Supporting Information

Enantioselective Transformation of Na_2SO_3 into Allylic Sulfonic Acids under Pd catalysis

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General Experimental Details

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

All reagents were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent (3.31 ppm for CD_3OD; 7.26 ppm for $CDCl_3$). ^{13}C NMR spectra were obtained at 100 MHz, and chemical shifts were recorded relative to the solvent resonance (CD_3OD, 49.00 ppm; $CDCl_3$, 77.0 ppm). ^{19}F NMR spectra were obtained at 377 MHz and CF_3COOH (δ = -76.55) was used as internal standard. Data for NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration).

General Procedure for Pd-catalyzed Allylic Sulfonations of the Symmetrical Allylic Acetates

In a reaction tube equipped with a magnetic stirring bar were added in sequence allylic aceate **1** (1.0 mmol, 5 equiv.) and a mixture of THF (2.0 mL) and H_2O (0.5 mL) at room temperature under argon. To this solution were sequentially added catalyst made from $Pd_2(dba)_3$ (0.01 mmol, 5 mol%) and (*R*)-BINAP(0.02 mmol, 10 mol%) and sodium sulfite Na_2SO_3 **2a** (0.20 mmol, 1 equiv.). The reaction was vigorously stirred at room temperature.

Work-up was performed through a plug of freshly activated acidic ion exchange resin.[1] The crude residue was purified by flash column chromatography (methanol/ethyl acetate) to give the desired products **3**.[2] The allylic sulfonic acid **3** (0.10 mmol) was added into the mixture of DCM (2.0 mL) and HBF_4 (50% aq, 20 μL) at room temperature, and then trimethylsilyl diazomethane (Me_3SiCHN_2, 0.5 mmol, 0.5 mL) was added dropwise into the above-mentioned solution. The reaction mixture was stirred for 1 hour then the volatile solvent was removed under reduced pressure. The methylated sulfonic acids **3aa-3ja** was obtained by purifying the crude residue with column chromatography (petroleum ether/ethyl acetate).

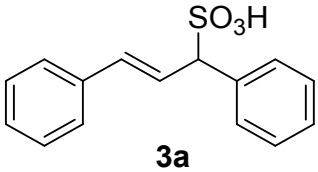
Methanol-d4 was chosen as an internal standard and the peak at 3.31 ppm is distributed to MeOD. The peak at 4.87 ppm is assigned to H_2O. After purification, there was a peak at 4.87 ppm for H_2O in ^{1}H NMR spectra of the sulfonic acids due to the hygroscopic property of the sulfonic acids. The allylic sulfonic acids are difficult to be dried absolutely and this phenomena is in accord with previous works.[2] The yields of products were reduced the weight of water according the integration of H_2O in all cases.

Reference

[1] F. Fini, M. Nagabelli, M. F. A. Adamo, *Adv. Synth. Catal.* 2010, **352**, 3163.

[2] The sulfonic acids **3** with water were obtained after purification, which are inseparable, see: (a) Moccia, M.; Fini, F.; Scagnetti, M.; Adamo, M. F. A. *Angew. Chem. Int. Ed.* 2011, **50**, 6893; b) Koch, F. M.; Peters, R. *Chem. -Eur. J.* 2011, **17**, 3679.

Characterization Data



3a

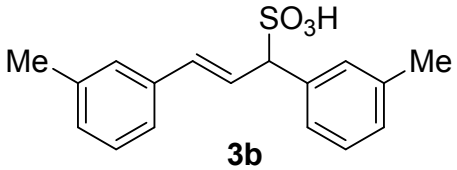
(*E*)-1,3-Diphenylprop-2-ene-1-sulfonic acid (**3a**)
The isolated hydrated sulfonic acid **3a** is 30.9 mg, which contains 2.4 mg of H_2. The integration of the hydrogen of H_2O was determined as 2.19 by ^1H NMR at 4.87 ppm and the calculated yield was calculated by the following equations:

$[H_2O]\% = ([H]*18/2)/([H]*18/2+MW)$
$W[H_2O] = W*[H_2O]\%$
$CW = W - W[H_2O]$

W = weight of the hydrated sulfonic acid
MW = molecular weight of the sulfonic acid
$[H_2O]\%$ = the percent of water in the hydrated sulfonic acid
$W[H_2O]$ = weight of H_2O
CW = calculated weight of the sulfonic acid
[H] = the integration of the hydrogen of H_2O in ^1H NMR spectra.

For example, CW of **3a** was calculated by the following equations:
$[H_2O]\% = 2.19*9/(2.19*9+237) = 7.7\%$
$W[H_2O] = 30.9*7.7\% = 2.4$ mg
CW = 30.9 mg-2.4 mg = 28.5 mg

Calculated yield: 60% (28.5 mg). White solid. The sulfonic acid **3a** is hygroscopic[2] and is decomposed over 300 °C.
^1H NMR (400 MHz, CD_3OD) δ = 7.58 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.78 (dd, *J* = 15.8, 8.7 Hz, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 4.82 (d, *J* = 8.6 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ = 138.61, 138.31, 135.38, 130.52, 130.44, 129.56, 129.30, 129.13, 128.71, 128.56, 127.49, 126.86, 71.38.
HRMS (ESI) found: 237.0597, $C_{15}H_{13}O_3S$ $[M-H]^-$ requires: 237.0591.
Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3a** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 19.06 min (major); 22.02 min (minor); hexane/2-propanol = 80/20, 1.0 mL/min] to be 90%. $[\alpha]_{20}^{D}$ = -13.5° (c 1.0, MeOH).
IR (KBr): ν max (cm^{-1}) = 3480, 2960, 2913, 2852, 1633, 1511, 1489, 1396, 1357, 1169, 1089, 1070, 984, 775, 587, 510, 453.



3b

(*E*)-1,3-Di-m-tolylprop-2-ene-1-sulfonic acid (**3b**)

The isolated hydrated sulfonic acid **3b** is 31.5 mg, which contains 0.8 mg of H_2O (the integration of the hydrogen of H_2O was determined as 0.89 by ^1H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 51% (30.7 mg). White solid. The sulfonic acid **3b** is hygroscopic[2] and is decomposed over 300 °C.

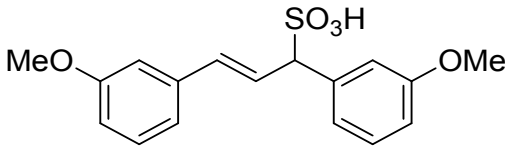
^1H NMR (400 MHz, CD_3OD) δ = 7.29 – 7.24 (m, 2H), 7.13 – 7.01 (m, 4H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.62 (dd, *J* = 15.8, 8.7 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 4.68 (d, *J* = 8.7 Hz, 1H), 2.21 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ = 139.09, 138.87, 138.27, 138.09, 135.44, 131.01, 129.39, 129.22, 129.17, 128.06, 127.47, 126.44, 124.62, 71.27, 21.51, 21.38.

HRMS (ESI) found: 301.0891, $C_{17}H_{17}O_3S$ $[M-H]^-$ requires: 301.0904.

Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3b** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 12.56 min (major); 14.68 min (minor); hexane/2-propanol = 70/30, 1.0 mL/min] to be 83%. $[\alpha]_{20}^{D}$ = -14.0° (c 1.0, MeOH).

IR (KBr): ν max (cm^{-1}) = 3493, 2978, 2958, 2851, 1625, 1502, 1474, 1387, 1351, 1160, 1081, 1065, 974, 763, 597, 525, 441.



3c

(*E*)-1,3-Bis(3-methoxyphenyl)prop-2-ene-1-sulfonic acid (**3c**)

The isolated hydrated sulfonic acid **3c** is 46.3 mg, which contains 1.0 mg of H_2O (the integration of the hydrogen of H_2O was determined as 0.80 by ^1H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 68% (45.3 mg).

White solid. The sulfonic acid **3c** is hygroscopic[2] and is decomposed over 300 °C.

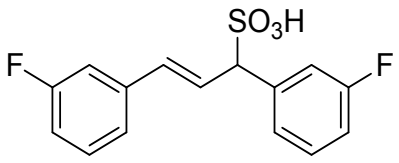
1H NMR (400 MHz, CD_3OD) δ = 7.26 – 7.12 (m, 4H), 7.04 – 6.97 (m, 2H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.73 (dd, *J* = 15.7, 8.6 Hz, 1H), 6.59 (d, *J* = 15.8 Hz, 1H), 4.78 (d, *J* = 8.6 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ = 161.31, 161.01, 139.90, 139.69, 135.33, 130.52, 130.26, 127.07, 122.78, 120.11, 116.15, 114.47, 114.06, 112.70, 71.25, 55.69, 55.63.

HRMS (ESI) found: 333.0808, $C_{17}H_{17}O_5S$ $[M-H]^-$ requires: 333.0802.

Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3c** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 21.91 min (major); 24.10 min (minor); hexane/2-propanol = 70/30, 1.0 mL/min] to be 91%. $[\alpha]_{20}^{D}$ = -15.9° (c 1.1, MeOH).

IR (KBr): ν max (cm^{-1}) = 3486, 3450, 2980, 2923, 2868, 1645, 1578, 1441, 1385, 1352, 1162, 1087, 1067, 963, 752, 578, 528, 468.



3d

(*E*)-1,3-Bis(3-fluorophenyl)prop-2-ene-1-sulfonic acid (**3d**)

The isolated hydrated sulfonic acid **3d** is 34.0 mg, which contains 1.2 mg of H_2O (the integration of the hydrogen of H_2O was determined as 1.3 by ^1H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 53% (32.8 mg).

White solid. The sulfonic acid **3d** is hygroscopic[2] and is decomposed over 300 °C.

^1H NMR (400 MHz, CD_3OD) δ = 7.34 – 7.14 (m, 6H), 7.10 – 6.91 (m, 2H), 6.78 (dd, *J* = 15.8, 8.9 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 4.82 (d, *J* = 8.7 Hz, 1H).

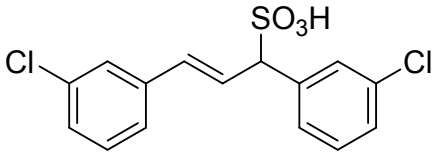
^{13}C NMR (100 MHz, CD_3OD) δ = 165.45 (d, *J* = 47.3 Hz), 163.03 (d, *J* = 46.9 Hz), 134.28 (d, *J* = 2.2 Hz), 131.25 (d, *J* = 8.4 Hz), 130.86 (d, *J* = 8.3 Hz), 130.44 (d, *J* = 8.5 Hz), 129.03 (s), 128.35 (s), 126.34 (d, *J* = 2.6 Hz), 123.58 (d, *J* = 2.4 Hz), 117.00 (d, *J* = 22.5 Hz), 115.31 (d, *J* = 10.8 Hz), 115.10 (d, *J* = 10.4 Hz), 113.72 (d, *J* = 22.1 Hz), 70.65 (s).

^{19}F NMR (377 MHz, MeOD) δ = -115.52, -115.69.

HRMS (ESI) found: 309.0407, $C_{15}H_{11}F_2O_3S$ $[M-H]^-$ requires: 309.0402.

Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3d** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 11.49 min (minor); 13.36 min (major); hexane/2-propanol = 70/30, 1.0 mL/min] to be 85%. $[\alpha]_{20}^{D}$ = -14.2° (c 0.9, MeOH).

IR (KBr): ν max (cm^{-1}) = 3495, 2971, 2925, 2868, 1689, 1544, 1475, 1386, 1341, 1156, 1025, 1010, 956, 796, 575, 569, 457.



3e

(*E*)-1,3-Bis(3-chlorophenyl)prop-2-ene-1-sulfonic acid (**3e**)

The isolated hydrated sulfonic acid **3e** is 42.8 mg, which contains 1.3 mg of H_2O (the integration of the hydrogen of H_2O was determined as 1.22 by ^1H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 61% (41.5 mg).

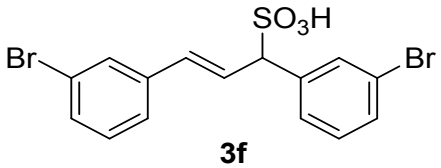
White solid. The sulfonic acid **3e** is hygroscopic[2] and is decomposed over 300 °C.

^1H NMR (400 MHz, CD_3OD) δ = 7.58 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.78 (dd, *J* = 15.8, 8.7 Hz, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 4.82 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (100 MHz, CD_3OD) δ = 140.71, 140.22, 135.51, 135.00, 134.33, 131.06, 130.80, 130.53, 130.34, 129.10, 128.88, 128.64, 128.61, 128.09, 127.35, 125.90, 70.49.

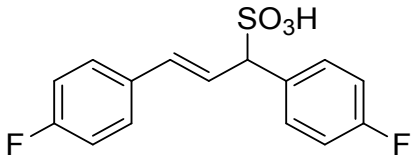
HRMS (ESI) found: 340.9814, $C_{15}H_{11}Cl_2O_3S$ $[M-H]^-$ requires: 340.9811.

Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3e** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 12.67 min (minor); 15.46 min (major); hexane/2-propanol = 70/30, 1.0 mL/min] to be 81%. $[\alpha]_{20}^{D}$ = -15.3° (c 1.0, MeOH).
IR (KBr): ν max (cm^{-1}) = 3489, 2986, 2942, 2874, 1656, 1529, 1480, 1342, 1311, 1109, 1056, 1014, 963, 761, 556, 512, 482.



3f

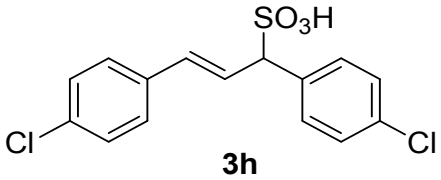
(*E*)-1,3-Bis(3-bromophenyl)prop-2-ene-1-sulfonic acid (**3f**)
The isolated hydrated sulfonic acid **3f** is 47.0 mg, which contains 0.7 mg of H_2O (integration of the hydrogen of H_2O was determined as 0.70 by ^1H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 54% (46.3 mg).
White solid. The sulfonic acid **3f** is hygroscopic[2] and is decomposed over 300 °C.
^1H NMR (400 MHz, CD_3OD) δ = 7.65 (s, 1H), 7.46 – 7.38 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.11 (m, 1H), 7.07 – 7.00 (m, 1H), 6.61 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 4.74 (d, *J* = 8.7 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ = 140.69, 140.23, 134.34, 133.20, 131.63, 131.56, 131.26, 131.08, 130.25, 129.26, 127.75, 126.24, 123.52, 123.05, 70.28.
HRMS (ESI) found: 428.8800, $C_{15}H_{11}Br_2O_3S$ $[M-H]^-$ requires: 428.8801.
Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3f** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 13.98 min (minor); 17.57 min (major); hexane/2-propanol = 70/30, 1.0 mL/min] to be 86%. $[\alpha]_{20}^{D}$ = -15.7° (c 1.0, MeOH).
IR (KBr): ν max (cm^{-1}) = 3452, 2963, 2922, 2888, 2802, 1683, 1602, 1522, 1475, 1348, 1316, 1108, 1012, 1027, 959, 729, 587, 509, 469.



3g

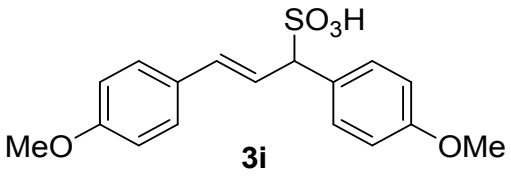
(*E*)-1,3-Bis(4-fluorophenyl)prop-2-ene-1-sulfonic acid (**3g**)
The isolated hydrated sulfonic acid **3g** is 38.9 mg, which contains 1.4 mg of H_2O (the integration of the hydrogen of H_2O was determined as 1.32 by ^1H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 61% (37.5 mg).
White solid. The sulfonic acid **3g** is hygroscopic[2] and is decomposed over 300 °C.
^1H NMR (400 MHz, CD_3OD) δ = 7.60 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.45 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.14 – 7.06 (m, 2H), 7.06 – 6.99 (m, 2H), 6.70 (dd, *J* = 15.7, 8.3 Hz, 1H), 6.60 (d, *J* = 15.7 Hz, 1H).

^{13}C NMR (100 MHz, CD_3OD) δ = 164.89 (d, *J* = 9.6 Hz), 162.45 (d, *J* = 8.6 Hz), 134.69 (d, *J* = 3.1 Hz), 134.63 (d, *J* = 3.3 Hz), 134.16 (s), 132.21 (d, *J* = 8.1 Hz), 129.26 (d, *J* = 8.0 Hz), 126.67 (s), 116.23 (d, *J* = 21.8 Hz), 115.87 (d, *J* = 21.6 Hz), 70.28 (s).
^{19}F NMR (377 MHz, CD_3OD) δ = -116.21, -116.92.
HRMS (ESI) found: 309.0402, $C_{15}H_{11}F_2O_3S$ $[M-H]^-$ requires: 309.0402.
Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3g** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK OD, 0.46 cm × 25 cm). t_R = 6.40 min (minor); 6.89 min (major); hexane/2-propanol = 70/30, 1.0 mL/min] to be 83%. $[\alpha]_{20}^{D}$ = -13.4 ° (c1.0, MeOH).
IR (KBr): ν max (cm^{-1}) = 3460, 2981, 2901, 2859, 1652, 1524, 1492, 1385, 1369, 1175, 1090, 1075, 996, 780, 590, 530, 456.



3h

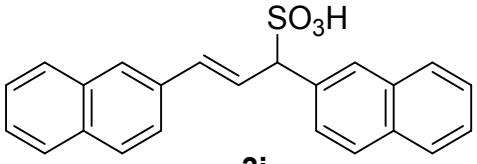
(*E*)-1,3-Bis(4-chlorophenyl)prop-2-ene-1-sulfonic acid (**3h**)
The isolated hydrated sulfonic acid **3h** is 38.5 mg, which contains 1.2 mg of H_2O (integration of the hydrogen of H_2O was determined as 1.21 by ^{1}H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 55% (37.3 mg).
White solid. The sulfonic acid **3h** is hygroscopic[2] and is decomposed over 300 °C.
^{1}H NMR (400 MHz, CD_3OD) δ = 7.57 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.76 (dd, *J* = 15.7, 8.6 Hz, 1H), 6.59 (d, *J* = 15.8 Hz, 1H), 4.88 (d, *J* = 8.6 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ = 137.07, 136.74, 134.33, 134.23, 131.96, 129.55, 129.29, 128.91, 127.12, 70.22.
HRMS (ESI) found: 340.9811, $C_{15}H_{11}Cl_2O_3S$ $[M-H]^-$ requires: 340.9811.
Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3h** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK AD, 0.46 cm × 25 cm). t_R = 20.00 min (major); 22.24 min (minor); hexane/2-propanol = 70/30, 1.0 mL/min] to be 87%. $[\alpha]_{20}^{D}$ = -14.6° (c 1.0, MeOH).
IR (KBr): ν max (cm^{-1}) = 3501, 2963, 2927, 2845, 1670, 1569, 1432, 1352, 1359, 1174, 1092, 1085, 950, 763, 585, 532, 440.



3i

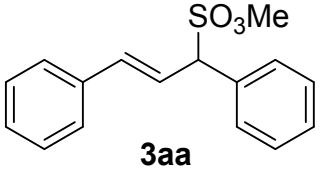
(*E*)-1,3-Bis(4-methoxyphenyl)prop-2-ene-1-sulfonic acid (**3i**)
The isolated hydrated sulfonic acid **3i** is 65.0 mg, which contains 3.7 mg of H_2O (the integration of the hydrogen of H_2O was determined as 2.25 by ^{1}H NMR at 4.87 ppm). Calculated yield by the same method as shown in **3a**: 92% (61.3 mg).
White solid. The sulfonic acid **3i** is hygroscopic[2] and is decomposed over 300 °C.

^{1}H NMR (400 MHz, CD_3OD) δ = 7.48 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.60 (dd, *J* = 15.7, 8.0 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 4.74 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ = 160.85, 160.61, 134.73, 131.50, 131.08, 130.65, 128.71, 124.59, 114.96, 114.70, 70.73.
HRMS (ESI) found: 333.0799, $C_{17}H_{17}O_5S$ $[M-H]^-$ requires: 333.0802.
Enantiomeric excess was determined with the sulfonic acid **3i** and analyzed by HPLC (267 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK IB, 0.46×25 cm, 5 μm). t_R = 17.62 min (major); 26.42 min (minor); hexane/2-propanol/diethyl amine = 50/50/0.2, 0.7 mL/min] to be 98%. $[\alpha]_{20}^{D}$ = -10.8° (c 1.0, MeOH).
IR (KBr): ν max (cm^{-1}) = 3510, 2996, 2905, 2849, 1626, 1505, 1493, 1382, 1369, 1189, 1050, 1010, 970, 785, 575, 520, 442.



