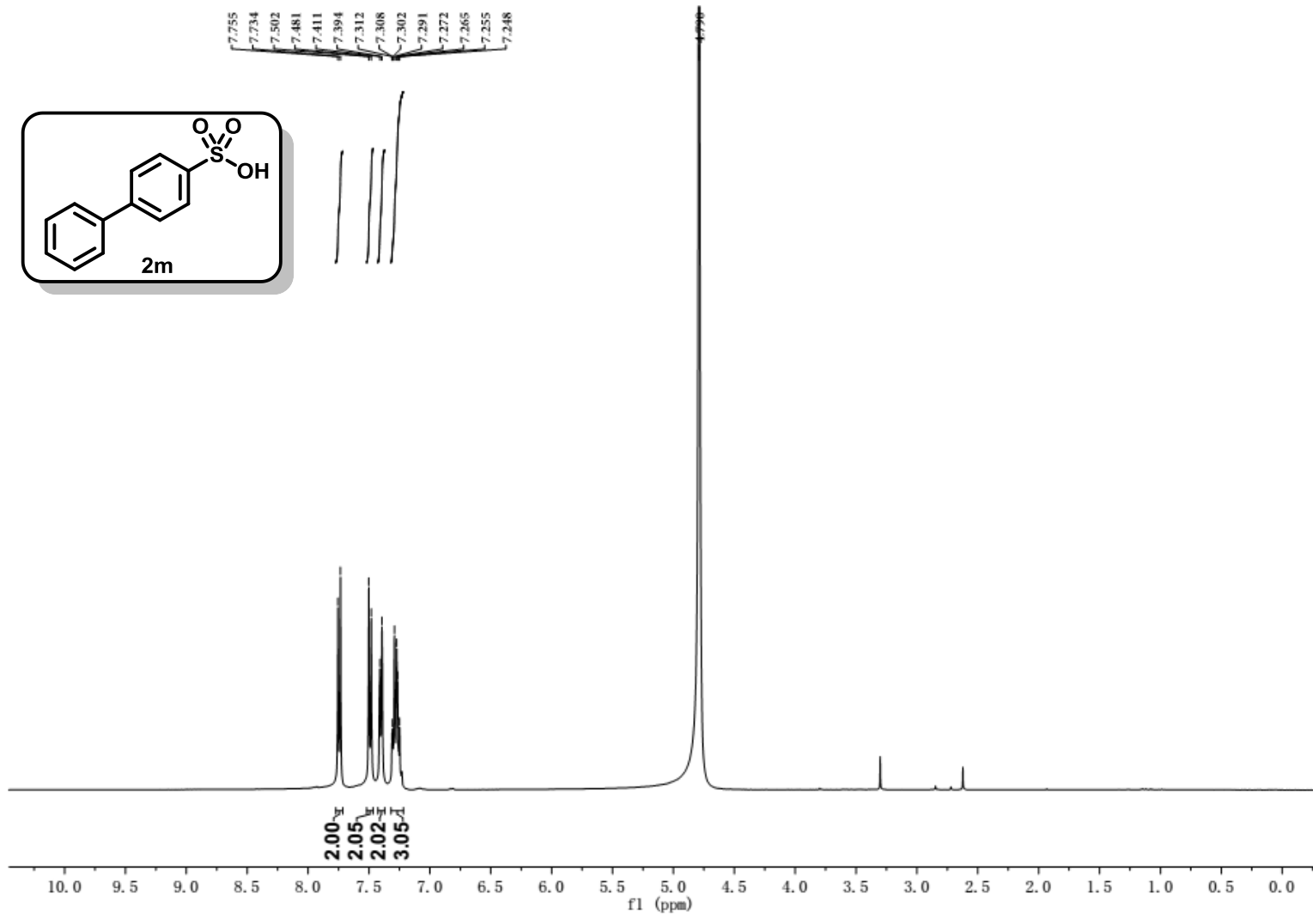


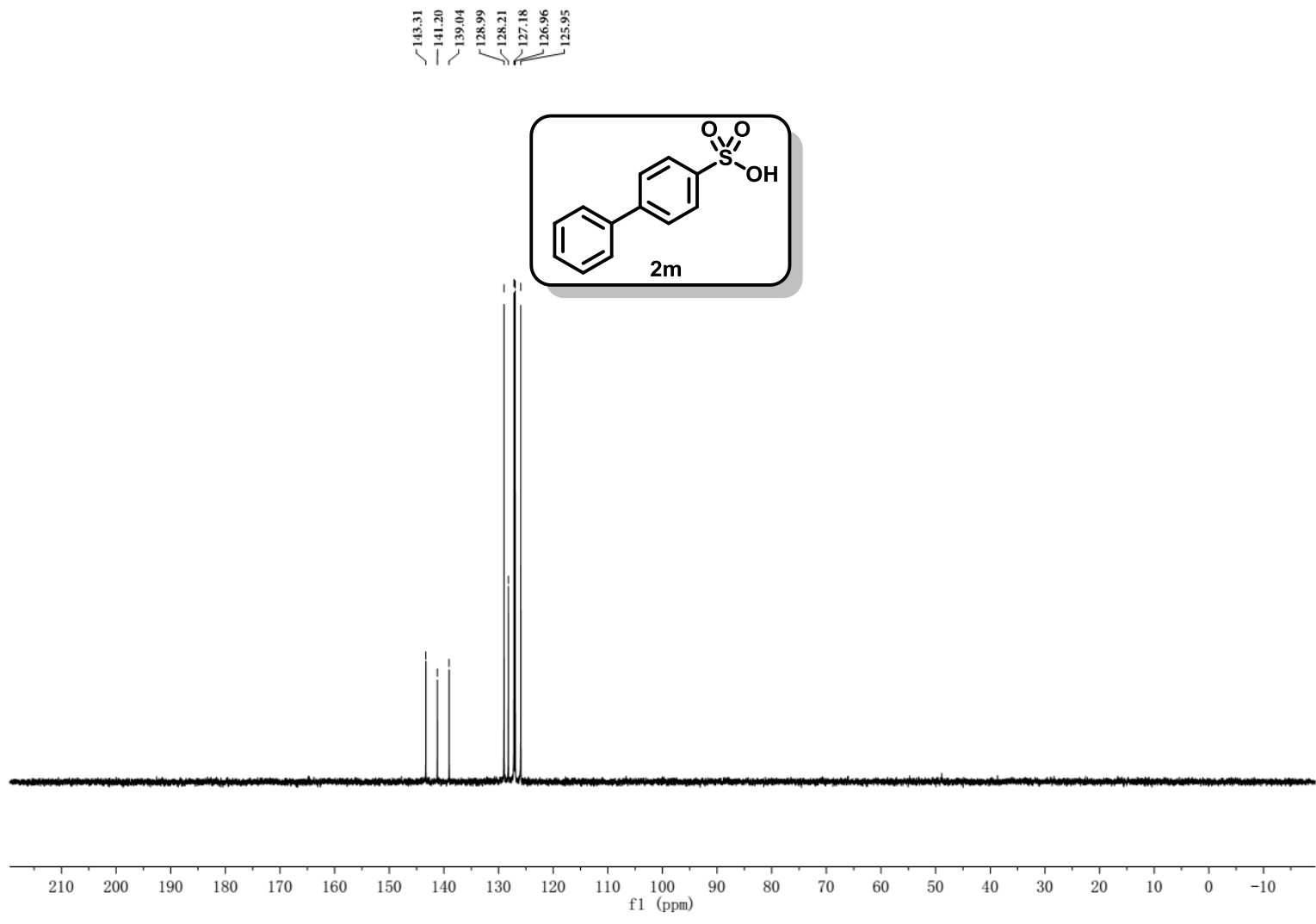


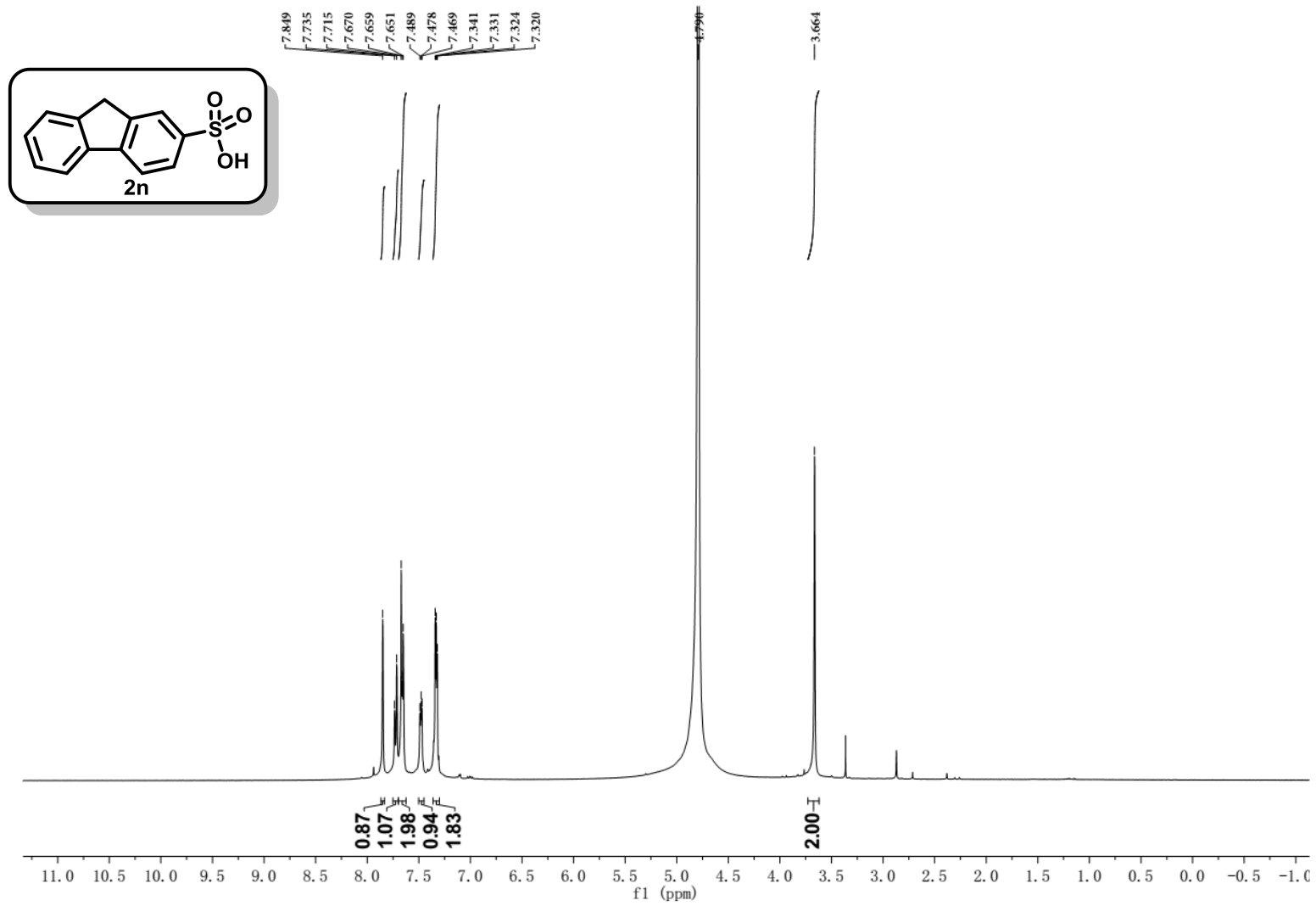


