Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Electrochemical Synthesis of Sulfinic and Sulfonic Esters from Sulfonyl Hydrazides

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1. General Information

All reagents were purchased and used without further purification. ^{1}H NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2SO$ on 500 MHz NMR spectrometers and data are reported as follows: chemical shift, multiplicity [singlet (s), doublet (d), triplet (t), septet (sept), doublet of doublets (dd), doublet of triplet (dt), doublet of quartet (dq), doublet of doublet of doublet (ddd), and multiplet (m)], coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2SO$ on 126 MHz NMR spectrometers and resonances (δ) are given in ppm. High resolution mass spectra was recorded on a time of flight (TOF) mass spectrometer.

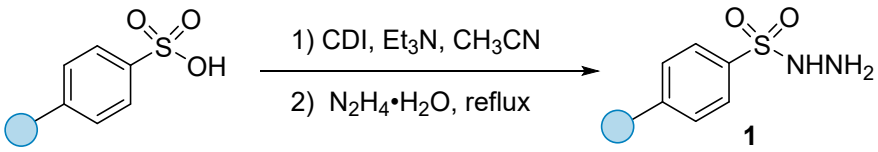
2. Electrochemical apparatus and Electrode materials

All reactions for Sulfinic and Sulfonic Esters were performed using an ElectraSyn 2.0 Pro from IKA.

(a) **(b)**

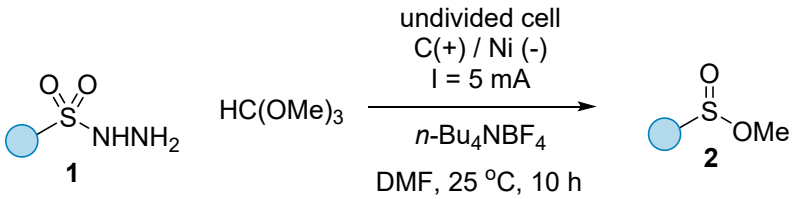
Figure S1. (a) ElectraSyn 2.0 Pro purchased from IKA. (b) Graphite SK-50 plated electrode (8 mm × 2mm × 52 mm) (left side) (IKA) and nickel plated electrode (8 mm × 2mm × 52 mm) (right side) (IKA).

3. Experimental Procedures for arylsulfonyl hydrazides.



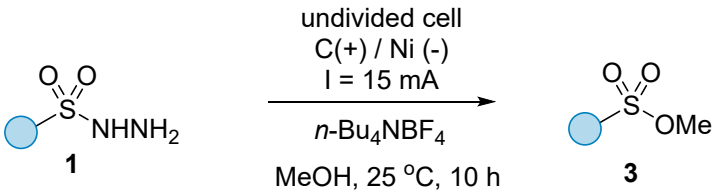
Arylsulfonic acids (1 mmol), triethylamine (1.2 mmol) and 1,1'-carbonyldiimidazole (1.0 mmol) mixed in acetonitrile (5.0 mL) and reflux for 30 min. Then, eighty percent hydrazine hydrate (2.5 mmol) was added into the reaction mixture and reflux for 6 h. The resulting mixture was diluted with ethyl acetate, and washed with distilled water, and the organic layer was separated and dried over $MgSO_4$. The organic layer was concentrated, and added to petroleum ether and stirred for 30 min. The formed precipitates were filtered and washed with water and then with n-hexane. The collected solid was dried in vacuum. The yields for the formation of arylsulfonyl hydrazides range from 51% to 82%

4. General procedure for the synthesis of sulfinic ester



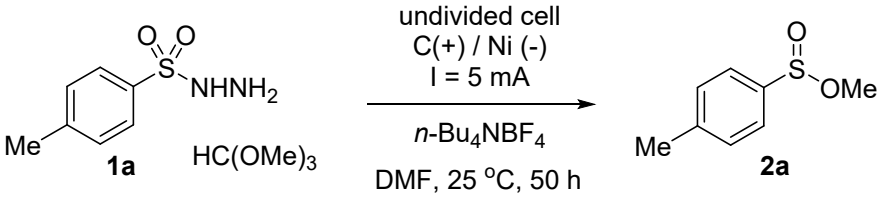
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added sulfonyl hydrazide **1** (0.6 mmol), trimethyl orthoformate (3.0 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in DMF (5mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 5 mA at 25 °C for 10 h. After the reaction, the mixture was extracted with ethyl acetate (1 × 30 mL). The combined organic layers were washed with brine, dried over anhydride $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel. The product **2** was eluted with *n*-hexane/EtOAc (95:5)

5. General procedure for the synthesis of sulfonic ester

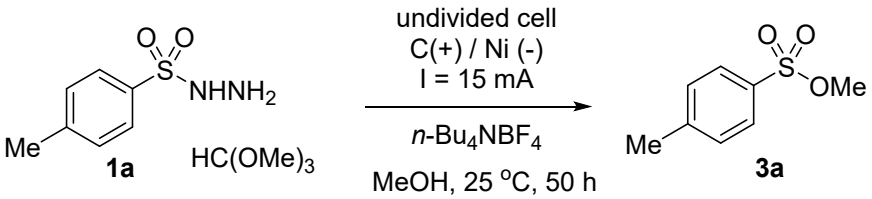


Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added sulfonyl hydrazide **1** (0.6 mmol) followed by 0.1 M *n*-Bu_4NBF_4 in MeOH (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 15 mA at 25 °C for 10 h. After the reaction, the mixture was extracted with ethyl acetate (1 × 30 mL). The combined organic layers were washed with brine, dried over anhydride $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel. The product **3** was eluted with *n*-hexane/EtOAc (95:5)

6. Procedure for gram scale synthesis



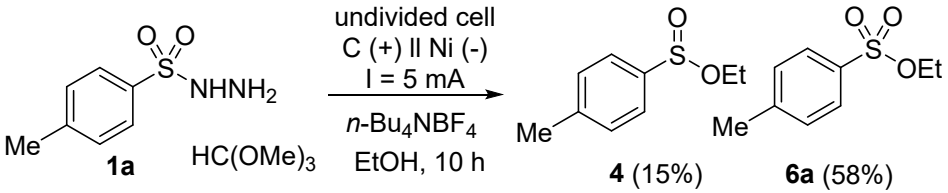
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added *p*-toluenesulfonyl hydrazide (**1a**) (5.48 mmol, 1.02 g), trimethyl orthoformate (27.5 mmol, 2.92 g), followed by 0.1 M *n*-Bu_4NBF_4 in DMF (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 5 mA at 25 °C for 50 h. After the reaction, the mixture was extracted with ethyl acetate (1 × 30 mL). The combined organic layers were washed with brine, dried over anhydride $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel and then the product **2a** (0.62 g, 3.64 mmol, 66%) was obtained.



Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added *p*-toluenesulfonyl hydrazide (**1a**) (5.48 mmol, 1.02 g) followed by 0.1 M *n*-Bu_4NBF_4 in MeOH (5mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 5 mA at 25 °C for 50 h. After the reaction, the mixture was extracted with ethyl acetate (1 × 30 mL). The combined organic layers were washed with brine, dried over anhydride $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel. The product **3a** (0.64 g, 3.44 mmol, 63%) was obtained.

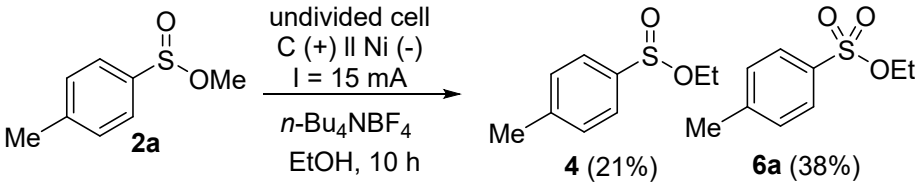
7. Experimental procedures for the control experiments

a)



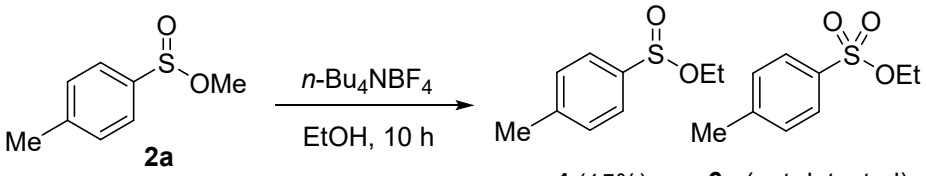
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added *p*-toluenesulfonyl hydrazide (**1a**) (0.3 mmol), trimethyl orthoformate (1.5 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in ethyl alcohol (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 5 mA at 25 °C for 10 h. The yield of **4** and **6a** were determined by gas chromatography with an internal standard (2-methoxynaphthalene).

b)



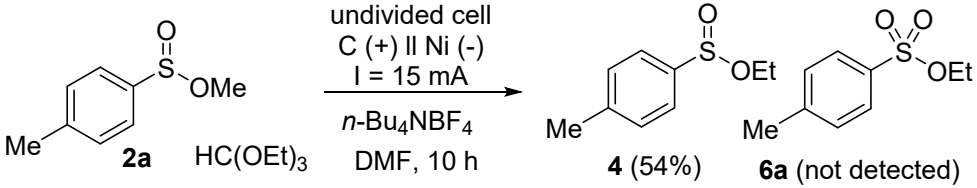
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added methyl 4-methylbenzenesulfinate (**2a**) (0.3 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in ethyl alcohol (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 15 mA at 25 °C for 10 h. The yield of **4** and **6a** were determined by gas chromatography with an internal standard (2-methoxynaphthalene).

c)



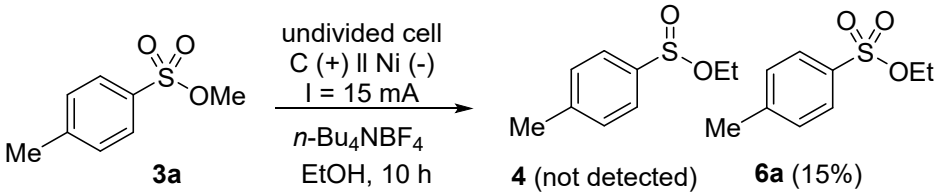
To a clean and dry 10 mL vial was added methyl 4-methylbenzenesulfinate (**2a**) (0.3 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in ethyl alcohol (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at 25 °C for 10 h. The yield of **6a** was determined by gas chromatography with an internal standard (2-methoxynaphthalene).

d)



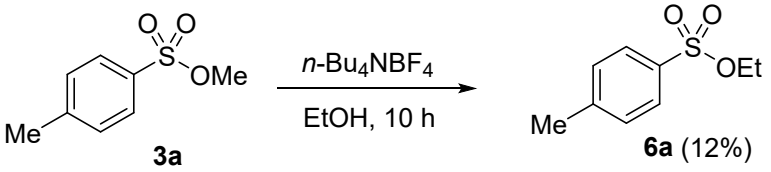
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added Methyl 4-methylbenzenesulfinate (**2a**) (0.3 mmol), triethyl orthoformate (1.5 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in DMF (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 15 mA at 25 °C for 10 h. The yield of **4** was determined by gas chromatography with an internal standard (2-methoxynaphthalene).

e)



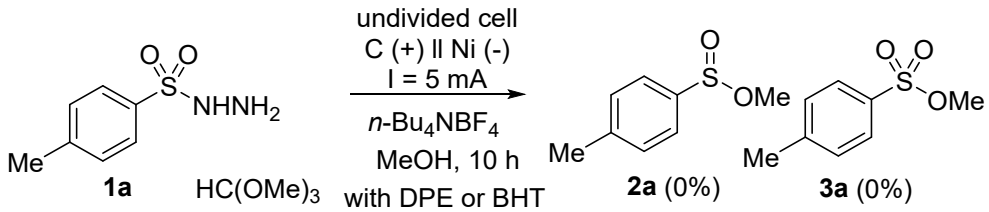
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added methyl 4-methylbenzenesulfonate (**3a**) (0.3 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in ethyl alcohol (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 15 mA at 25 °C for 10 h. The yield of **6a** was determined by gas chromatography with an internal standard (2-methoxynaphthalene).

f)



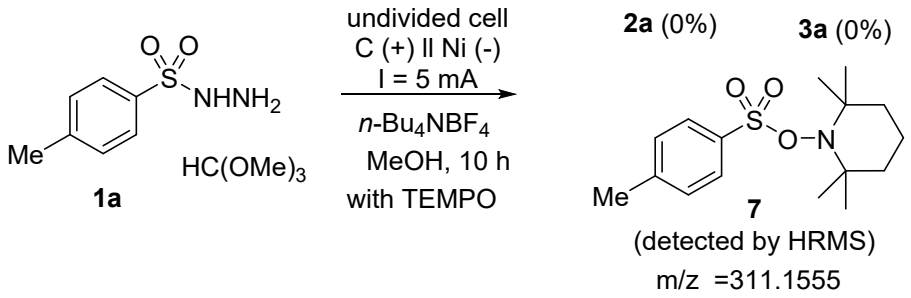
To a clean and dry 10 mL vial was added methyl 4-methylbenzenesulfonate (**3a**) (0.3 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in ethyl alcohol (5mL) under air. The electrolyte was allowed to stir and the reaction was carried out at 25 °C for 10 h. The yield of **6a** was determined by gas chromatography with an internal standard (2-methoxynaphthalene).

g)



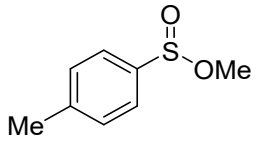
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added *p*-toluenesulfonyl hydrazide (**1a**) (0.3 mmol), trimethyl orthoformate (1.5 mmol), DPE (0.6 mmol) or BHT (0.6 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in methyl alcohol (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 5 mA at 25 °C for 10 h.

h)



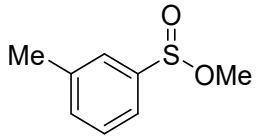
Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added sulfonyl hydrazide **1a** (0.3 mmol), trimethyl orthoformate (1.5 mmol), TEMPO (0.6 mmol), followed by 0.1 M *n*-Bu_4NBF_4 in methyl alcohol (5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 5 mA at 25 °C for 10 h. The yield of **7** was determined by gas chromatography with an internal standard (2-methoxynaphthalene) and the molecular weight was confirmed by HRMS.

8. Analytical data

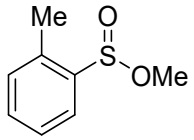


Methyl 4-methylbenzenesulfinate (2a)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (77.5 mg, 0.46 mmol, 76%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dt, J = 8.3, 1.8 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 3.46 (s, 3H), 2.43 (s,3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.97, 141.08, 129.85, 125.51, 49.52, 21.65;
MS (EI) *m/z* = 170.0 (M^+)

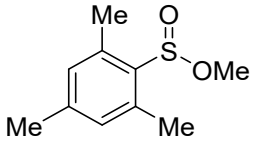


Methyl 3-methylbenzenesulfinate (2b)[1]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (65.3 mg, 0.38 mmol, 64%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 3.47 (s, 3H), 2.42 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.89, 139.37, 133.13, 129.02, 125.75, 122.61, 49.78, 21.48;
MS (EI) *m/z* = 170.0 (M^+)

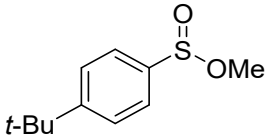


Methyl 2-methylbenzenesulfinate (2c)[2]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (69.4 mg, 0.41 mmol, 68%).
^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.76 (dd, J = 7.8, 1.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.49 – 7.45 (m, 1H), 7.37 (d, J = 7.5 Hz, 1H), 3.43 (s, 3H), 2.43 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2SO$) δ 141.07, 136.33, 132.37, 131.36, 126.33, 123.94, 50.38, 17.49
MS (EI) m/z = 170.0 (M^+)

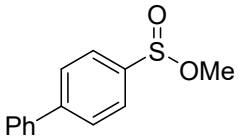


Methyl 2,4,6-trimethylbenzenesulfinate (2d)[1]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (87.9 mg, 0.44 mmol, 74%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (s, 2H), 3.78 (s, 3H), 2.58 (s, 6H), 2.27 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.12, 137.92, 137.80, 130.79, 54.51, 21.19, 19.10.
MS (EI) m/z = 198.1 (M^+)



Methyl 4-(*tert*-butyl)benzenesulfinate (2e)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (84.0 mg, 0.40 mmol, 66%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dt, J = 7.6, 2.0 Hz, 2H), 7.55 (dt, J = 9.0, 2.0 Hz, 2H), 3.48 (s, 3H), 1.34 (s, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.04, 140.98, 126.21, 125.31, 49.82, 35.23, 31.30.
MS (EI) m/z = 212.1 (M^+)



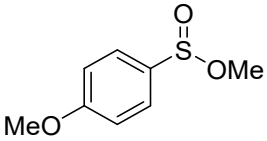
Methyl [1,1'-biphenyl]-4-sulfinate (2f)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (89.1 mg, 0.38 mmol, 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.77 – 7.74 (m, 2H), 7.63 – 7.60 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.40 (m, 1H), 3.53 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.38, 142.66, 139.77, 129.12, 128.41, 127.91, 127.44, 126.05, 49.87.

MS (EI) *m/z* = 232.1 (M^+)



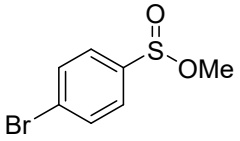
Methyl 4-methoxybenzenesulfinate (2g)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (80.4 mg, 0.43 mmol, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dt, J = 9.0, 2.5 Hz, 2H), 7.01 (dt, J = 9.0, 2.5 Hz, 2H), 3.85 (s, 3H), 3.44 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.81, 135.53, 127.28, 114.49, 55.64, 49.27.

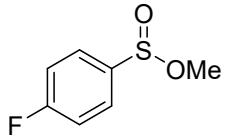
MS (EI) *m/z* = 186.0 (M^+)



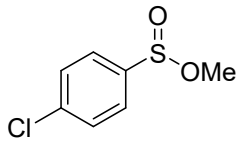
Methyl 4-bromobenzenesulfinate (2h)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (101.0 mg, 0.43 mmol, 72%).

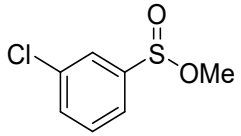
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dt, J = 8.7, 2.1 Hz, 2H), 7.56 (dt, J = 8.7, 2.1 Hz, 2H), 3.48 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.13, 132.48, 127.22, 127.20, 49.90.
HRMS (FD-TOF) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_3S$ 233.9350; Found 233.9345



Methyl 4-fluorobenzenesulfinate (2i)[1]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (61.6 mg, 0.35 mmol, 59%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.25 – 7.21 (m, 2H), 3.48 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.19 (d, J = 253.6 Hz), 139.92 (d, J = 3.1 Hz), 128.01 (d, J = 9.2 Hz), 116.50 (d, J = 22.6 Hz), 49.79.
^{19}F NMR (470 MHz, $CDCl_3$) δ -106.77 (m)
MS (EI) *m/z* = 174.0 (M^+)



Methyl 4-chlorobenzenesulfinate (2j)[1]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (77.5 mg, 0.41 mmol, 68%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.54 – 7.51 (m, 2H), 3.48 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.59, 138.79, 129.54, 127.06, 49.90.
MS (EI) *m/z* = 190.0 (M^+)



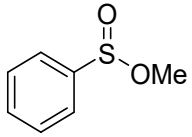
Methyl 3-chlorobenzenesulfinate (2k)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (74.1 mg, 0.39 mmol, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.68 (m, 1H), 7.58-7.56 (m, 1H), 7.53-7.51 (m, 1H), 7.48 – 7.46 (m, 1H), 3.49 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.01, 135.64, 132.48, 130.51, 125.69, 123.76, 50.04.

MS (EI) *m/z* = 190.0 (M^+)



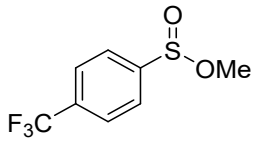
Methyl benzenesulfinate (2l)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (64.6 mg, 0.42 mmol, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.58 – 7.52 (m, 3H), 3.48 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.06, 132.34, 129.19, 125.53, 49.74.

MS (EI) *m/z* = 156.0 (M^+)

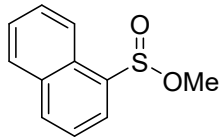


Methyl 4-(trifluoromethyl)benzenesulfinate (2m)[1]

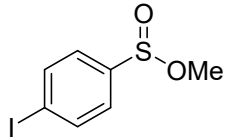
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (56.4 mg, 0.25 mmol, 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 4H), 3.51 (s, 3H).

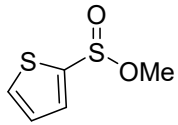
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 147.96, 134.26 (q, J = 33.0 Hz), 126.33 (q, J = 273.4 Hz), 126.25, 123.55 (q, J = 4.0 Hz), 50.32.
^{19}F NMR (470 MHz, $CDCl_3$) δ -63.01.
MS (EI) m/z = 224.0 (M^+)



Methyl 4-naphthalene-1-sulfinate (2n)[1]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (63.0 mg, 0.31 mmol, 51%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 1H), δ 8.16 – 8.14 (m, 1H), δ 8.04 – 8.02 (m, 1H), δ 7.95 – 7.93 (m, 1H), δ 7.64 – 7.56 (m, 3H), δ 3.43 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 138.33, 133.80, 133.03, 129.47, 128.90, 127.65, 126.88, 124.85, 124.84, 122.37, 49.59.
MS (EI) m/z = 206.0 (M^+)



Methyl 4-iodobenzenesulfinate (2o)[7]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (49.0 mg, 0.17 mmol, 29%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.41 – 7.38 (m, 2H), 3.45 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 143.75, 138.28, 127.05, 99.50, 49.83.
MS (EI) m/z = 281.9 (M^+)



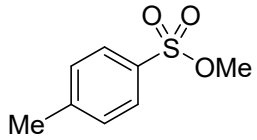
Methyl thiophene-2-sulfinate (2s)[2]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (25.1 mg, 0.17 mmol, 29%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 4.9, 1.2 Hz, 1H), 7.49 (dd, J = 3.7, 1.3 Hz, 1H), 7.17–7.15 (m, 1H), 3.60 (s, 3H)

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.16, 131.79, 130.09, 127.92, 49.47.

MS (EI) m/z = 144.0 (M^+)



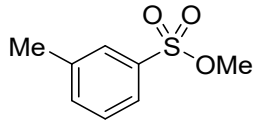
Methyl 4-methylbenzenesulfonate (3a)[3]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (80.4 mg, 0.43 mmol, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.72 (s, 3H), 2.44 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.04, 132.22, 129.97, 128.12, 56.28, 21.69.

MS (EI) m/z = 186.0 (M^+)



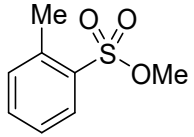
Methyl 3-methylbenzenesulfonate (3b)[3]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (64.7 mg, 0.35 mmol, 58%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.77 (m, 2H), 7.36 – 7.33 (m, 2H), 3.72 (s, 3H), 2.44 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.76, 135.17, 134.78, 129.22, 128.46, 125.30, 56.40, 21.43.

MS (EI) *m/z* = 186.0 (M^+)



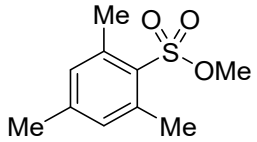
Methyl 2-methylbenzenesulfonate (3c)[4]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (65.8 mg, 0.35 mmol, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, J = 7.8, 1.5 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.38 – 7.32 (m, 2H), 3.72 (s, 3H), 2.64 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.57, 133.95, 133.69, 132.73, 130.35, 126.27, 56.12, 20.32.

MS (EI) *m/z* = 186.0 (M^+)



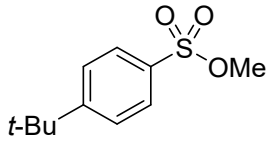
Methyl 2,4,6-trimethylbenzenesulfonate (3d)

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (83.5 mg, 0.39 mmol, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 3.69 (s, 3H), 2.62 (s, 6H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.46, 140.16, 131.83, 129.88, 55.20, 22.63, 21.12.

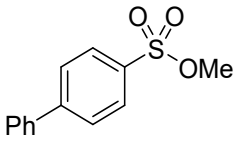
HRMS (FD-TOF) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_3S$ 214.0664; Found 214.0658



Methyl 4-(*tert*-butyl)benzenesulfonate (3e)[3]

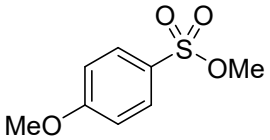
According to the general procedure, the product was purified by chromatography on silica gel

eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (95.8 mg, 0.42 mmol, 70%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.58 – 7.55 (m, 2H), 3.75 (s, 3H), 1.35 (s, 9H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 157.96, 132.24, 128.03, 126.39, 56.33, 35.40, 31.14.
MS (EI) *m/z* = 228.1 (M^+)



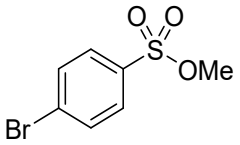
Methyl [1,1′-Biphenyl]-4-sulfonate (3f)[4]

According to the general procedure, the product was purified by chromatography on silica gel
eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (86.3 mg, 0.35 mmol, 58%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.78 – 7.75 (m, 2H), 7.63 – 7.60 (m, 2H), 7.52 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 3.81 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 147.02, 139.16, 133.86, 129.27, 128.90, 128.72, 128.01, 127.51, 56.48.
MS (EI) *m/z* = 248.1 (M^+)



Methyl 4-methoxybenzenesulfonate (3g)[3]

According to the general procedure, the product was purified by chromatography on silica gel
eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (87.3 mg, 0.43 mmol, 72%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dt, J = 8.9, 2.5 Hz, 2H), 7.00 (dt, J = 9.0, 2.5 Hz, 2H), 3.86 (s, 3H), 3.70 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 163.91, 130.28, 126.49, 114.53, 56.12, 55.79.
MS (EI) *m/z* = 202.0 (M^+)



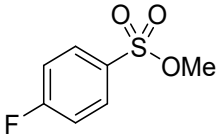
Methyl 4-bromobenzenesulfonate (3h)[5]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (105.0 mg, 0.42 mmol, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dt, J = 8.8, 2.1 Hz, 2H), 7.71 (dt, J = 8.8, 2.1, 2H), 3.77 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.40, 132.76, 129.63, 129.26, 56.62.