3j

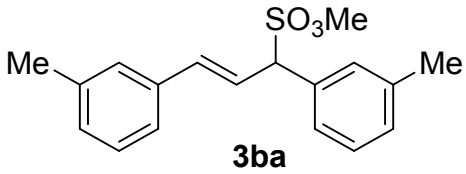
(*E*)-1,3-Di(naphthalen-2-yl)prop-2-ene-1-sulfonic acid (**3j**)
The isolated hydrated sulfonic acid **3j** is 31.1 mg, which contains 1.1 mg of H_2O (the integration of the hydrogen of H_2O was determined as 1.51 by ^{1}HNMR at 4.87 ppm). Calculated yield by the same method as shown in **3a** : 40% (30.0 mg).
White solid. The sulfonic acid **3j** is hygroscopic[2] and is decomposed over 300 °C.
^{1}H NMR (400 MHz, CD_3OD) δ = 8.06 (s, 1H), 7.87 – 7.79 (m, 3H), 7.75 – 7.71 (m, 3H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.36 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.03 (dd, *J* = 15.8, 8.7 Hz, 1H), 6.80 (d, *J* = 15.9 Hz, 1H), 5.08 (d, *J* = 8.6 Hz, 1H).
^{13}C NMR (100 MHz, CD_3OD) δ = 136.11, 135.74, 135.65, 134.99, 134.82, 134.48, 134.32, 130.53, 129.55, 129.16, 129.01, 128.79, 128.58, 128.55, 128.36, 127.55, 127.28, 127.24, 127.03, 126.97, 126.93, 124.58, 71.57.
HRMS (ESI) found: 373.0917, $C_{23}H_{17}O_3S$ $[M-H]^-$ requires: 373.0904.
Enantiomeric excess was determined with the sulfonic acid methyl ester generated by esterification of **3j** with Me_3SiCHN_2 and analyzed by HPLC (254 nm, 25 °C) on a chiral stationary phase [(Daicel CHIRALPAK OD, 0.46 cm × 25 cm). t_R = 31.28 min (minor); 38.62 min (major); hexane/2-propanol = 90/10, 1.0 mL/min] to be 87%. $[\alpha]_{20}^{D}$ = -11.5° (c 0.9, MeOH).
IR (KBr): ν max (cm^{-1}) = 3475, 2997, 2956, 2810, 2755, 1652, 1506, 1475, 1380, 1342, 1175, 1093, 1052, 974, 769, 574, 532, 442.



3aa

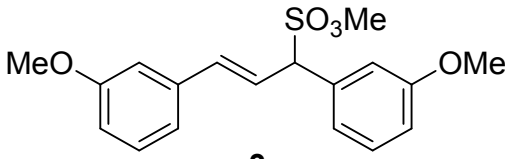
(*E*)-Methyl 1,3-diphenylprop-2-ene-1-sulfonate (**3aa**)

Yield: 45%, 15.0 mg. White solid. Melting point: 118-119 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.54 (m, 2H), 7.50 – 7.40 (m, 5H), 7.39 – 7.30 (m, 3H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.63 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.09 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.50, 135.59, 132.57, 129.32, 129.22, 129.06, 128.70, 126.86, 120.48, 70.81, 57.53.
HRMS (ESI) found: 311.0707, $C_{16}H_{16}O_3SNa$ $[M+Na]^+$ requires: 311.0712.
IR (KBr): ν max (cm^{-1}) = 3460, 2982, 2978, 2810, 2715, 1650, 1515, 1463, 1392, 1322, 1155, 1096, 1014, 961, 779, 563, 512, 478.



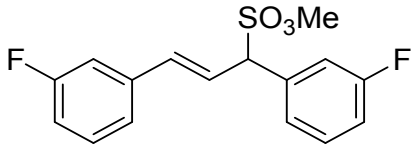
3ba

(*E*)-Methyl 1,3-di-m-tolylprop-2-ene-1-sulfonate (**3ba**)
Yield: 42%, 12.8 mg. White solid. Melting point: 124-125 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.27 (m, 3H), 7.26 – 7.16 (m, 4H), 7.13 – 7.04 (m, 1H), 6.71 (d, *J* = 15.7 Hz, 1H), 6.58 (dd, *J* = 15.6, 8.9 Hz, 1H), 5.02 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.88, 138.35, 137.50, 135.61, 132.53, 130.03, 129.92, 129.50, 128.96, 128.63, 127.48, 126.40, 124.17, 120.45, 70.84, 57.65, 21.50, 21.39.
HRMS (ESI) found: 339.1025, $C_{18}H_{20}O_3SNa$ $[M+Na]^+$ requires: 339.1025.
IR (KBr): ν max (cm^{-1}) = 3347, 2913, 1547, 1526, 1505, 1473, 1406, 1372, 1170, 1178, 1049, 806, 659, 676, 618, 600, 495.



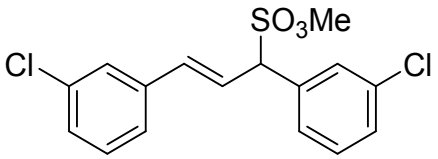
3ca

(*E*)-Methyl 1,3-bis(3-methoxyphenyl)prop-2-ene-1-sulfonate (**3ca**)
Yield: 48%, 16.7 mg. White solid. Melting point: 153-154 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.11 (s, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 6.4 Hz, 2H), 6.87 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.75 (d, *J* = 15.7 Hz, 1H), 6.59 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.04 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.96, 159.88, 137.41, 136.99, 133.89, 130.08, 129.71, 121.56, 120.77, 119.57, 115.09, 114.61, 114.43, 112.11, 70.72, 55.39, 55.33.
HRMS (ESI) found: 371.0916, $C_{18}H_{20}O_5SNa$ $[M+Na]^+$ requires: 371.0924.
IR (KBr): ν max (cm^{-1}) = 3510, 2969, 2930, 2847, 1601, 1556, 1478, 1312, 1300, 1156, 1089, 1020, 960, 785, 563, 520, 463.



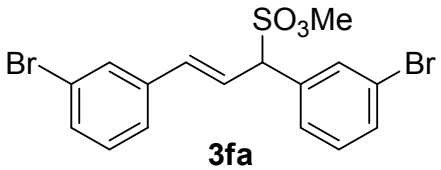
3da

(E)-Methyl 1,3-bis(3-fluorophenyl)prop-2-ene-1-sulfonate (**3da**)
Yield: 50%, 16.2 mg. White solid. Melting point: 107-108 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.39 (m, 1H), 7.38 – 7.28 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 13.1, 5.5 Hz, 2H), 7.05 – 6.99 (m, 1H), 6.76 (d, *J* = 15.7 Hz, 1H), 6.58 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.08 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.18 (d, *J* = 19.8 Hz), 161.72 (d, *J* = 21.4 Hz), 137.64 (d, *J* = 7.7 Hz), 136.74 (d, *J* = 2.6 Hz), 134.59 (d, *J* = 7.5 Hz), 130.71 (d, *J* = 8.2 Hz), 130.30 (d, *J* = 8.3 Hz), 125.08 (d, *J* = 3.1 Hz), 122.83 (d, *J* = 2.8 Hz), 121.39 (s), 116.50 (d, *J* = 4.0 Hz), 116.28 (d, *J* = 5.9 Hz), 115.72 (d, *J* = 21.3 Hz), 113.41 (d, *J* = 22.1 Hz), 69.88 (d, *J* = 1.7 Hz), 57.52 (s).
^{19}F NMR (377 MHz, $CDCl_3$) δ = -111.19, -112.84.
HRMS (ESI) found: 347.0530, $C_{16}H_{14}F_2O_3SNa$ $[M+Na]^+$ requires: 347.0524.
IR (KBr): ν max (cm^{-1}) = 3486, 2951, 2900, 2847, 1679, 1552, 1415, 1312, 1358, 1126, 1048, 1000, 923, 796, 585, 547, 452.



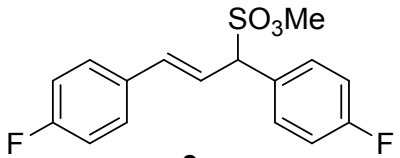
3ea

(*E*)-Methyl 1,3-bis(3-chlorophenyl)prop-2-ene-1-sulfonate (**3ea**)
Yield: 53%, 18.9 mg. White solid. Melting point: 127-128 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (s, 1H), 7.49 – 7.39 (m, 4H), 7.37 – 7.29 (m, 3H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.57 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.03 (d, *J* = 8.7 Hz, 1H), 3.83 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.14, 136.59, 135.02, 134.81, 134.21, 130.37, 130.02, 129.58, 129.36, 128.85, 127.46, 126.79, 125.16, 121.42, 69.88, 57.49.
HRMS (ESI) found: 378.9937, $C_{16}H_{14}Cl_2O_3SNa$ $[M+Na]^+$ requires: 378.9933.



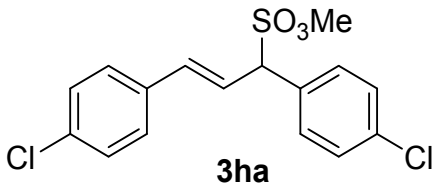
3fa

(E)-Methyl 1,3-bis(3-bromophenyl)prop-2-ene-1-sulfonate (**3fa**)
Yield: 46%, 20.5 mg. White solid. Melting point: 150-151 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.55 – 7.38 (m, 4H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.53 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.00 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.40, 136.51, 134.46, 132.52, 132.21, 131.76, 130.66, 130.30, 129.69, 127.92, 125.64, 123.06, 122.94, 121.42, 69.78, 57.58.
HRMS (ESI) found: 466.8915, $C_{16}H_{14}BrO_3SNa$ $[M+Na]^+$ requires: 466.8923.



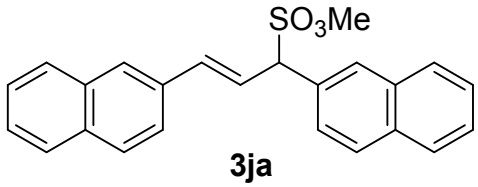
3ga

(*E*)-Methyl 1,3-bis(4-fluorophenyl)prop-2-ene-1-sulfonate (**3ga**)
Yield: 55%, 18.0 mg. White solid. Melting point: 125-126°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.40 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.17 – 7.09 (m, 2H), 7.06 – 7.00 (m, 2H), 6.71 (d, *J* = 15.7 Hz, 1H), 6.48 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.04 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.32 (d, *J* = 16.2 Hz), 161.84 (d, *J* = 15.9 Hz), 136.49 (s), 131.64 (d, *J* = 3.3 Hz), 131.12 (d, *J* = 8.4 Hz), 128.57 (d, *J* = 8.2 Hz), 128.35 (d, *J* = 3.4 Hz), 119.93 (d, *J* = 2.1 Hz), 116.19 (d, *J* = 21.8 Hz), 115.78 (d, *J* = 21.8 Hz), 69.77 (s), 57.44 (s).
^{19}F NMR (377 MHz, $CDCl_3$) δ = -111.66, -112.25.
HRMS (ESI) found: 347.0518, $C_{16}H_{14}F_2O_3SNa$ $[M+Na]^+$ requires: 347.0524.
IR (KBr): ν max (cm^{-1}) = 3496, 2985, 2974, 2823, 1656, 1585, 1452, 1332, 1300, 1170, 1089, 1070, 910, 777, 559, 512, 427.



3ha

(*E*)-Methyl 1,3-bis(4-chlorophenyl)prop-2-ene-1-sulfonate (**3ha**)
Yield: 56%, 20.0 mg. White solid. Melting point:128-129 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.43 (m, 4H), 7.40 – 7.37 (m, 1H), 7.37 – 7.33 (m, 3H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.54 (dd, *J* = 15.7, 8.7 Hz, 1H), 5.05 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.58, 135.48, 134.65, 133.87, 130.87, 130.80, 130.62, 129.56, 129.38, 129.25, 128.98, 128.10, 120.60, 69.81, 57.47.
HRMS (ESI) found: 378.9934, $C_{16}H_{14}Cl_2O_3SNa$ $[M+Na]^+$ requires: 378.9933.
IR (KBr): ν max (cm^{-1}) = 3461, 3061, 2963, 2843, 1895, 1692, 1596, 1492, 1403, 1356, 1163, 1095, 987, 846, 821, 781, 590, 529, 504, 443.

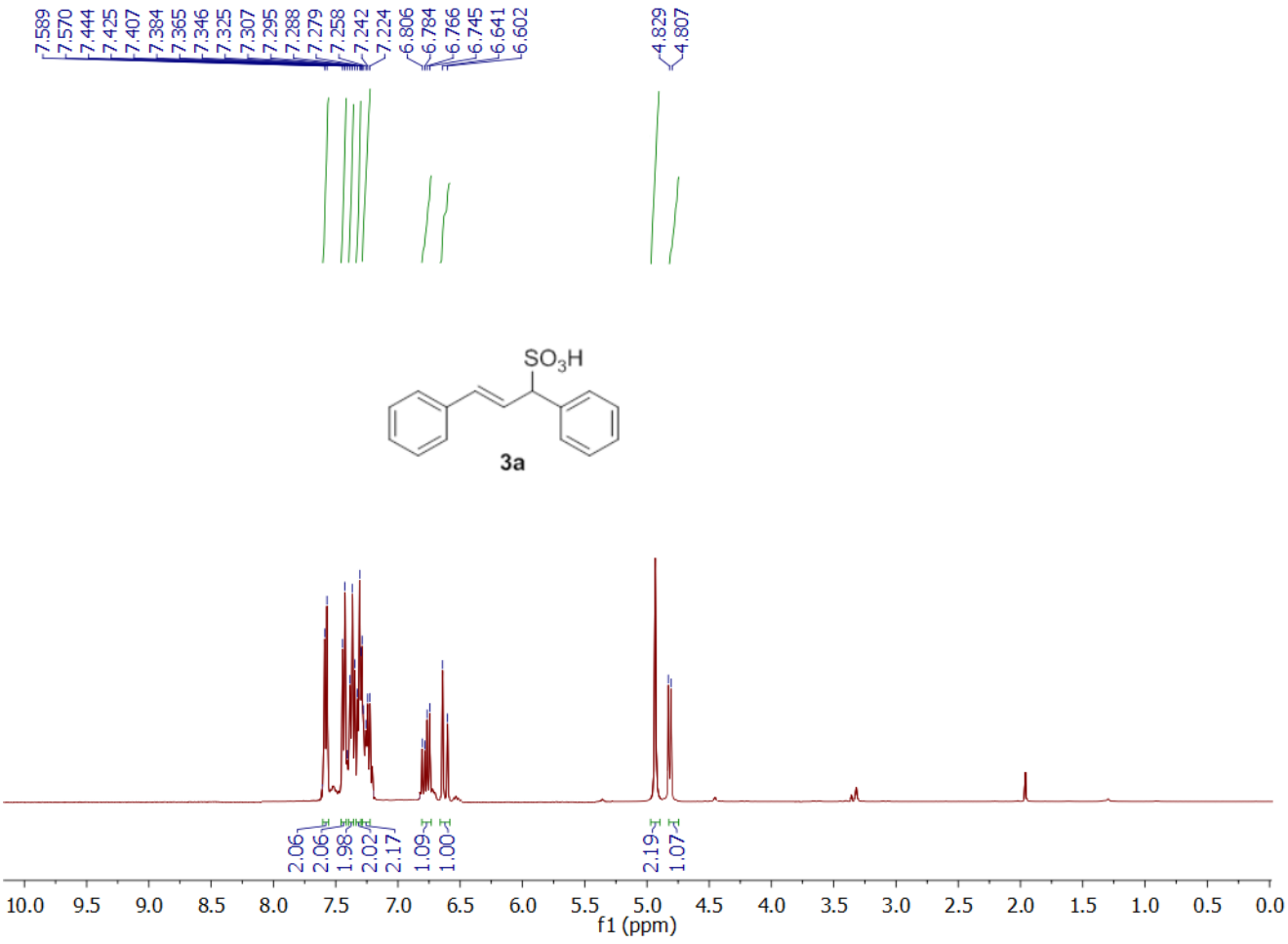


3ja

(*E*)-Methyl 1,3-di(naphthalen-2-yl)prop-2-ene-1-sulfonate (**3ja**)
Yield: 45%, 13.9 mg. White solid. Melting point: 164-165°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.86 – 7.79 (m, 4H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.57 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.53 – 7.47 (m, 2H), 6.99 (d, *J* = 15.7 Hz, 1H), 6.86 (dd, *J* = 15.7, 8.5 Hz, 1H), 5.33 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.74, 133.47, 133.42, 133.29, 133.07, 129.92, 129.14, 128.96, 128.49, 128.23, 128.17, 127.78, 127.73, 127.46, 126.98, 126.71, 126.53, 126.48, 126.29, 123.45, 120.78, 71.08, 57.60.
HRMS (ESI) found: 411.1025, $C_{24}H_{20}O_3SNa$ $[M+Na]^+$ requires: 411.1025.
IR (KBr): ν max (cm^{-1}) = 3493, 2970, 2925, 2871, 1759, 1660, 1472, 1302, 1299, 1250, 1192, 1110, 989, 783, 570, 502, 463.