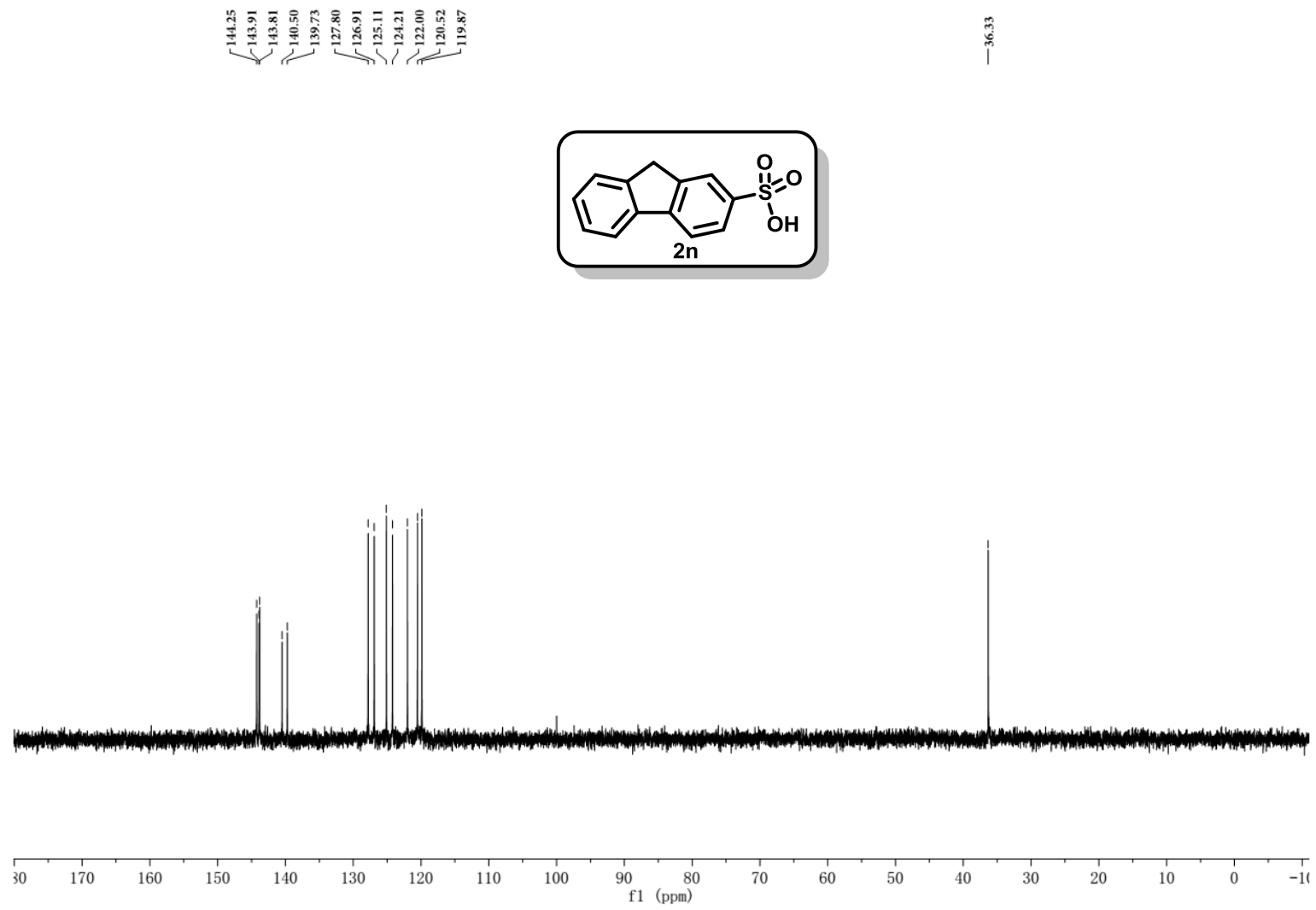
143.610
135.073
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130.043
129.394
118.547
111.893