HRMS (FD-TOF) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_3S$ 249.9299; Found 249.9294



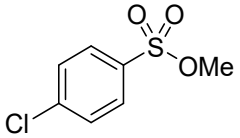
Methyl 4-fluorobenzenesulfonate (3i)[6]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (71.8 mg, 0.38 mmol, 63%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.20 – 7.16 (m, 2H), 3.71 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.94 (d, J = 257.1 Hz), 131.42 (d, J = 3.3 Hz), 131.0 (d, J = 9.6 Hz), 116.77 (d, J = 22.9 Hz), 56.48.

^{19}F NMR (470 MHz, $CDCl_3$) δ -103.12 (m)

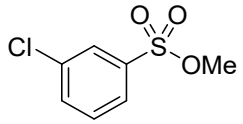


Methyl 4-chlorobenzenesulfinate (3j)[3]

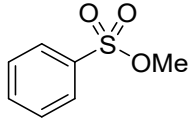
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (76.6 mg, 0.37mmol, 62%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.55 – 7.52 (m, 2H), 3.77 (s, 3H).

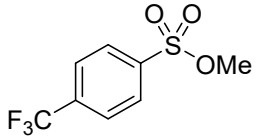
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 140.70, 133.82, 129.75, 129.57, 56.60.
MS (EI) *m/z* = 206.0 (M^+)



Methyl 3-chlorobenzenesulfonate (3k)[3]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (75.4 mg, 0.37 mmol, 61%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (t, J = 1.9 Hz, 1H), 7.80 (ddd, J = 7.8, 1.8, 1.0 Hz, 1H), 7.64 (ddd, J = 8.1, 2.1, 1.1 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 3.79 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 137.08, 135.68, 134.17, 130.72, 128.20, 126.24, 56.80.

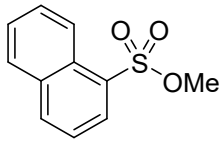


Methyl benzenesulfonate (3l)[3]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (69.1 mg, 0.40 mmol, 67%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.54 (m, 2H), 3.75 (s, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 135.32, 133.99, 129.39, 128.11, 56.45.
MS (EI) *m/z* = 172.0 (M^+)

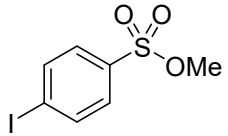


Methyl 4-(trifluoromethyl)benzenesulfinate (3m)
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (79.2 mg, 0.33 mmol, 55%).

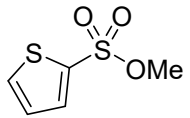
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 2H), 7.86 – 7.83 (m, 2H), 3.82 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.06, 135.70 (q, J = 33.4 Hz), 128.74, 126.60 (q, J = 3.7 Hz), 123.17 (q, J = 273.7 Hz), 56.88.
^{19}F NMR (470 MHz, $CDCl_3$) δ -63.46.
HRMS (FD-TOF) *m/z*: $[M]^+$ Calcd. for $C_8H_7F_3O_3S$ 240.0068; Found 240.0064



Methyl 4-naphthalene-1-sulfonate (3n)[3]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (86.6 mg, 0.39 mmol, 65%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 8.7 Hz, 1H), 8.29 (dd, J = 7.3, 1.4 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.3 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.64 – 7.60 (m, 1H), 7.58 – 7.54 (m, 1H), 3.71 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.47, 134.23, 130.86, 130.41, 128.95, 128.79, 128.49, 127.35, 124.96, 124.09, 56.52.
MS (EI) *m/z* = 222.0 (M^+)



Methyl 4-iodobenzenesulfonate (3o)[5]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (41.1 mg, 0.14 mmol, 23%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.60 – 7.58 (m, 2H), 3.75 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.63, 134.88, 129.32, 101.76, 56.64.
MS (EI) *m/z* = 297.9 (M^+)



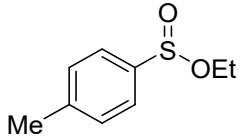
Methyl thiophene-2-sulfonate (3s)

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (20.2 mg, 0.13 mmol, 21%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.16-7.14 (m, 1H), 3.82 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 134.88, 134.64, 133.96, 127.70, 57.08.

HRMS (FD-TOF) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_3S$ 177.9758; Found 177.9753



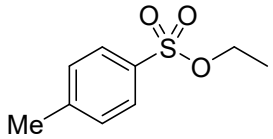
Ethyl 4-methylbenzenesulfinate (4)[2]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (79.2 mg, 0.40 mmol, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.31 – 7.30 (m, 2H), 4.10 – 4.04 (m, 1H), 3.72 – 3.66 (m, 1H), 2.40 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.67, 141.89, 129.72, 125.23, 60.72, 21.53, 15.61.

MS (EI) *m/z* = 184.1 (M^+)

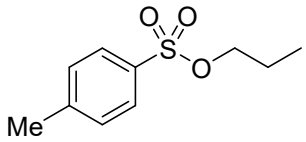


Ethyl 4-methylbenzenesulfonate (6a)[4]

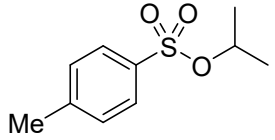
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (83.5 mg, 0.42 mmol, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.32 (m, 2H), 4.09 (q, J = 7.3 Hz, 2H), 2.44 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.79, 133.40, 129.93, 127.94, 66.92, 21.71, 14.86.
MS (EI) *m/z* = 200.1 (M^+)



Propyl 4-methylbenzenesulfonate (6b)[4]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (83.5 mg, 0.39 mmol, 65%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.34– 7.32 (m, 2H), 3.97 (t, J = 6.5 Hz, 2H), 2.43 (s, 3H), 1.65 (qt, J = 7.5, 6.5 Hz, 2H), 0.88 (t, J = 7.5 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.75, 133.31, 129.90, 127.93, 72.25, 22.38, 21.69, 10.04.
MS (EI) *m/z* = 214.1 (M^+)



Isopropyl 4-methylbenzenesulfonate (6c)[4]
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (95:5) and obtained as a colorless oil (78.4 mg, 0.37 mmol, 61%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.32 (d, J = 7.8 Hz, 2H), 4.71 (hept, J = 6.4 Hz, 1H), 2.42 (s, 3H), 1.25 (d, J = 6.4 Hz, 6H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.51, 134.61, 129.84, 127.72, 77.19, 22.83, 21.68
MS (EI) *m/z* = 214.1 (M^+)

9. Reference

(1) G. Zhang, Q. Fan, H, Wang, Y. Zhao and C. Ding, $NaHSO_3$-Mediated Direct Synthesis of Sulfinic Esters from Sulfonyl Hydrazides under Transition-Metal-Free Conditions, *Adv. Synth.Catal*., 2021, **363**, 833–837.

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(4) Y. Wang, L. Deng, Y. Deng and J. Han, Copper-Catalyzed Multicomponent Reaction of DABCO·$(SO_2)_2$, Alcohols, and Aryl Diazoniums for the Synthesis of Sulfonic Esters*, J. Org. Chem.,* 2018, **83**, 4674–4680.

(5) B. K. G. Bhatthula, J. R. Kanchani, V. R. Arava and S. M. C. Subbarao, A simple method for the synthesis of sulfonic esters, *Synth. Commun.,* 2020, **50**, 3133–3148

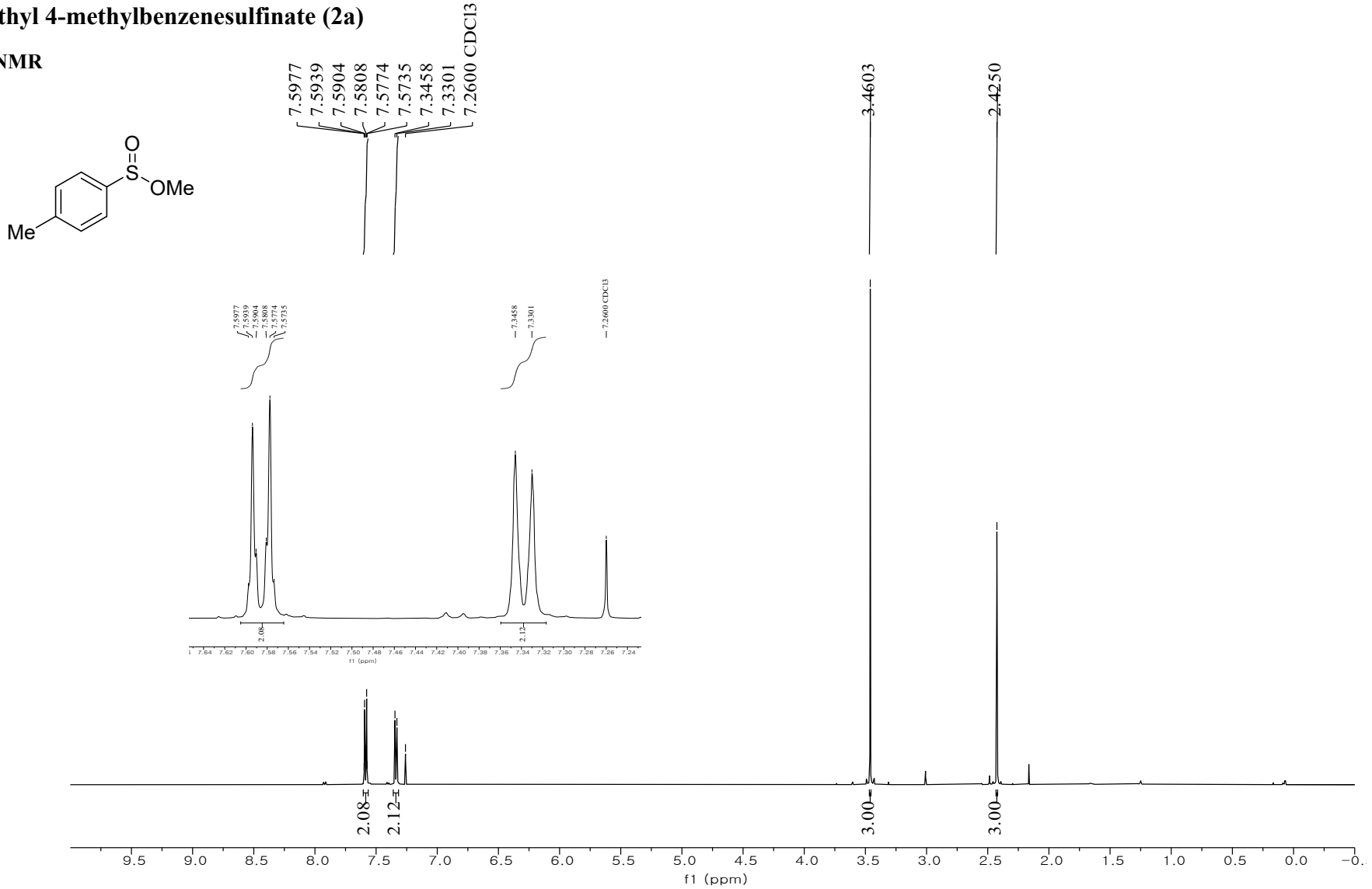
(6) A. K. Singh, H. Yi, G. Zhang, C. Bian, P. Pei and A. Lei, Photoinduced Oxidative Cross-Coupling for O–S Bond Formation: A Facile Synthesis of Alkyl Benzenesulfonates, *Synlett*., 2017, **28**, 1558–1563.

(7) B. Du, Z. Li, P. Qian, J. Han, Y. Pan, Copper-Catalyzed Aerobic Oxidative Reaction of Sulfonyl Hydrazides with Alcohols: An Easy Access to Sulfinates, *Chem. Asian J*., 2016, **11**, 478–481.

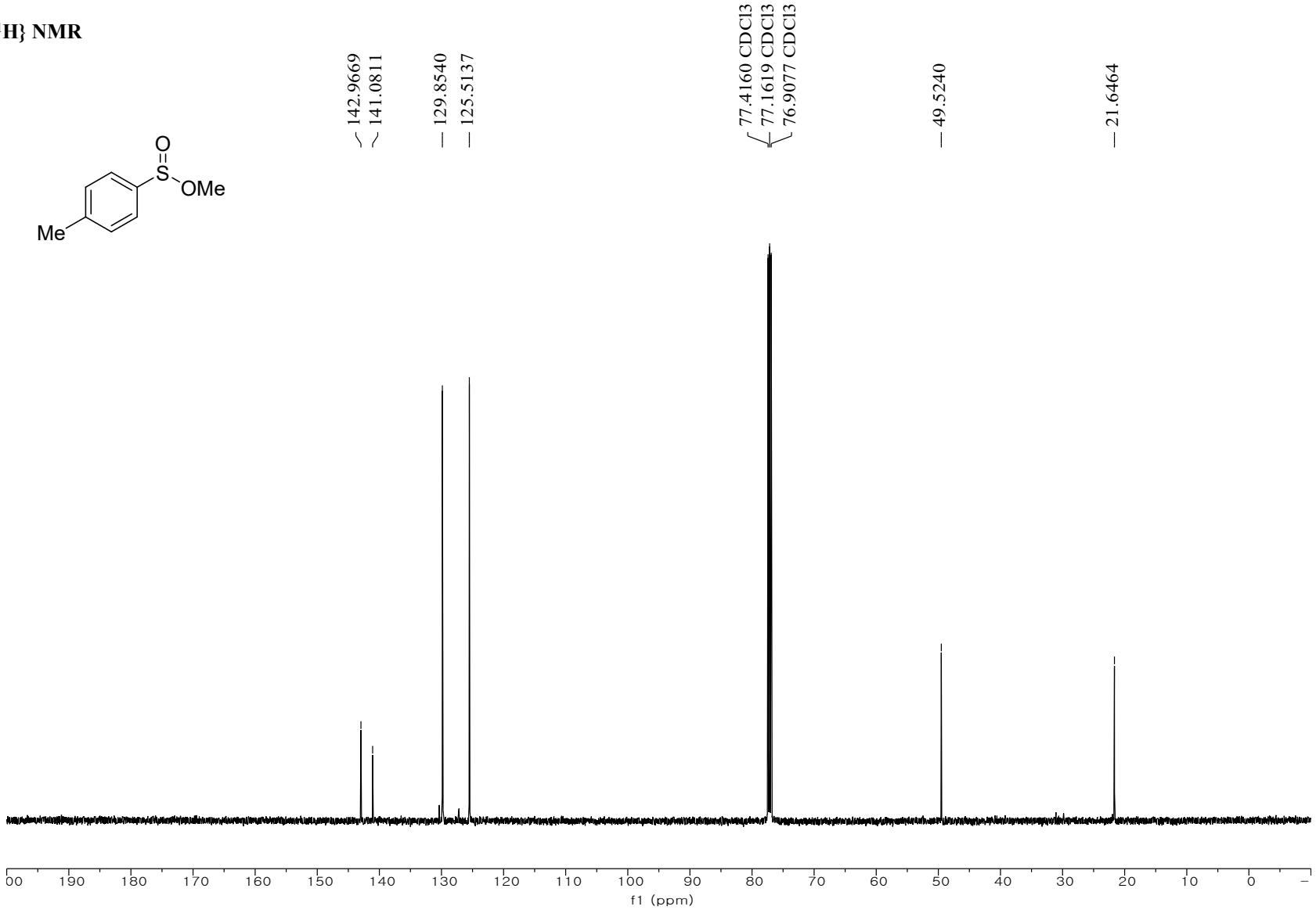
10. ^{1}H and ^{13}C NMR spectra of products

Methyl 4-methylbenzenesulfinate (2a)

^{1}H NMR

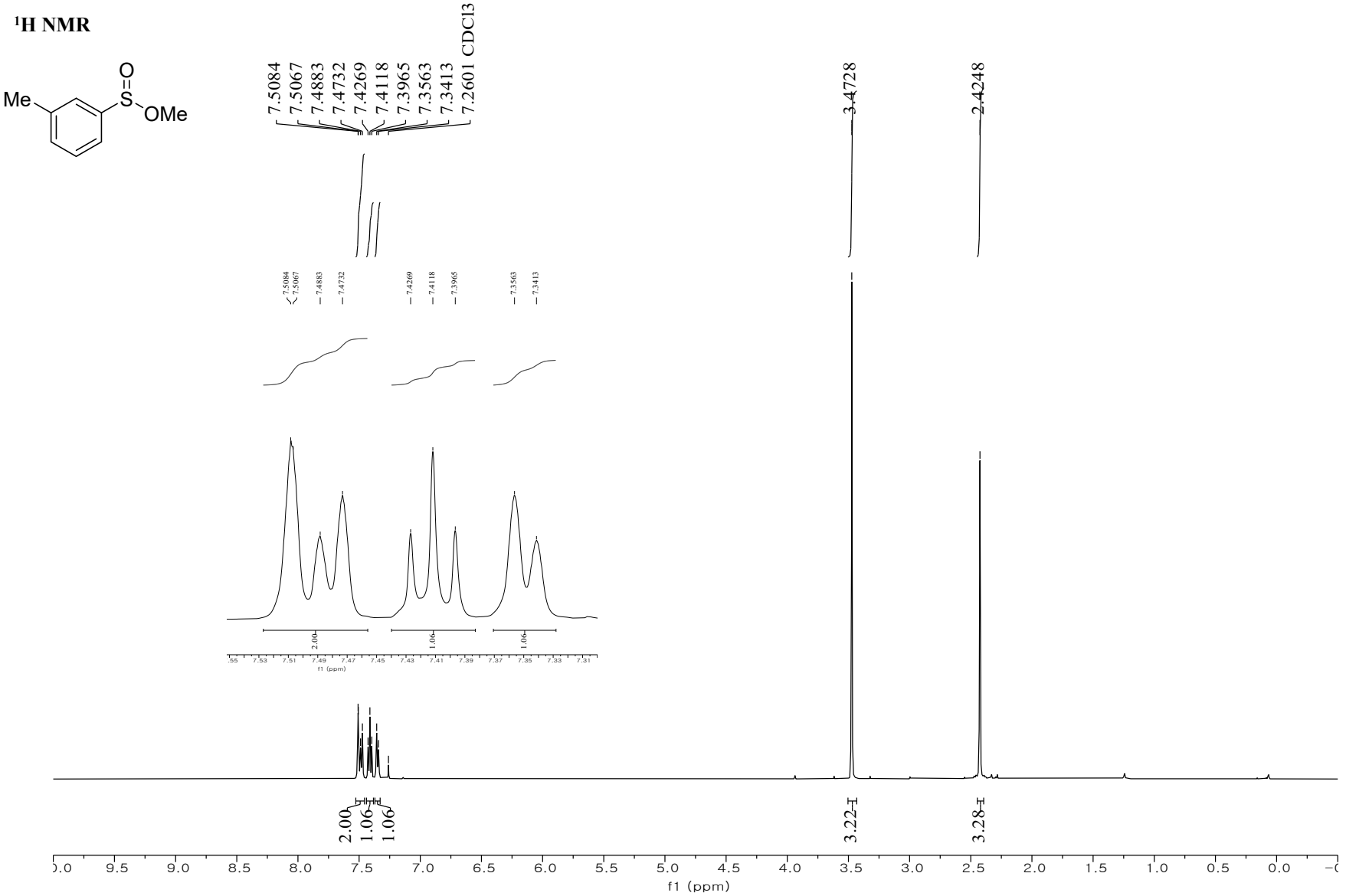


$^{13}C\{^{1}H\}$ NMR

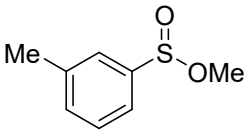

142.9669
141.0811
129.8540
125.5137
77.4160 CDCl3
77.1619 CDCl3
76.9077 CDCl3
49.5240
21.6464
O
S
OMe
Me
f1 (ppm)

Methyl 3-methylbenzenesulfinate (2b)

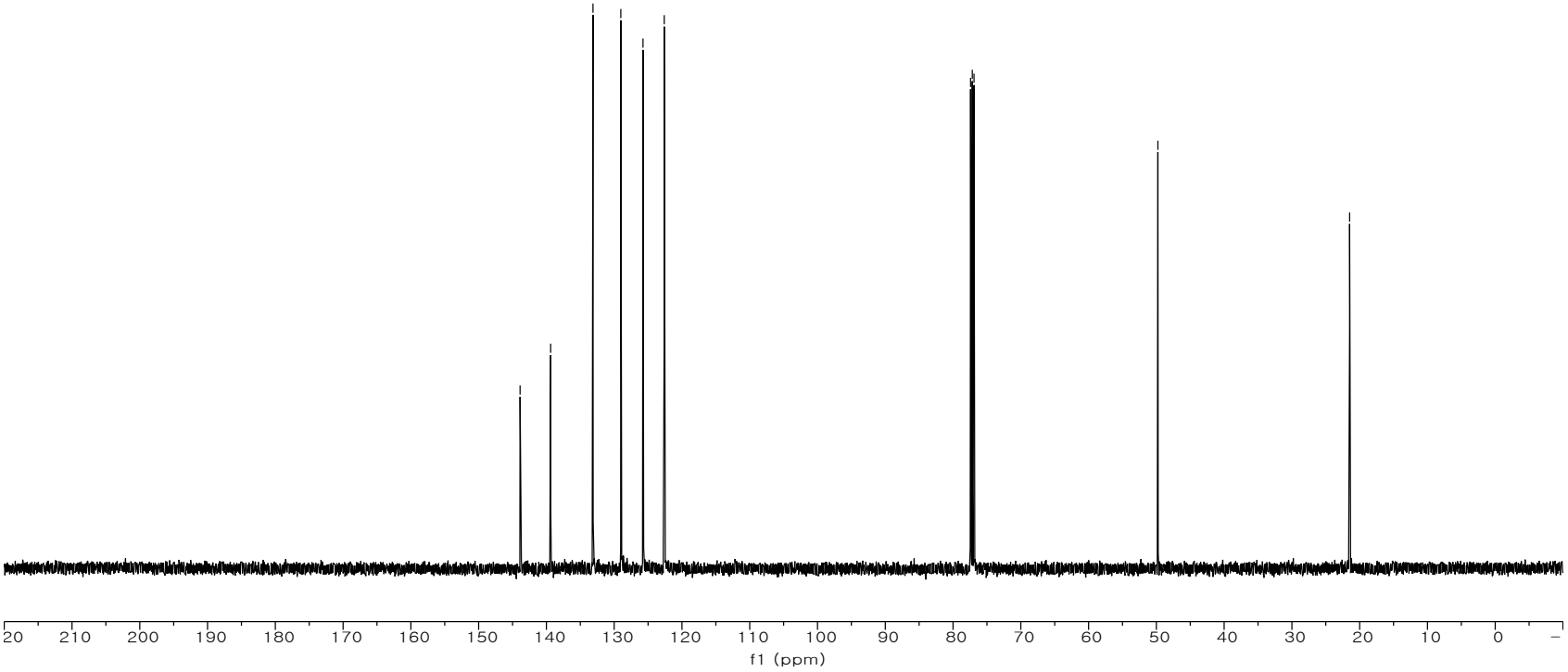
^{1}H NMR



$^{13}C\{^{1}H\}$ NMR

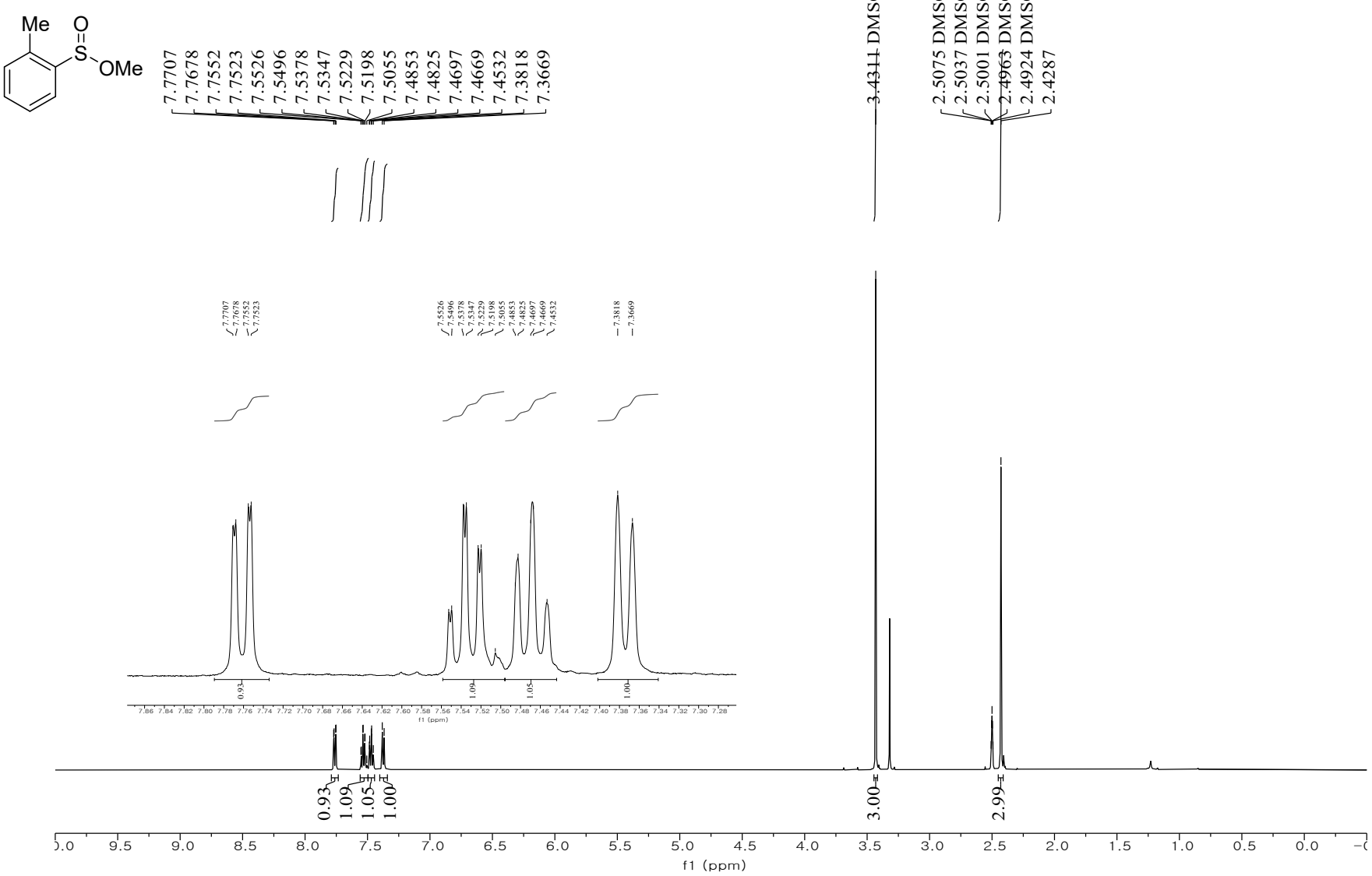


143.8860
139.3739
133.1283
129.0240
125.7485
122.6134
77.4146 CDCl3
77.1605 CDCl3
76.9064 CDCl3
49.7750
21.4848