NMR Spectra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1.00
2.19
1.07
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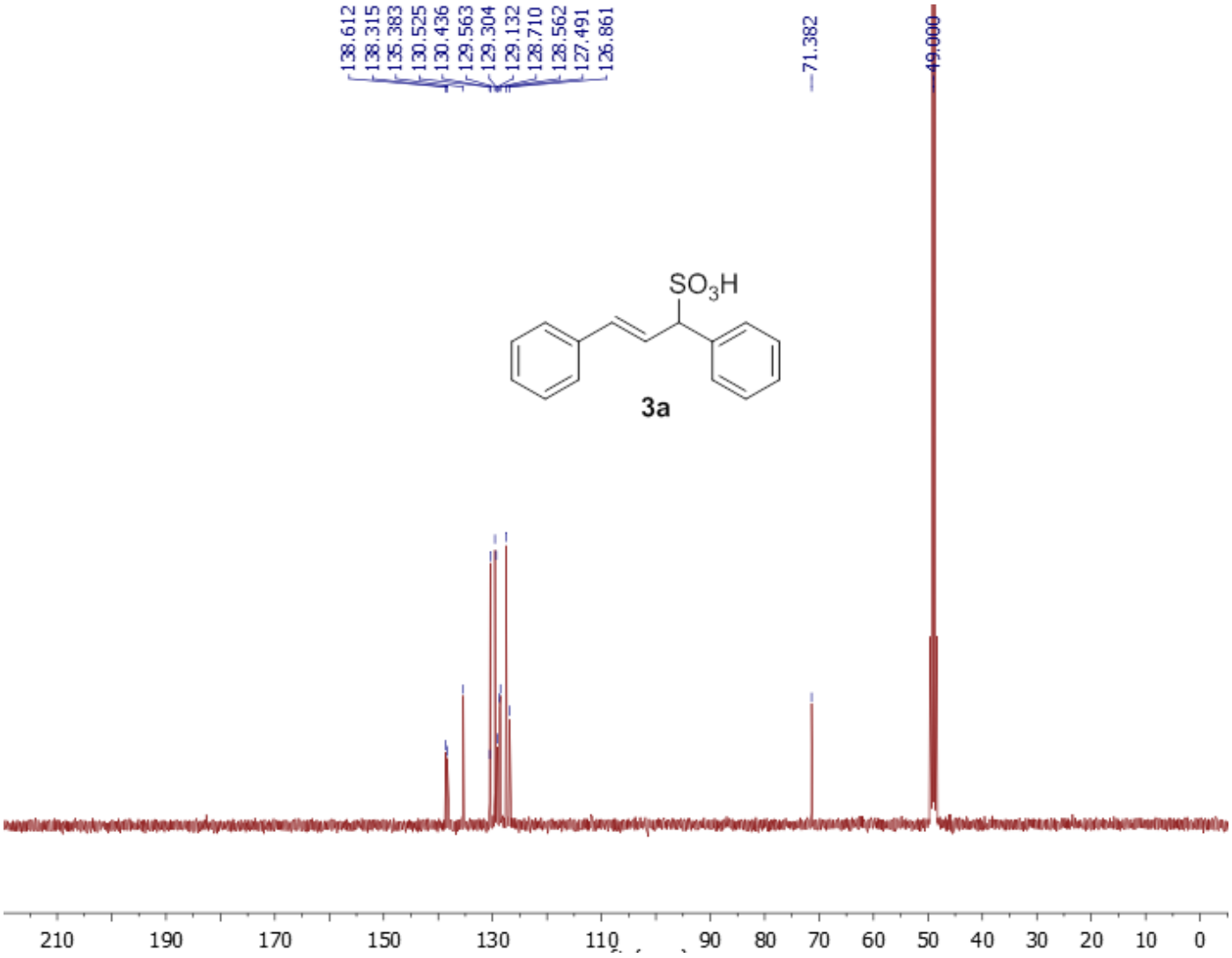
f1 (ppm)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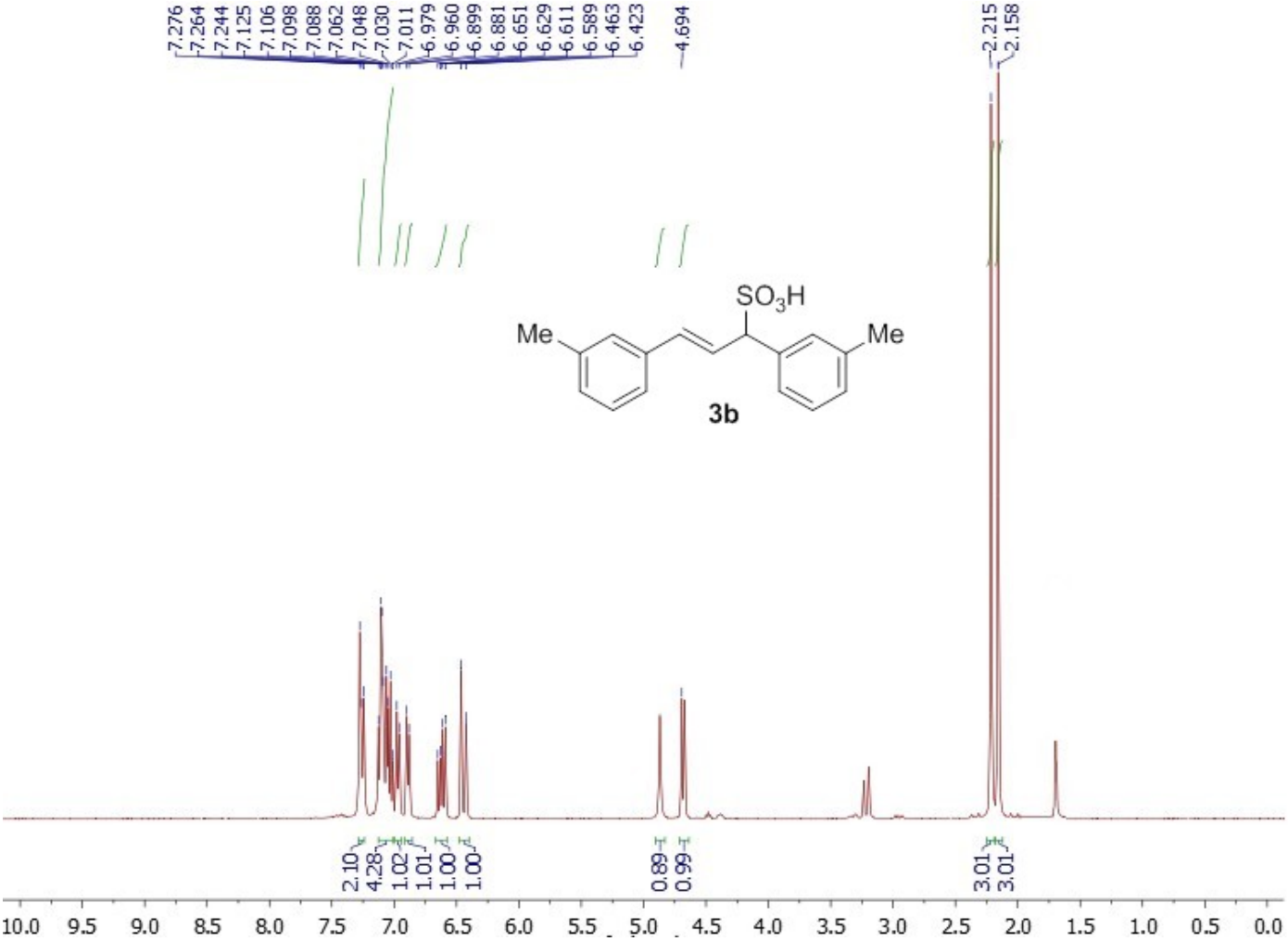
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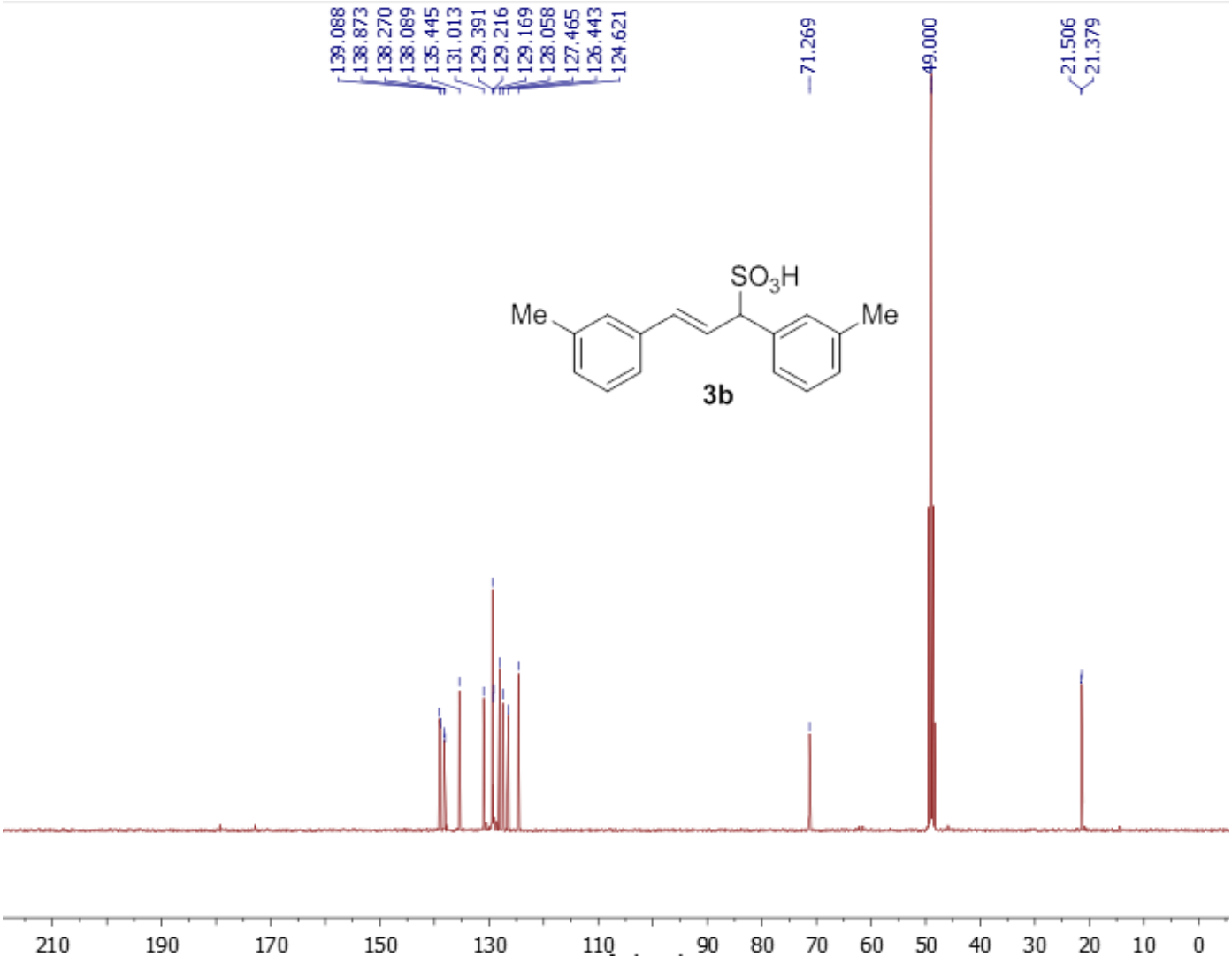
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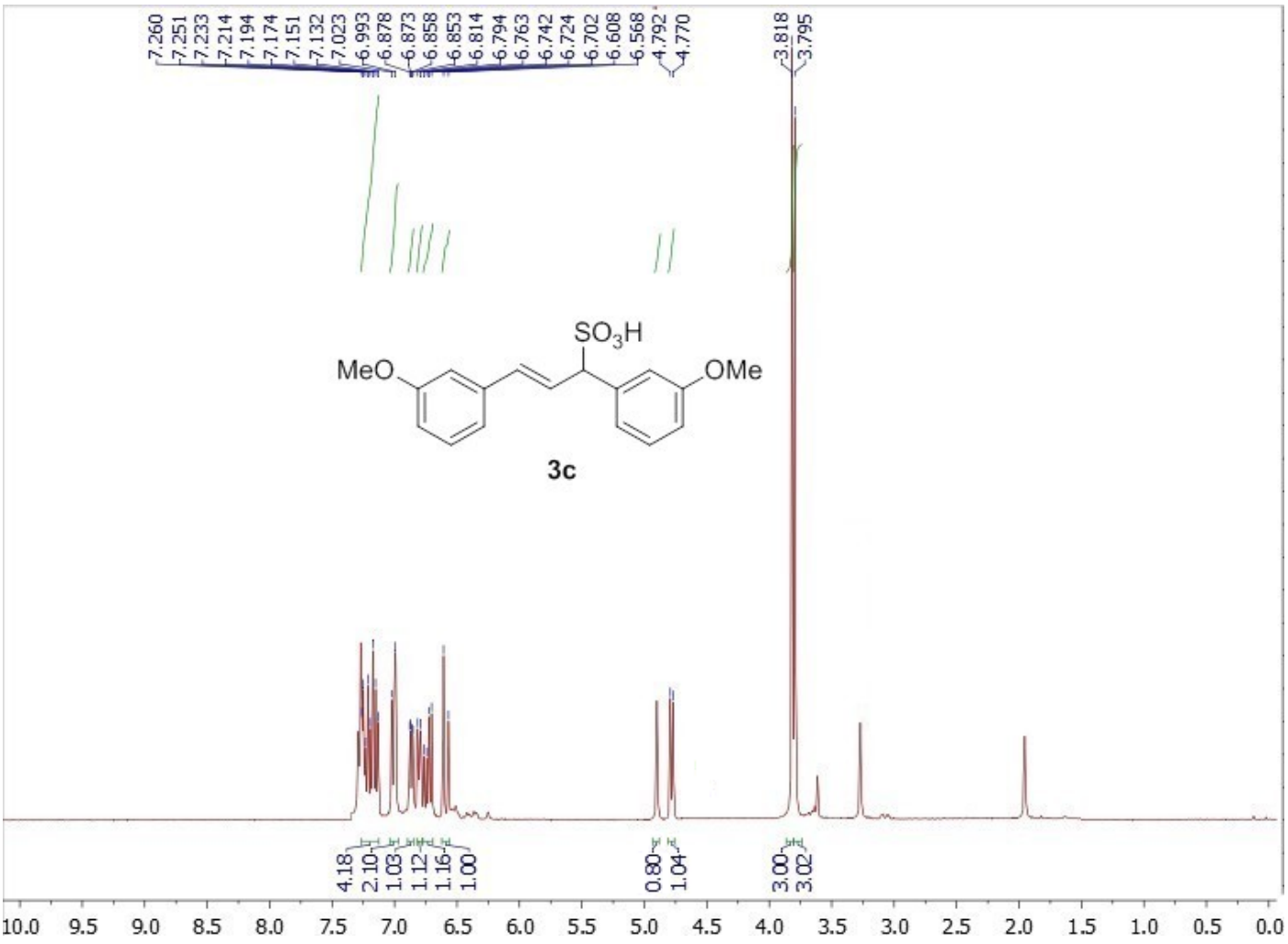
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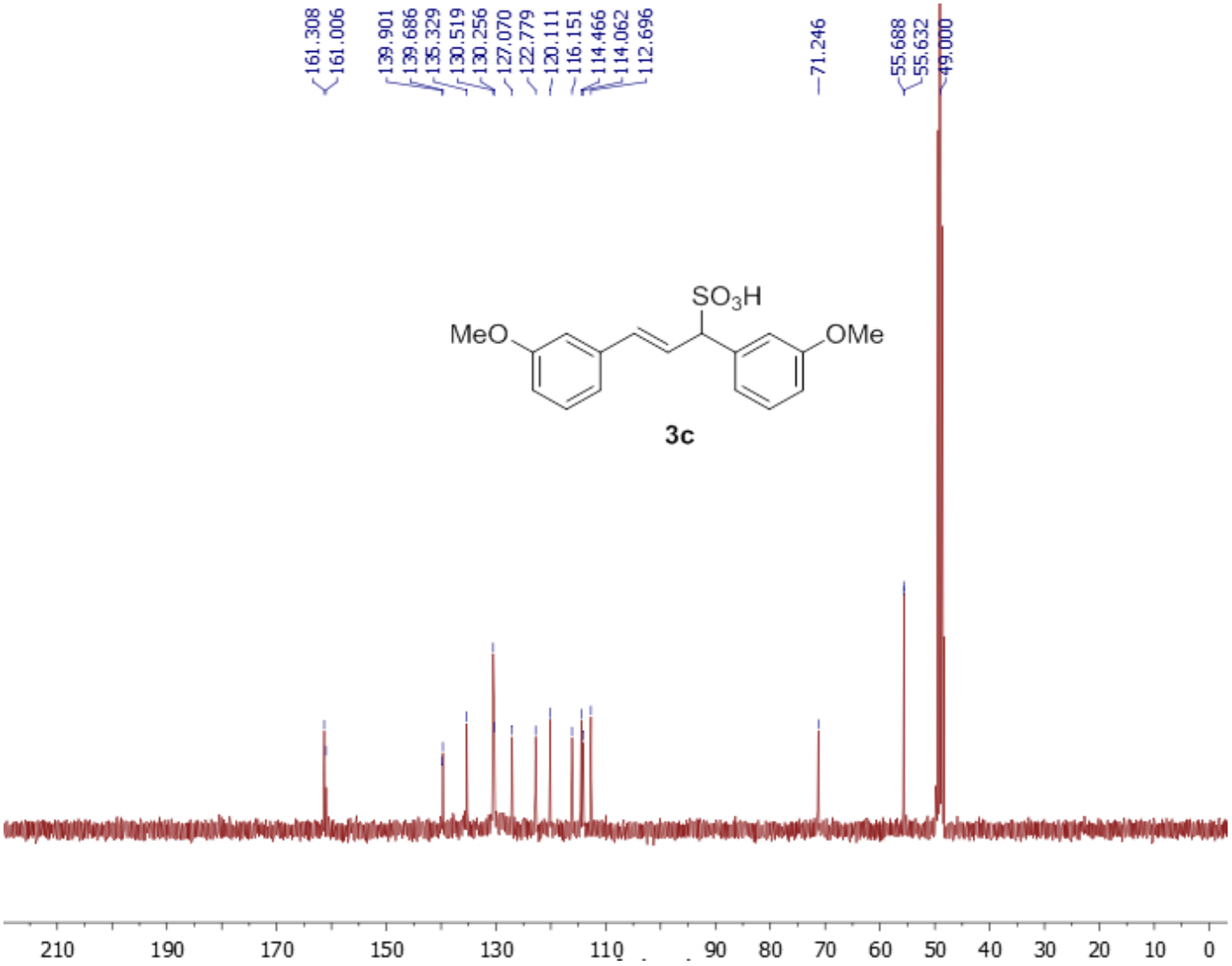
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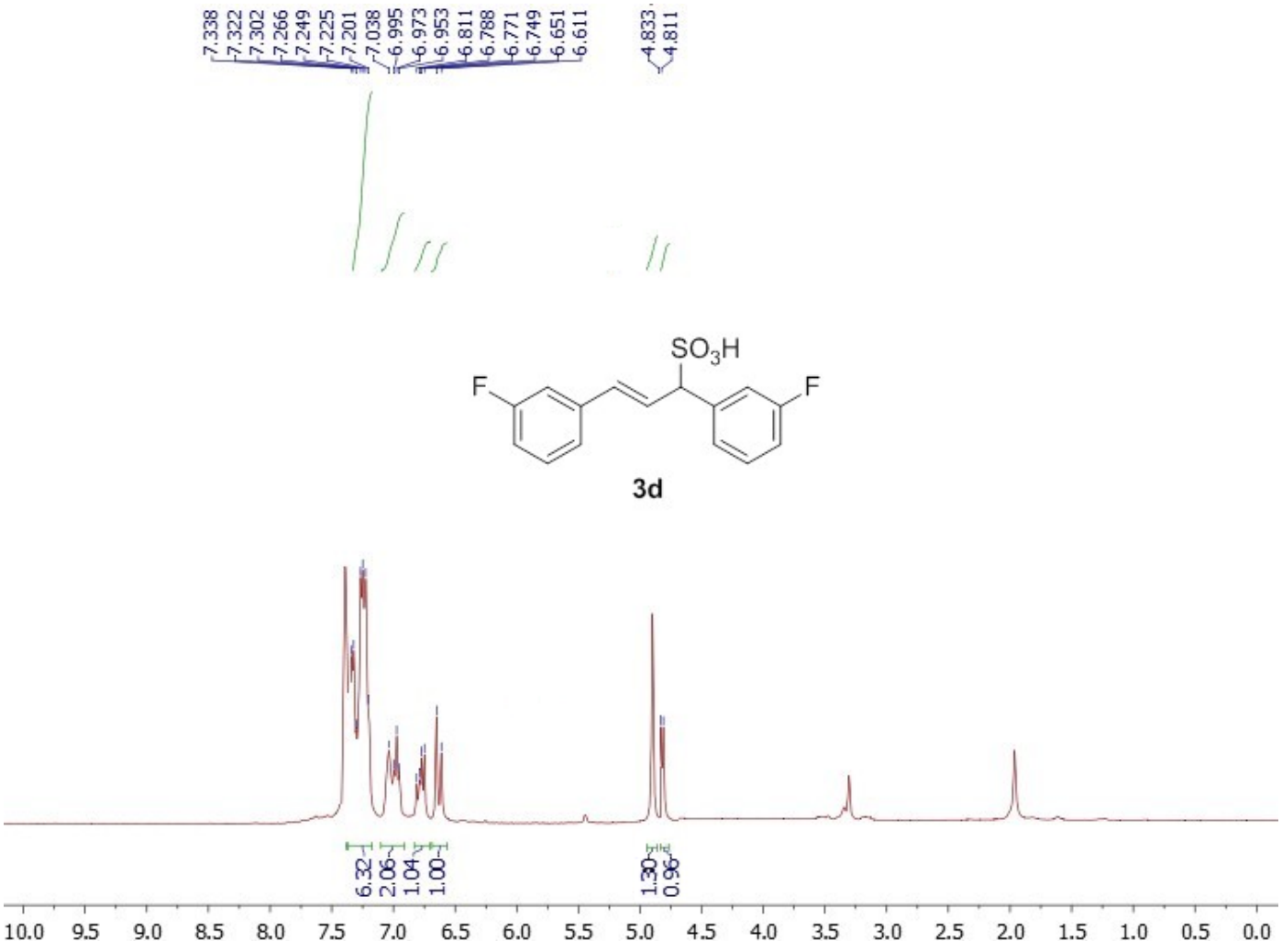
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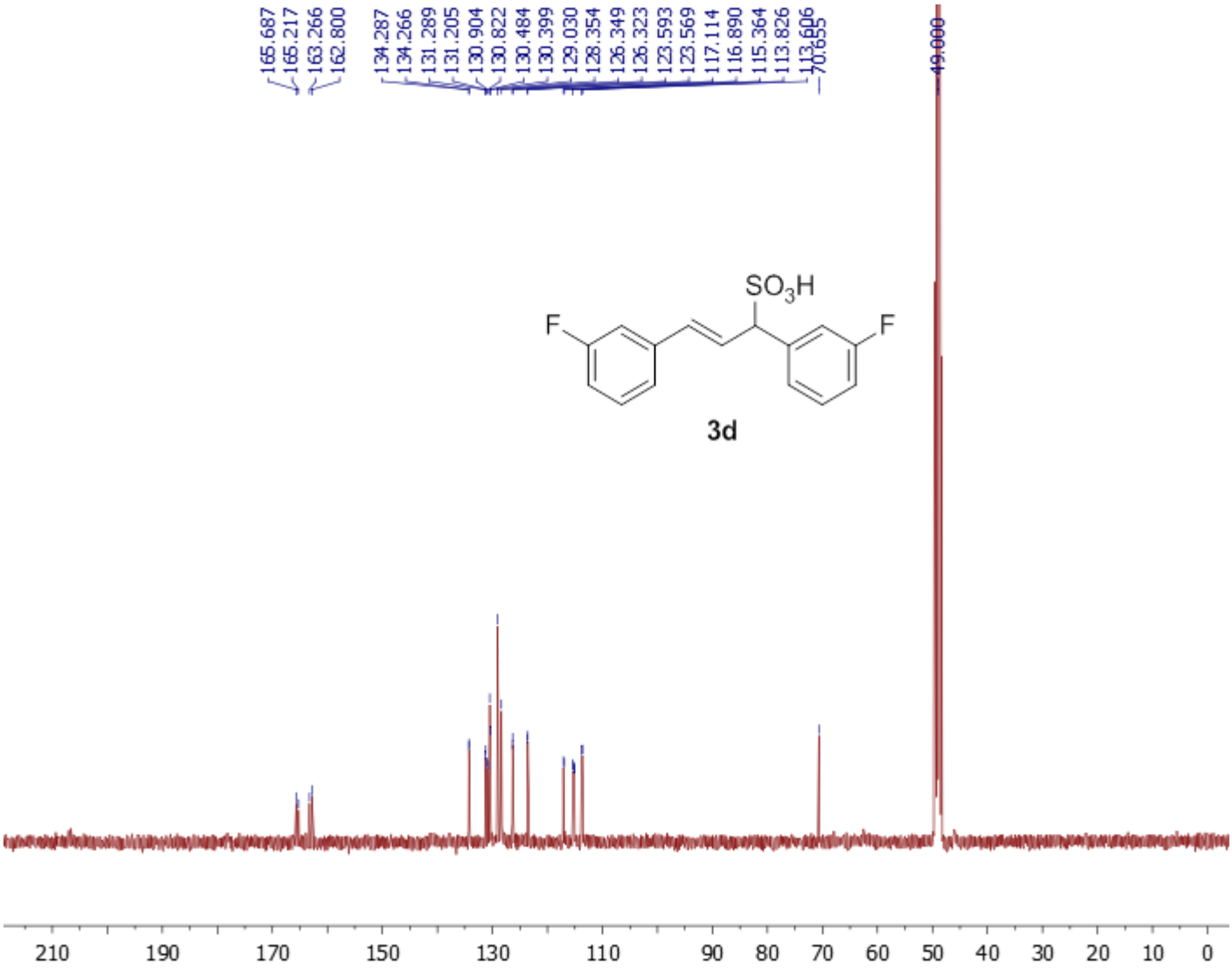
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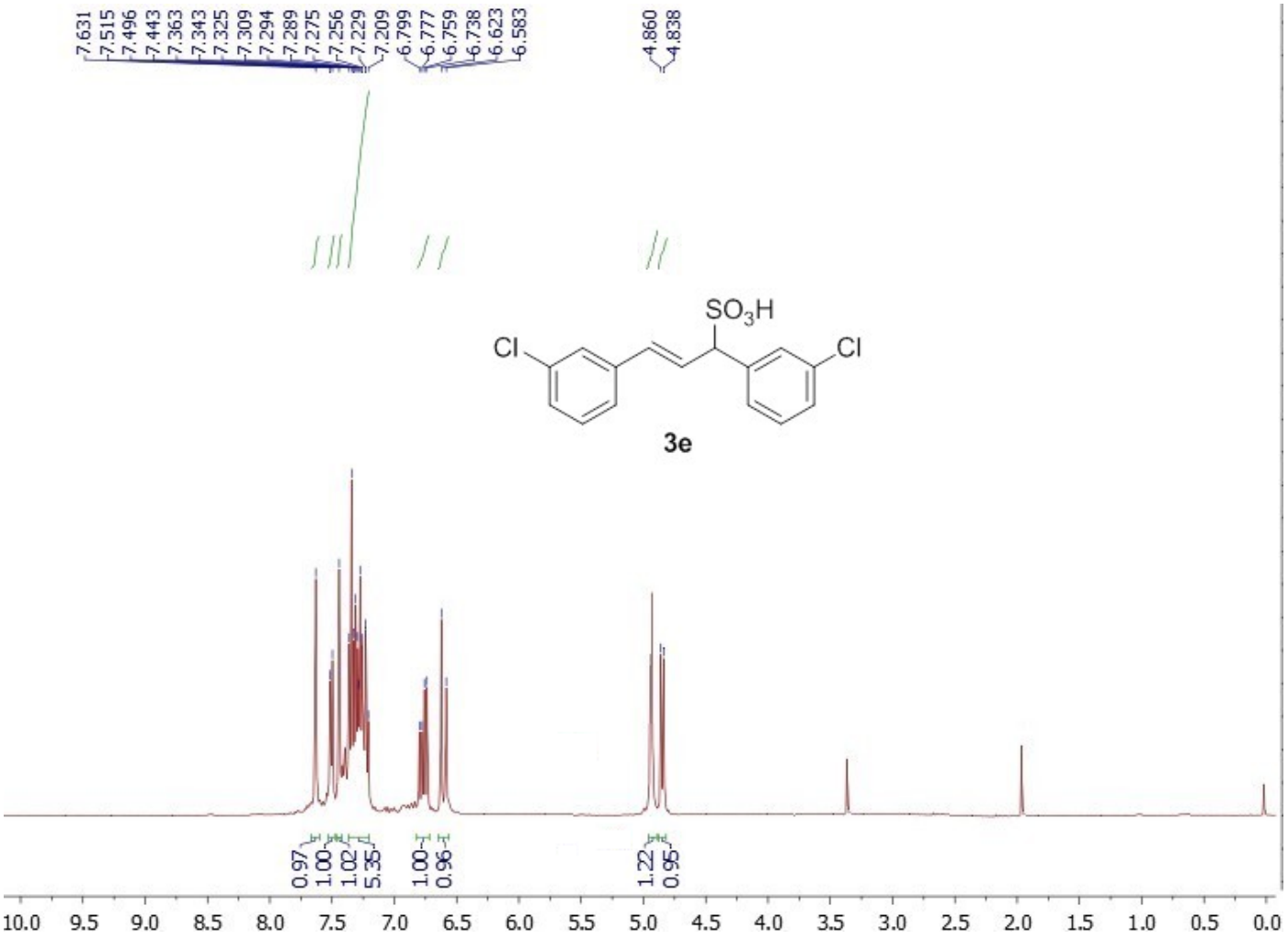