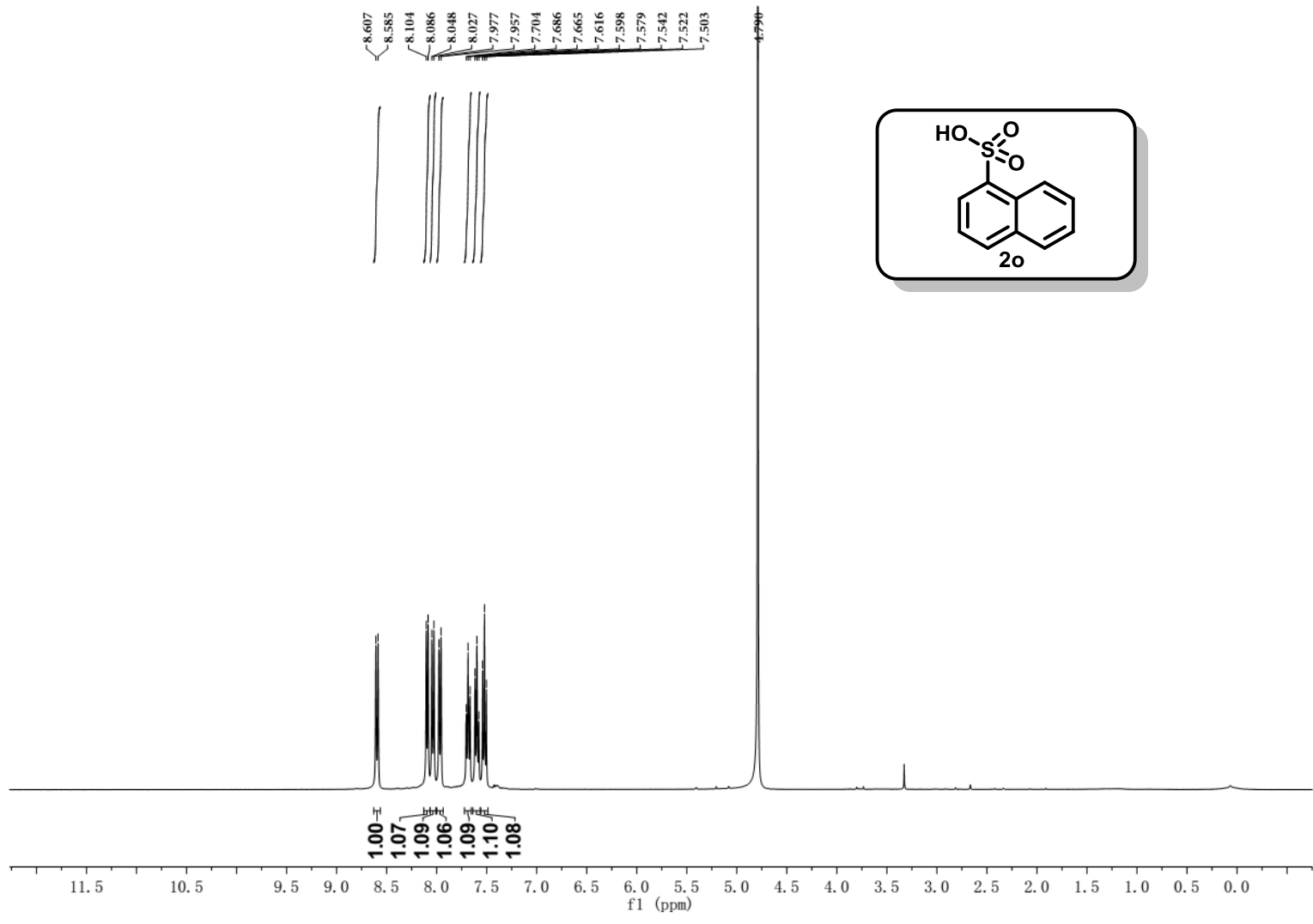




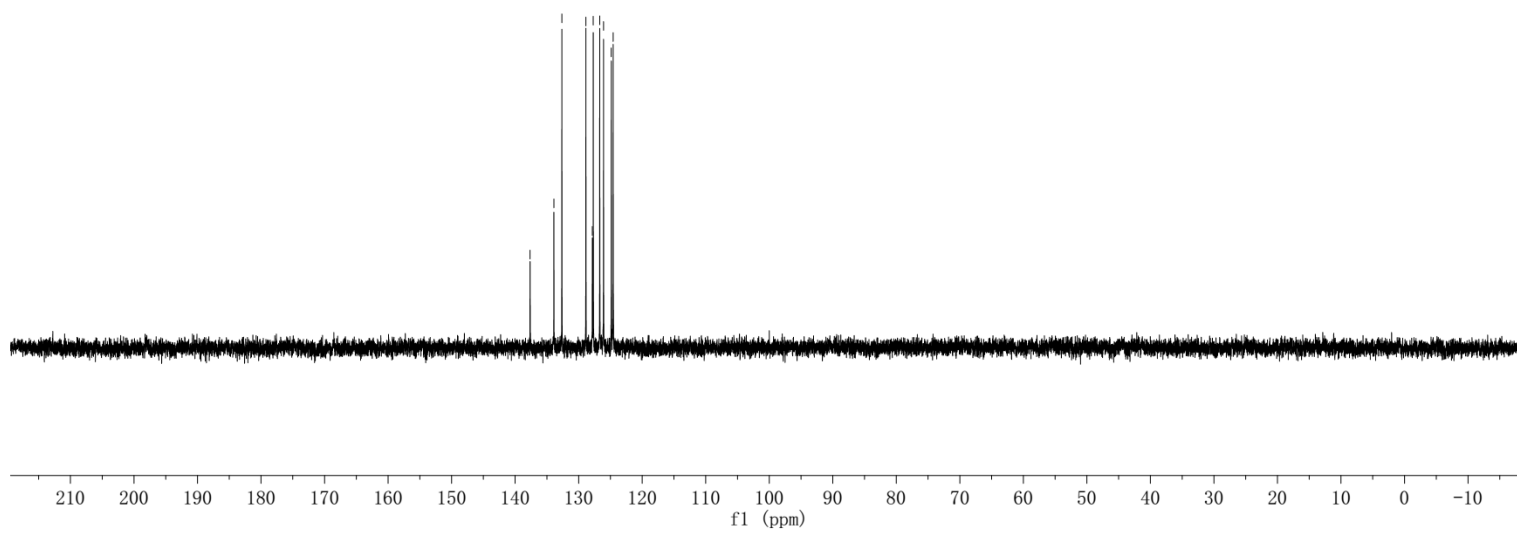
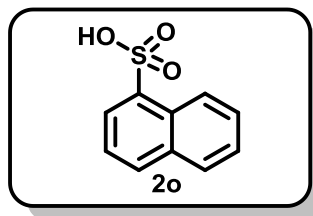