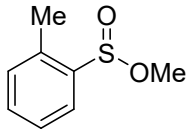


Methyl 2-methylbenzenesulfinate (2c)

^{1}H NMR



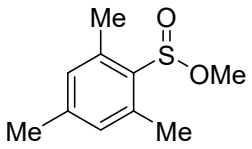
$^{13}C\{^{1}H\}$ NMR


Me
O
S
OMe

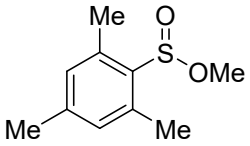
141.0661
136.3283
132.3701
131.3592
126.3331
123.9415
50.3847
40.0196 DMSO-d6
39.8546 DMSO-d6
39.6877 DMSO-d6
39.5208 DMSO-d6
39.3520 DMSO-d6
39.1851 DMSO-d6
39.0182 DMSO-d6
17.4915
f1 (ppm)

Methyl 2,4,6-trimethylbenzenesulfinate (2d)

^{1}H NMR



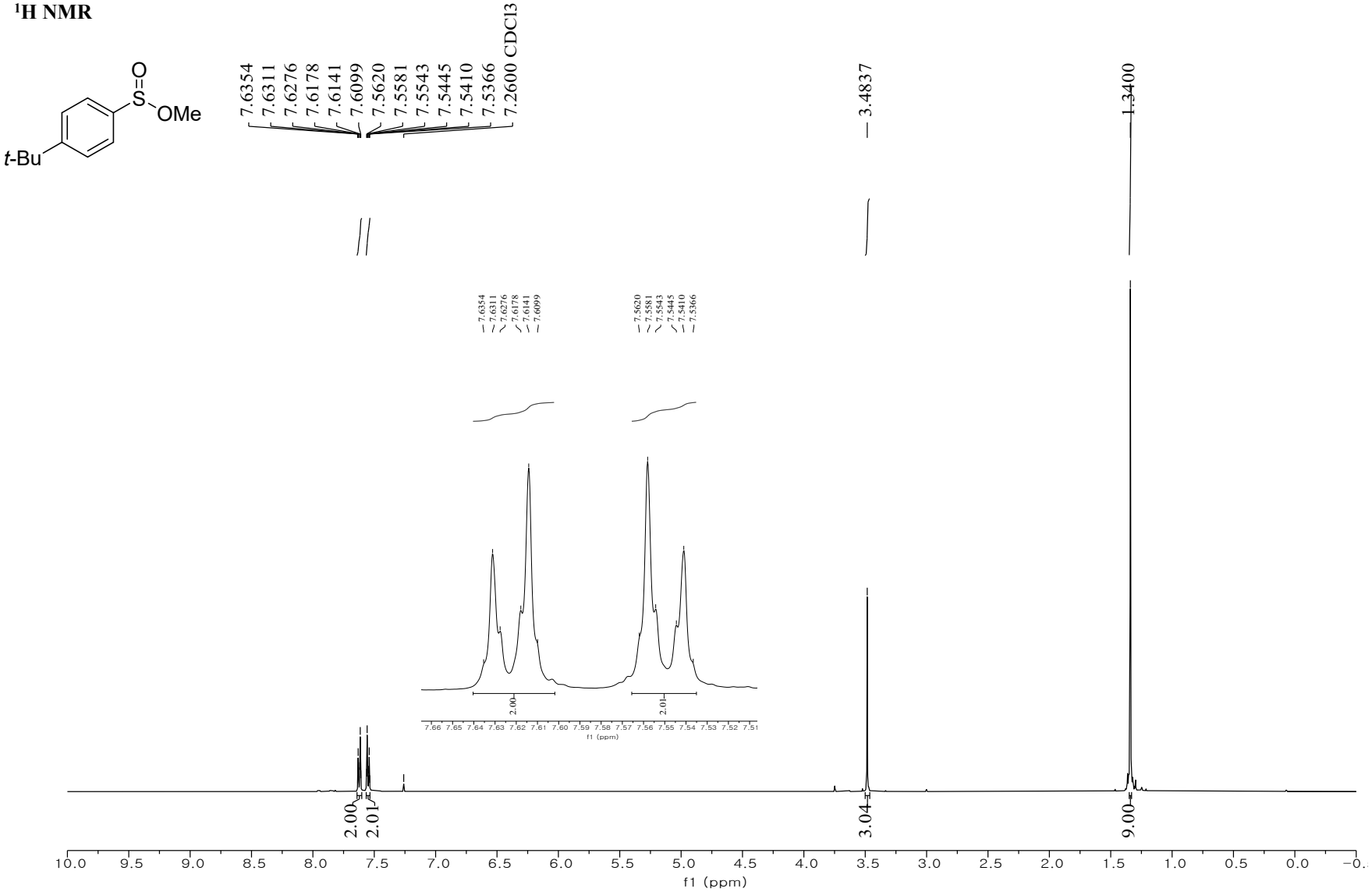
$^{13}C\{^{1}H\}$ NMR


Me
O
S
OMe
Me
Me

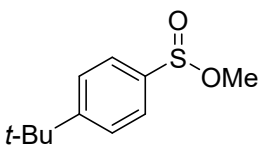
142.1225
137.9234
137.7982
130.7920
77.4150 CDCl3
77.1609 CDCl3
76.9049 CDCl3
54.5075
21.1912
19.1030
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

Methyl 4-(tert-butyl)benzenesulfinate (2e)

^{1}H NMR



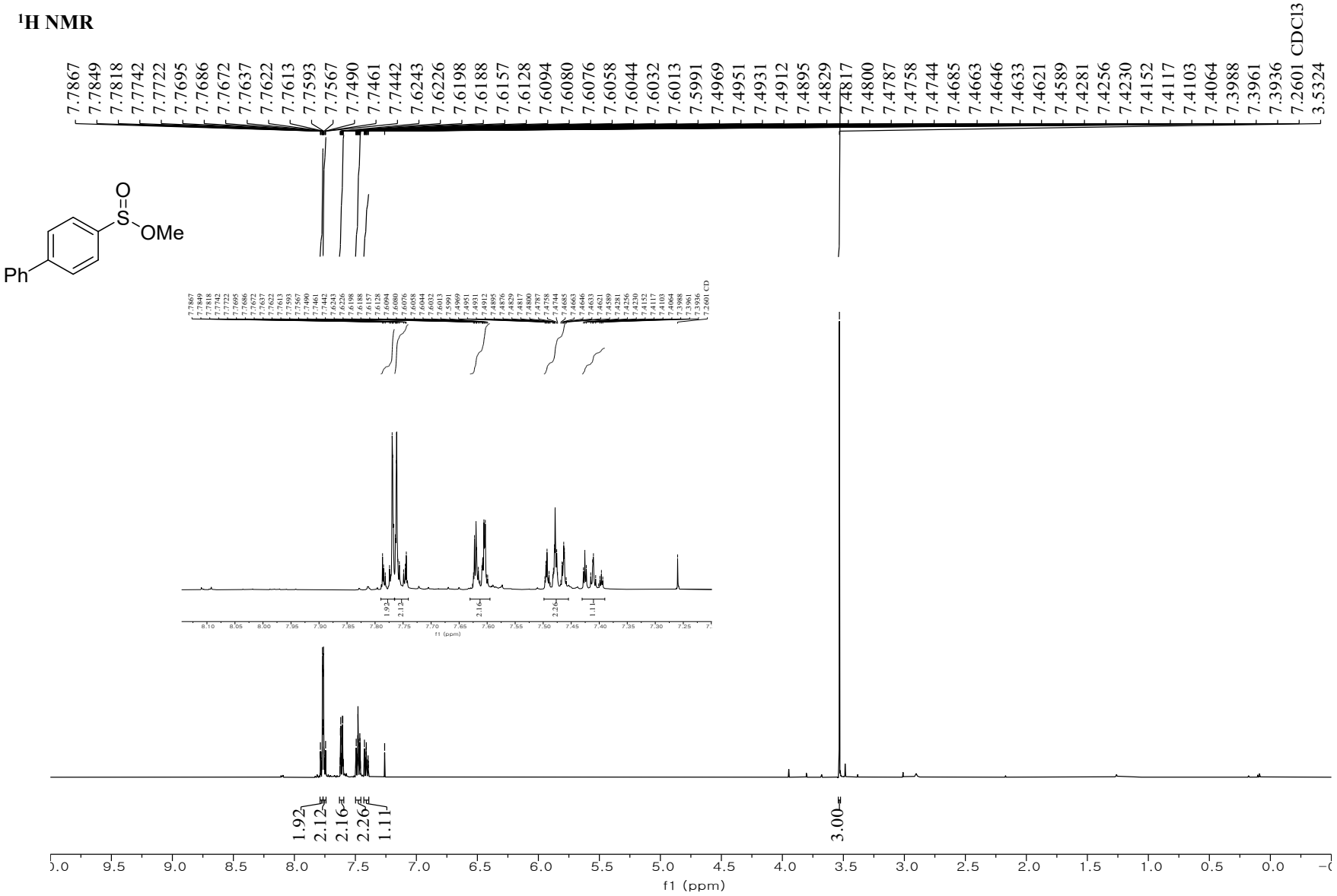
$^{13}C\{^{1}H\}$ NMR


O
S
OMe
t-Bu

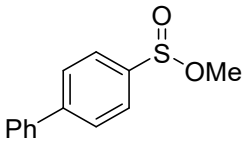
156.04
140.98
126.21
125.31
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
49.82
35.23
31.30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl [1,1'-biphenyl]-4-sulfinate (2f)

^{1}H NMR



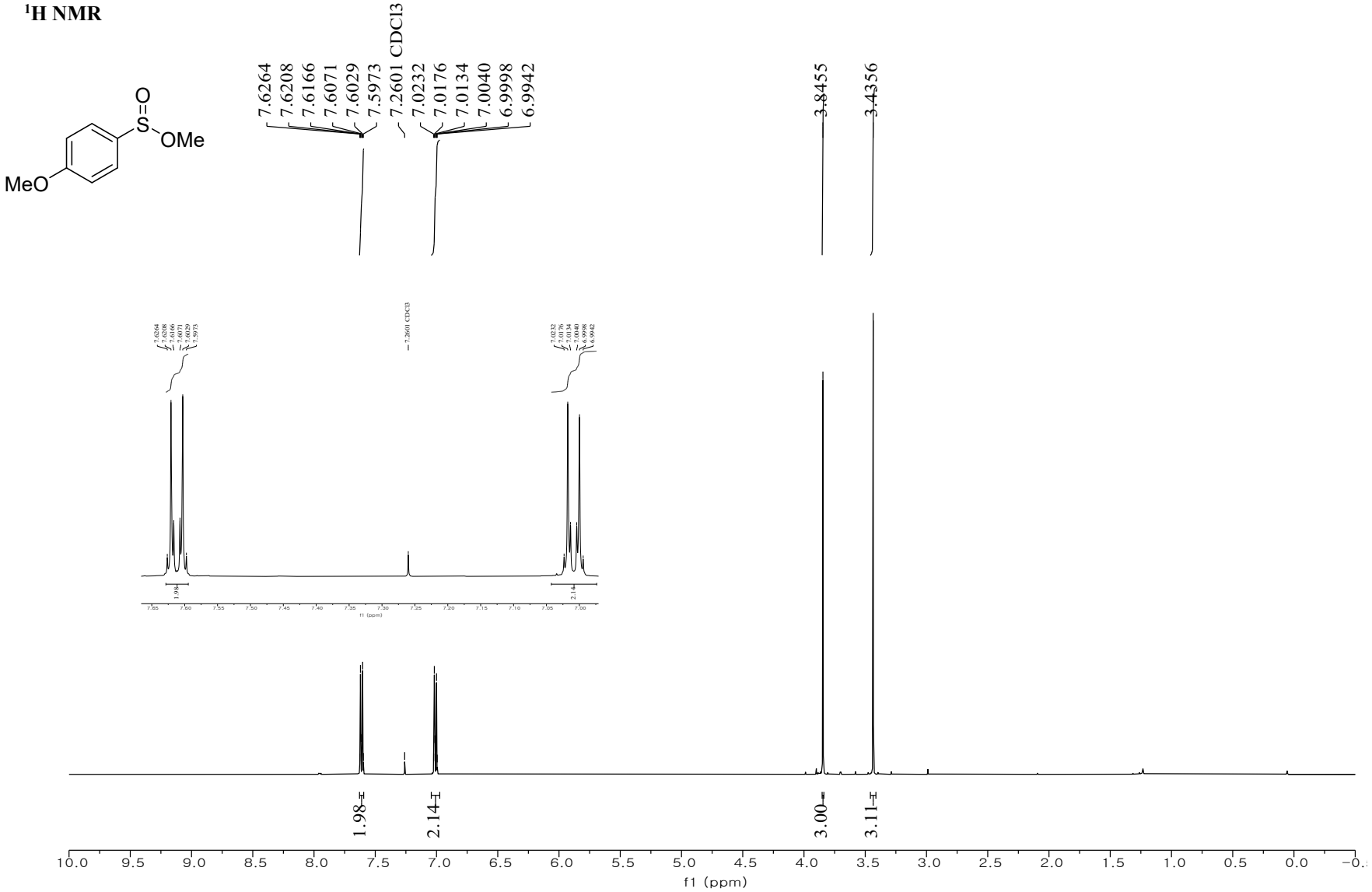
$^{13}C\{^{1}H\}$ NMR


O
S
OMe
Ph

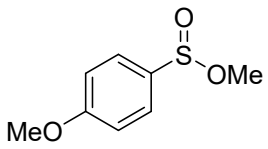
145.3775
142.6558
139.7653
129.1214
128.4083
127.9094
127.4429
126.0526
77.4153 CDCl3
77.1612 CDCl3
76.9051 CDCl3
49.8667
f1 (ppm)

Methyl 4-methoxybenzenesulfinate (2g)

^{1}H NMR



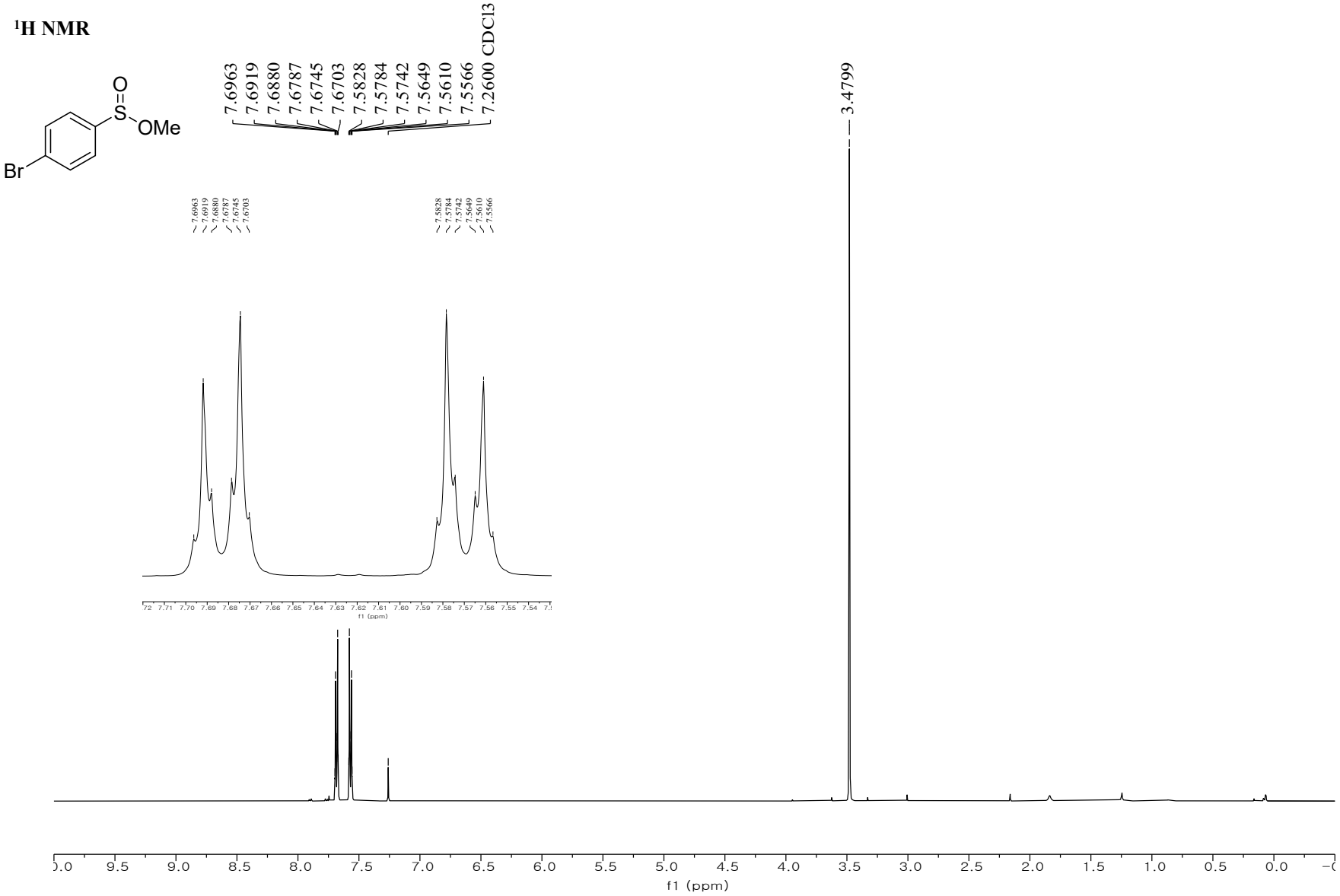
$^{13}C\{^{1}H\}$ NMR


O
S
OMe
MeO

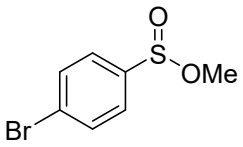
162.81
135.53
127.28
114.49
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
55.64
49.27
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 4-bromobenzenesulfinate (2h)

^{1}H NMR



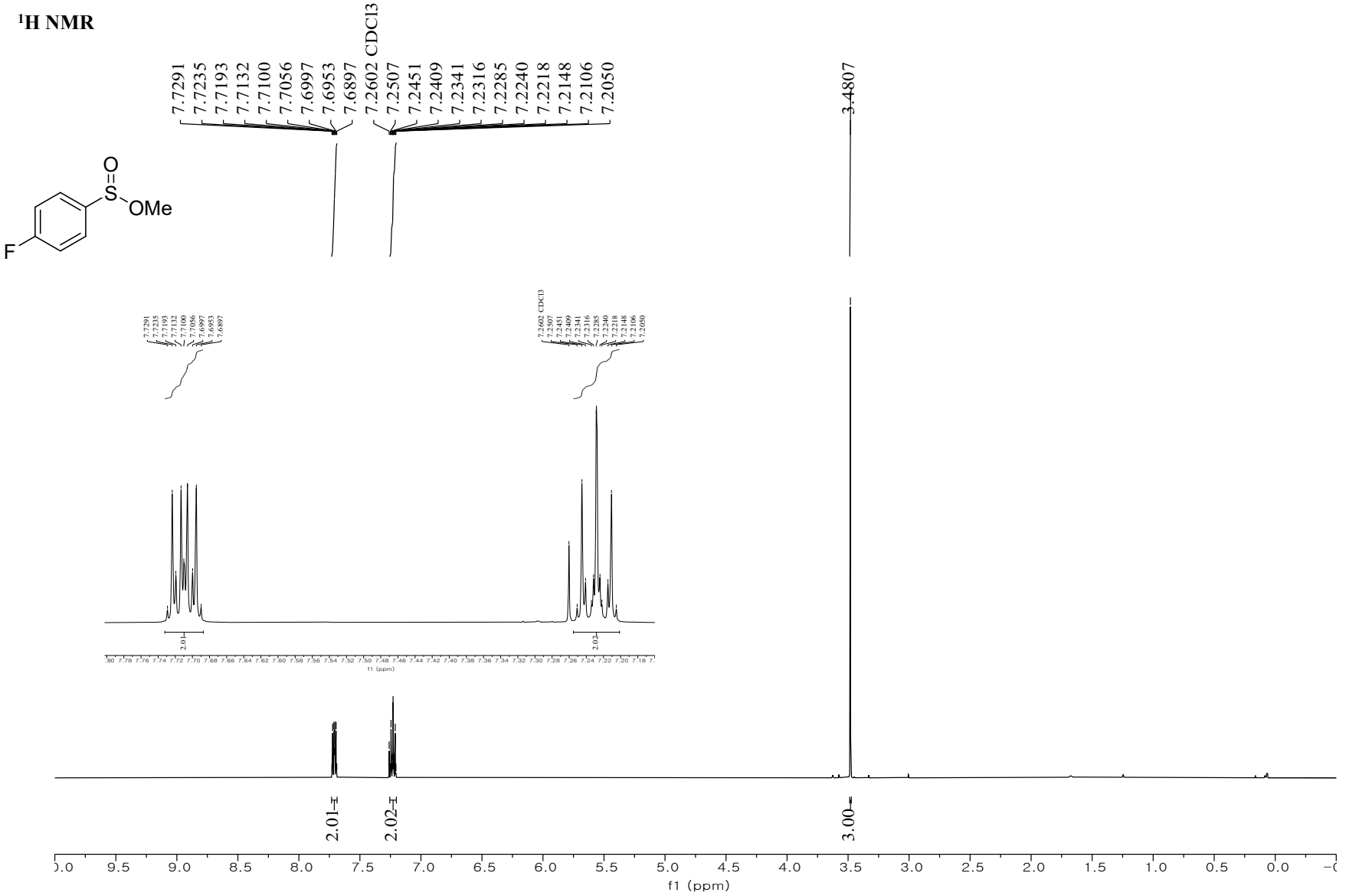
$^{13}C\{^{1}H\}$ NMR


O
S
OMe
Br

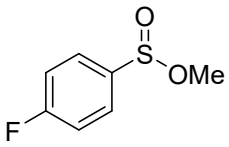
143.1335
132.4801
127.2207
127.2036
77.4150 CDCl3
77.1609 CDCl3
76.9068 CDCl3
49.9063
f1 (ppm)

Methyl 4-fluorobenzenesulfinate (2i)

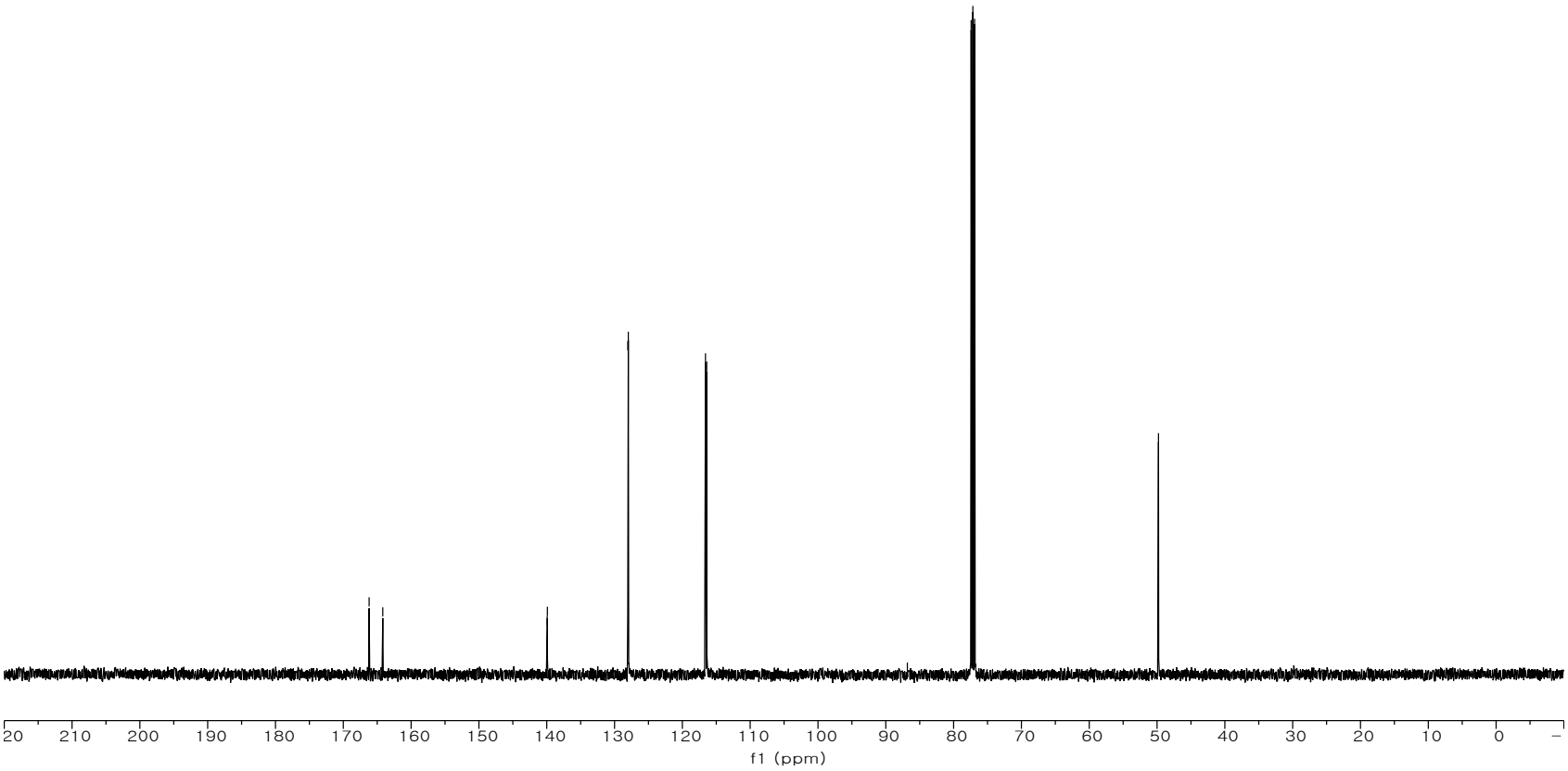
^{1}H NMR



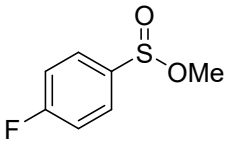
$^{13}C\{^{1}H\}$ NMR



166.1930
164.1801
139.9312
139.9063
128.0446
127.9719
116.5914
116.4120
86.8186
77.4154 CDCl3
77.1613 CDCl3
76.9072 CDCl3
49.7888