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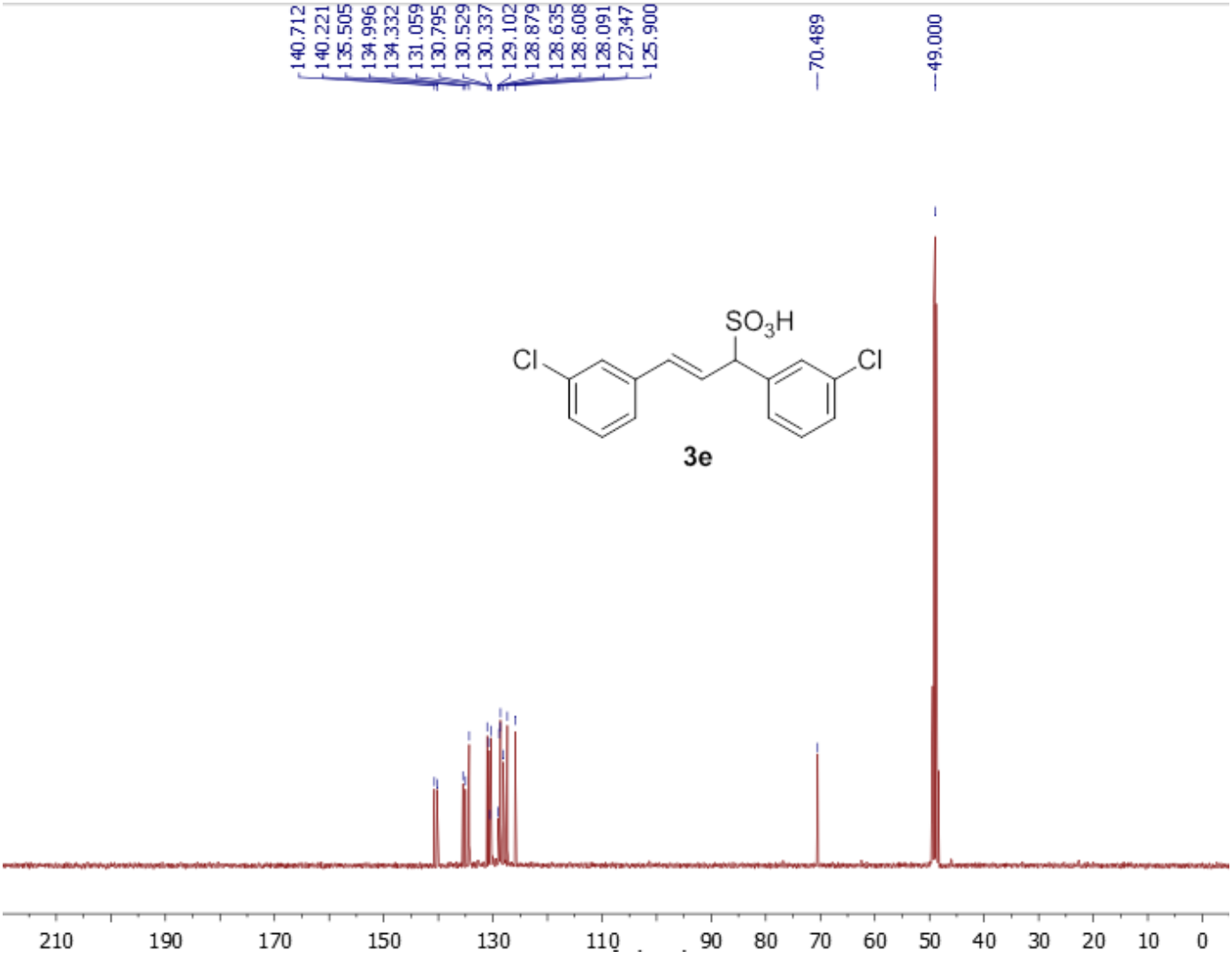
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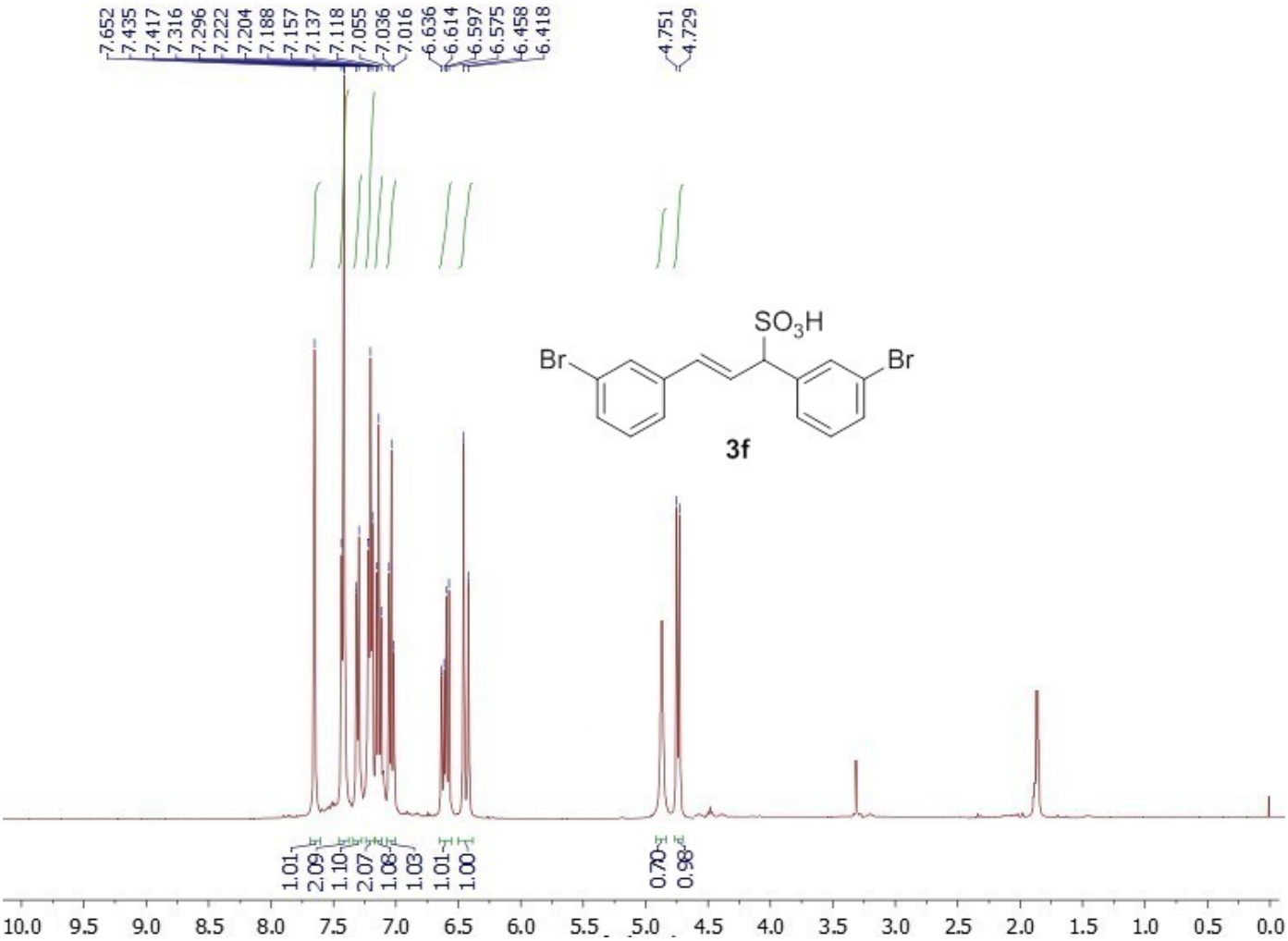
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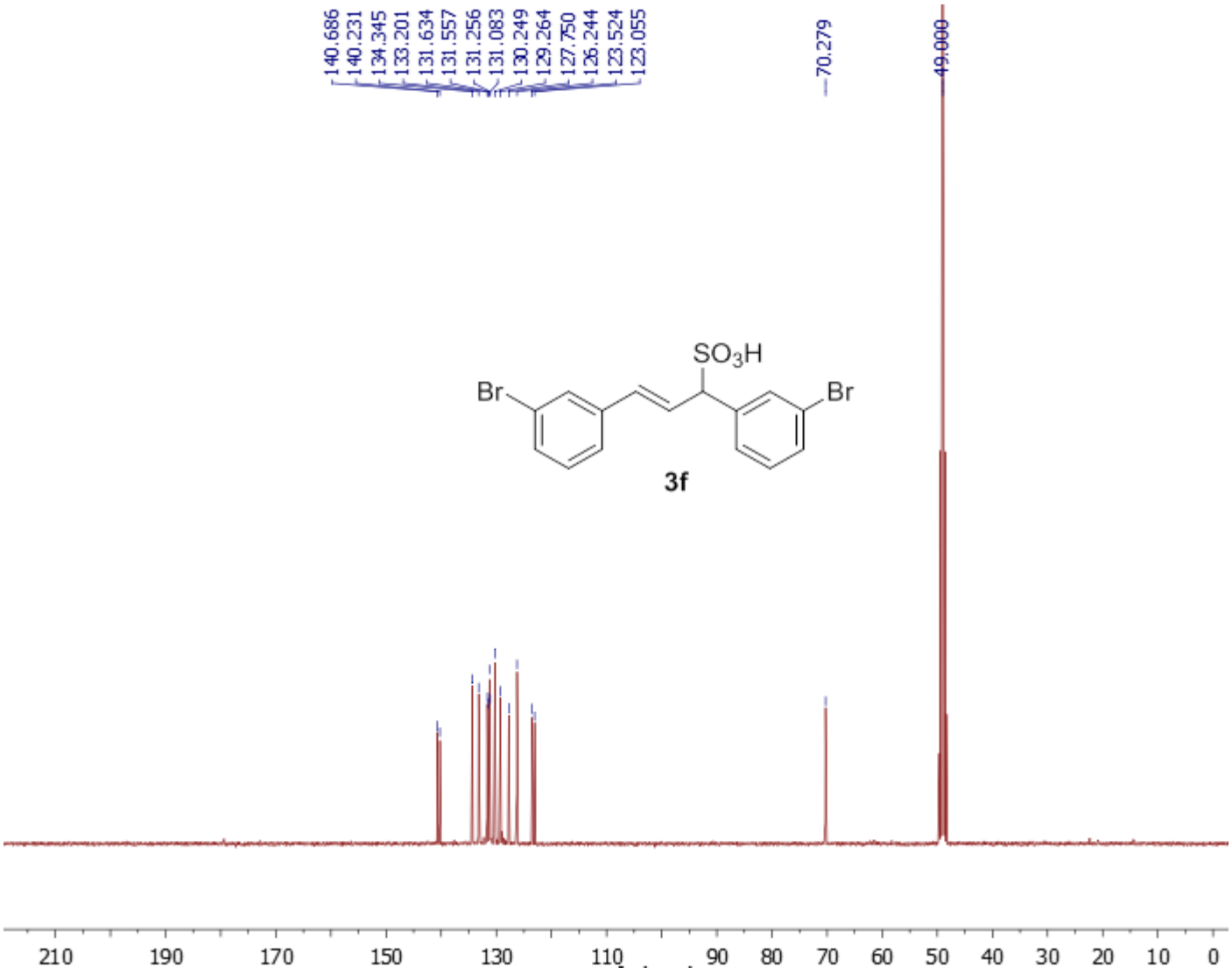
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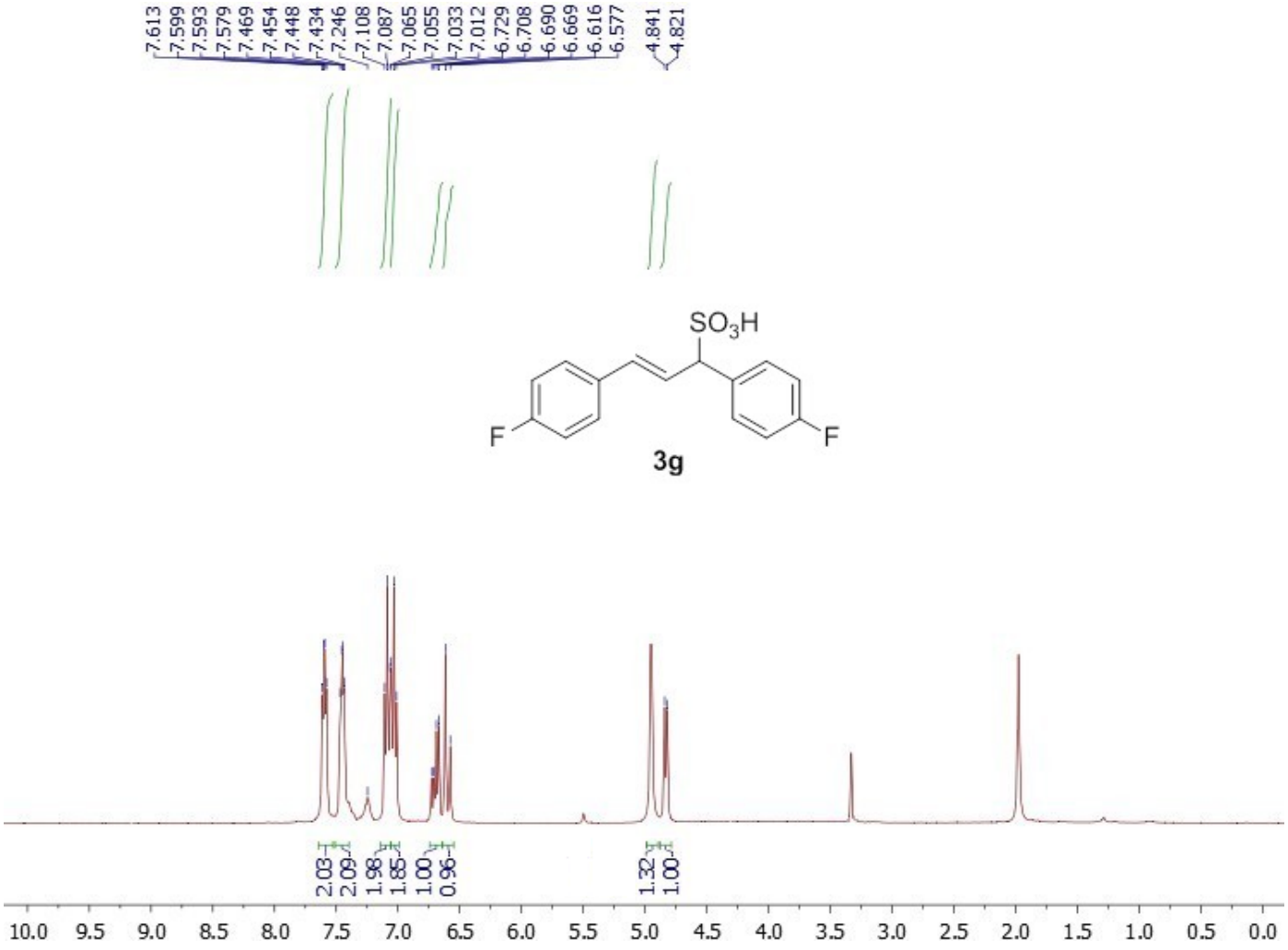
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7.055
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7.012
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6.690
6.669
6.616
6.577
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4.821
SO3H
F
F
3g
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2.09
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1.85