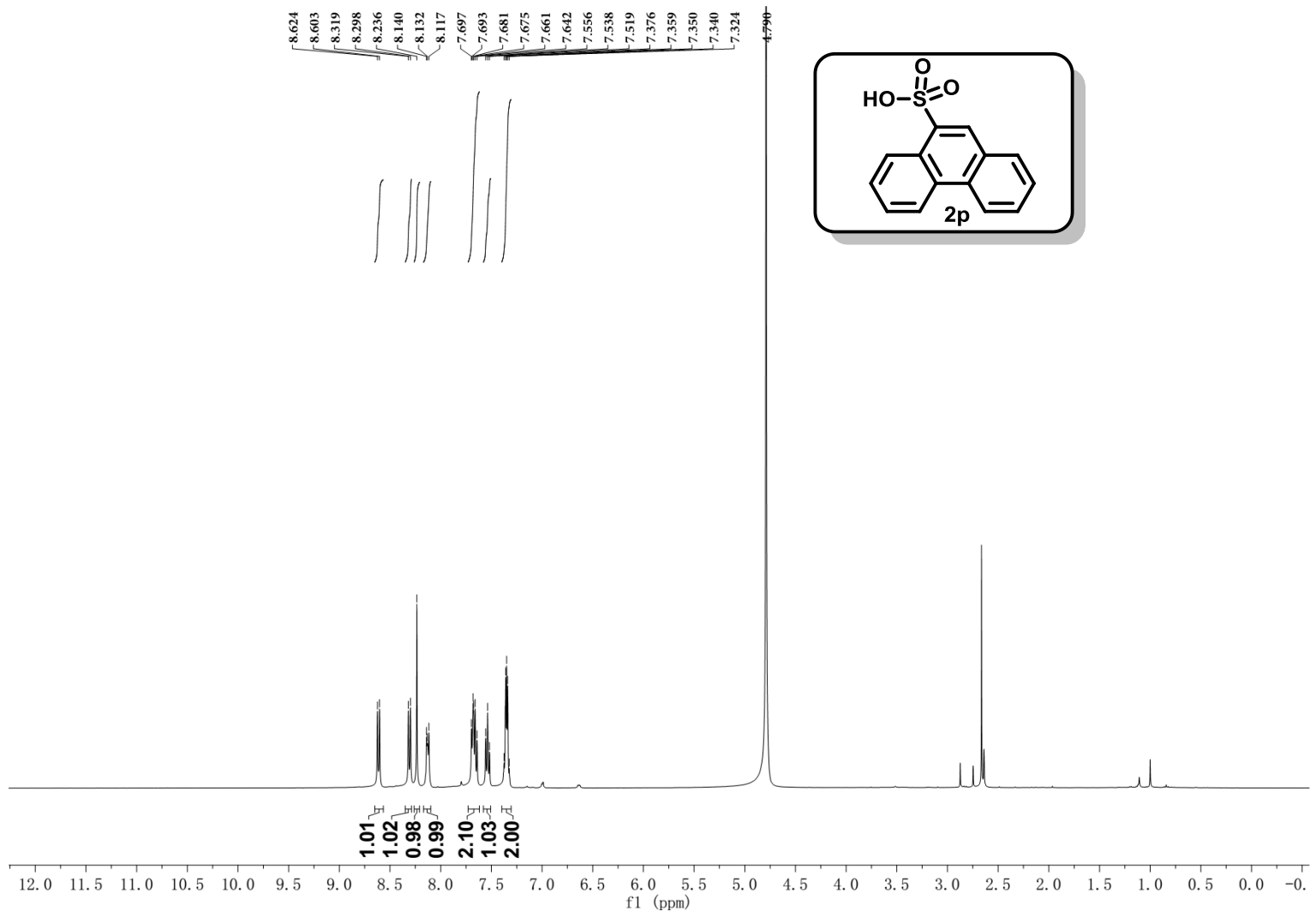




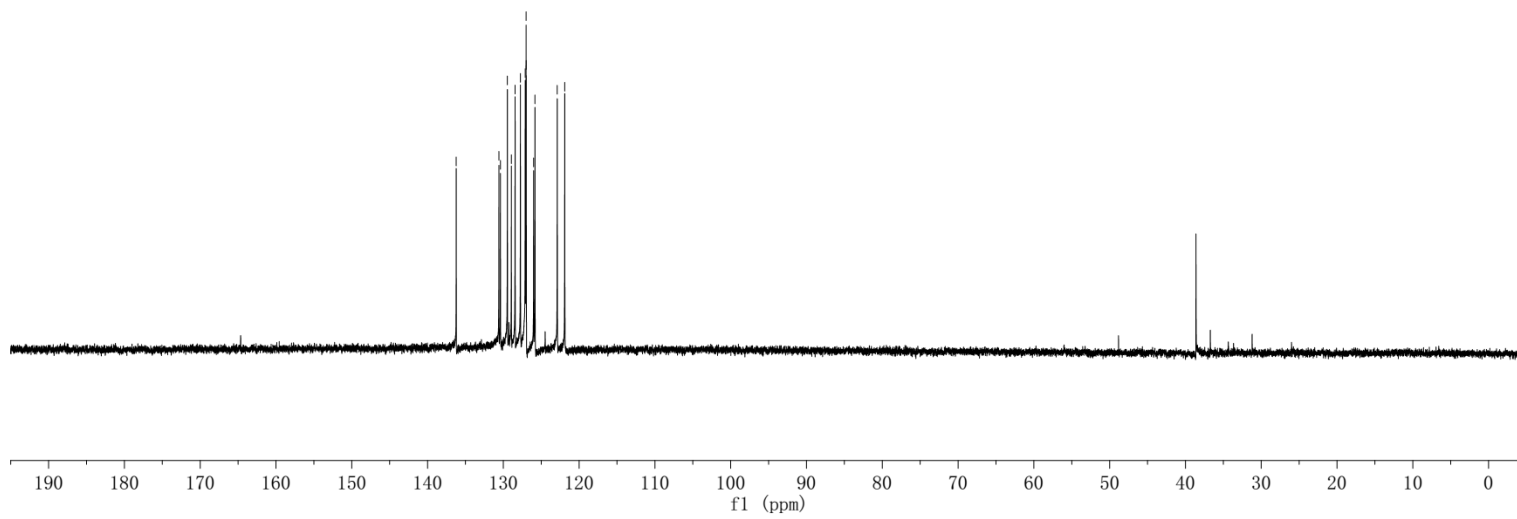
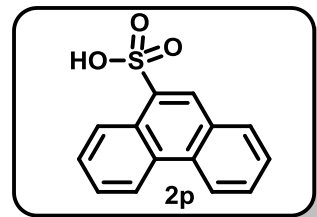