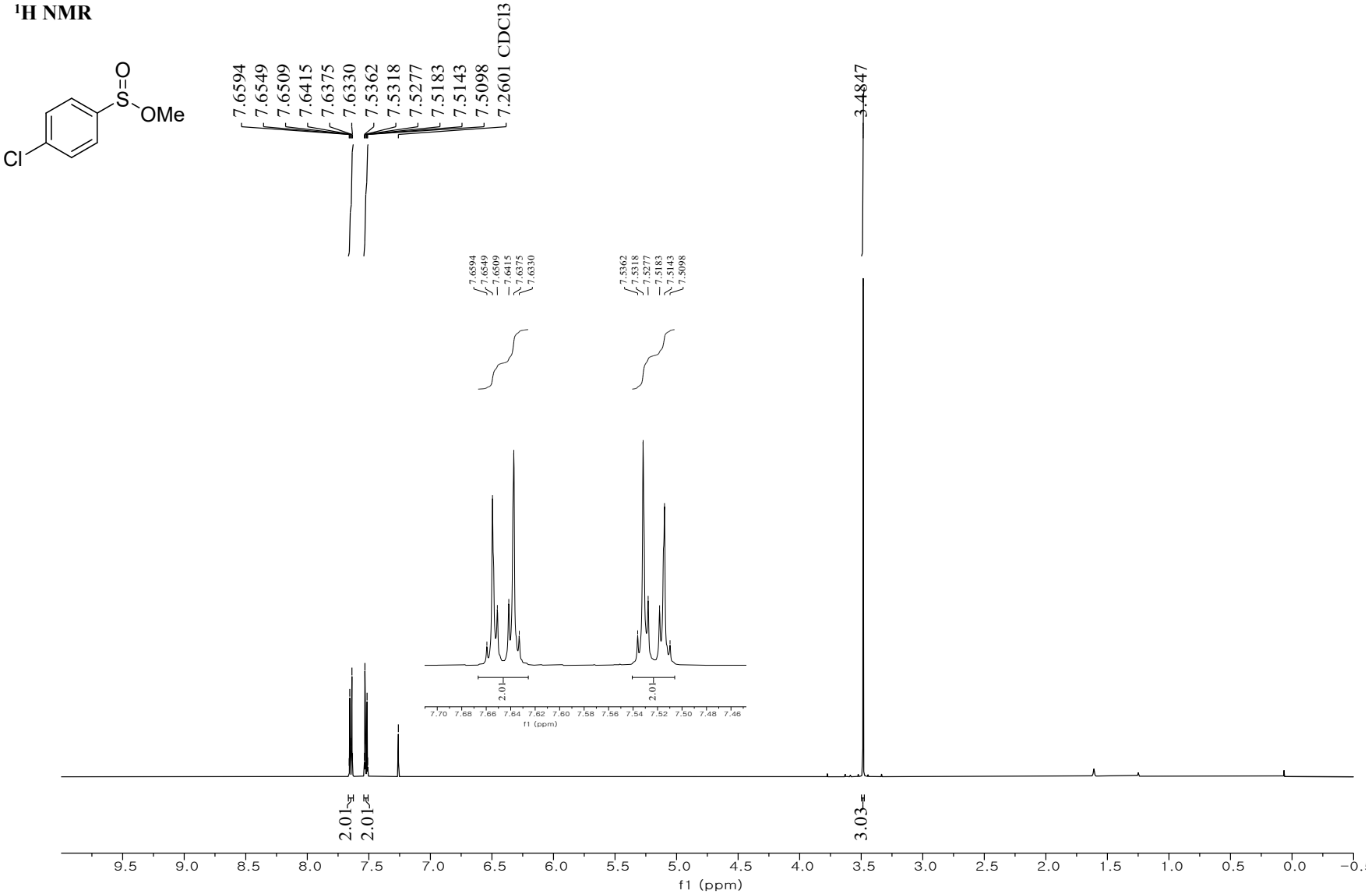
^{19}F NMR


O
S
OMe
F

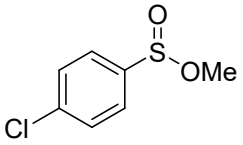
-106.74
-106.75
-106.76
-106.76
-106.77
-106.78
-106.78
-106.79
-106.80
f1 (ppm)
f1 (ppm)

Methyl 4-chlorobenzenesulfinate (2j)

^{1}H NMR



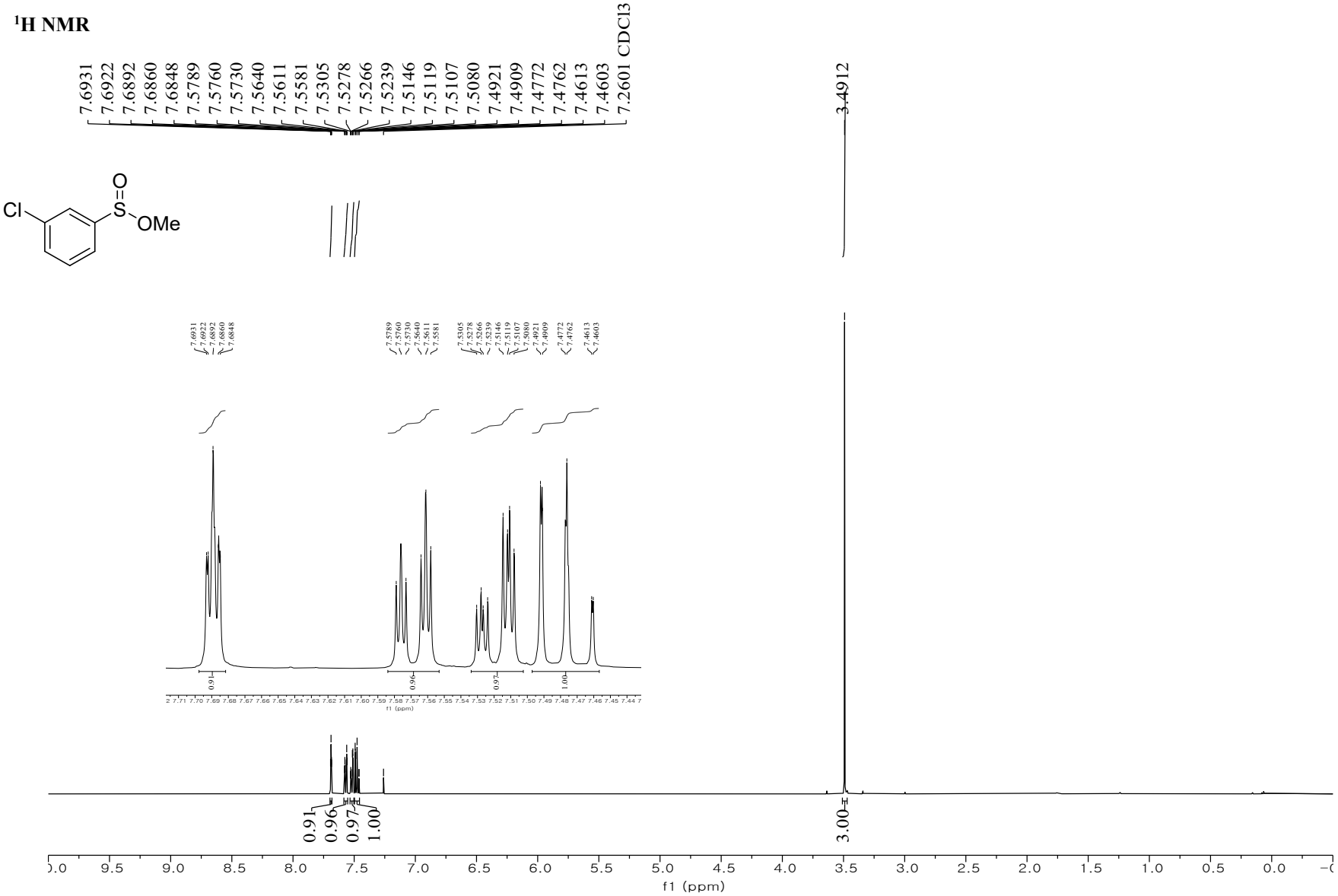
$^{13}C\{^{1}H\}$ NMR


O
S
OMe
Cl

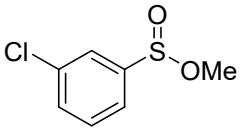
142.59
138.79
129.54
127.06
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
49.90
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 3-chlorobenzenesulfinate (2k)

^{1}H NMR



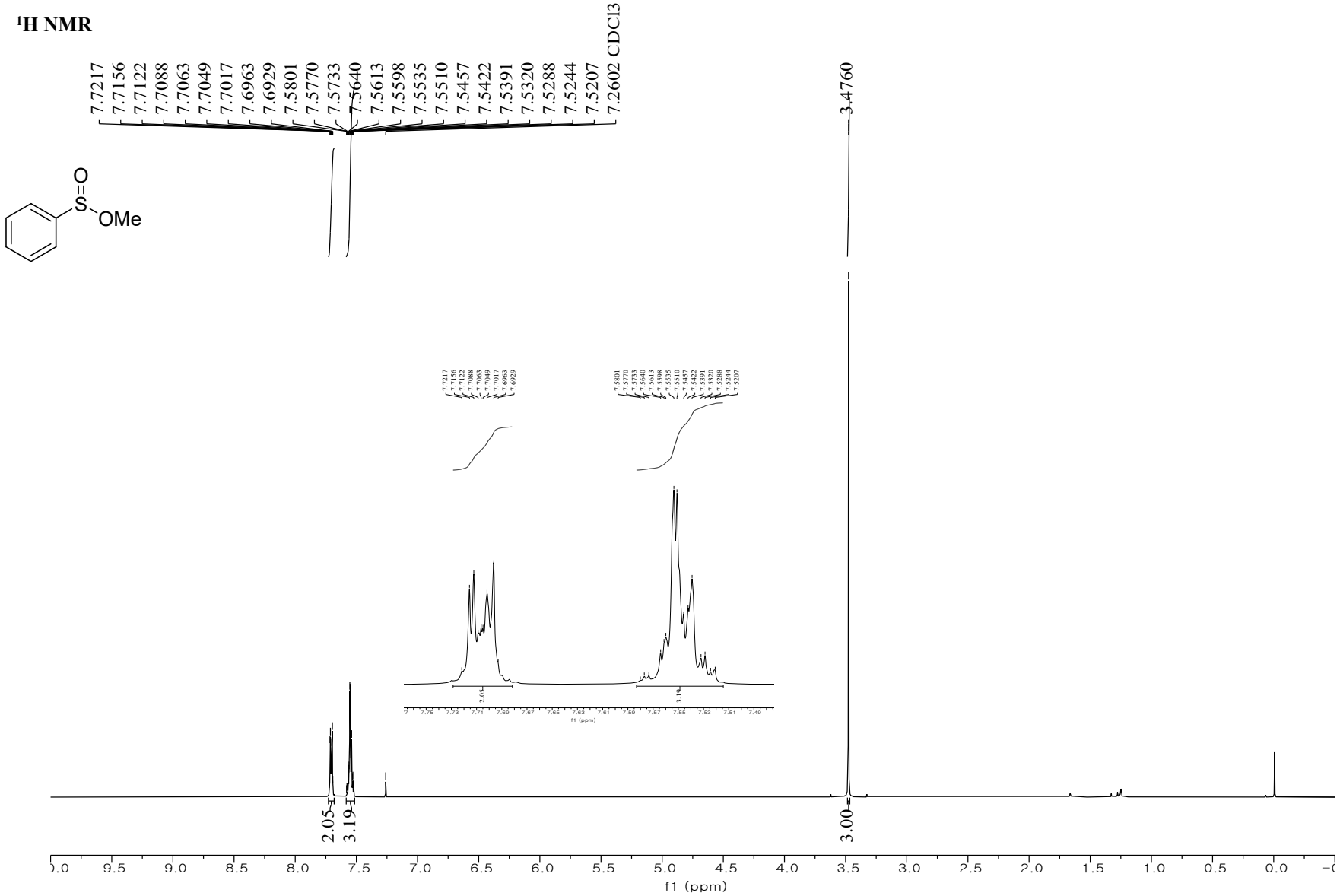
$^{13}C\{^{1}H\}$ NMR


Cl
O
S
OMe

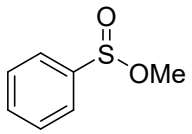
146.0111
135.6414
132.4810
130.5065
125.6930
123.7555
77.4139 CDCl3
77.1598 CDCl3
76.9057 CDCl3
50.0374
f1 (ppm)

Methyl benzenesulfinate (2l)

^{1}H NMR



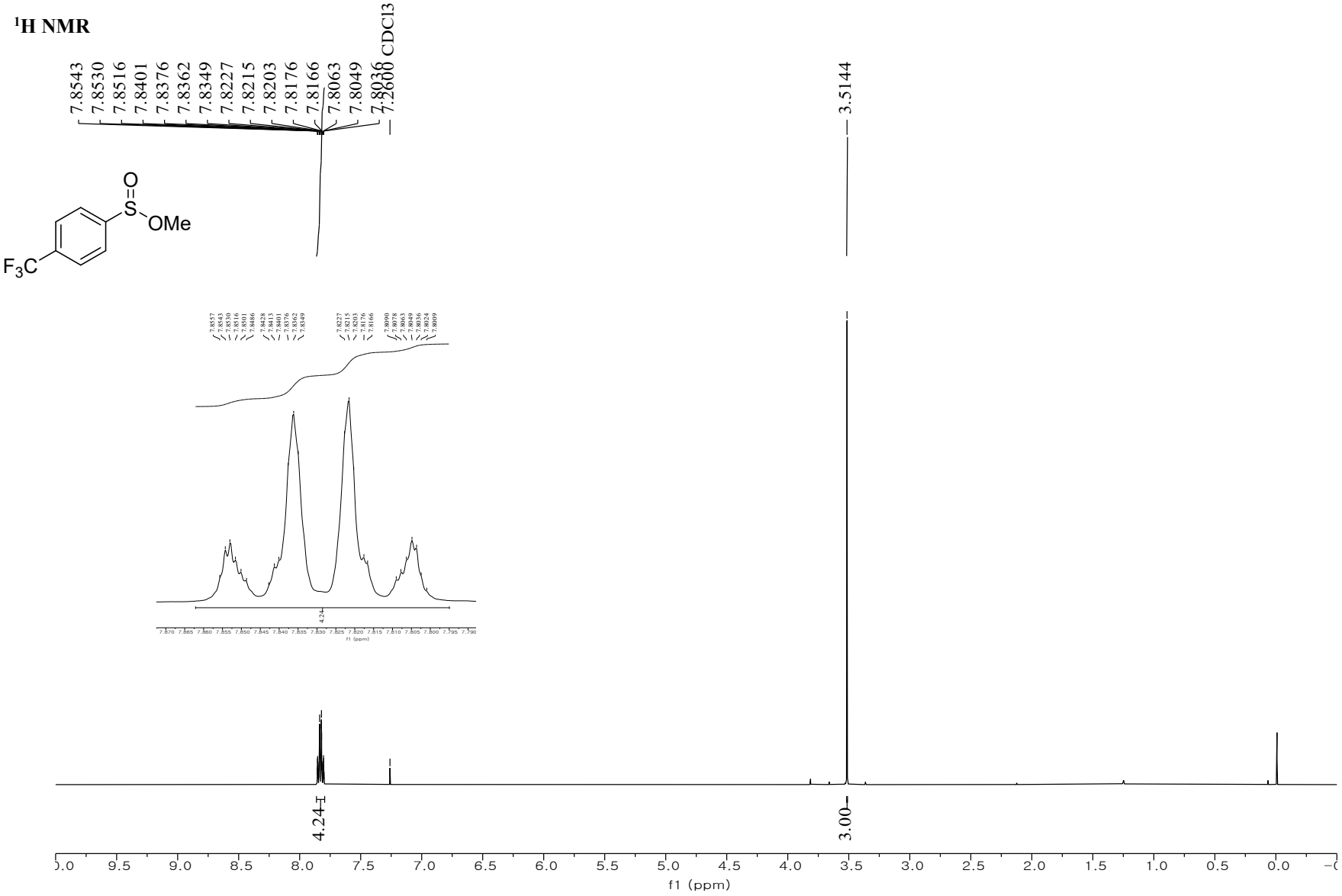
$^{13}C\{^{1}H\}$ NMR


O
S
OMe

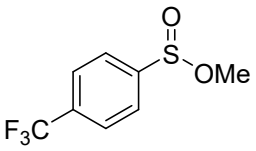
144.0589
132.3396
129.1931
125.5269
77.4149 CDCl3
77.1608 CDCl3
76.9067 CDCl3
49.7411
f1 (ppm)

Methyl 4-(trifluoromethyl)benzenesulfinate (2m)

^{1}H NMR

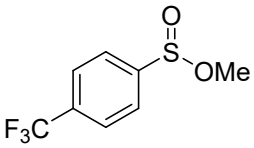


$^{13}C\{^{1}H\}$ NMR


O
S
OMe
F3C

147.9557
134.6546
134.3929
134.1311
133.8694
126.8044
126.3720
126.3416
126.3113
126.2829
126.2525
124.6347
122.4649
120.2952
77.4141 CDCl3
77.1600 CDCl3
76.9059 CDCl3
50.3226
f1 (ppm)

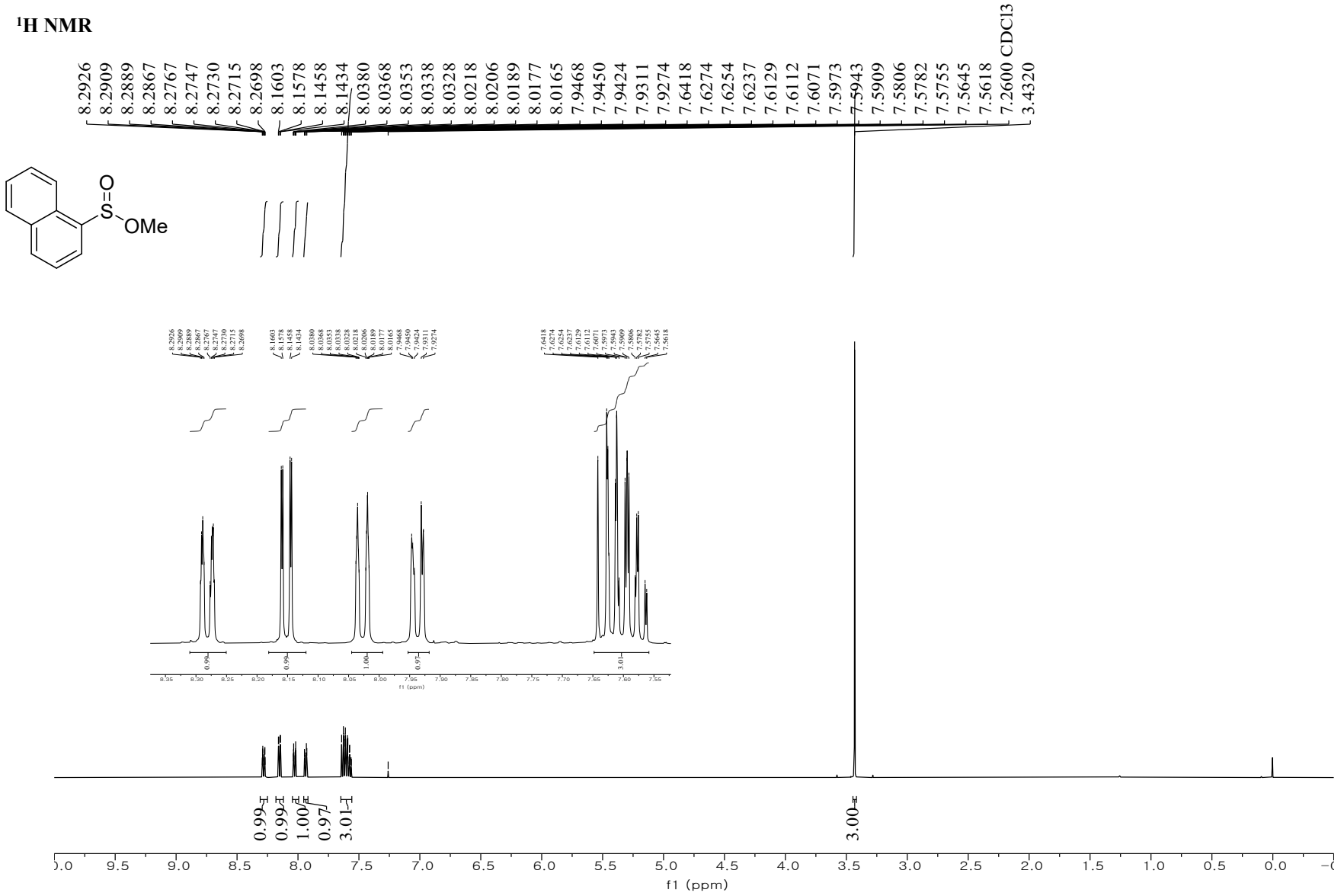
^{19}F NMR


O
S
OMe
F3C

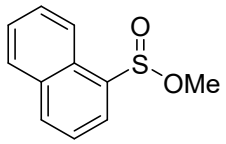
-63.01
30 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -1
f1 (ppm)

Methyl 4-naphthalene-1-sulfinate (2n)

^{1}H NMR



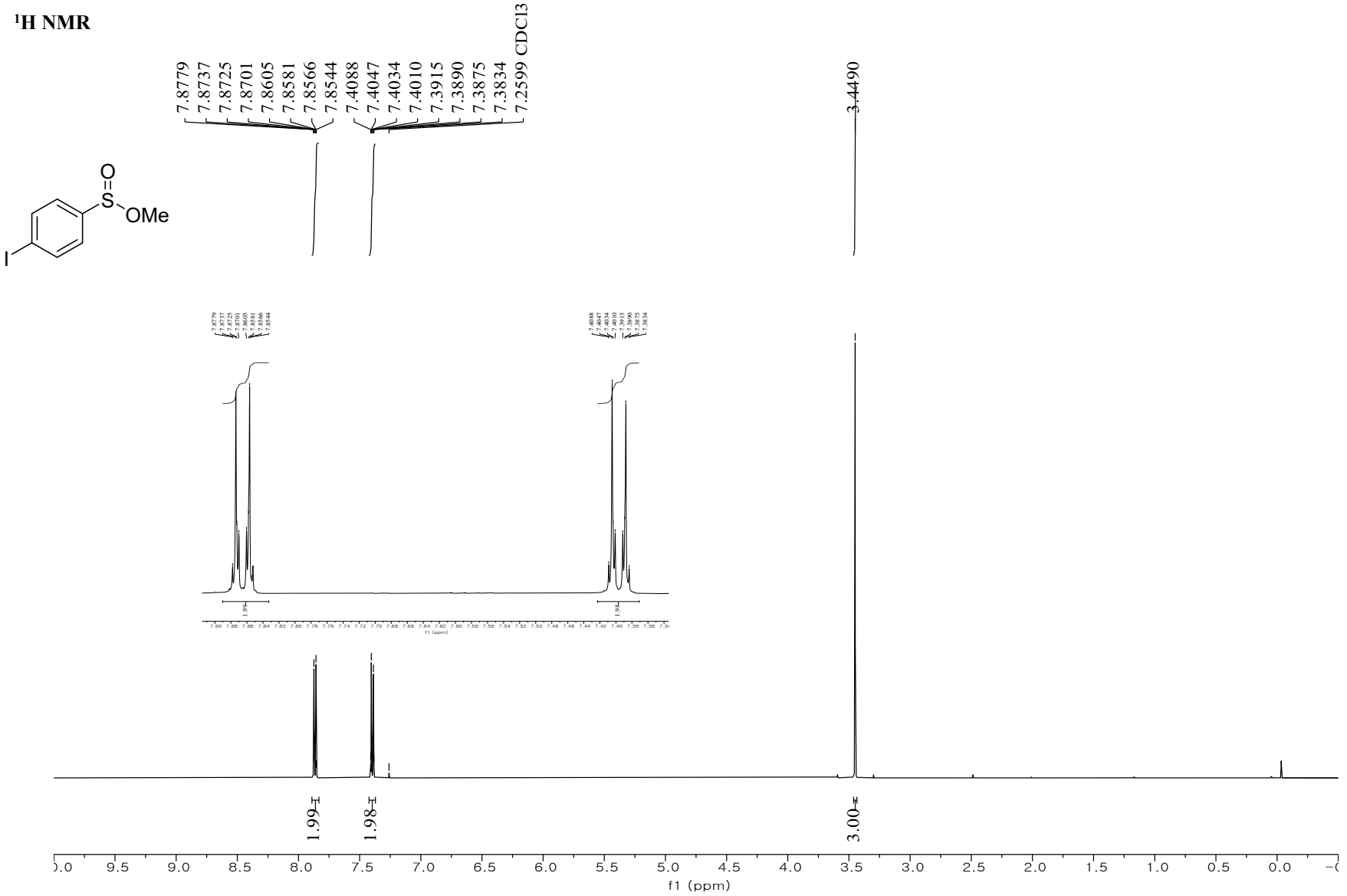
$^{13}C\{^{1}H\}$ NMR


O
S
OMe

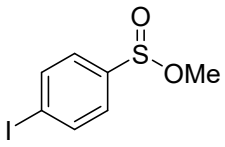
138.3266
133.7993
133.0312
129.4731
128.9022
127.6523
126.8785
124.8472
124.8377
122.3702
77.4142 CDCl3
77.1601 CDCl3
76.9059 CDCl3
49.5887
f1 (ppm)

Methyl 4-iodobenzenesulfinate (2o)