1.00
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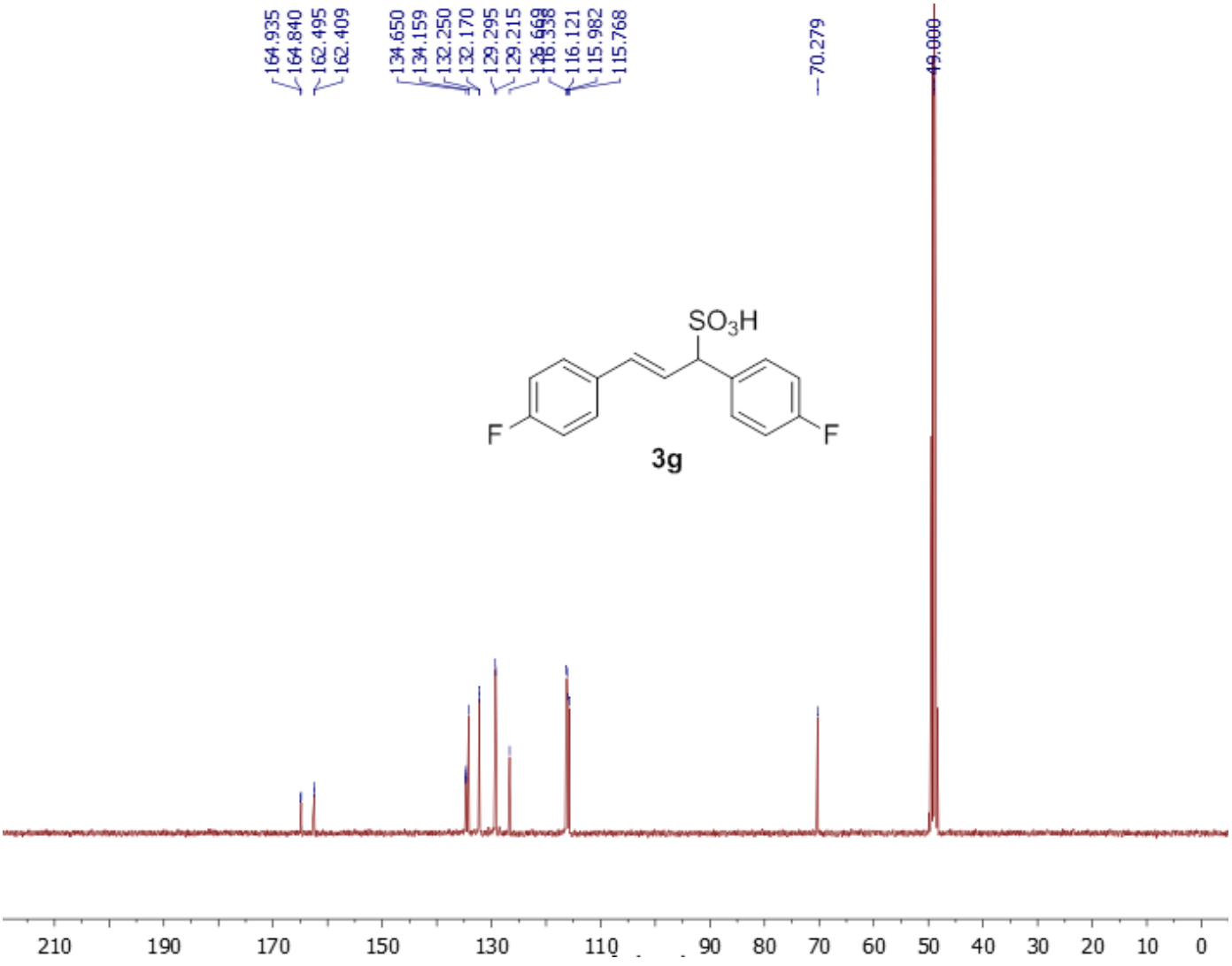
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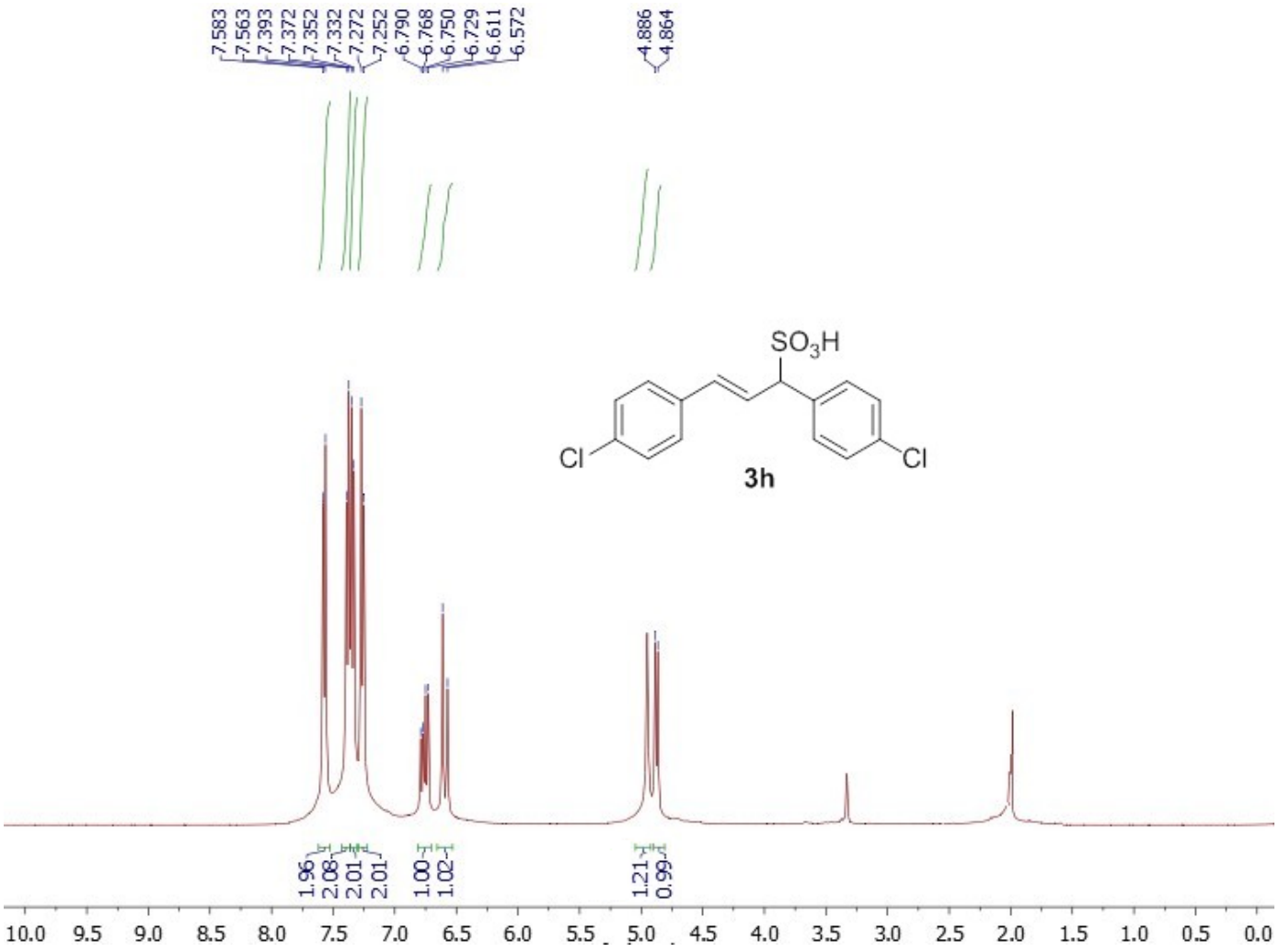
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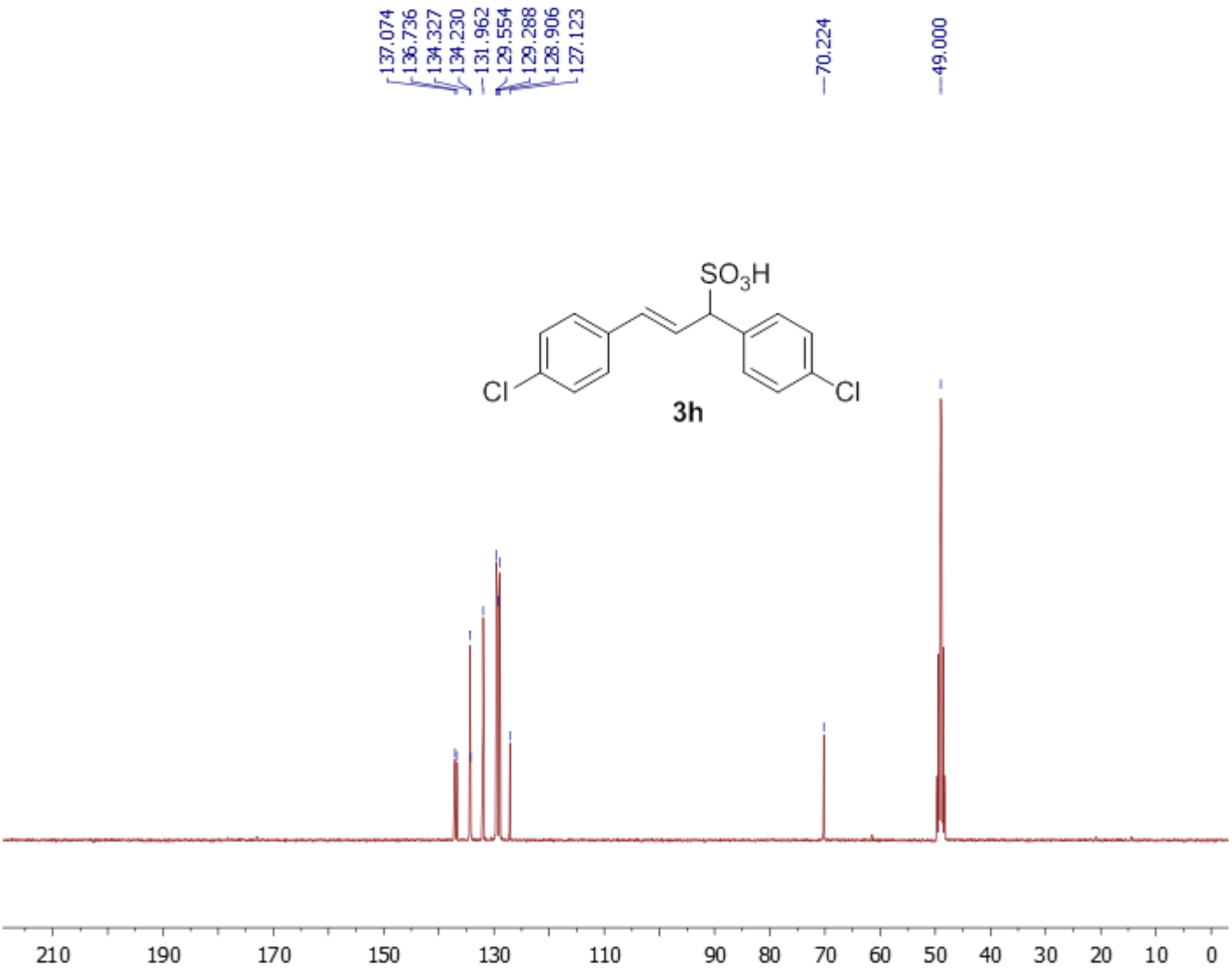
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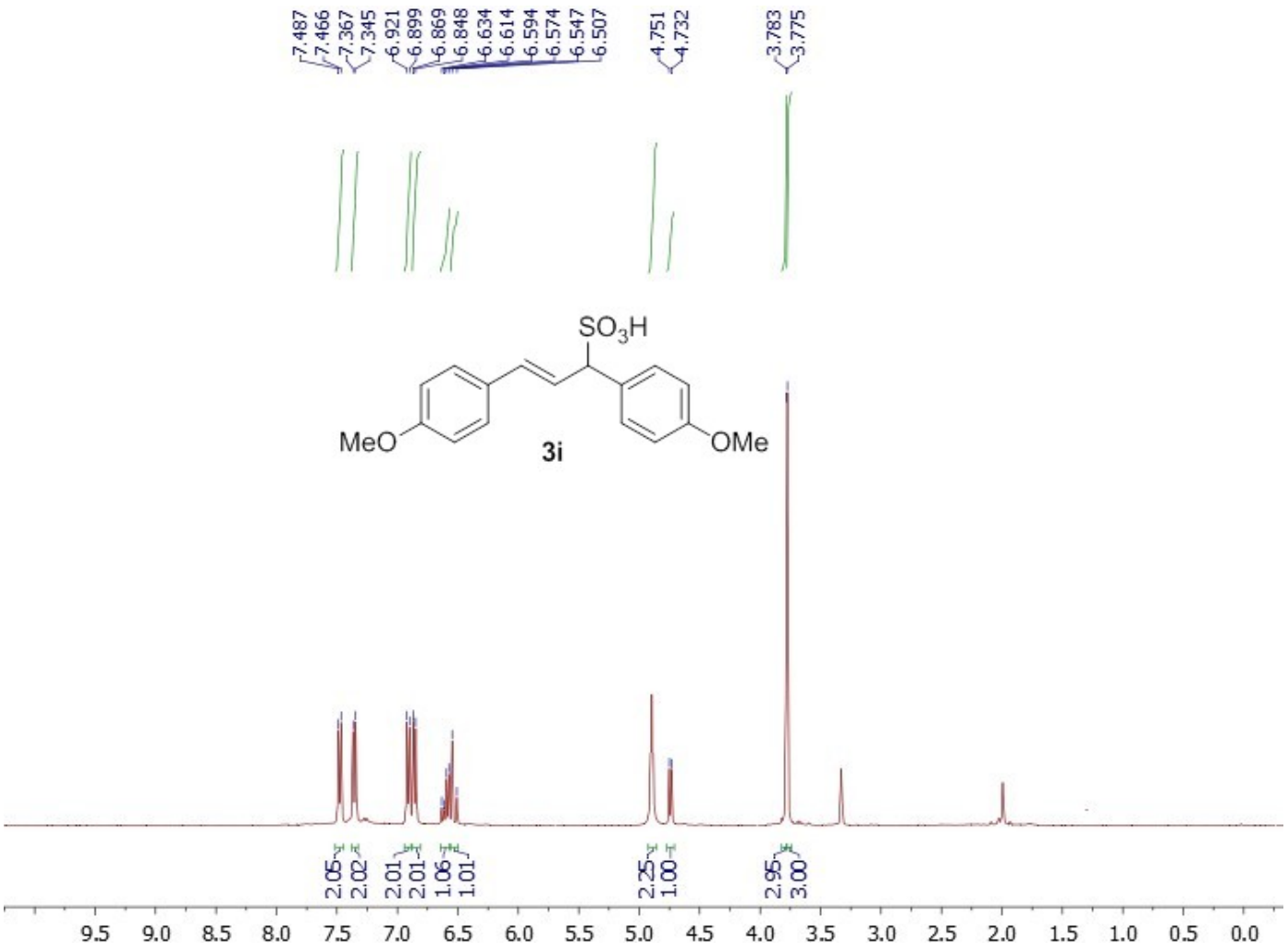
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OMe
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2.02
2.01
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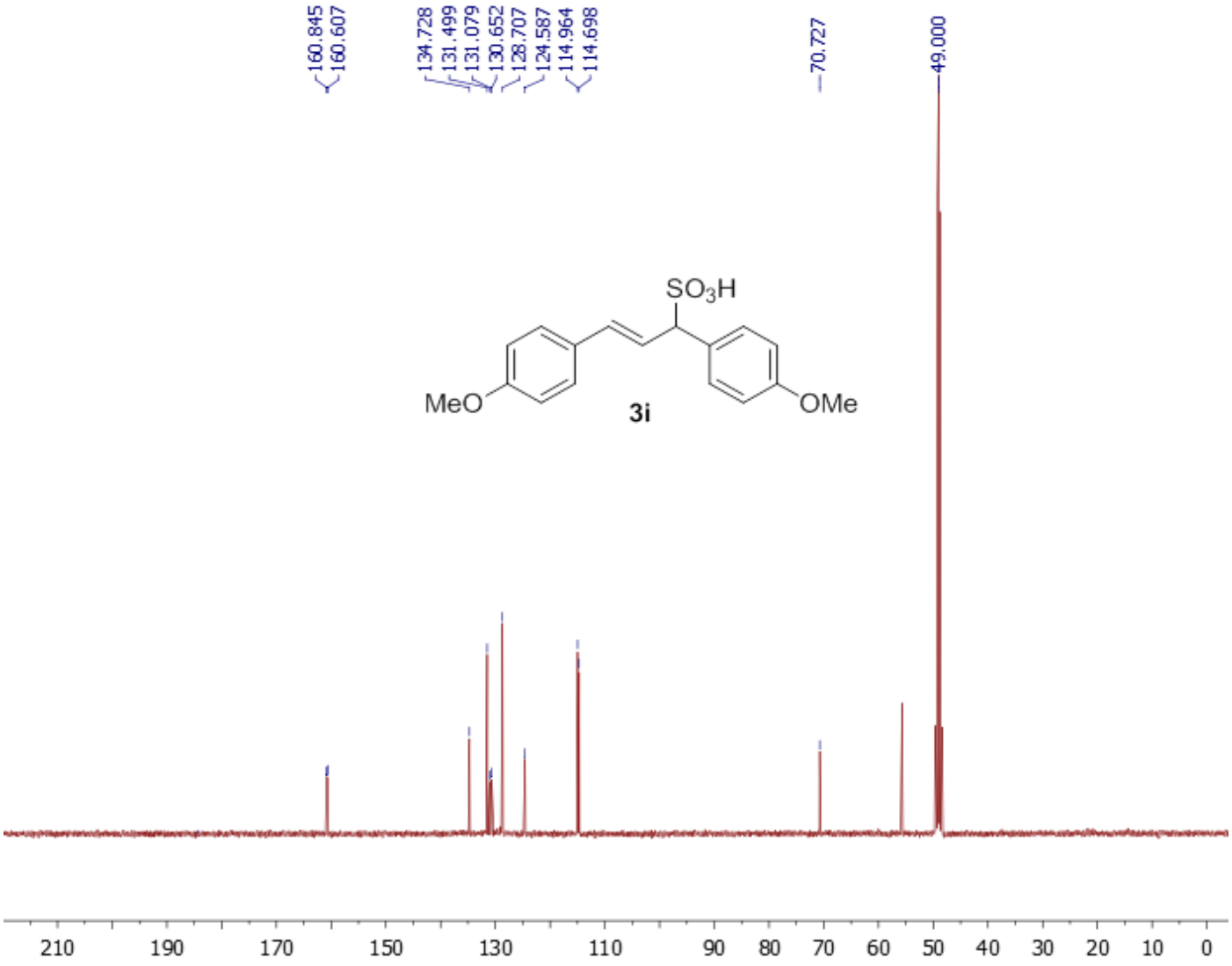
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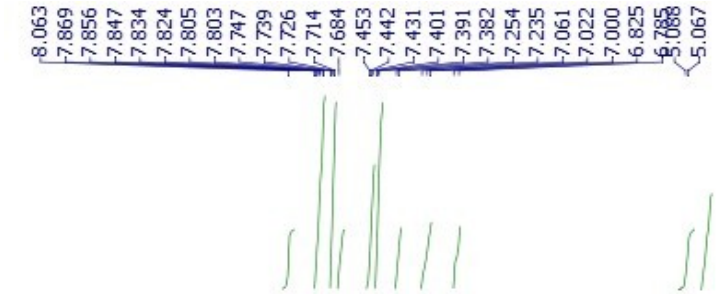
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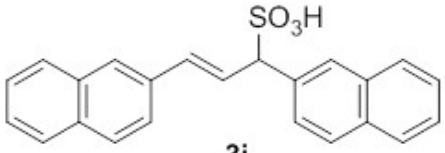
SO3H