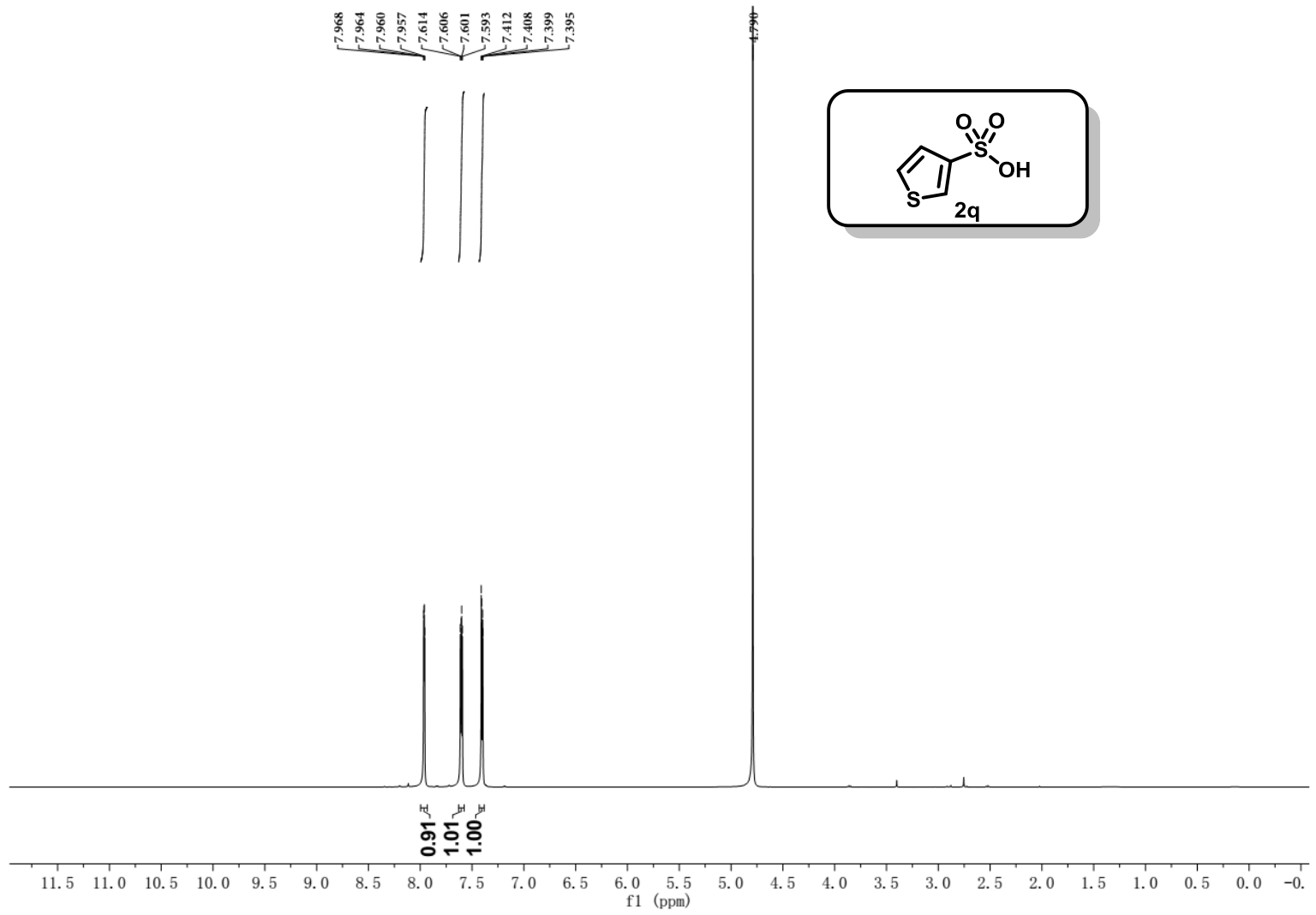
137.66
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127.71
126.69
126.09
124.87
124.57