^{1}H NMR



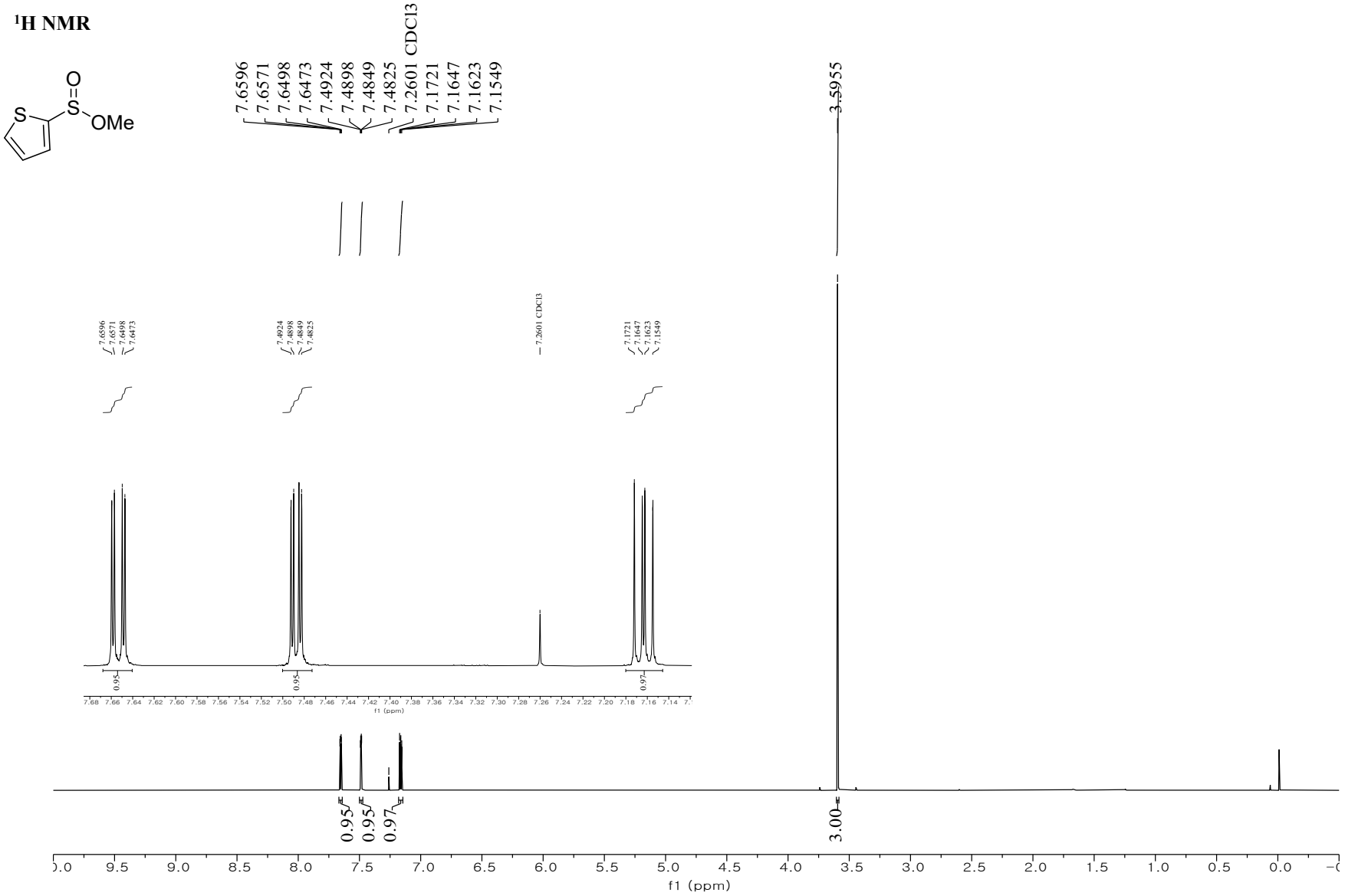
$^{13}C\{^{1}H\}$ NMR


O
S
OMe
I

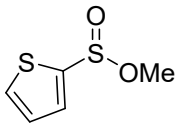
143.7524
138.2787
127.0487
99.4963
77.4157 CDCl3
77.1596 CDCl3
76.9055 CDCl3
49.8253
f1 (ppm)

Methyl thiophene-2-sulfinate (2s)

^{1}H NMR



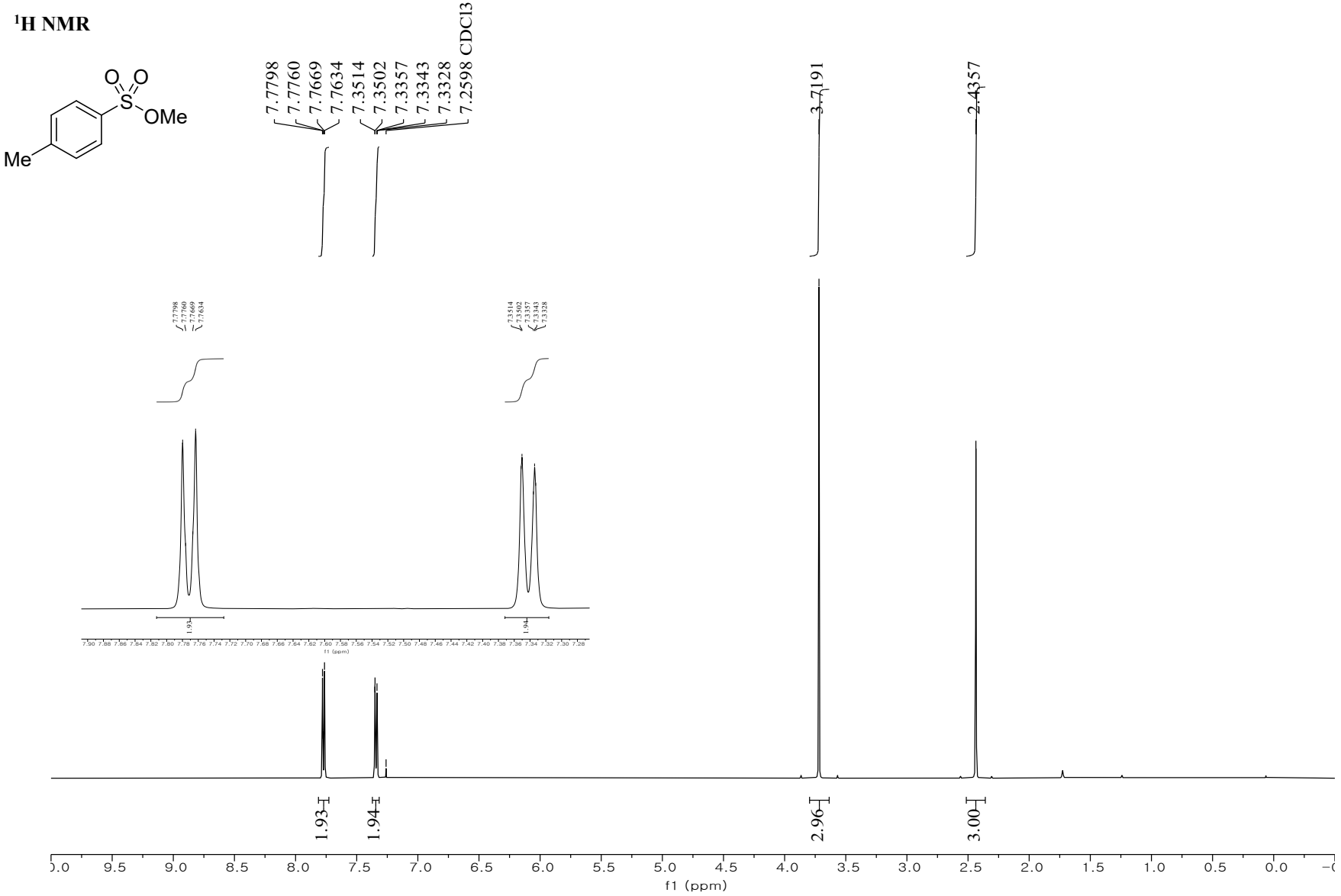
$^{13}C\{^{1}H\}$ NMR


O
S
S
OMe

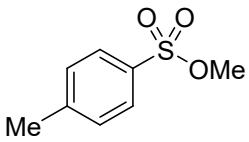
147.1569
131.7904
130.0929
127.9156
77.4138 CDCl3
77.1597 CDCl3
76.9056 CDCl3
49.4688
f1 (ppm)

Methyl 4-methylbenzenesulfonate (3a)

^{1}H NMR



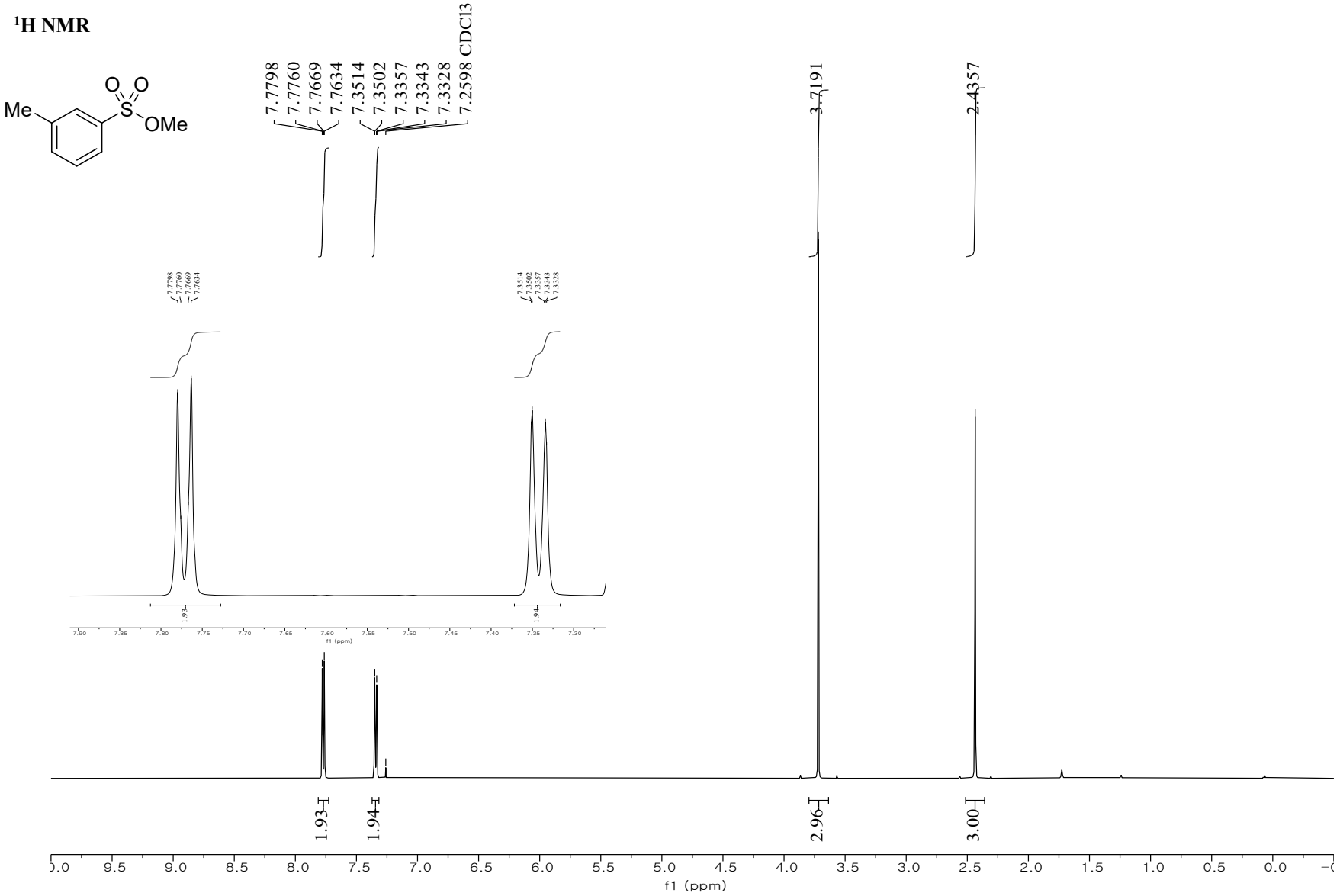
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
Me

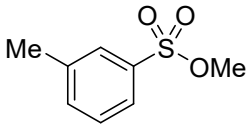
145.0411
132.2236
129.9666
128.1155
77.4146 CDCl3
77.1605 CDCl3
76.9064 CDCl3
56.2767
21.6915
f1 (ppm)

Methyl 3-methylbenzenesulfonate (3b)

^{1}H NMR



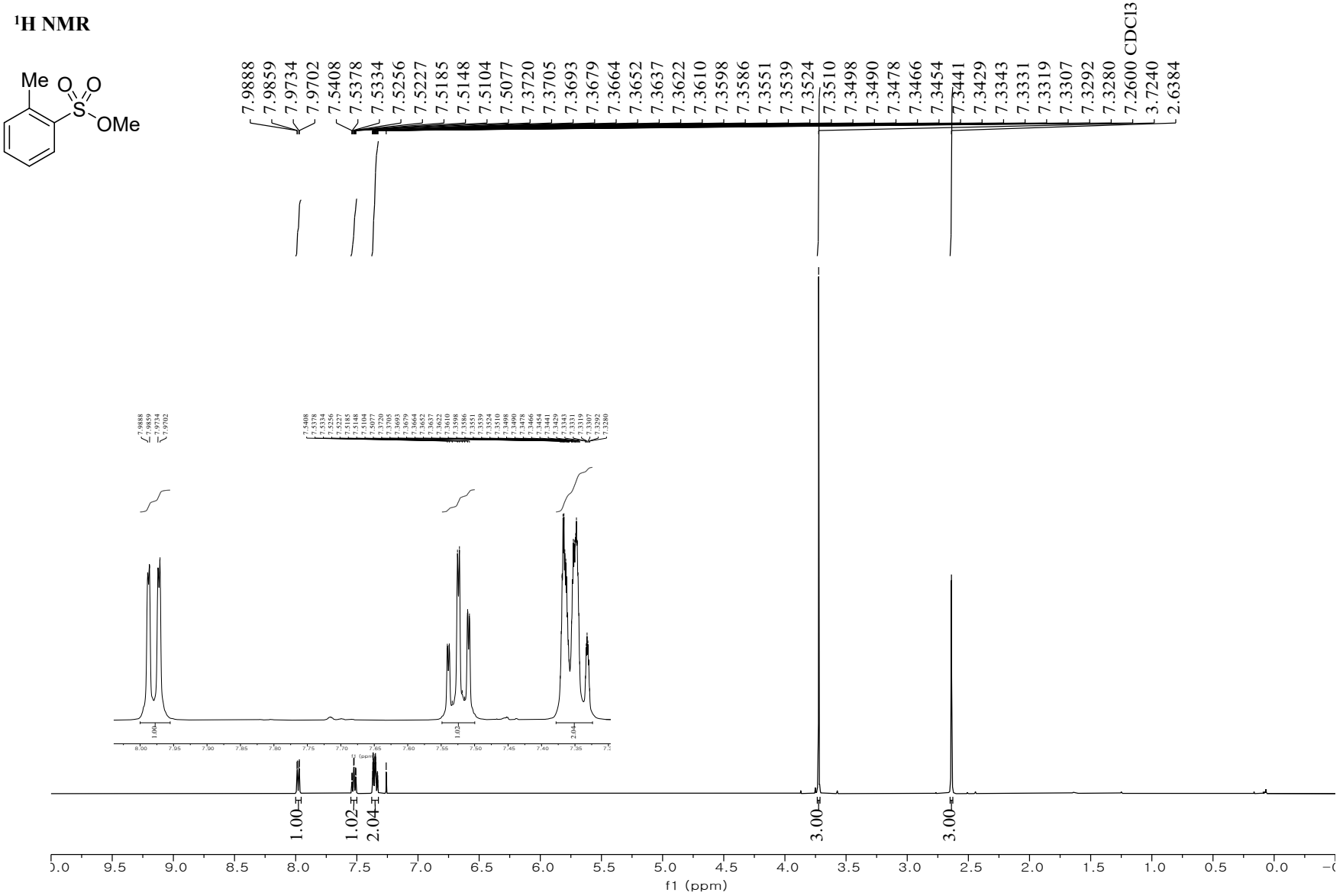
$^{13}C\{^{1}H\}$ NMR


Me
O
O
S
OMe

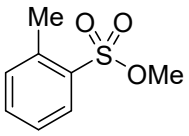
139.7560
135.1738
134.7831
129.2240
128.4559
125.3037
77.4136 CDCl3
77.1595 CDCl3
76.9054 CDCl3
56.3989
21.4250
f1 (ppm)

Methyl 2-methylbenzenesulfonate (3c)

^{1}H NMR



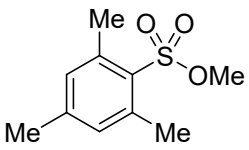
$^{13}C\{^{1}H\}$ NMR


Me
O
O
S
OMe

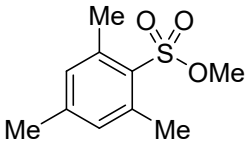
138.5728
133.9451
133.6909
132.7312
130.3452
126.2713
77.4140 CDCl3
77.1598 CDCl3
76.9057 CDCl3
56.1204
20.3176
f1 (ppm)

Methyl 2,4,6-trimethylbenzenesulfonate (3d)

^{1}H NMR



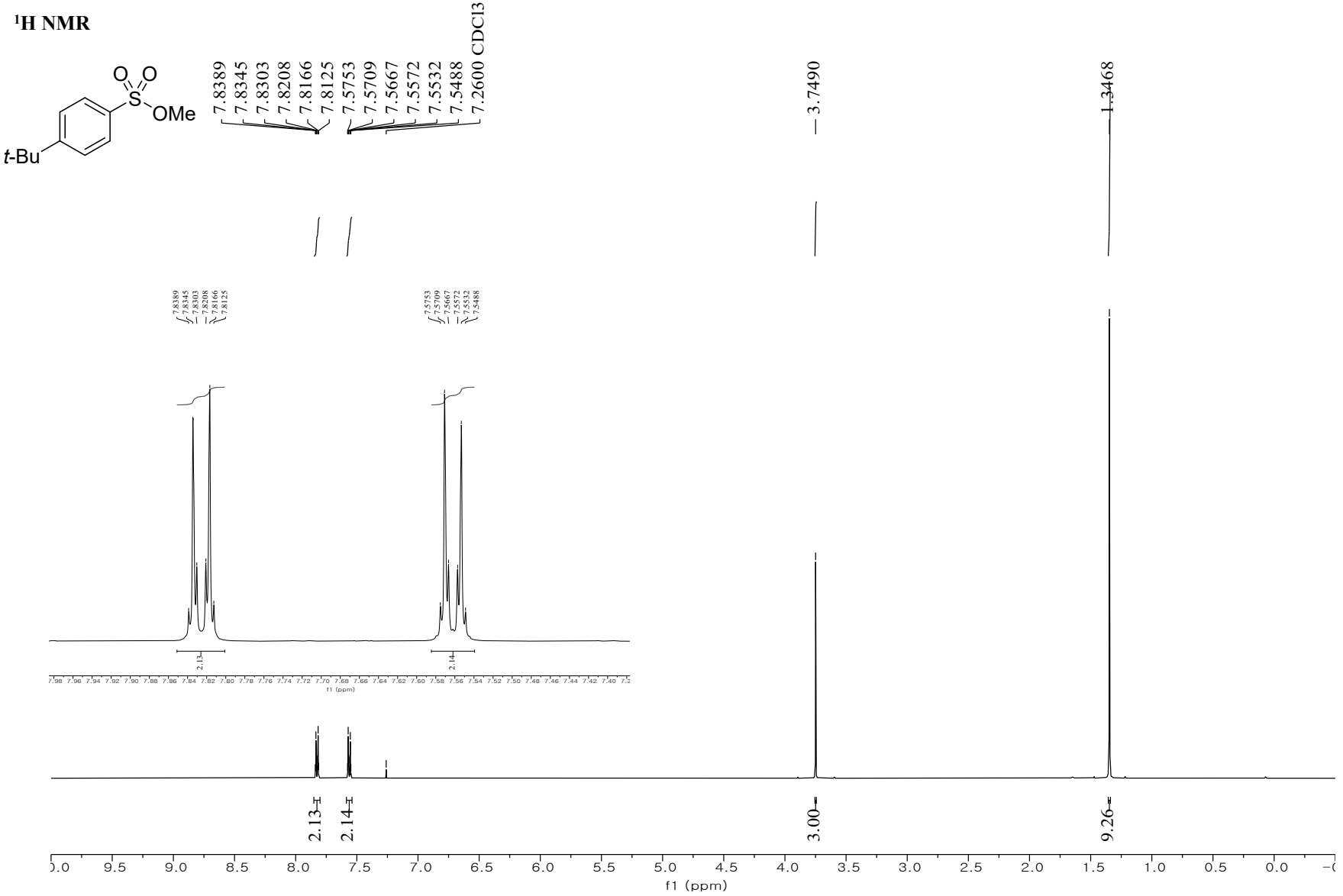
$^{13}C\{^{1}H\}$ NMR


Me
O
O
S
OMe
Me
Me

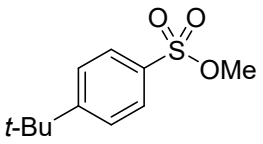
143.4590
140.1560
131.8334
129.8807
77.4151 CDCl3
77.1609 CDCl3
76.9068 CDCl3
55.1979
22.6346
21.1160
f1 (ppm)

Methyl 4-(tert-butyl)benzenesulfonate (3e)

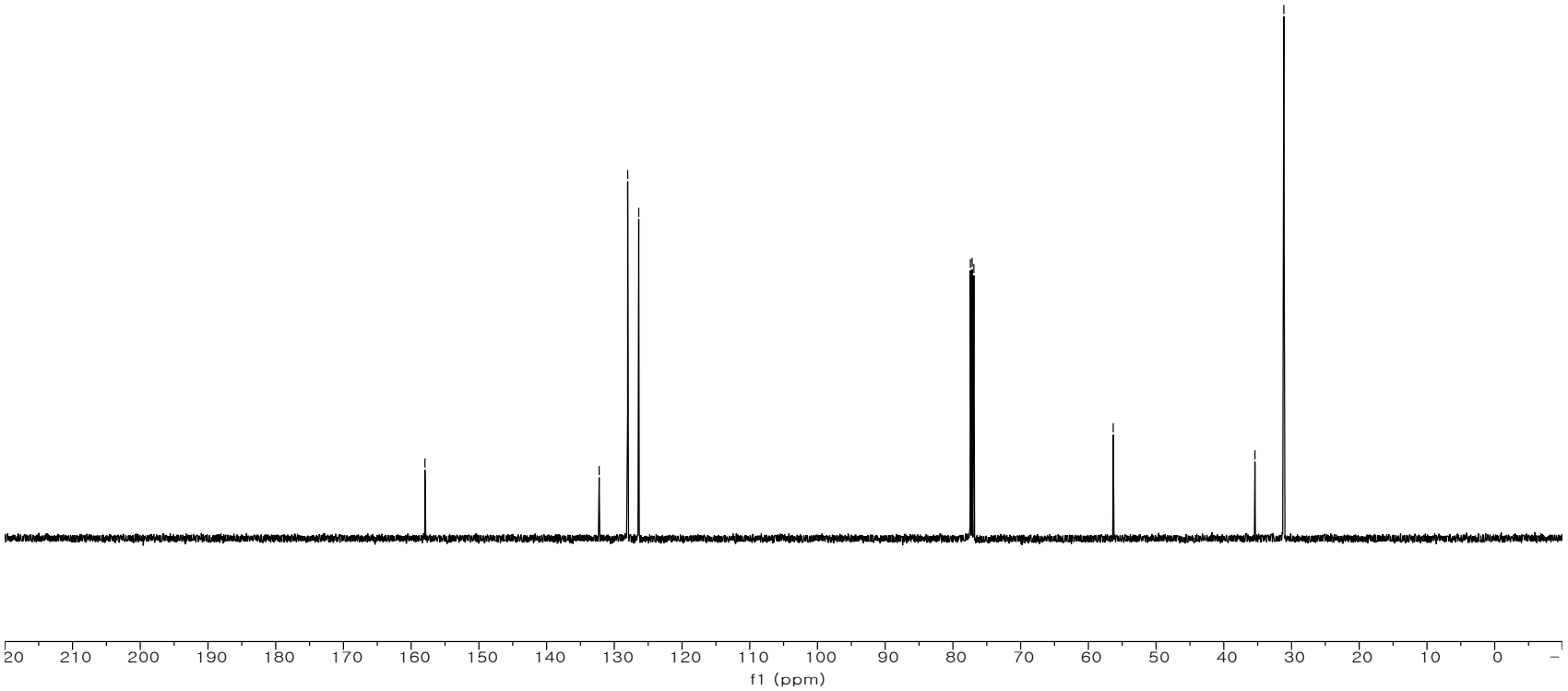
^{1}H NMR



$^{13}C\{^{1}H\}$ NMR

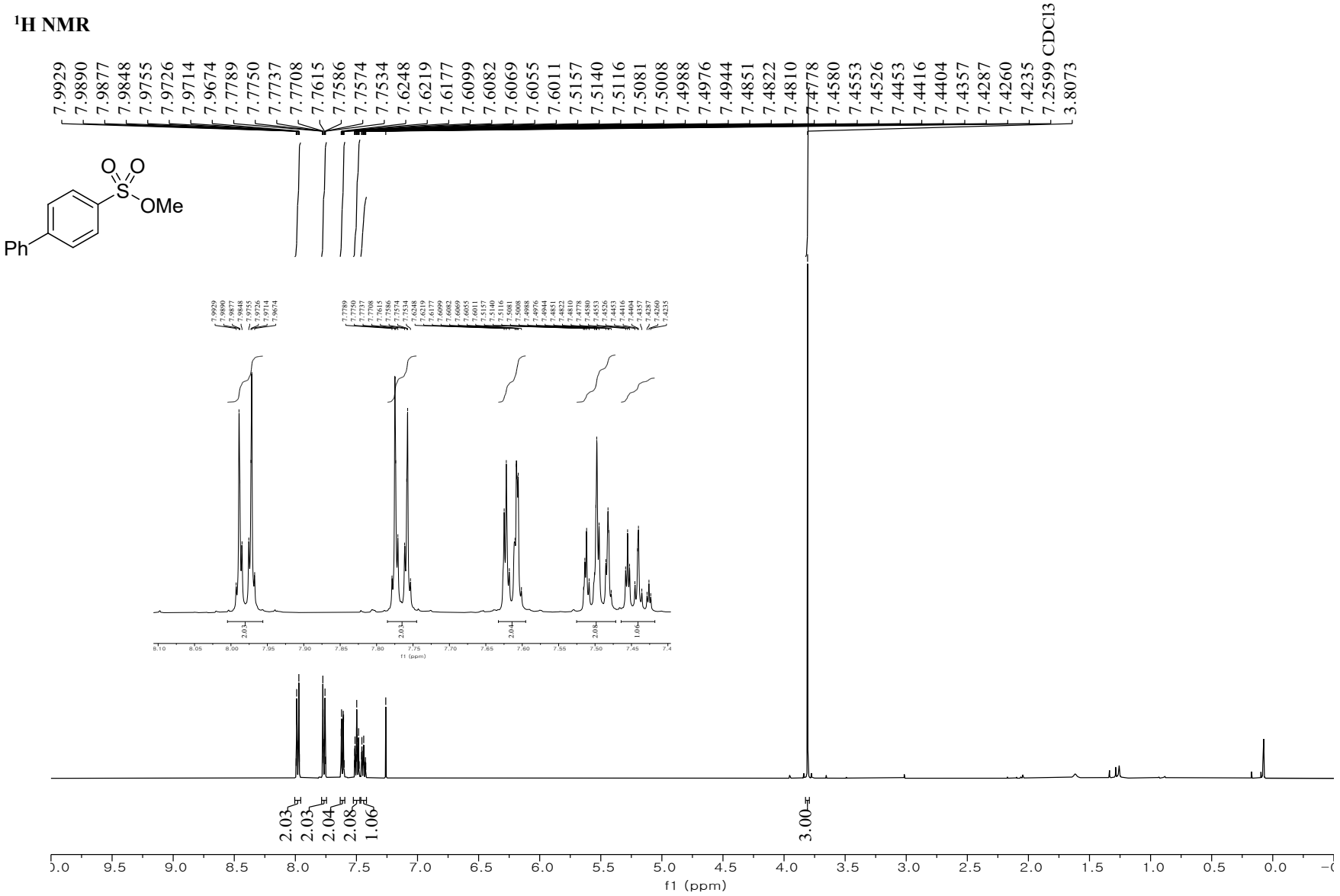


157.9607
132.2386
128.0281
126.3932
77.4144 CDCl3
77.1603 CDCl3
76.9061 CDCl3
56.3277
35.4021
31.1365