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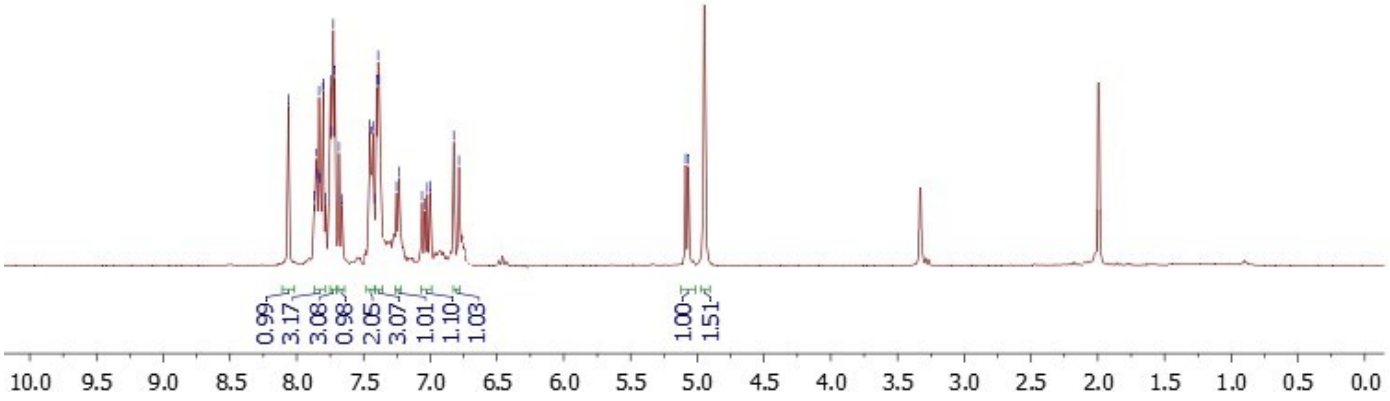
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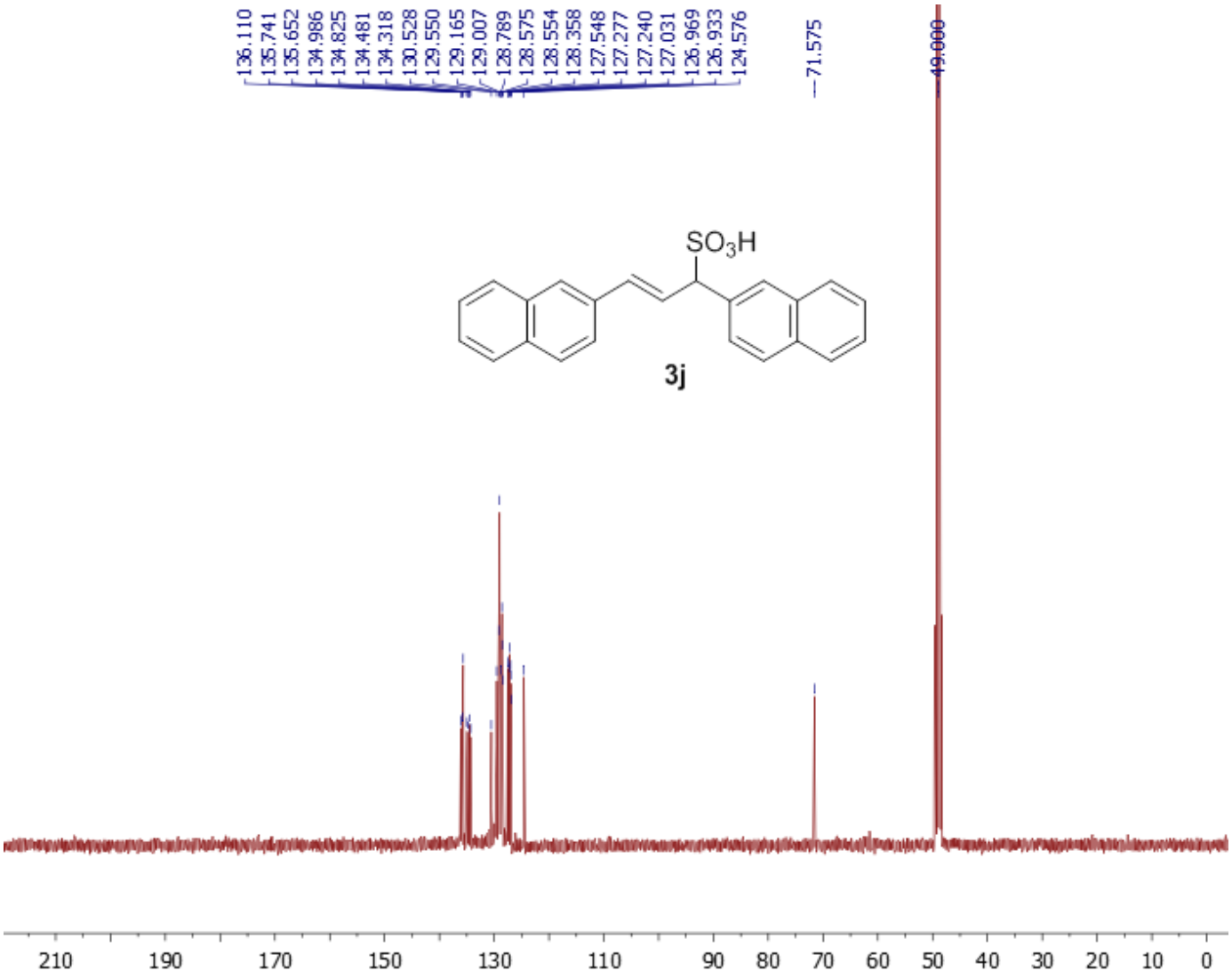
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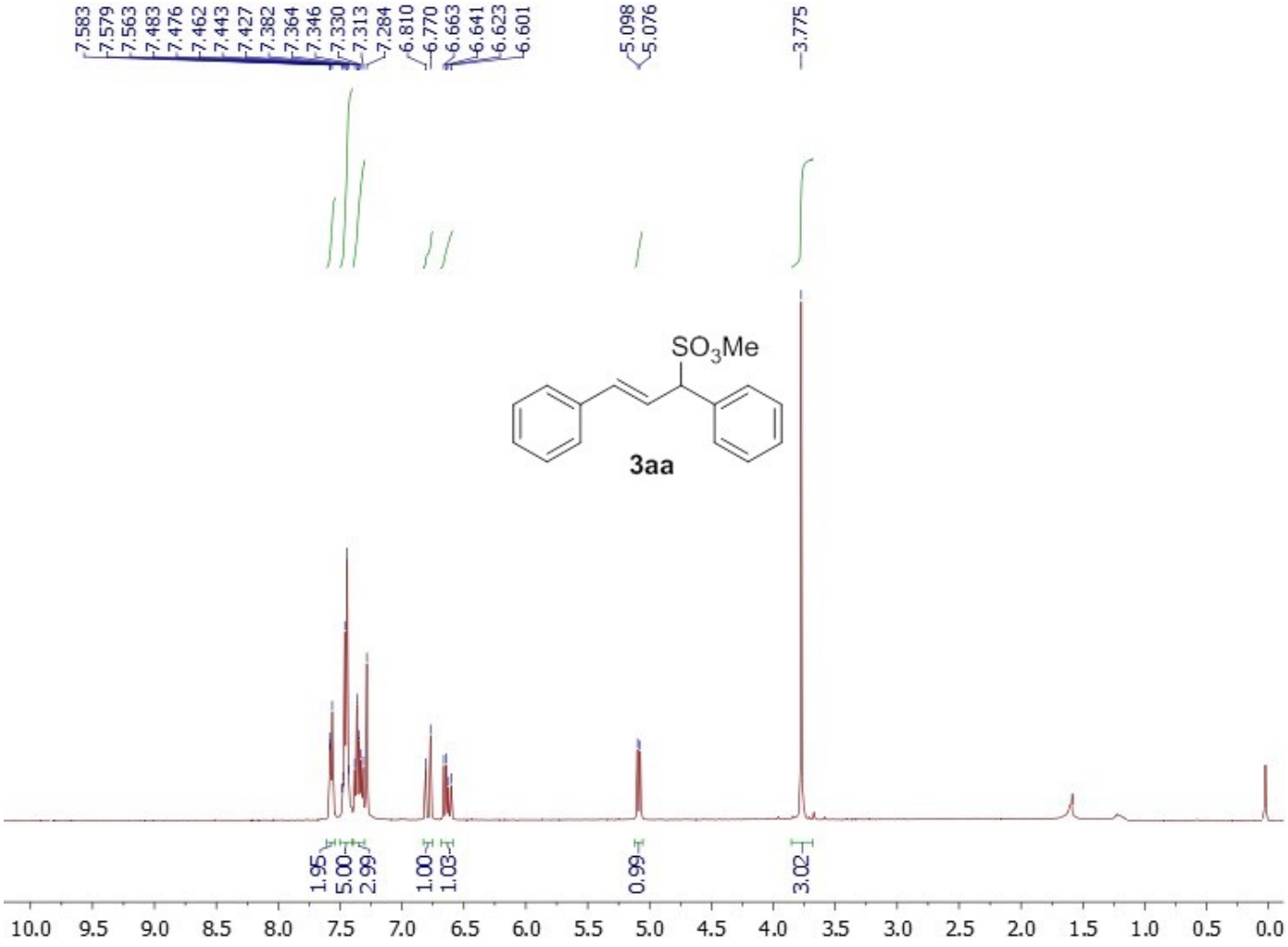
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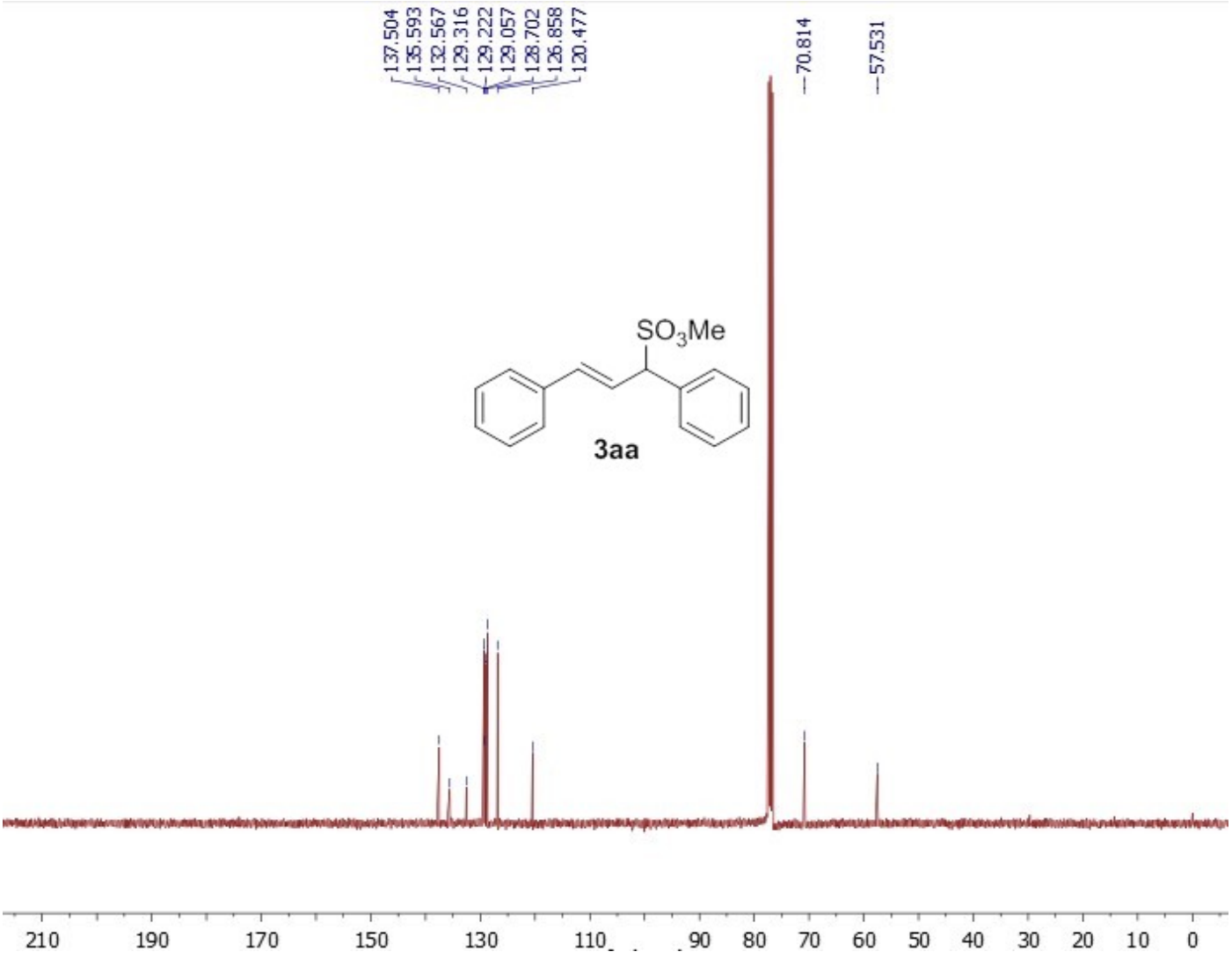
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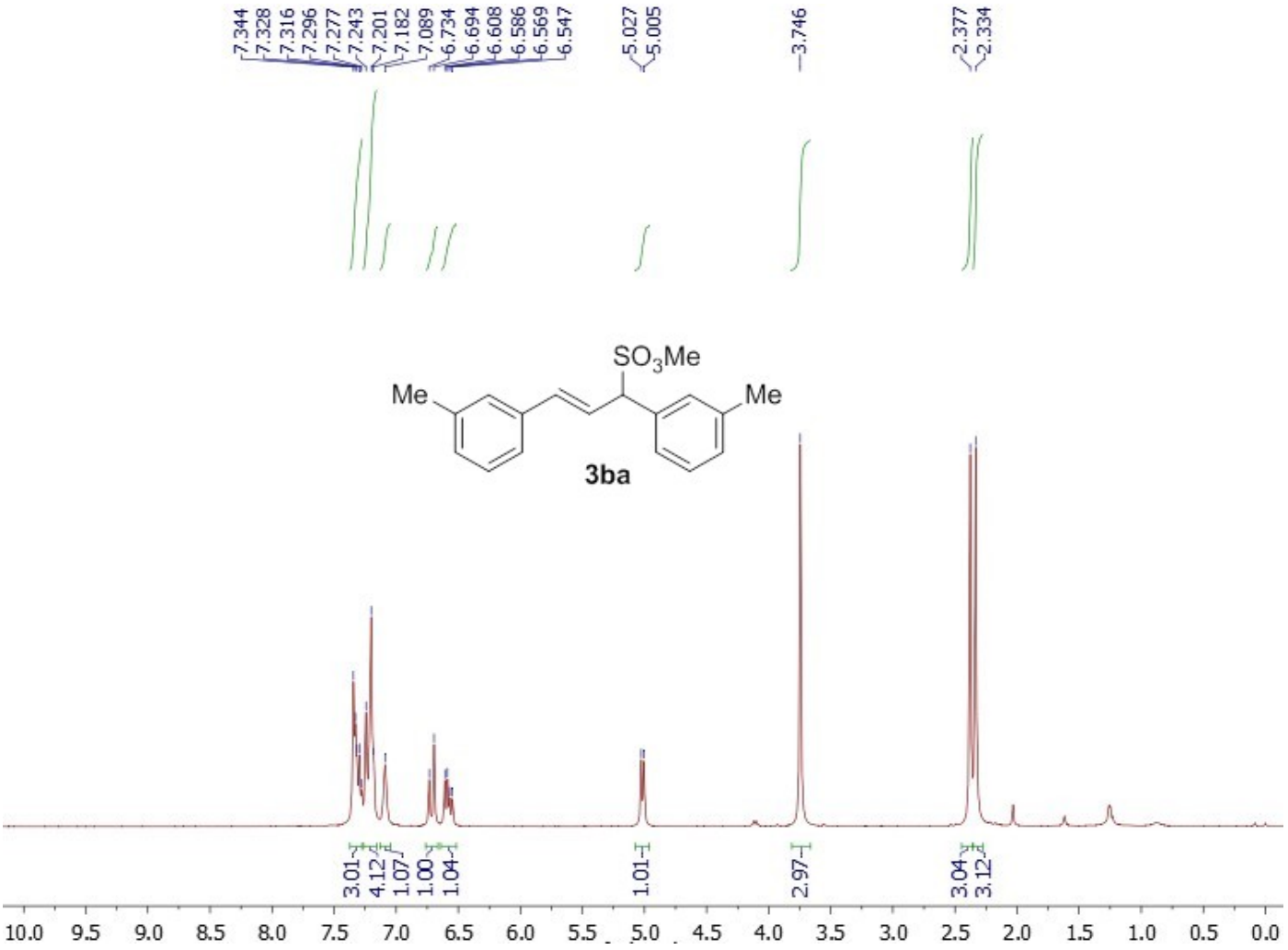
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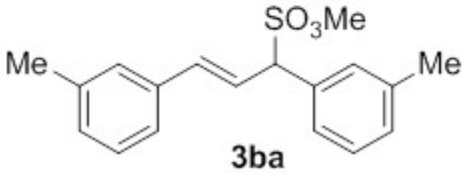
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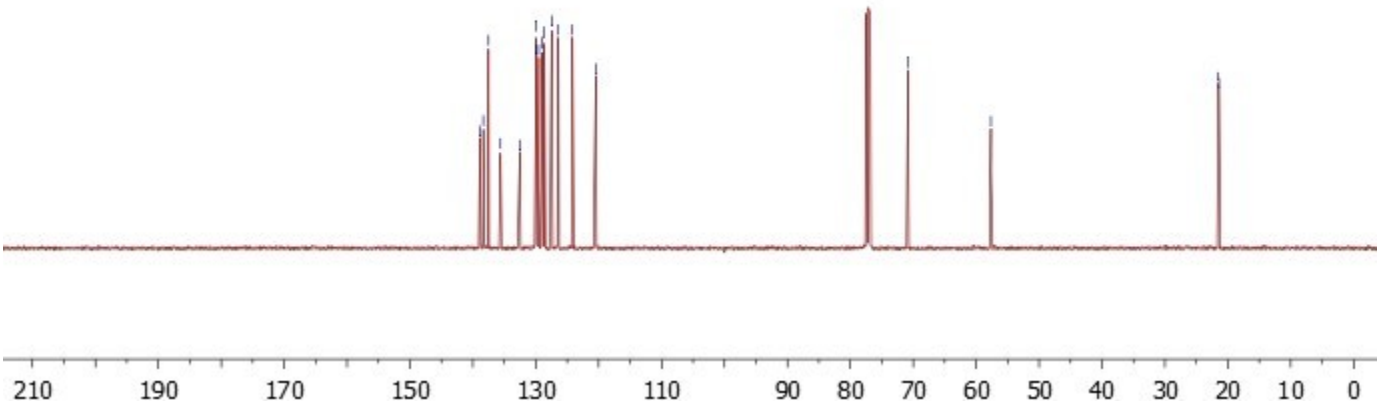
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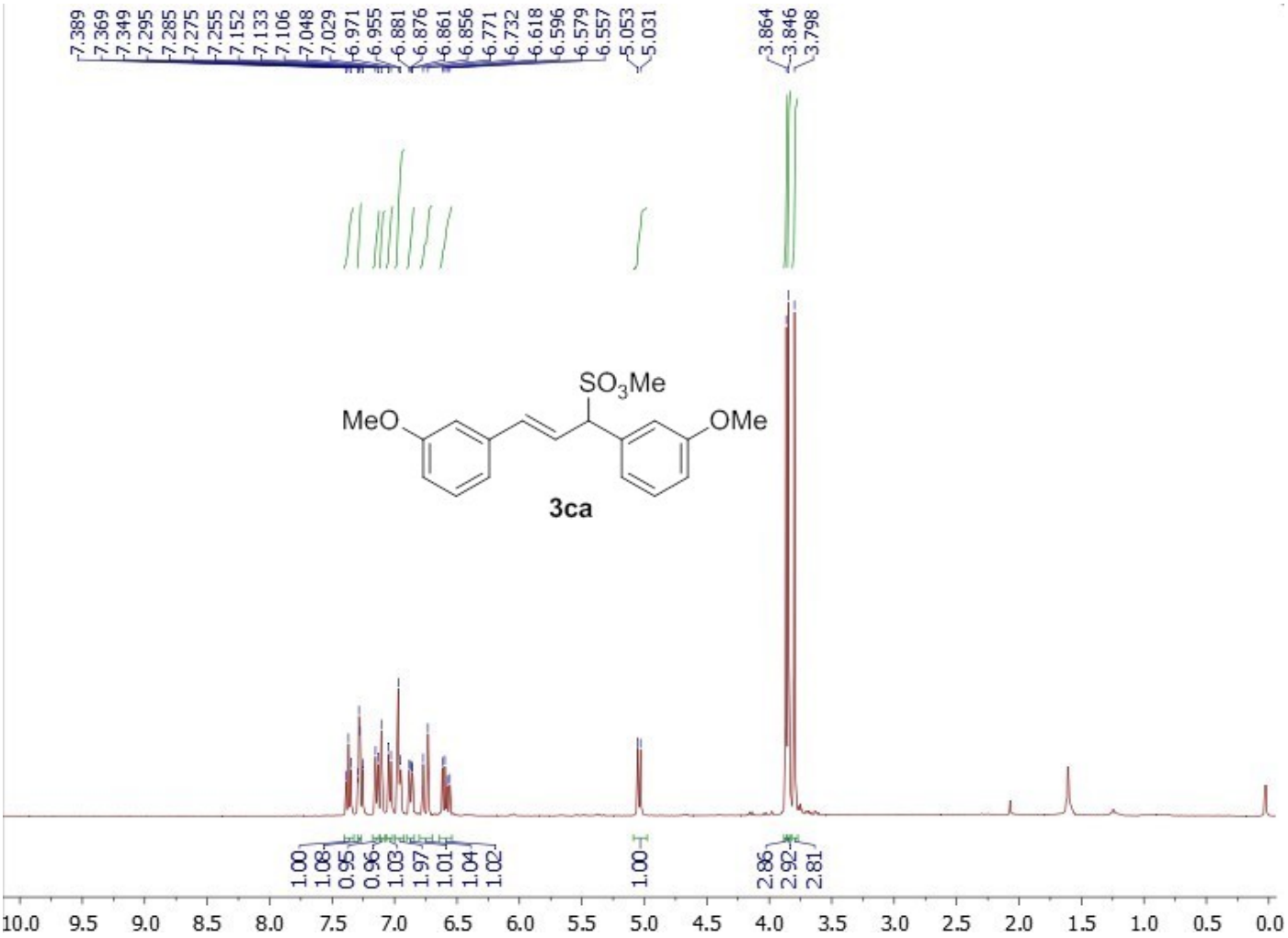
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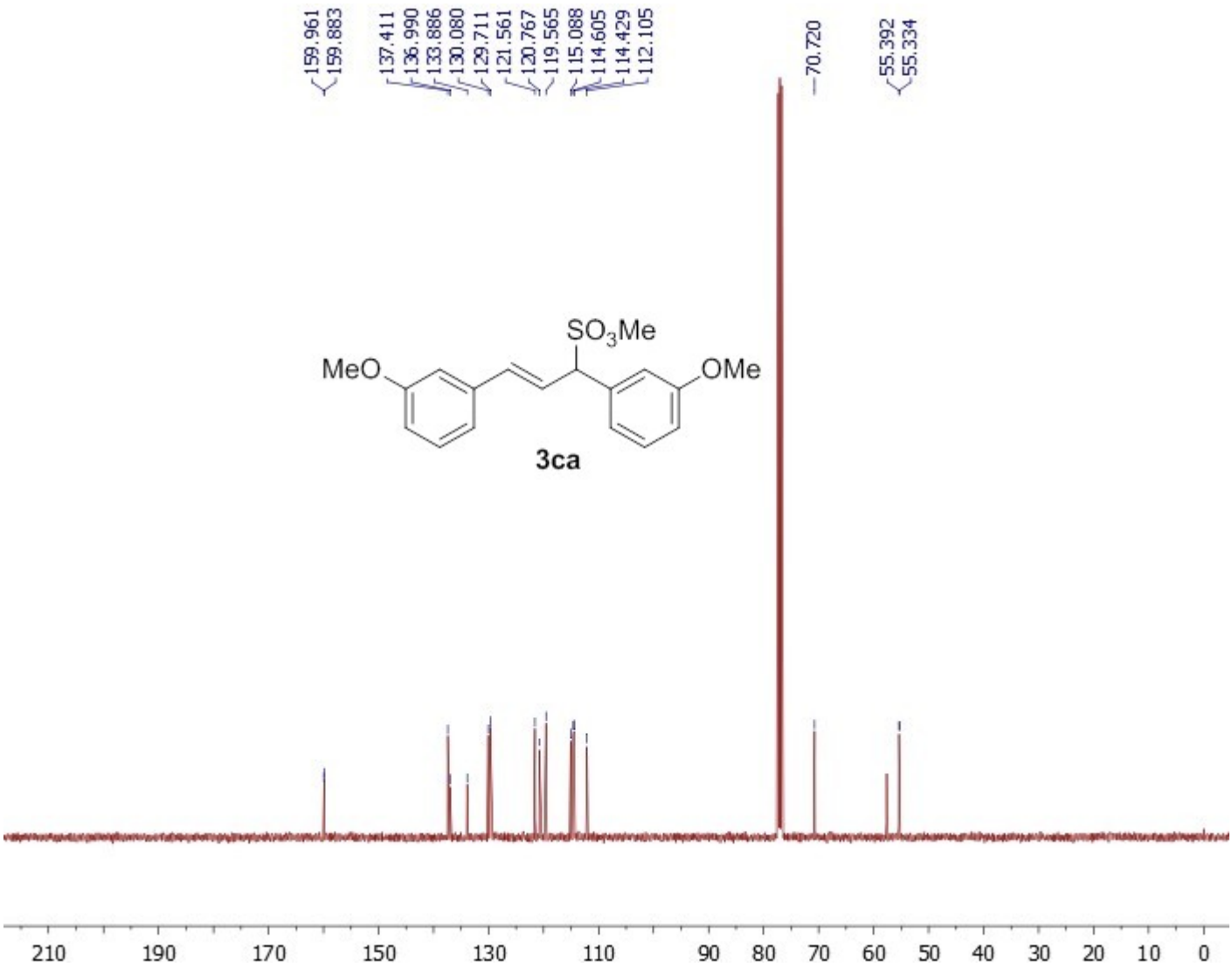