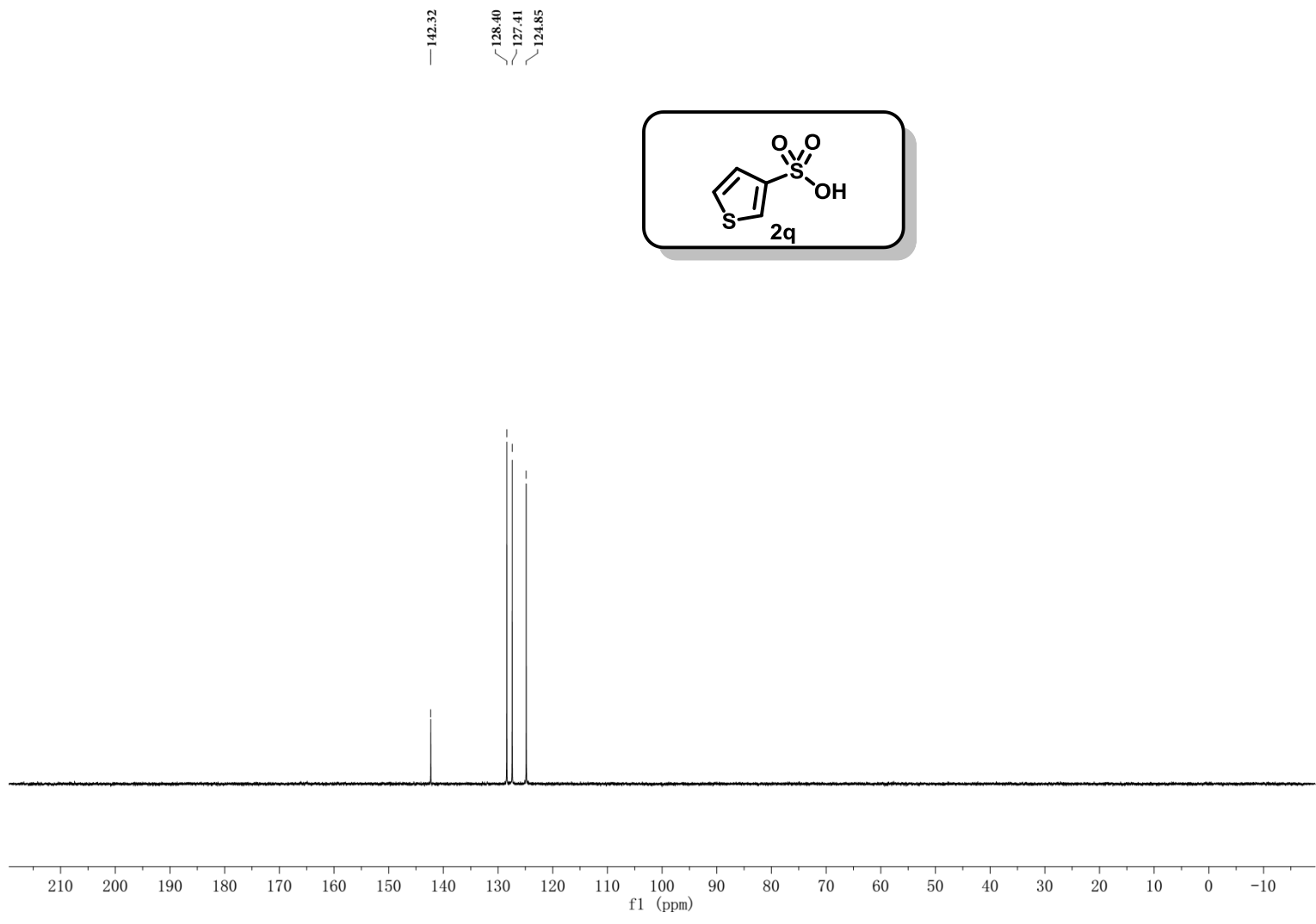


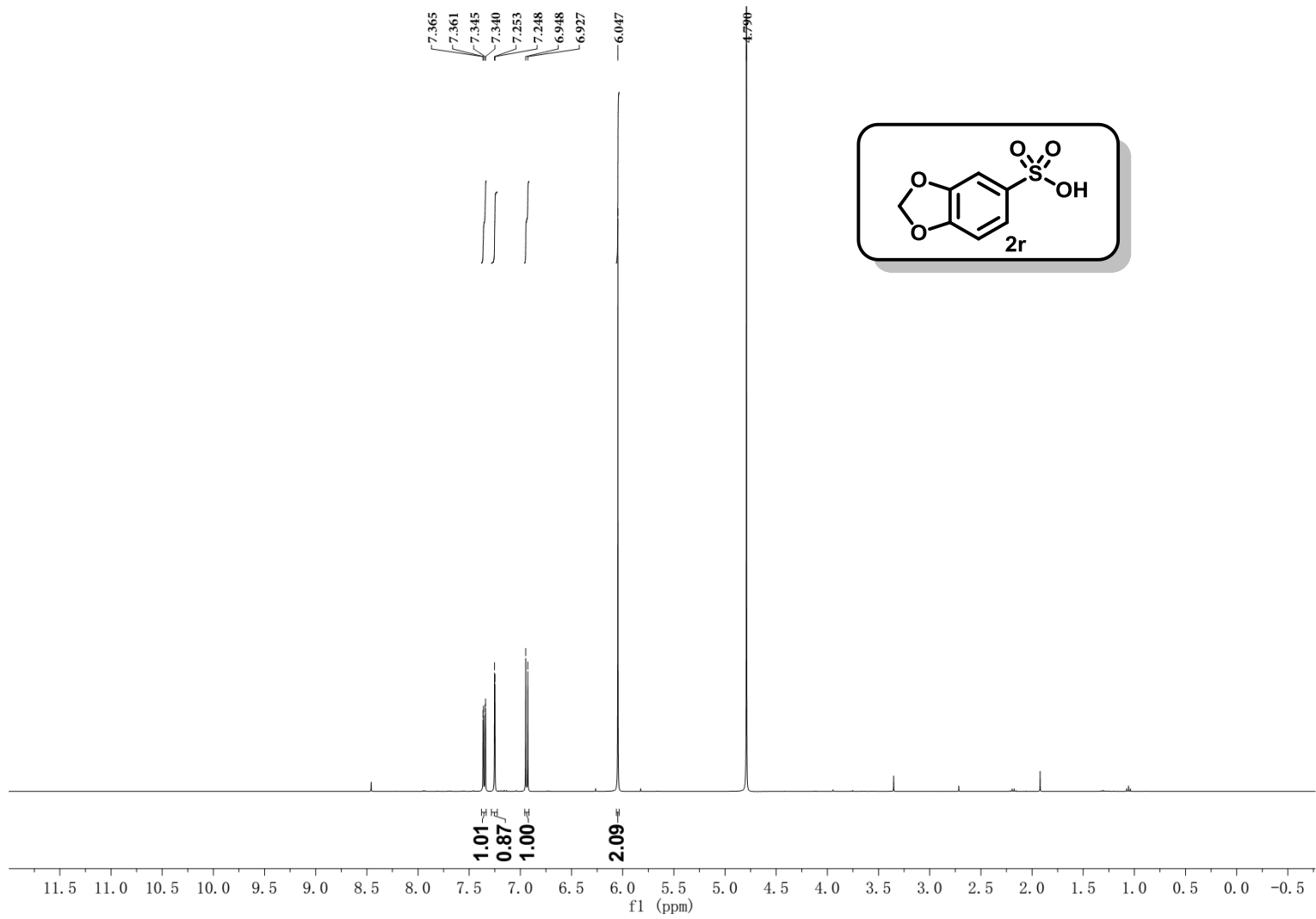


136.22
130.58
130.39
129.47
128.94
128.45
127.75
127.11
127.00
126.98
126.00
125.82
122.89
121.90