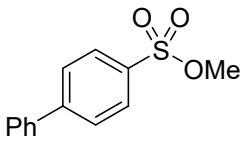


Methyl [1,1′-Biphenyl]-4-sulfonate (3f)

^{1}H NMR



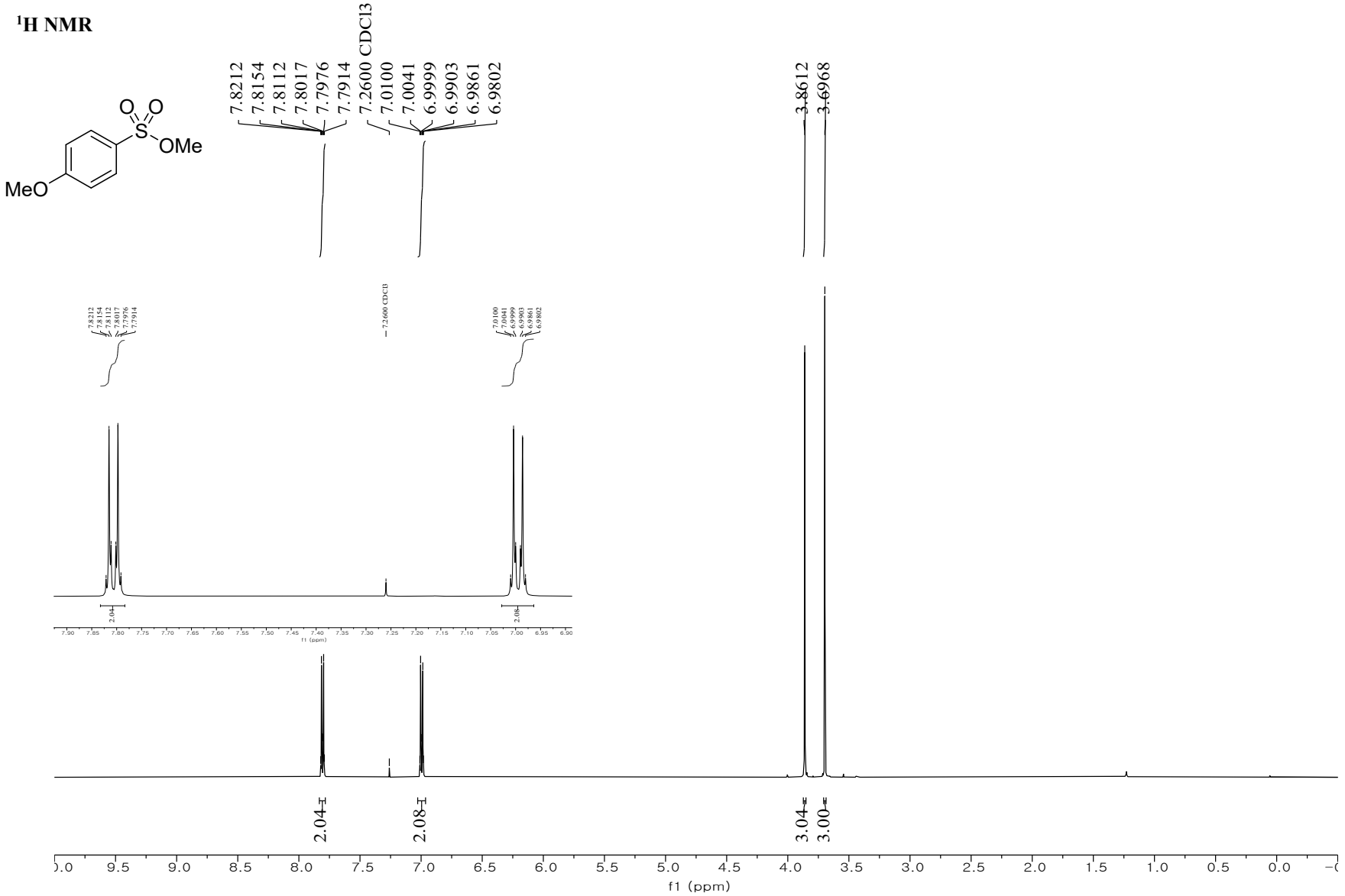
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
Ph

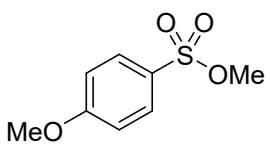
147.0188
139.1648
133.8599
129.2719
128.8983
128.7200
128.0107
127.5138
77.4141 CDCl3
77.1600 CDCl3
76.9059 CDCl3
56.4810
f1 (ppm)

Methyl 4- methoxybenzenesulfonate (3g)

^{1}H NMR



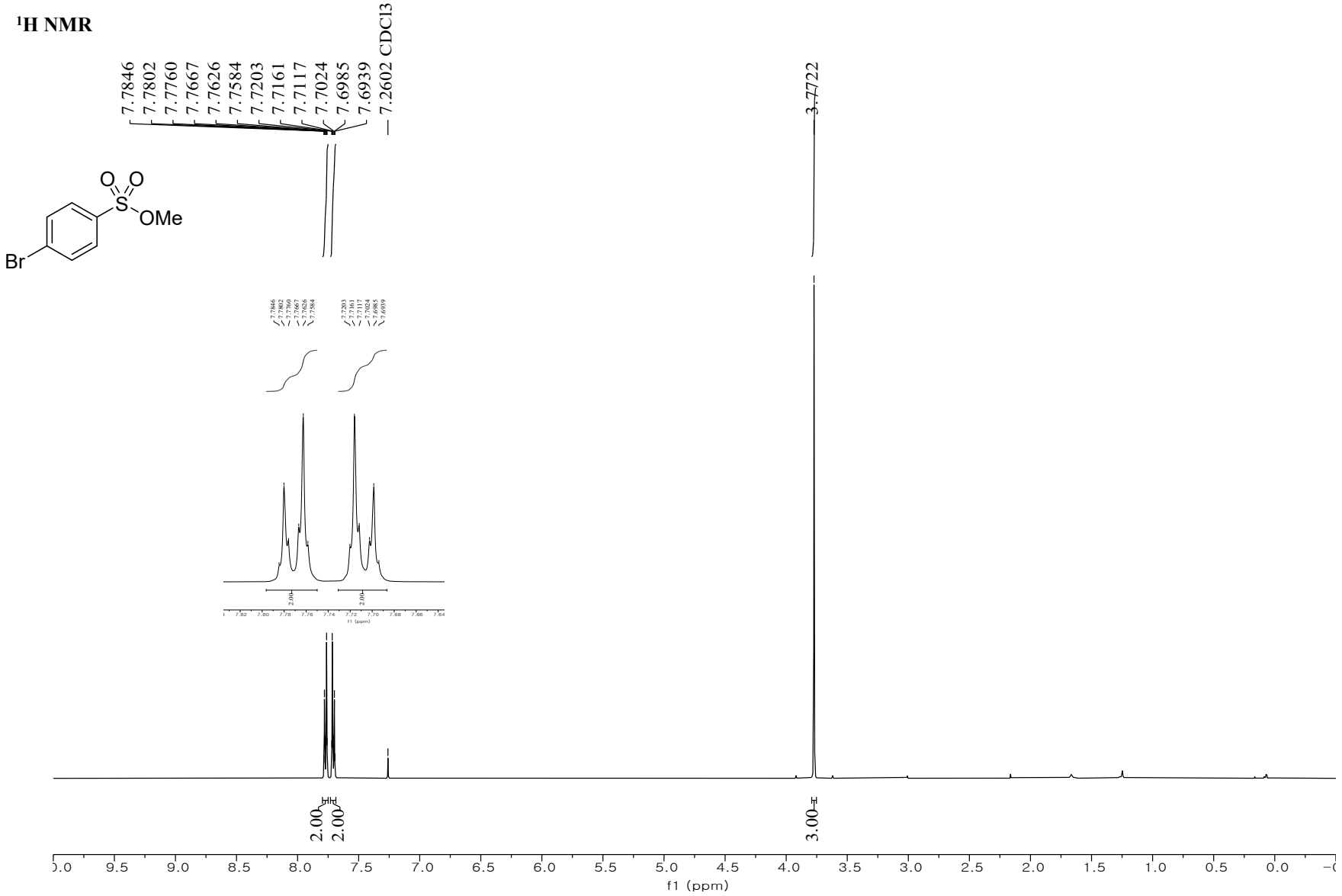
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
MeO

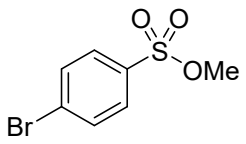
163.9129
130.2757
130.0327
126.4881
114.5344
77.4147 CDCl3
77.1606 CDCl3
76.9065 CDCl3
56.1250
55.7904
f1 (ppm)

Methyl 4-bromobenzenesulfonate (3h)

^{1}H NMR



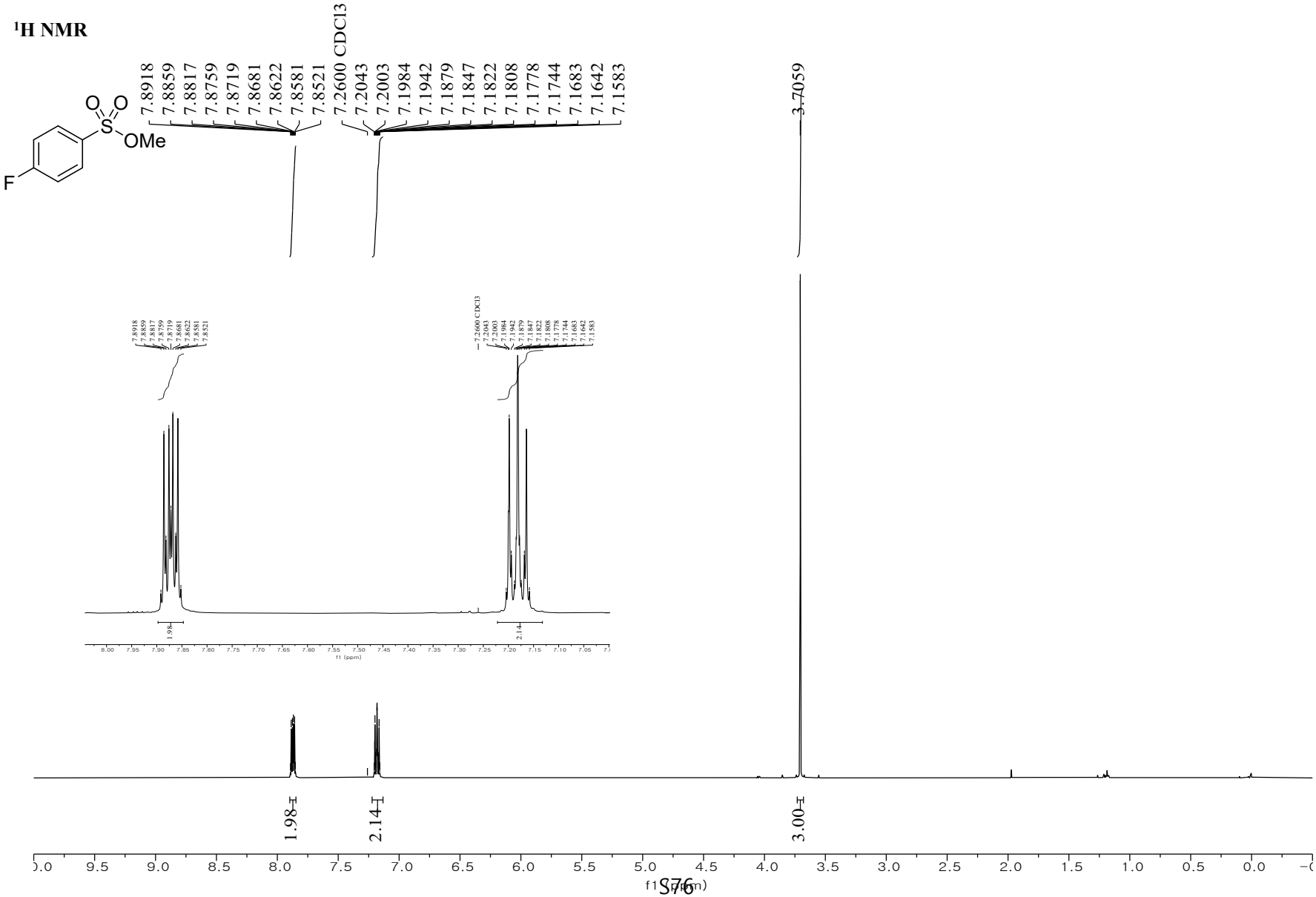
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
Br

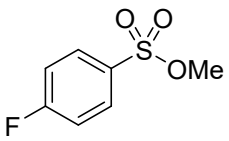
134.4005
132.7580
129.6361
129.2644
77.4179 CDCl3
77.1638 CDCl3
76.9096 CDCl3
56.6213
f1 (ppm)

Methyl 4-fluorobenzenesulfonate (3i)

^{1}H NMR

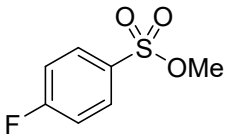


$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
F

166.9639
164.9231
131.4342
131.4077
131.0340
130.9582
116.8586
116.6765
77.4142 CDCl3
77.1601 CDCl3
76.9060 CDCl3
56.4849
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

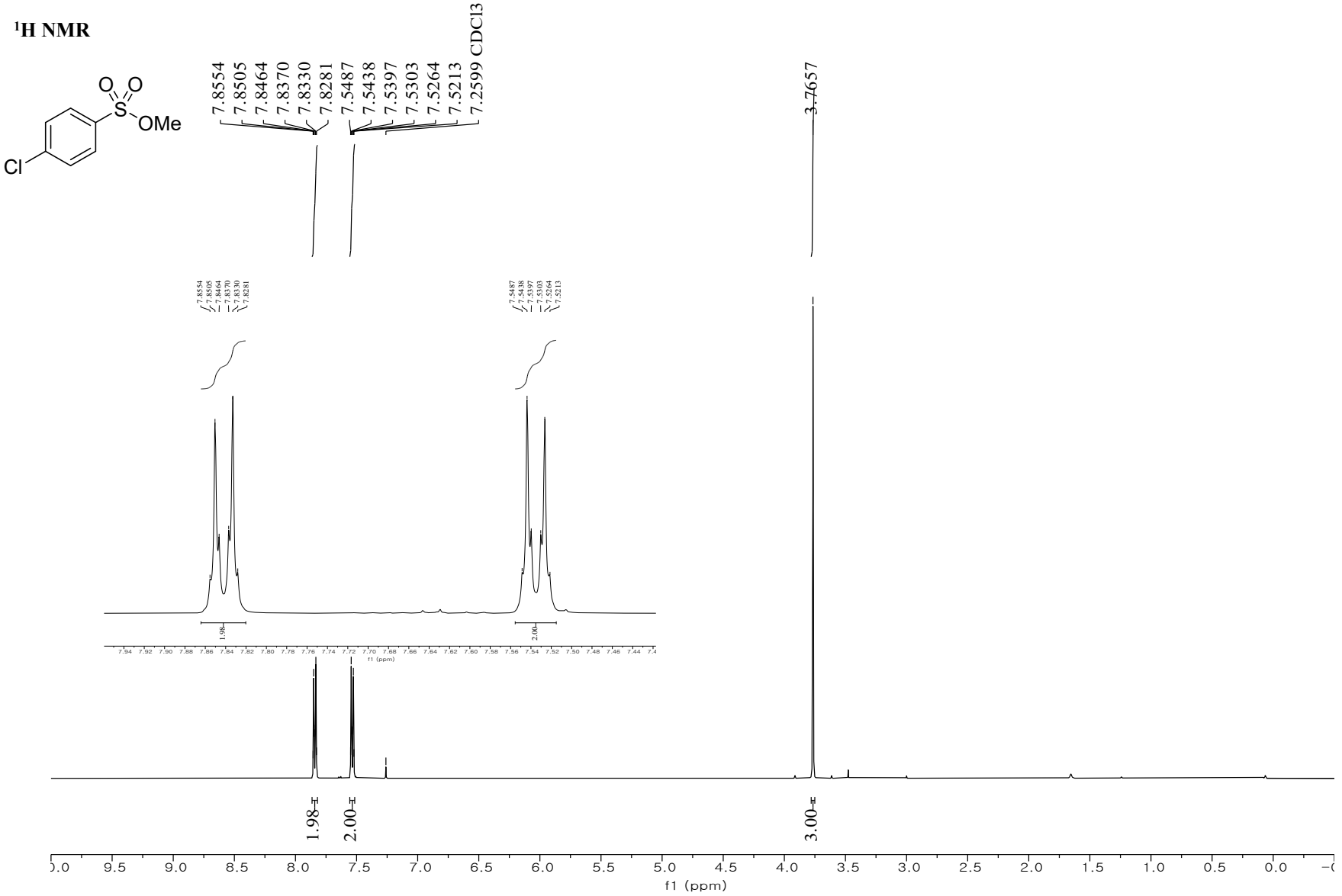
^{19}F NMR


O
O
S
OMe
F

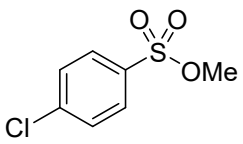
-103.09
-103.10
-103.11
-103.12
-103.12
-103.13
-103.13
-103.14
-103.15
3.00
−103.05
−103.10
−103.15
ppm)
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
f1 (ppm)

Methyl 4-chlorobenzenesulfinate (3j)

^{1}H NMR



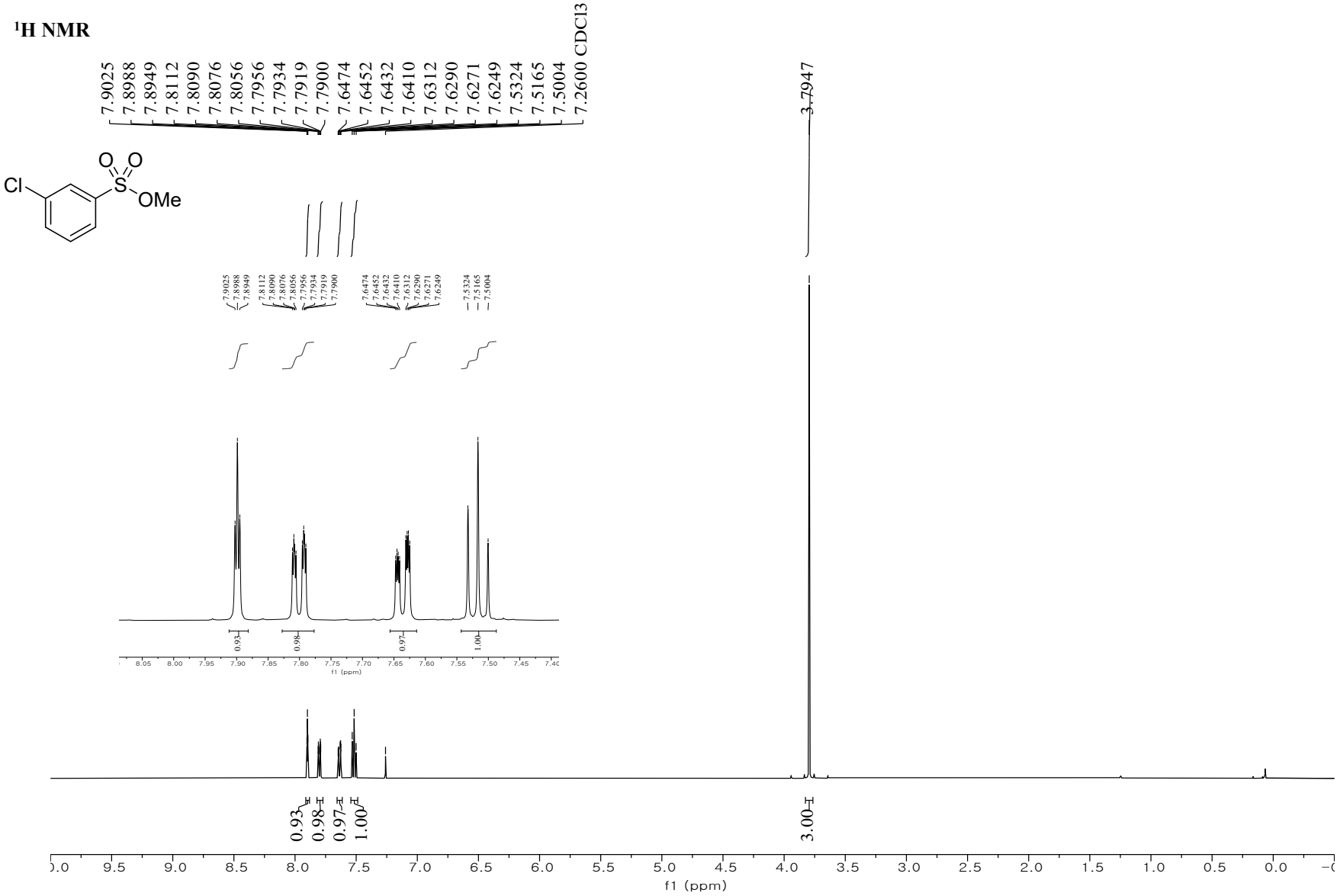
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
Cl

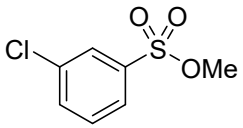
140.6996
133.8247
129.7462
129.5672
77.4149 CDCl3
77.1608 CDCl3
76.9066 CDCl3
56.6005
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl 3-chlorobenzenesulfonate (3k)

^{1}H NMR



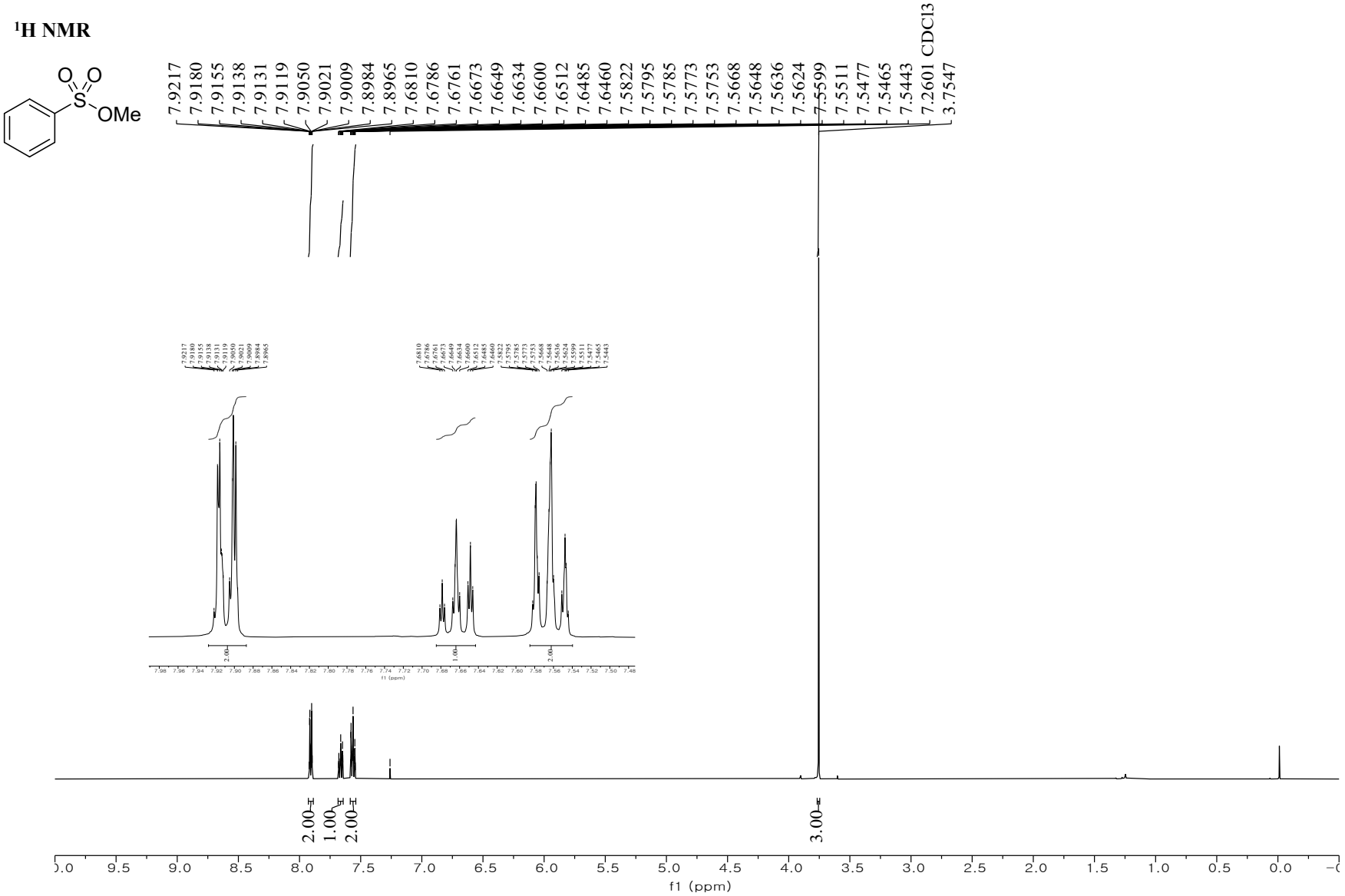
$^{13}C\{^{1}H\}$ NMR


Cl
O
O
S
OMe

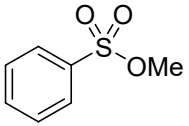
137.0846
135.6830
134.1695
130.7214
128.2046
126.2415
77.4146 CDCl3
77.1604 CDCl3
76.9063 CDCl3
56.8038
f1 (ppm)