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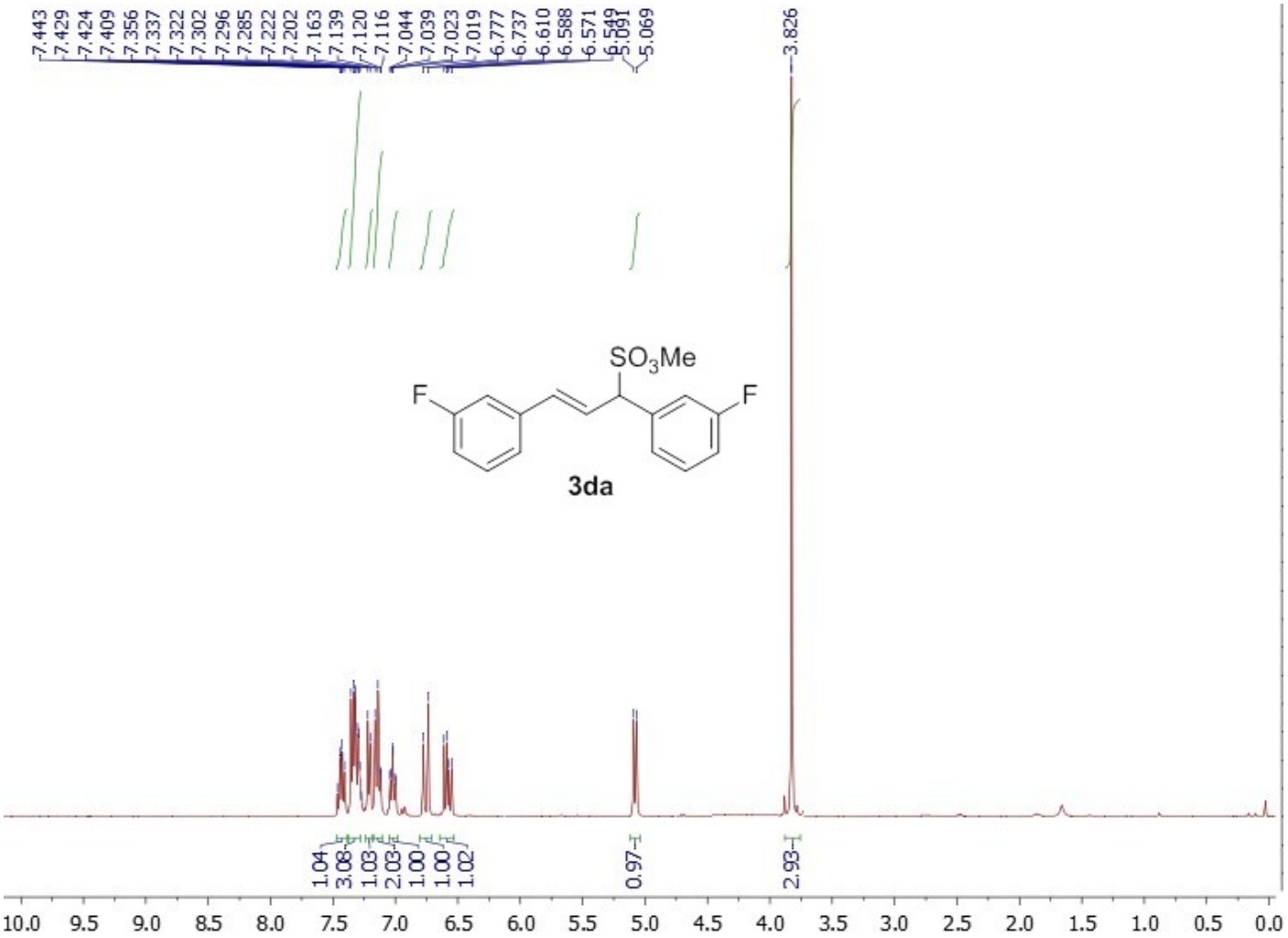
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F
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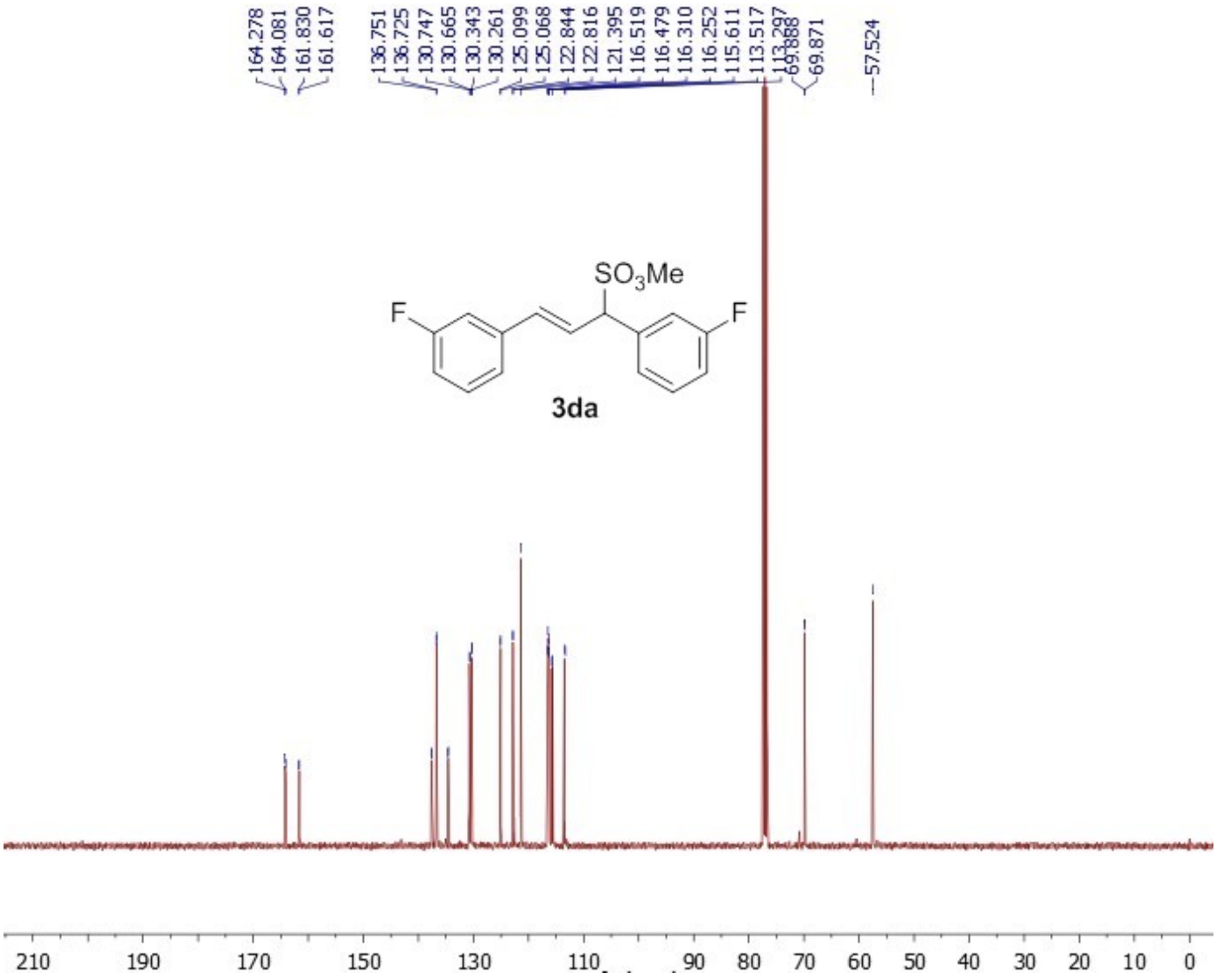
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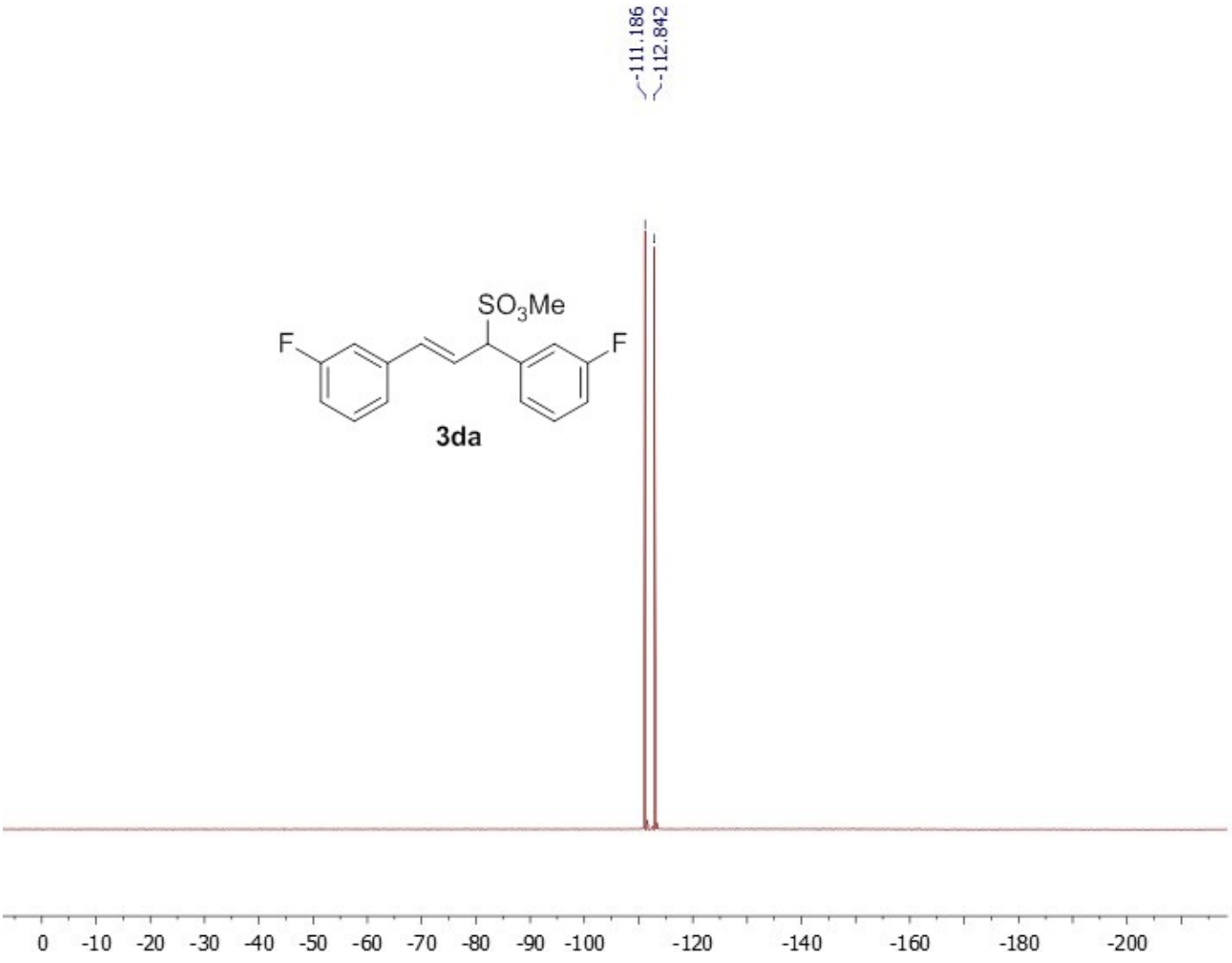
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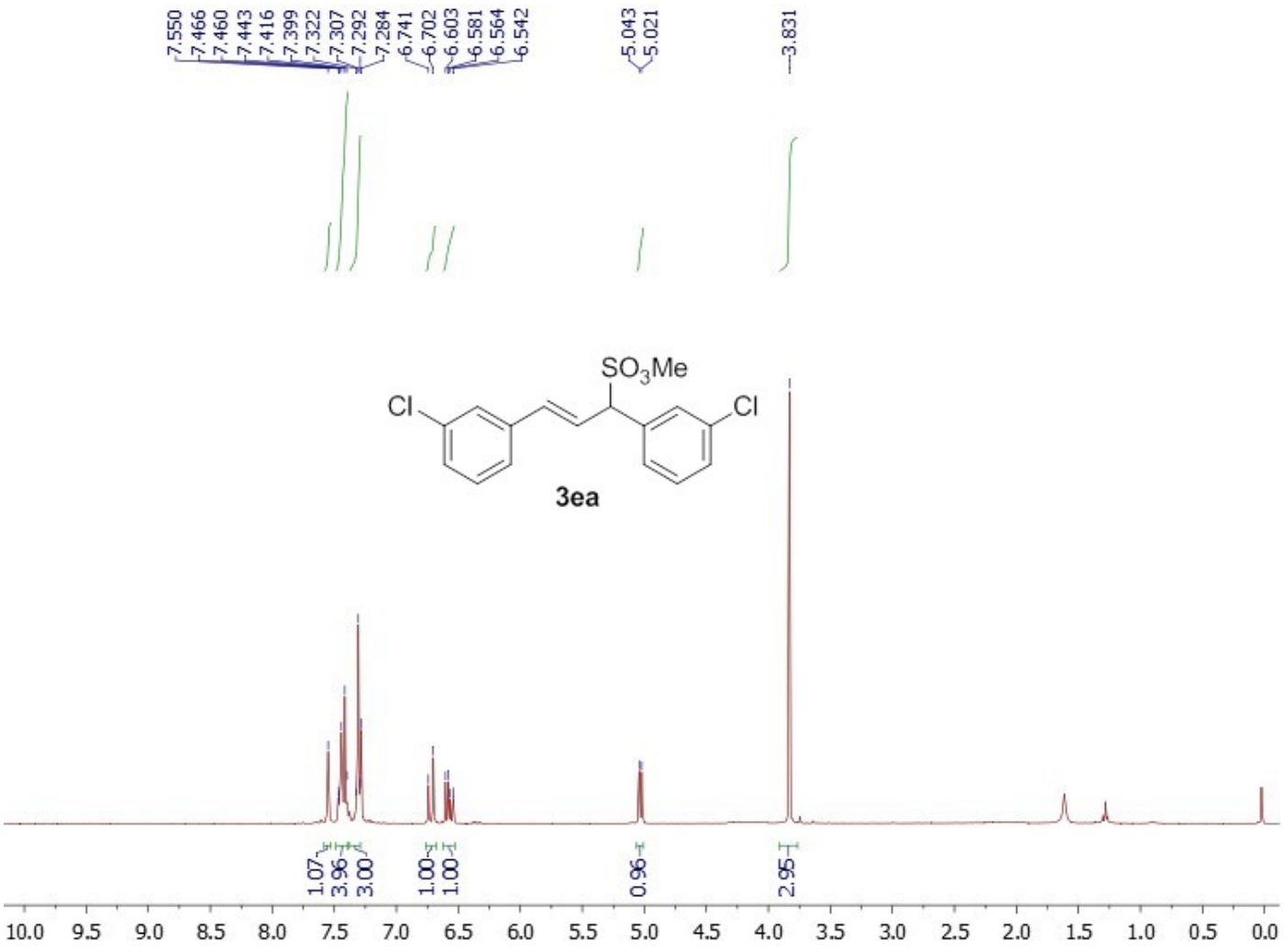
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Cl
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1.00
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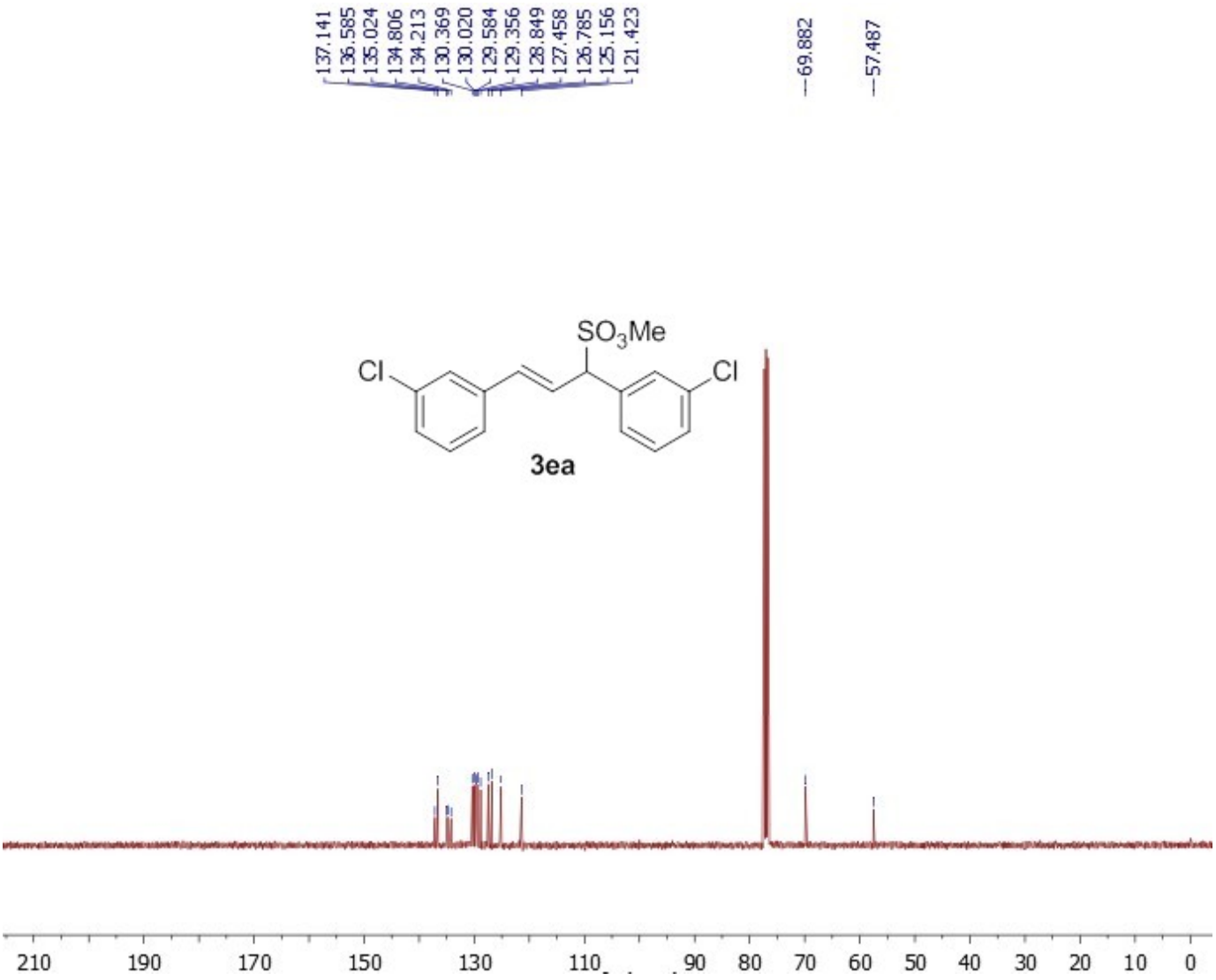
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Cl
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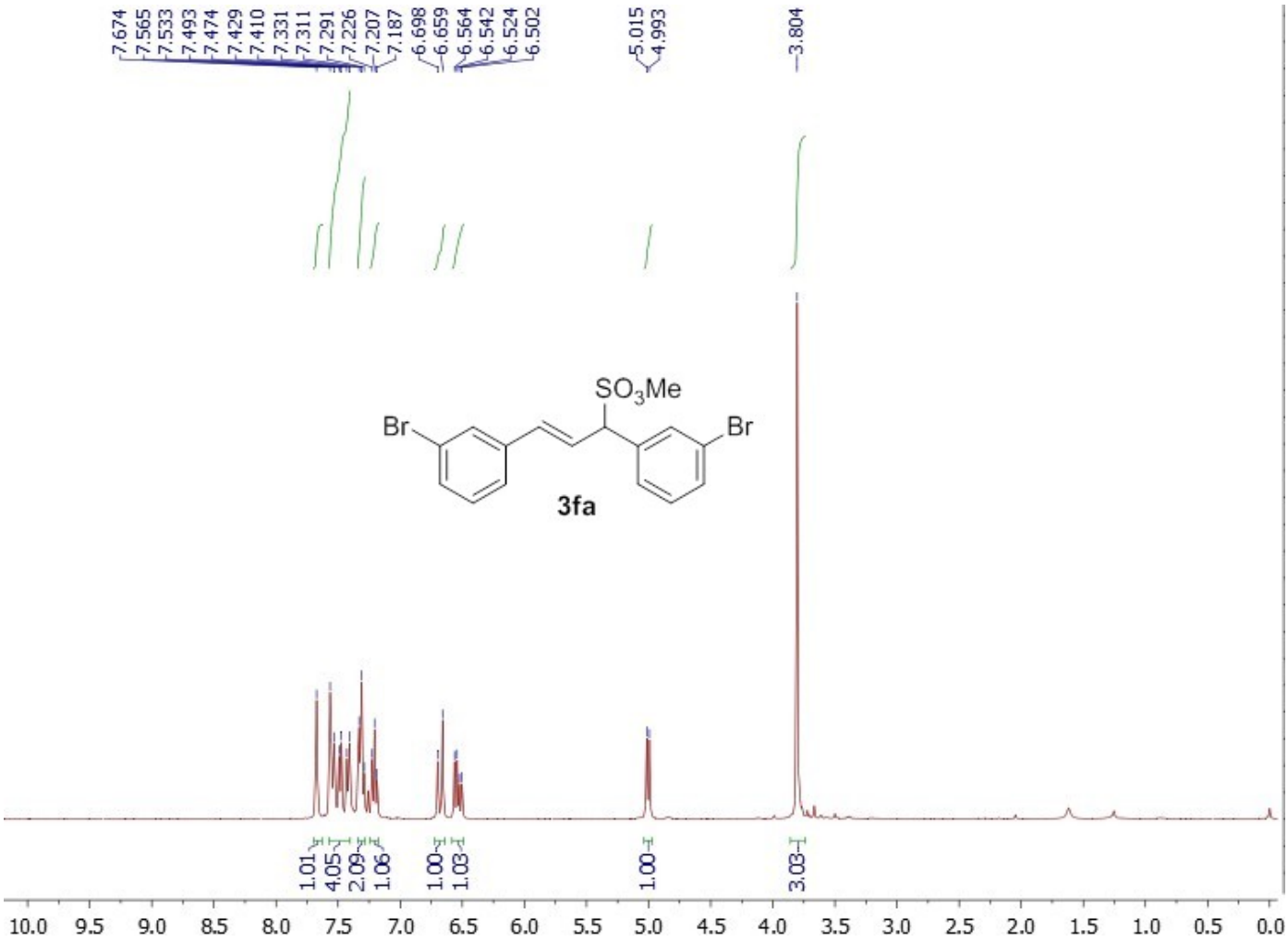
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Br