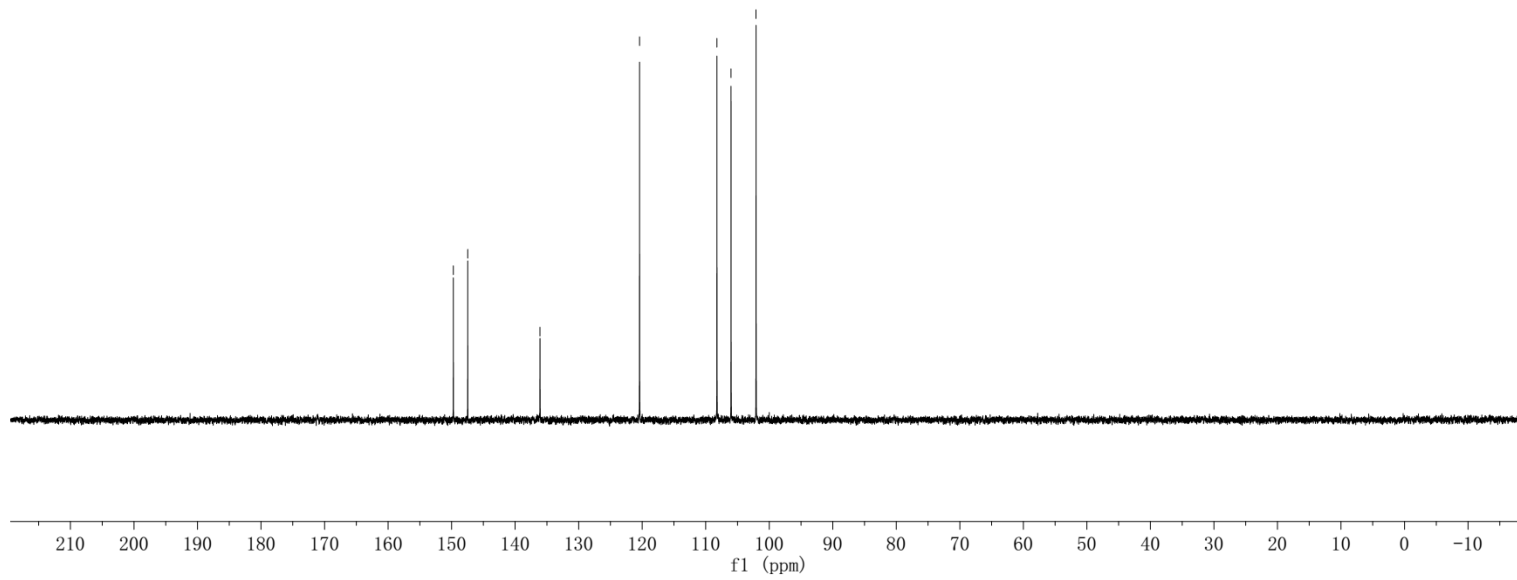
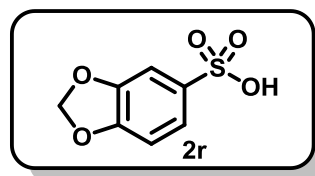