Methyl benzenesulfonate (3l)

^{1}H NMR



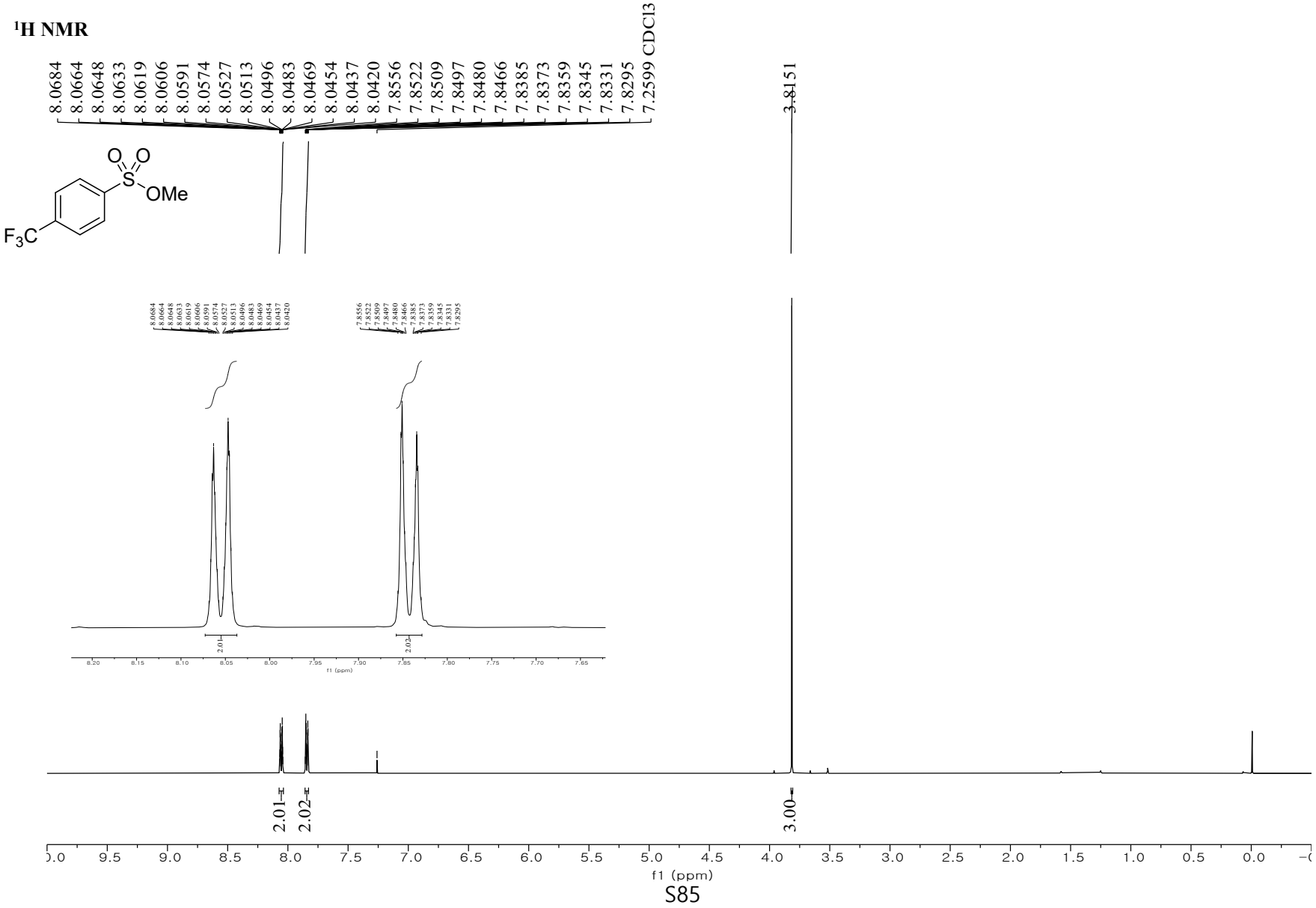
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe

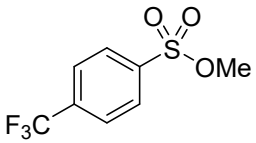
135.3165
133.9851
129.3876
128.1131
77.4141 CDCl3
77.1600 CDCl3
76.9059 CDCl3
56.4544
f1 (ppm)

Methyl 4-(trifluoromethyl)benzenesulfonate (3m)

^{1}H NMR

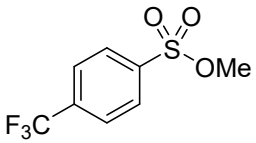


$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
F3C

139.0668
136.1042
135.8387
135.5732
135.3095
128.7491
126.6438
126.6135
126.5850
126.5547
124.2578
122.0843
119.9108
77.4147 CDCl3
77.1606 CDCl3
76.9064 CDCl3
56.8818
f1 (ppm)

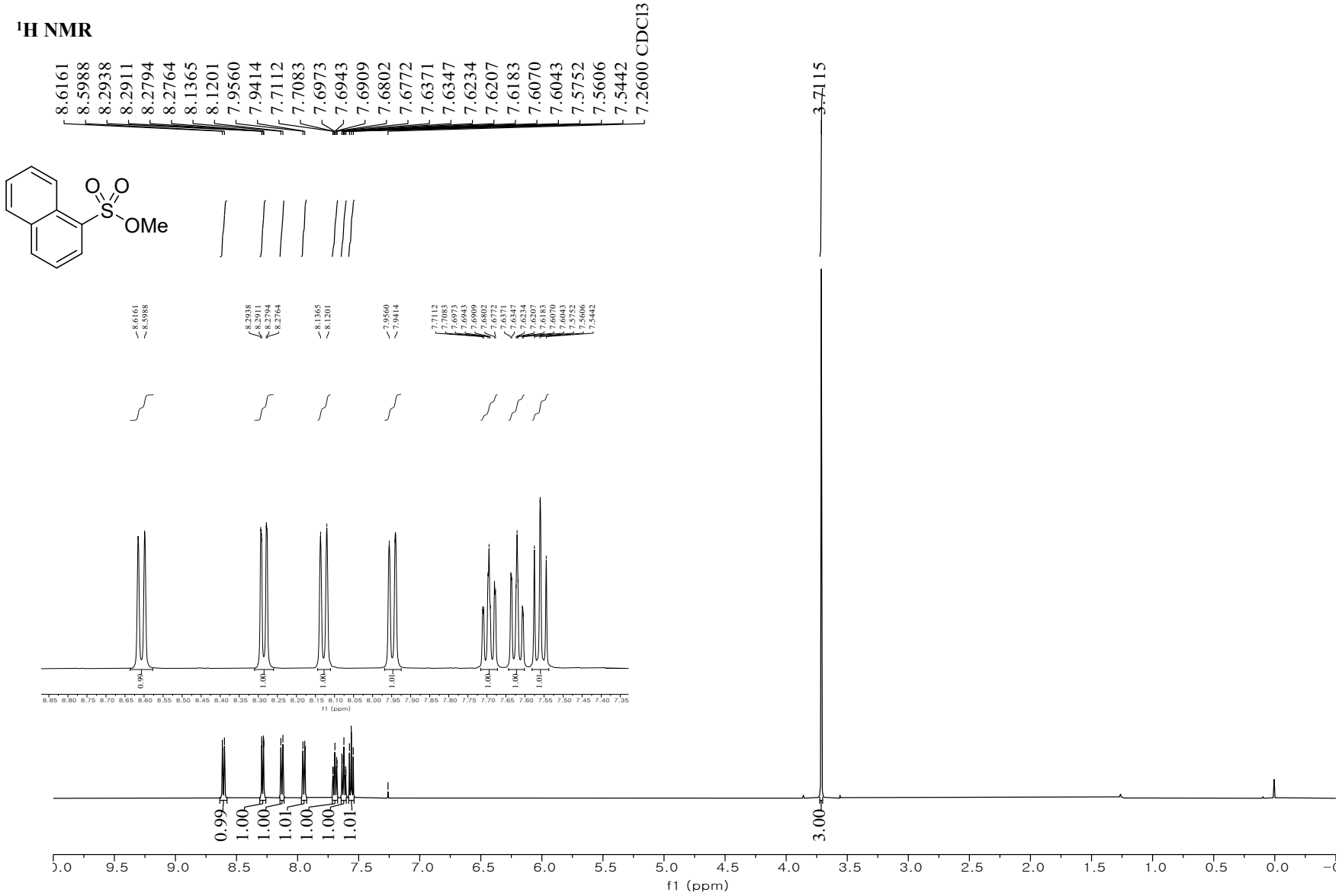
^{19}F NMR


O
O
S
OMe
F3C

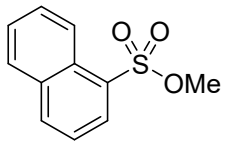
-63.46
120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120
f1 (ppm)

Methyl 4-naphthalene-1-sulfonate (3n)

^{1}H NMR



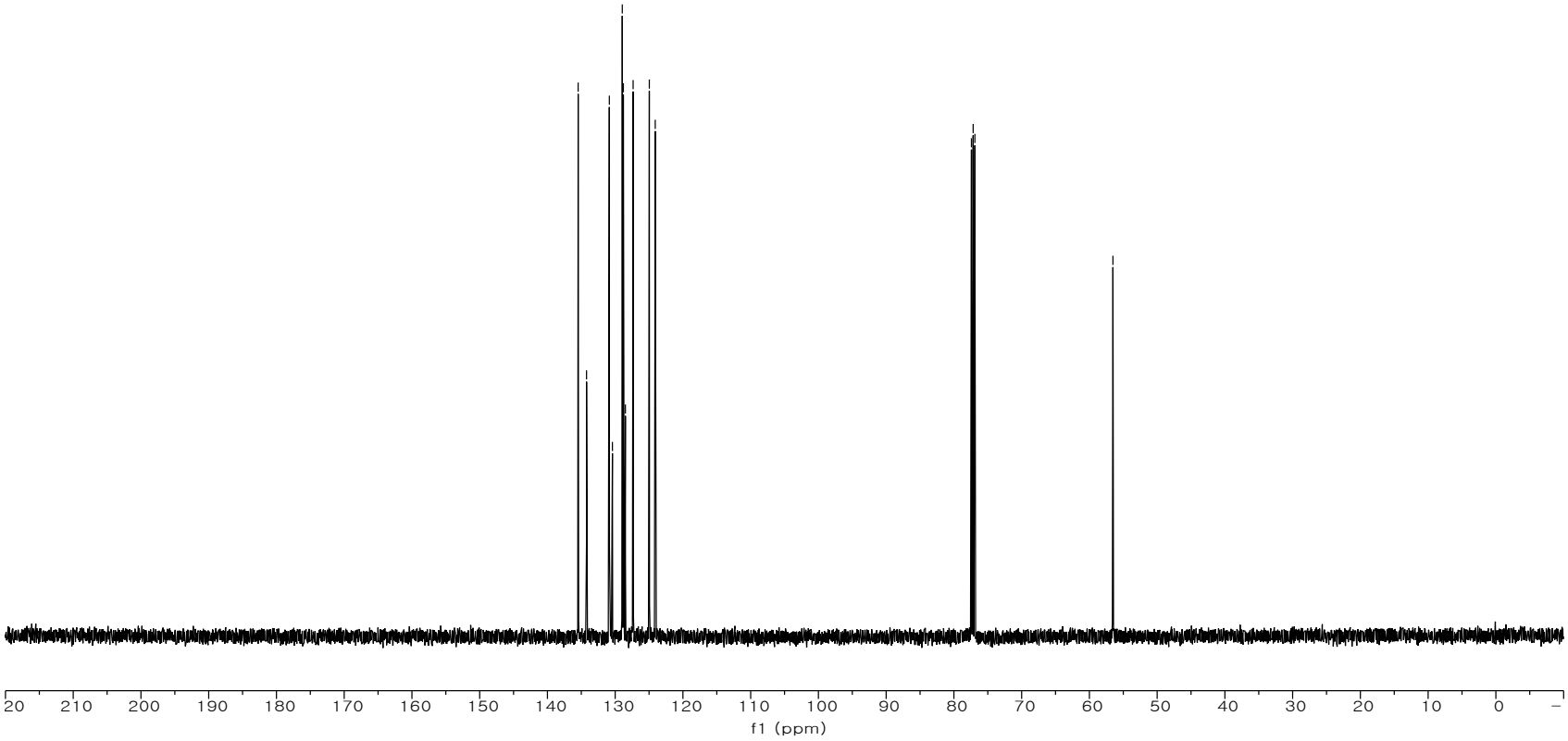
$^{13}C\{^{1}H\}$ NMR



135.4664
134.2279
130.8632
130.4080
128.9533
128.7921
128.4905
127.3526
124.9609
124.0865

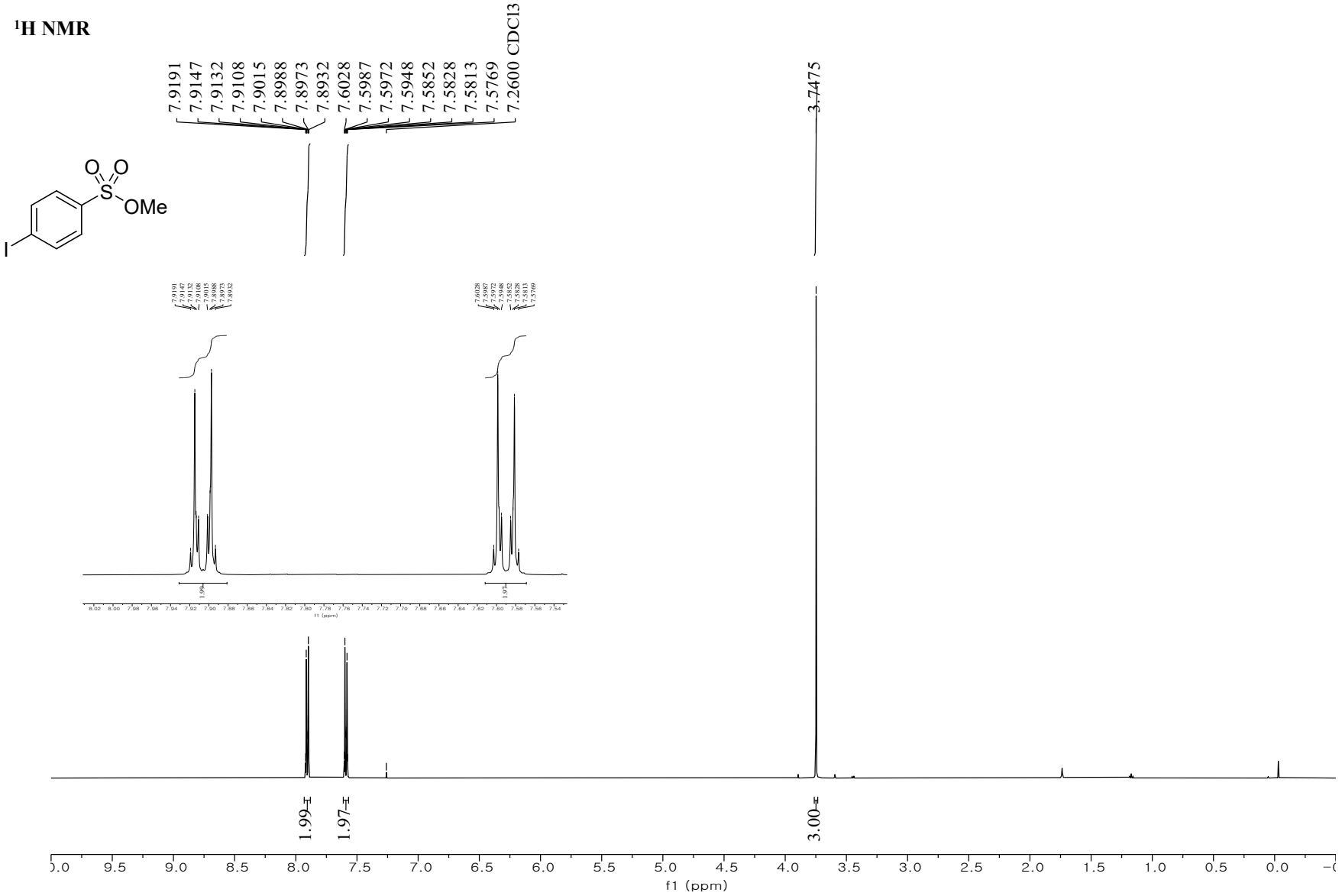
77.4142 CDCl3
77.1600 CDCl3
76.9059 CDCl3

56.5246

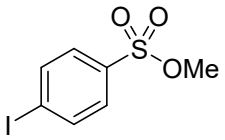


Methyl 4-iodobenzenesulfonate (3o)

^{1}H NMR



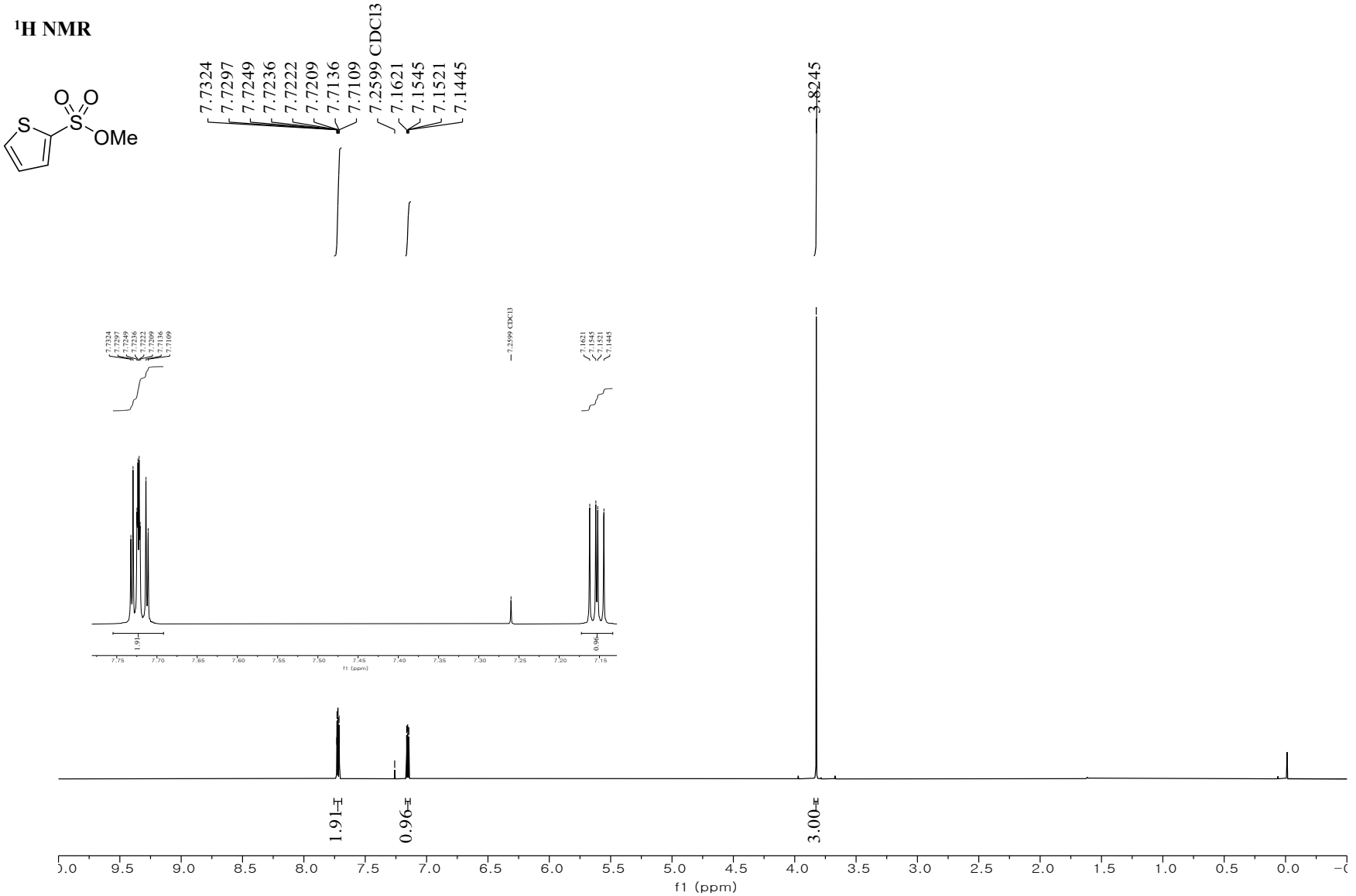
$^{13}C\{^{1}H\}$ NMR


O
O
S
OMe
I

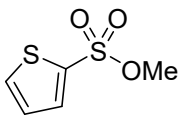
138.6301
134.8841
129.3192
101.7594
77.4161 CDCl3
77.1619 CDCl3
76.9059 CDCl3
56.6352
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Methyl thiophene-2-sulfonate (3s)

^{1}H NMR



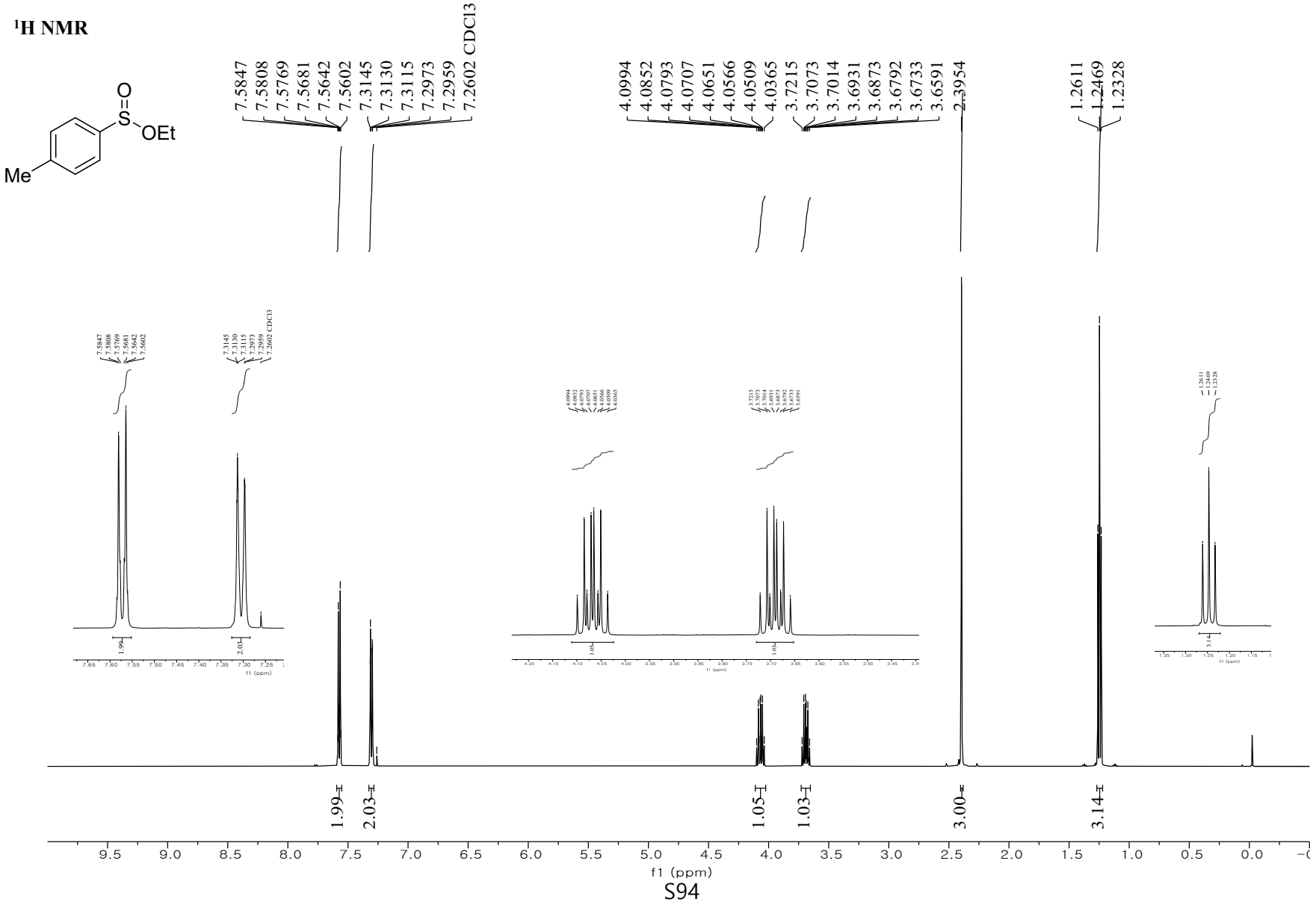
$^{13}C\{^{1}H\}$ NMR


O
O
S
S
OMe

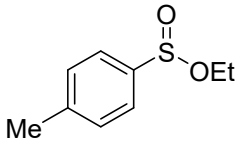
134.8821
134.6394
133.9642
127.7015
77.4141 CDCl3
77.1600 CDCl3
76.9058 CDCl3
57.0803
f1 (ppm)