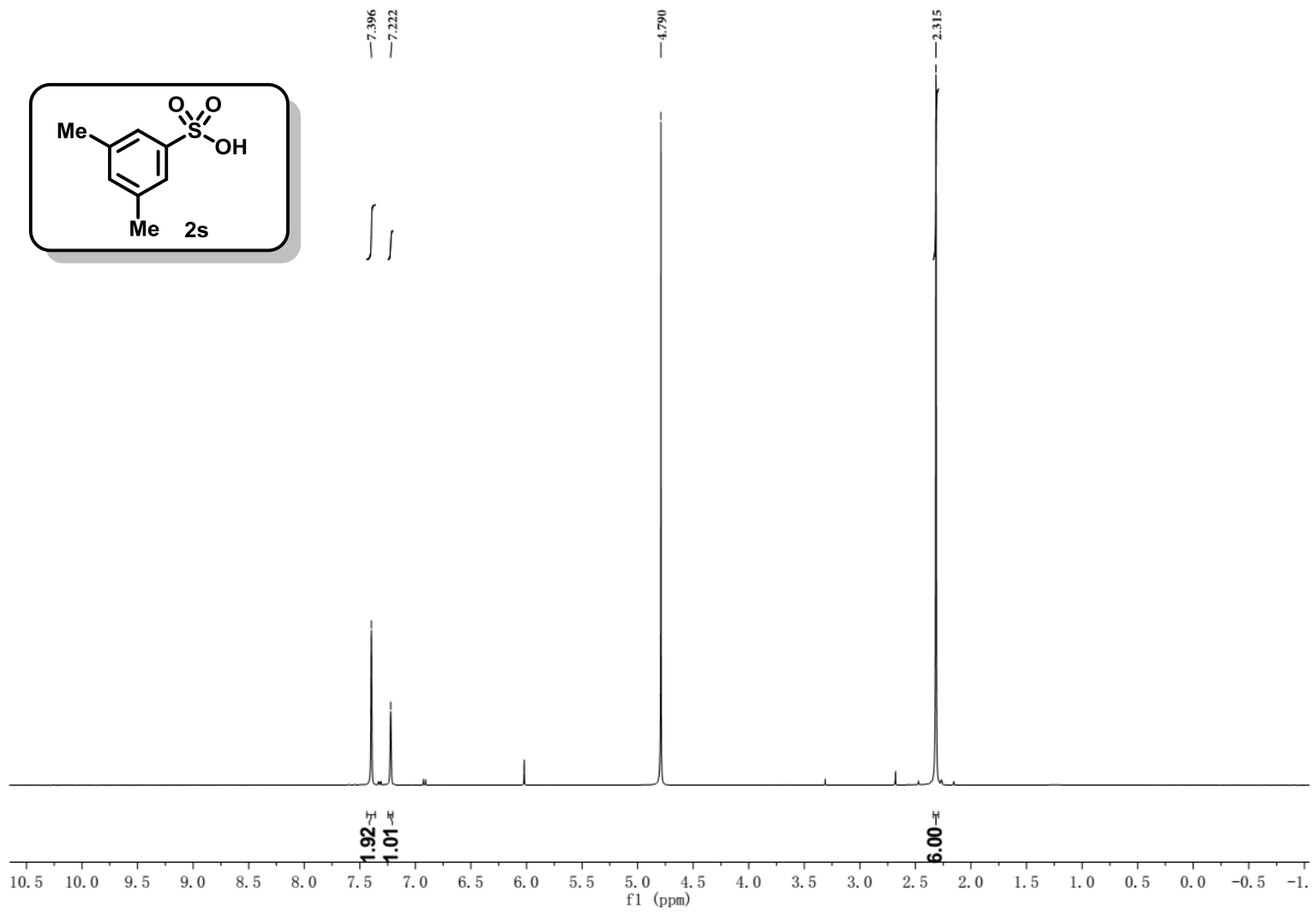


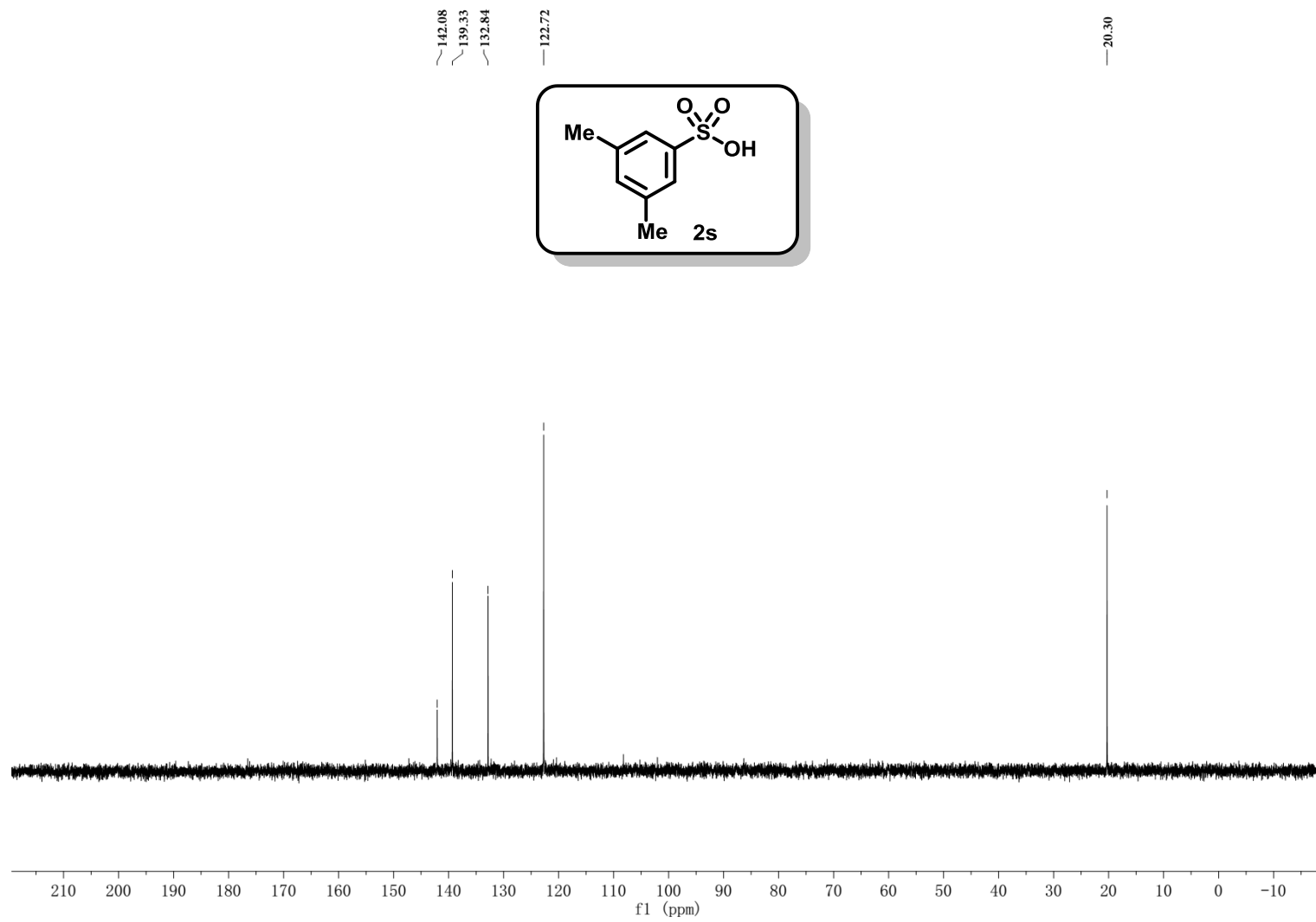


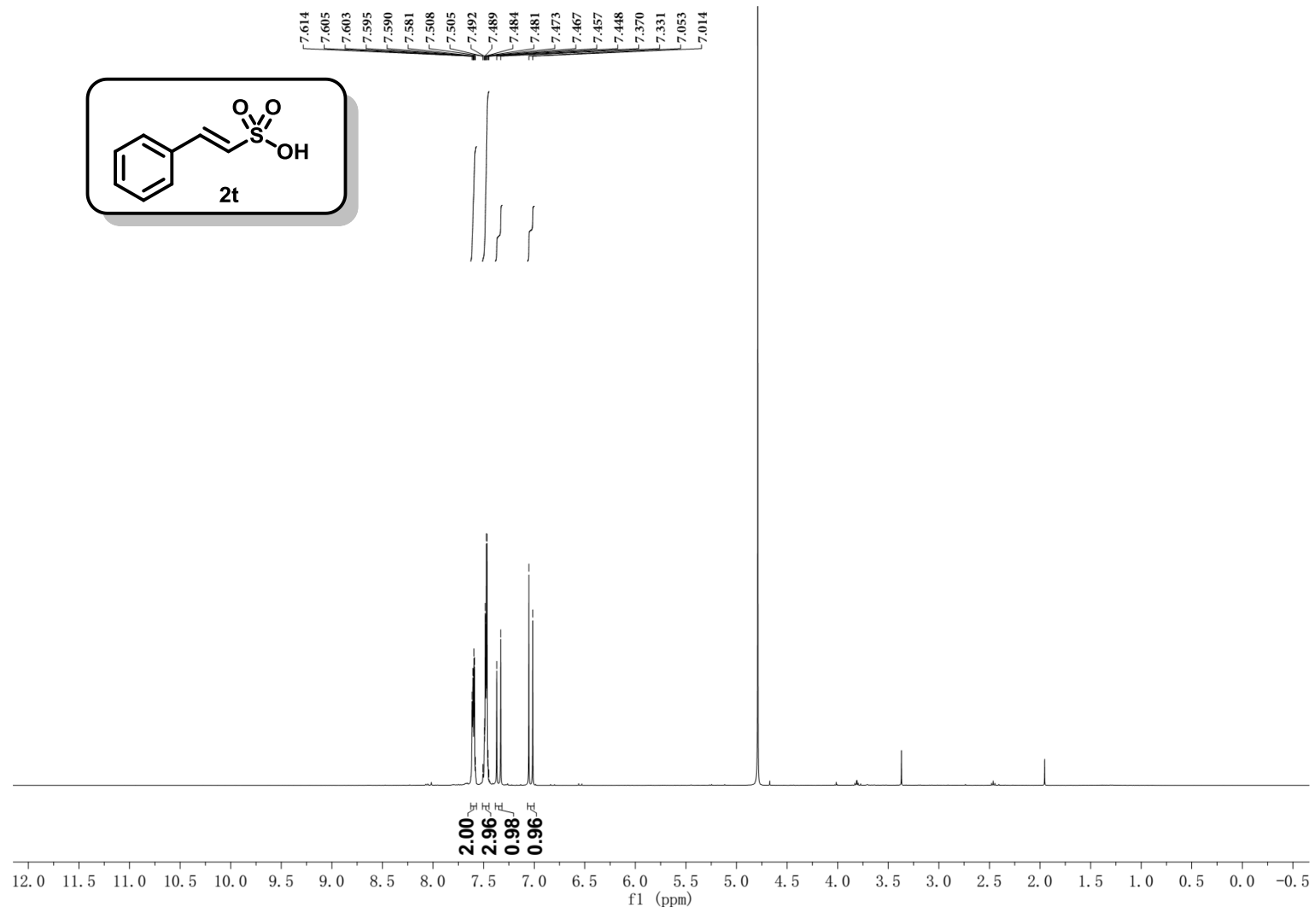


149.73
147.46
136.09
120.42
108.24
106.02
102.08









136.92
133.45
130.19
129.11
127.90
127.65