Ethyl 4-methylbenzenesulfinate (4)

^{1}H NMR



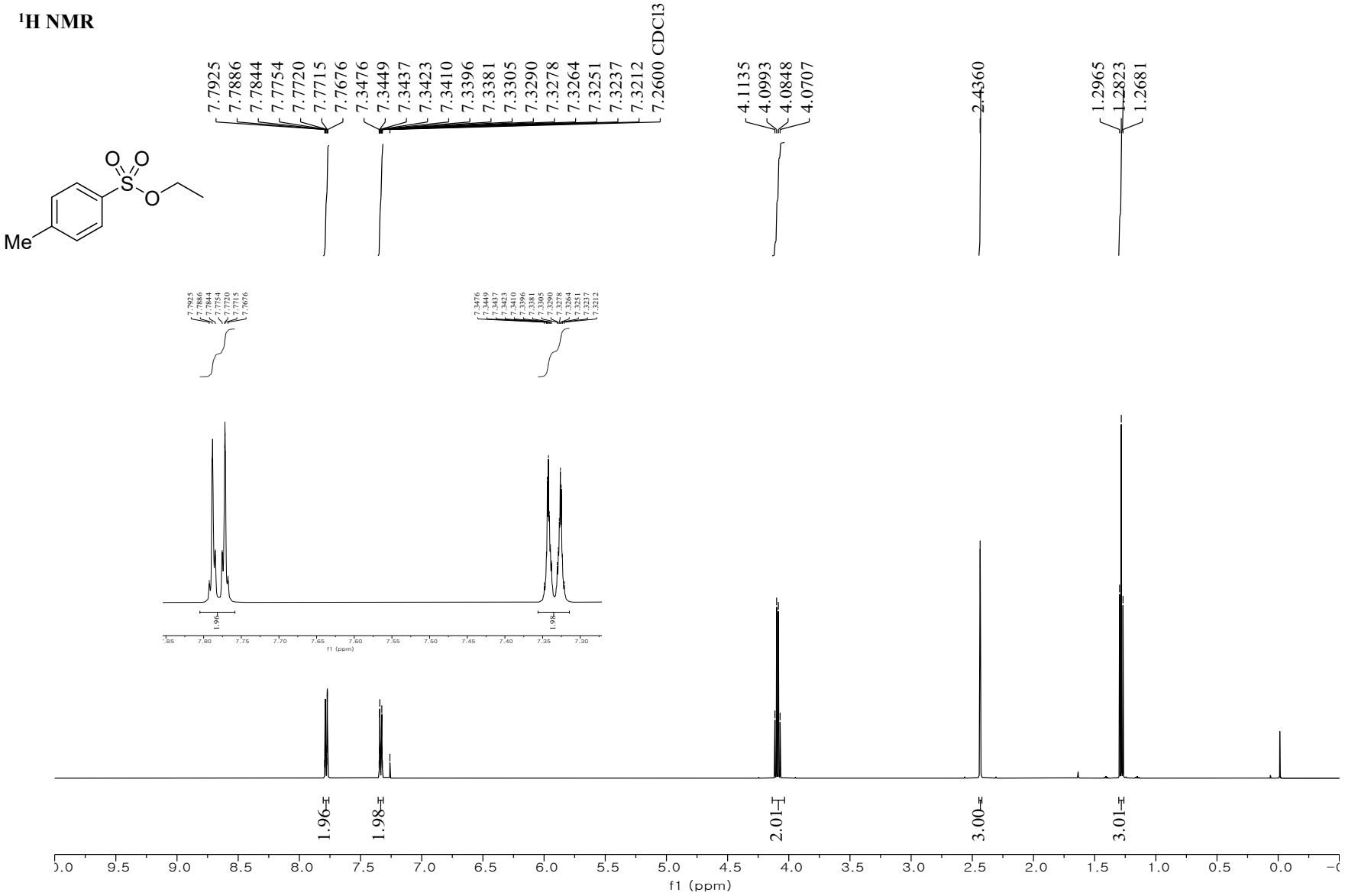
$^{13}C\{^{1}H\}$ NMR


O
S
OEt
Me

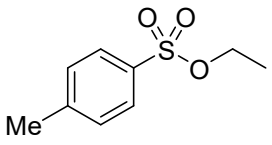
142.6679
141.8940
129.7195
125.2321
77.4141 CDCl3
77.1600 CDCl3
76.9059 CDCl3
60.7238
21.5298
15.6085
f1 (ppm)

Ethyl 4-methylbenzenesulfonate (6a)

^{1}H NMR



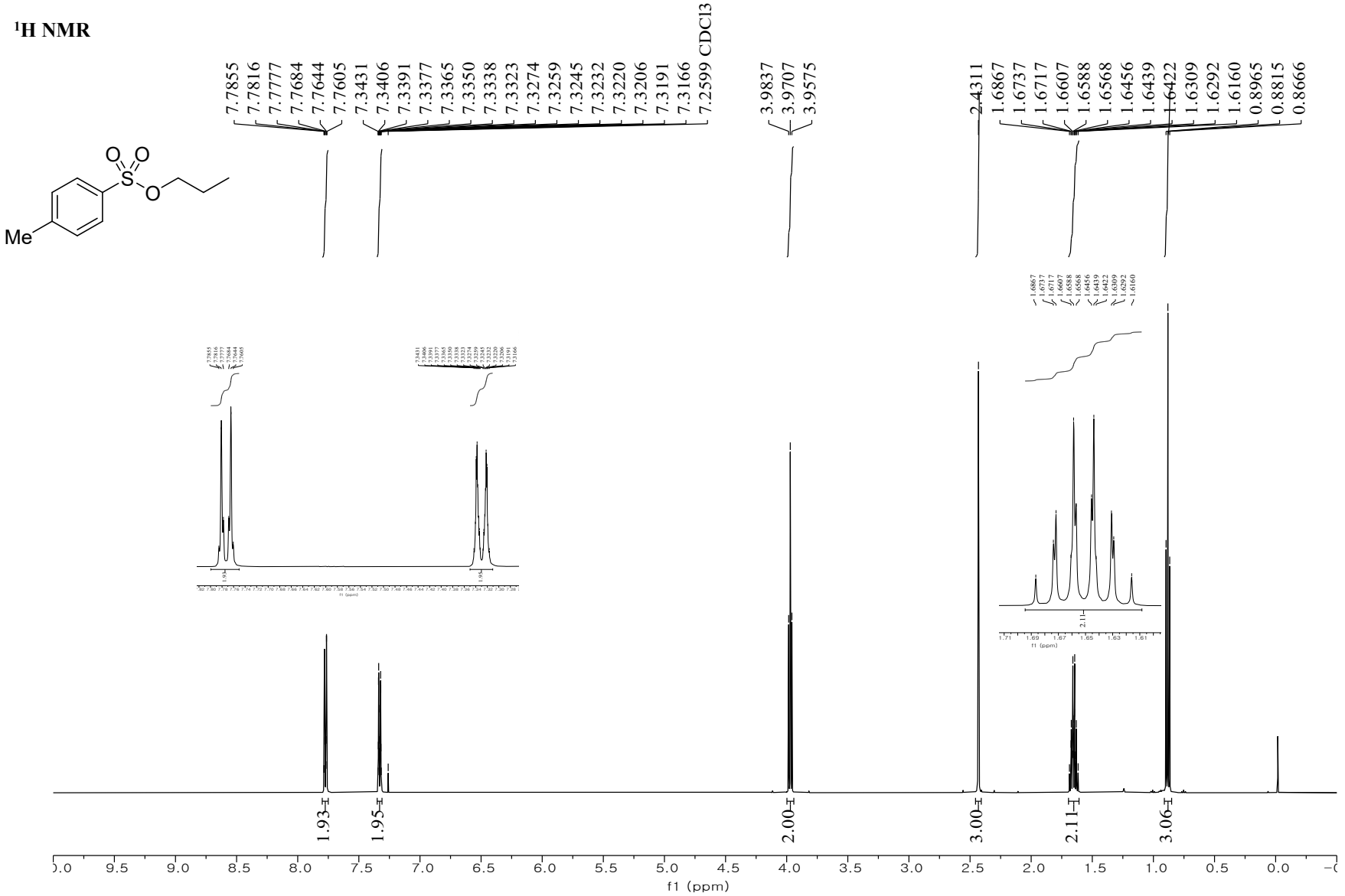
$^{13}C\{^{1}H\}$ NMR


O
O
S
O
Me

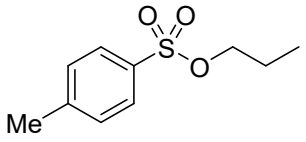
144.7889
133.3996
129.9288
127.9411
77.4147 CDCl3
77.1606 CDCl3
76.9064 CDCl3
66.9169
21.7106
14.8580
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 –
f1 (ppm)

Propyl 4-methylbenzenesulfonate (6b)

^{1}H NMR



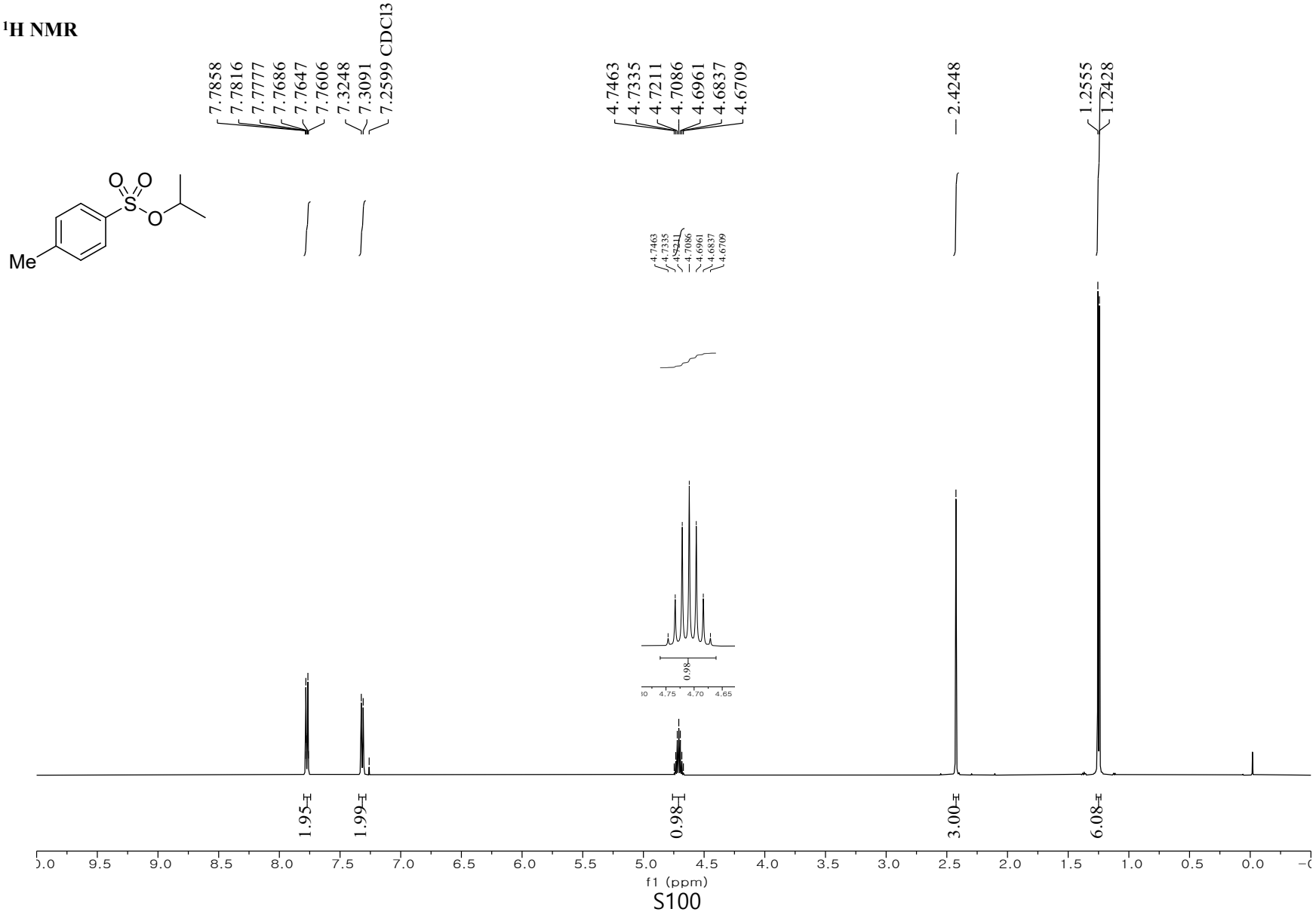
$^{13}C\{^{1}H\}$ NMR


O
O
S
O
Me

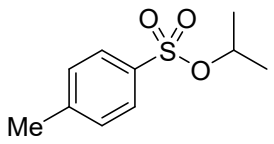
144.7470
133.3065
129.8964
127.9295
77.4146 CDCl3
77.1604 CDCl3
76.9063 CDCl3
72.2462
22.3818
21.6914
10.0366
f1 (ppm)

Isopropyl 4-methylbenzenesulfonate (6c)

^{1}H NMR



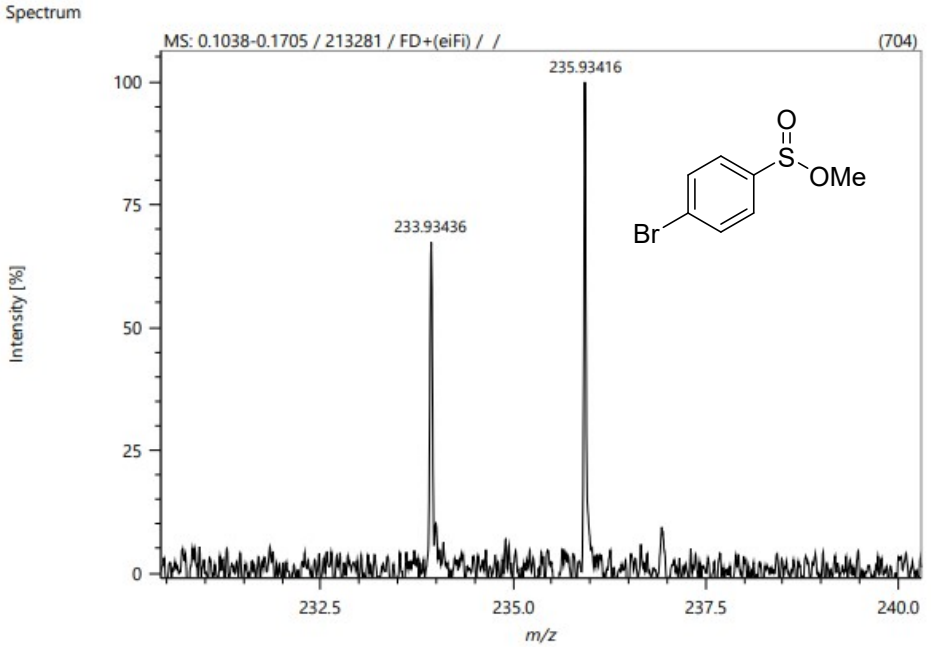
$^{13}C\{^{1}H\}$ NMR


O
O
S
O
Me

144.5114
134.6110
129.8371
127.7167
77.4141 CDCl3
77.1922
77.1600 CDCl3
76.9059 CDCl3
22.8309
21.6777
f1 (ppm)

11. HRMS data of products

Methyl 4-bromobenzenesulfinate (2h)



Elemental Composition

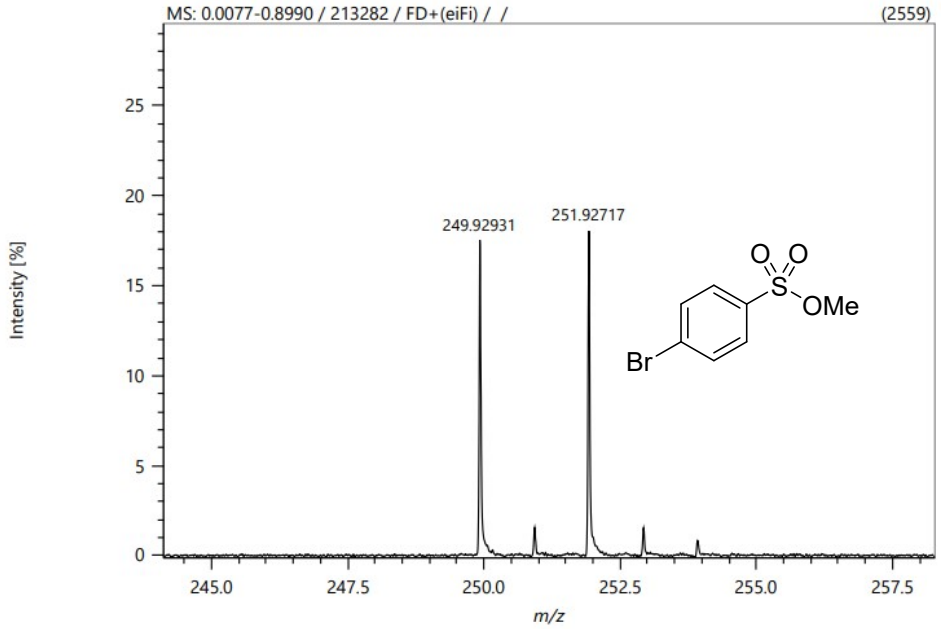
Parameters		Elements Set 1:					
Tolerance:	30.00 mDa	Symbol	C	H	O	S	Br
Electron:	Odd/Even	Min	5	6	1	1	1
Charge:	+1	Max	7	7	2	1	1
DBE:	-90.0 - 90.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
233.93436	474.23	C7 H7 O2 S Br	233.93446	-0.11	-0.45	4.0

Methyl 4-bromobenzenesulfonate (3h)

Spectrum



Elemental Composition

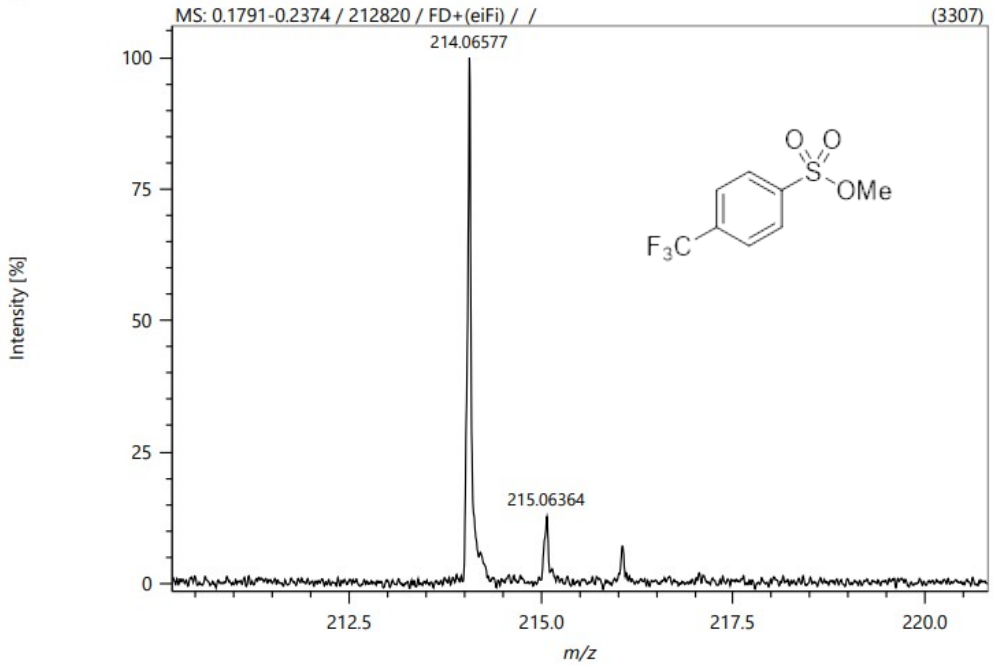
Parameters		Elements Set 1:					
Tolerance:	30.00 mDa	Symbol	C	H	O	S	Br
Electron:	Odd/Even	Min	5	6	1	1	1
Charge:	+1	Max	7	7	3	1	1
DBE:	-90.0 - 90.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
249.92931	2487.86	C7 H7 O3 S Br	249.92938	-0.07	-0.26	4.0

Methyl 4-(trifluoromethyl)benzenesulfinate (3m)

Spectrum



Elemental Composition

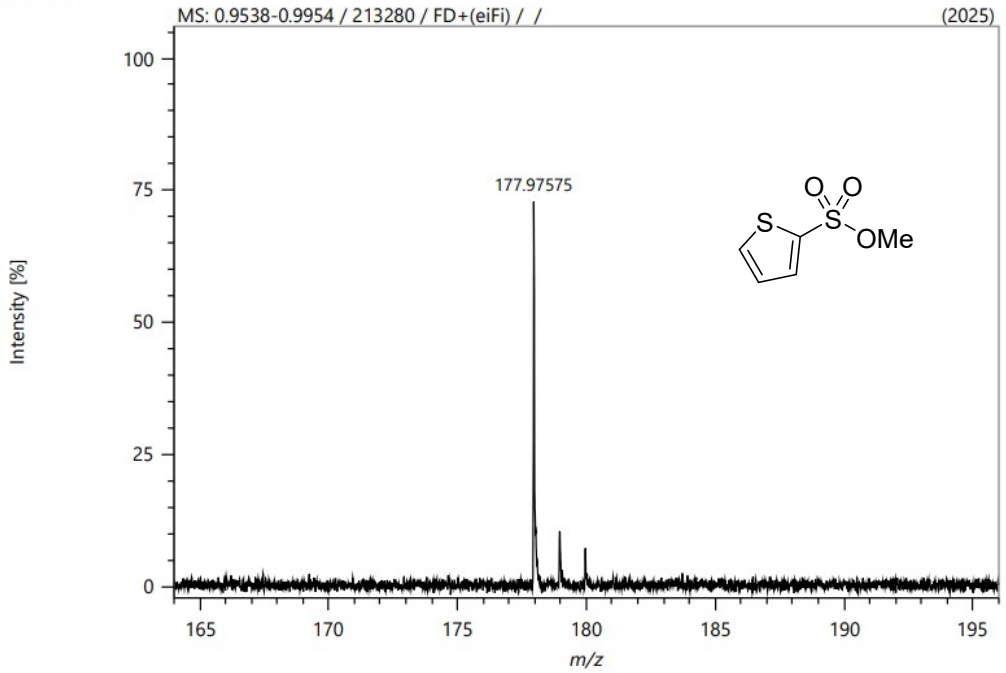
Parameters		Elements Set 1:				
Tolerance:	30.00 mDa	Symbol	C	H	O	S
Electron:	Odd/Even	Min	9	13	1	1
Charge:	+1	Max	10	14	3	1
DBE:	-90.0 - 90.0					

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
214.06577	3307.42	C10 H14 O3 S	214.06582	-0.04	-0.20	4.0

Methyl thiophene-2-sulfonate (3s)

Spectrum



Elemental Composition

Parameters	
Tolerance:	30.00 mDa
Electron:	Odd/Even
Charge:	+1
DBE:	-90.0 - 90.0

Elements Set 1:

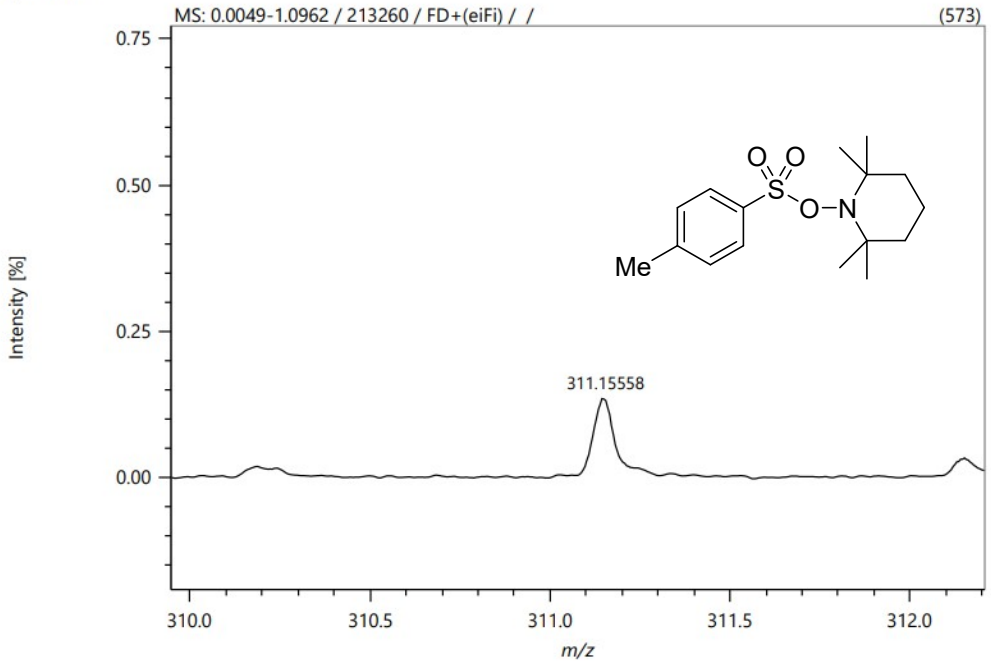
Symbol	C	H	O	S
Min	5	6	1	2
Max	5	6	3	2

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
177.97575	2024.68	C5 H6 O3 S2	177.97529	0.46	2.61	3.0

Product 7

Spectrum



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	30.00 mDa	Symbol	C	H	O	N	S
Electron:	Odd/Even	Min	6	9	1	1	1
Charge:	+1	Max	16	25	3	1	1
DBE:	-90.0 - 90.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
311.15558	573.20	C16 H25 N O3 S	311.15497	0.62	1.98	5.0