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4.05
2.09
1.06
1.00
1.03
1.00
3.03
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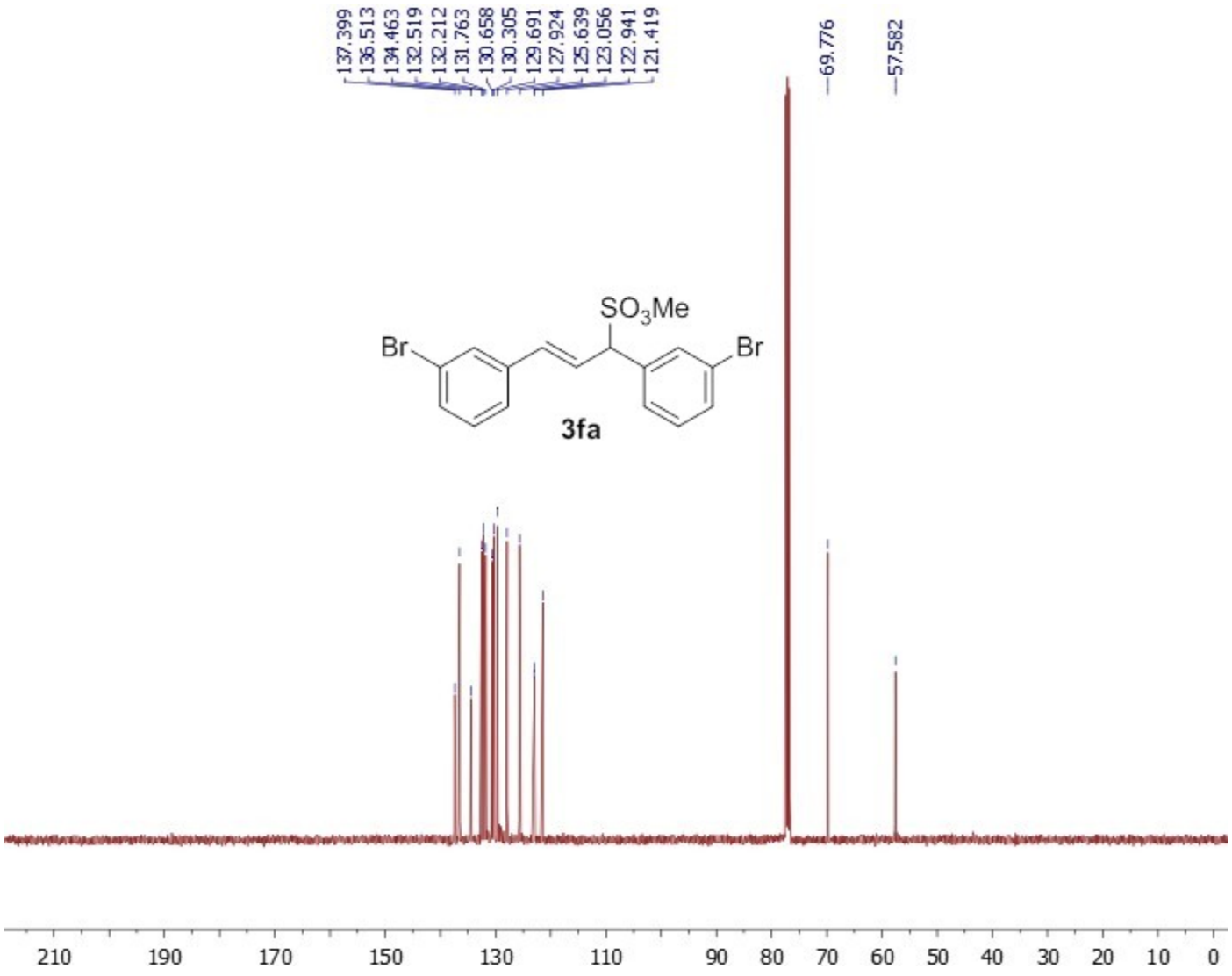
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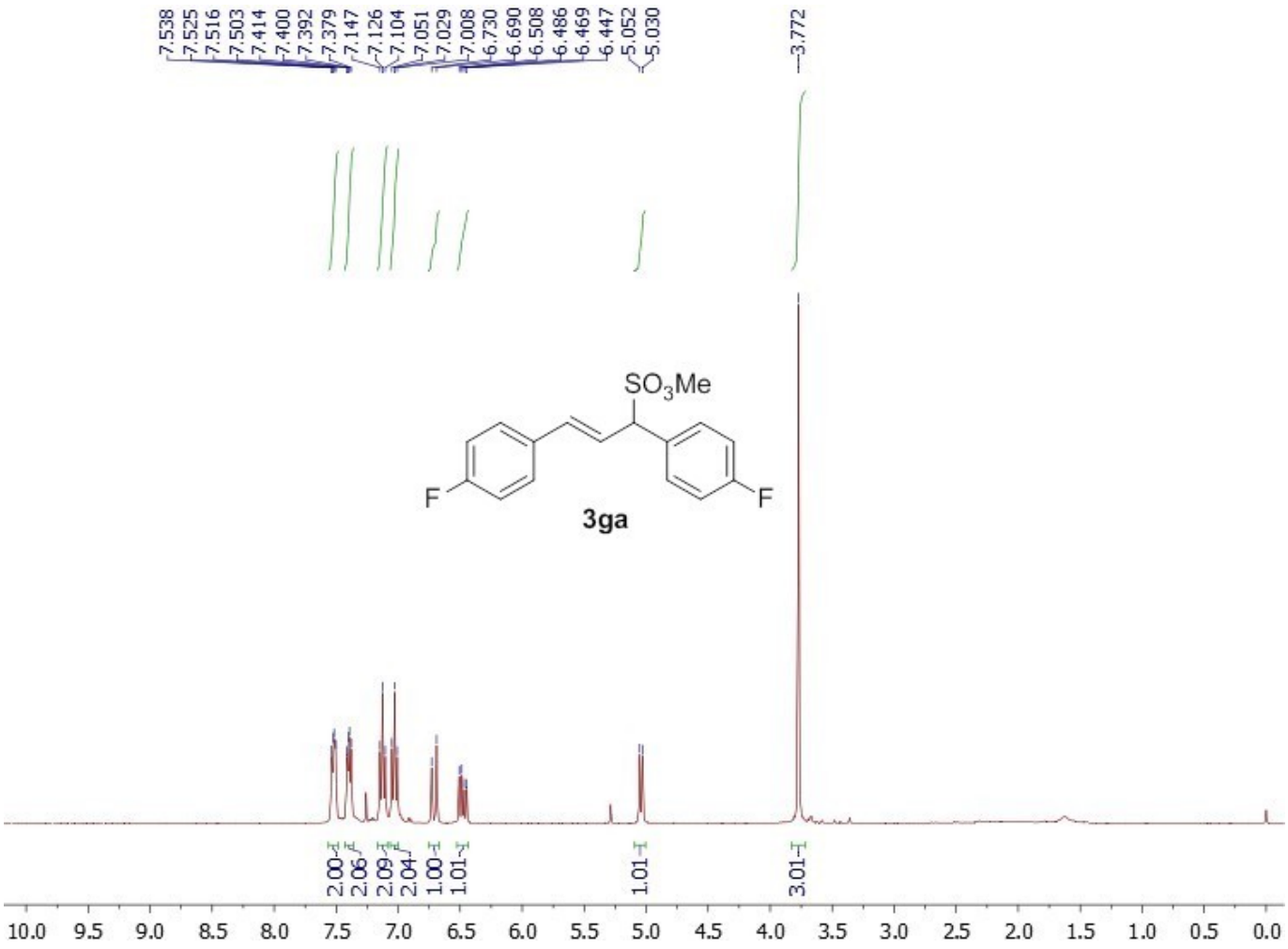
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F
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2.06
2.09
2.04
1.00
1.01
1.01
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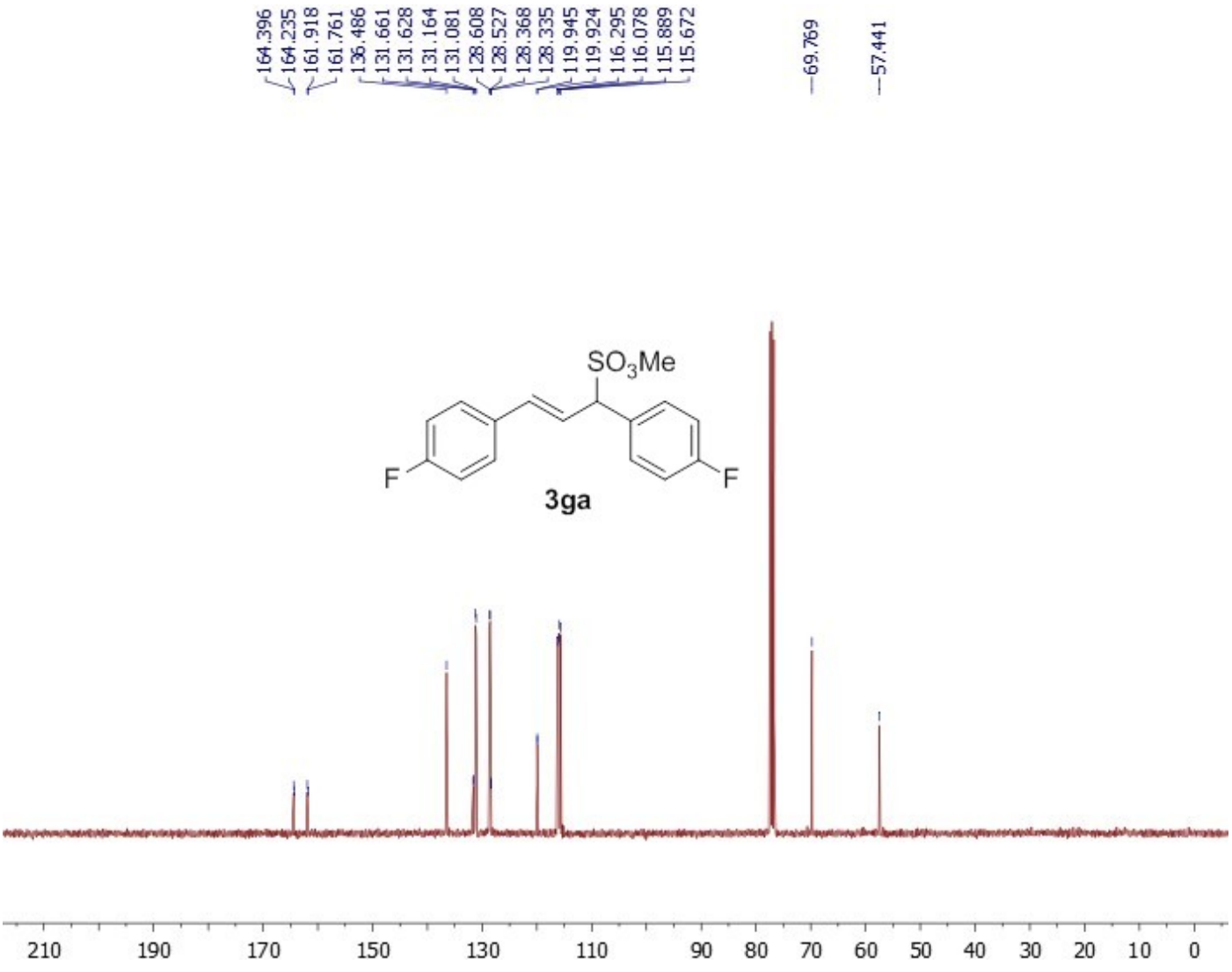
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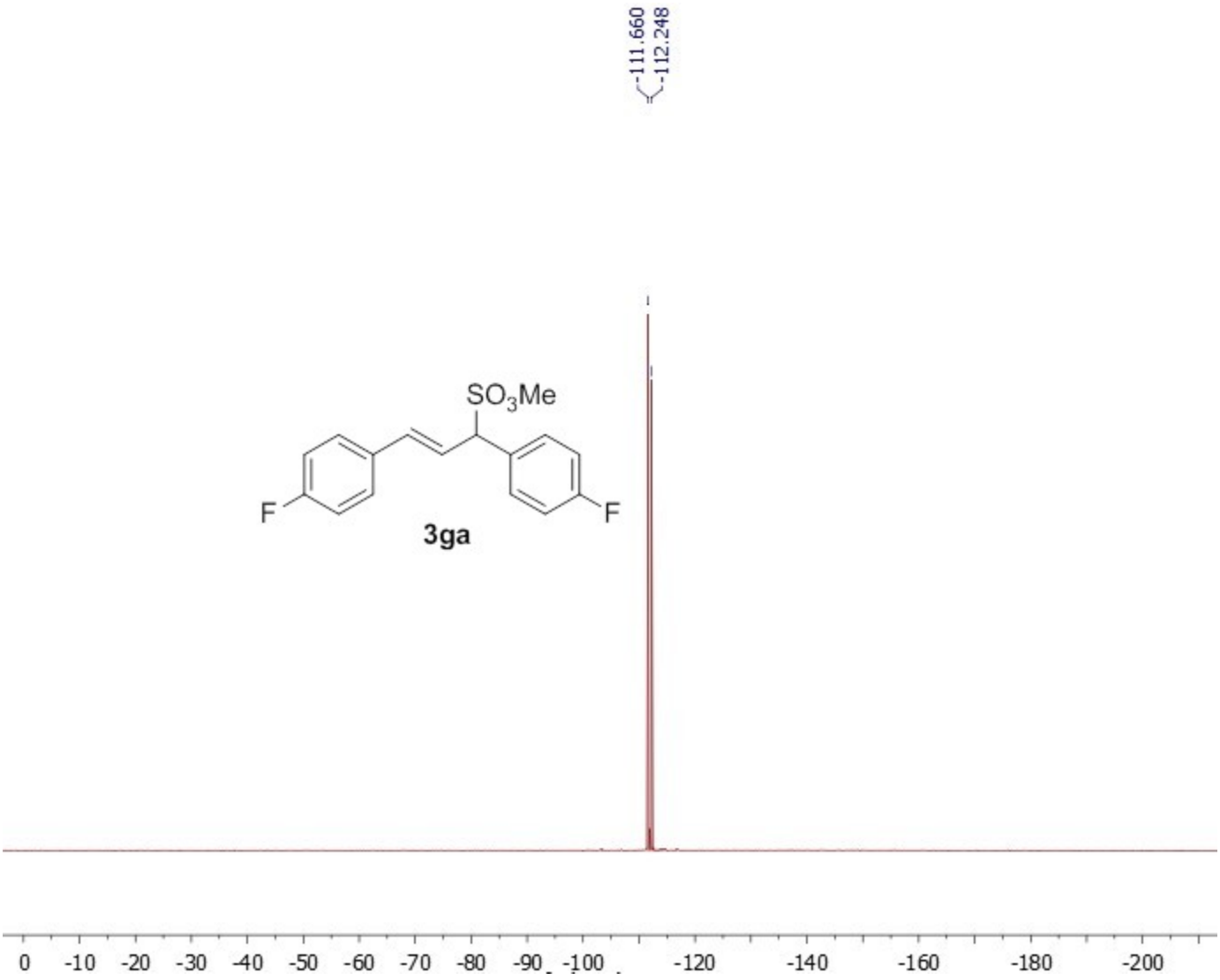
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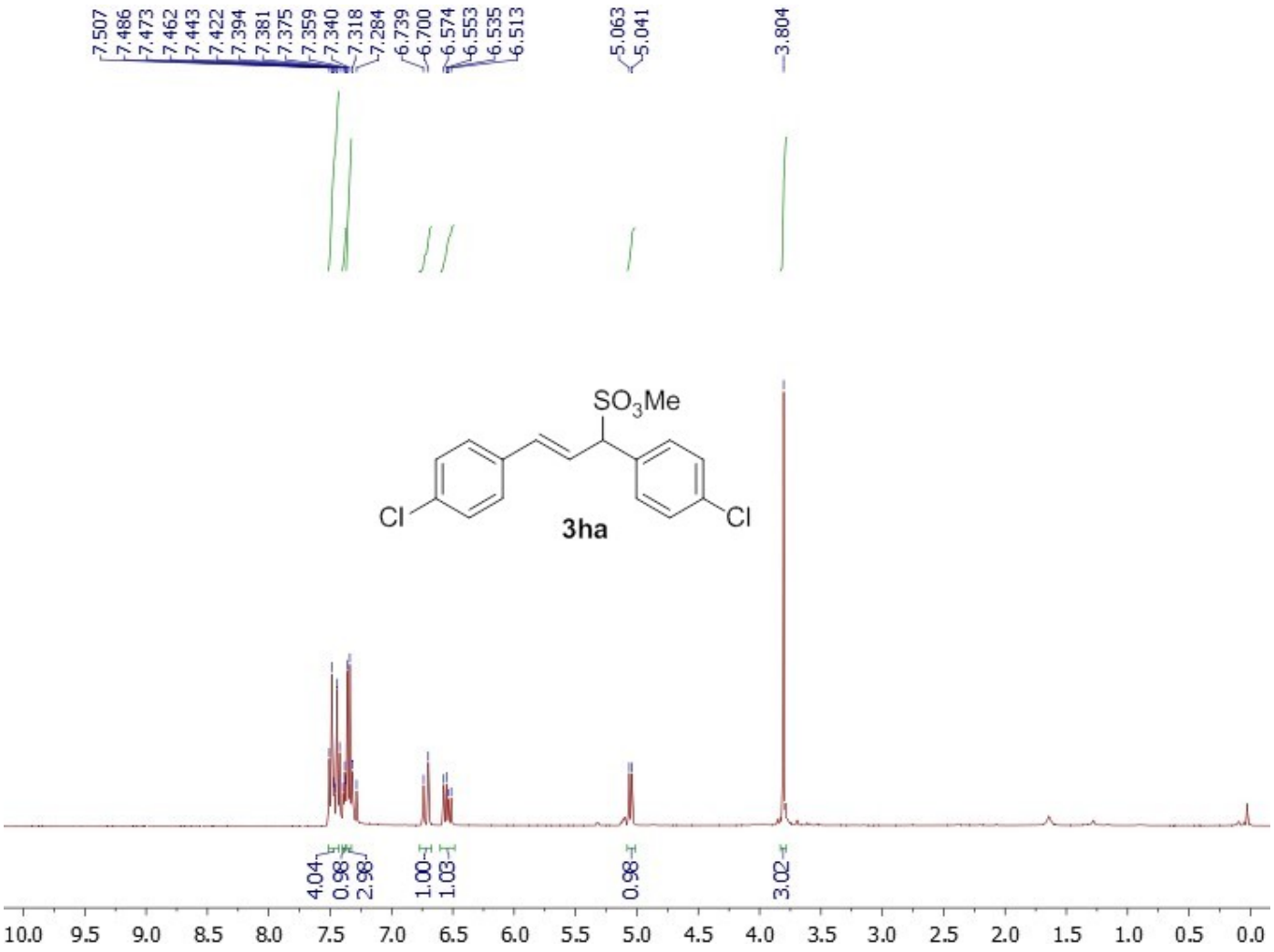
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SO3Me
Cl
Cl
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2.98
1.00
1.03
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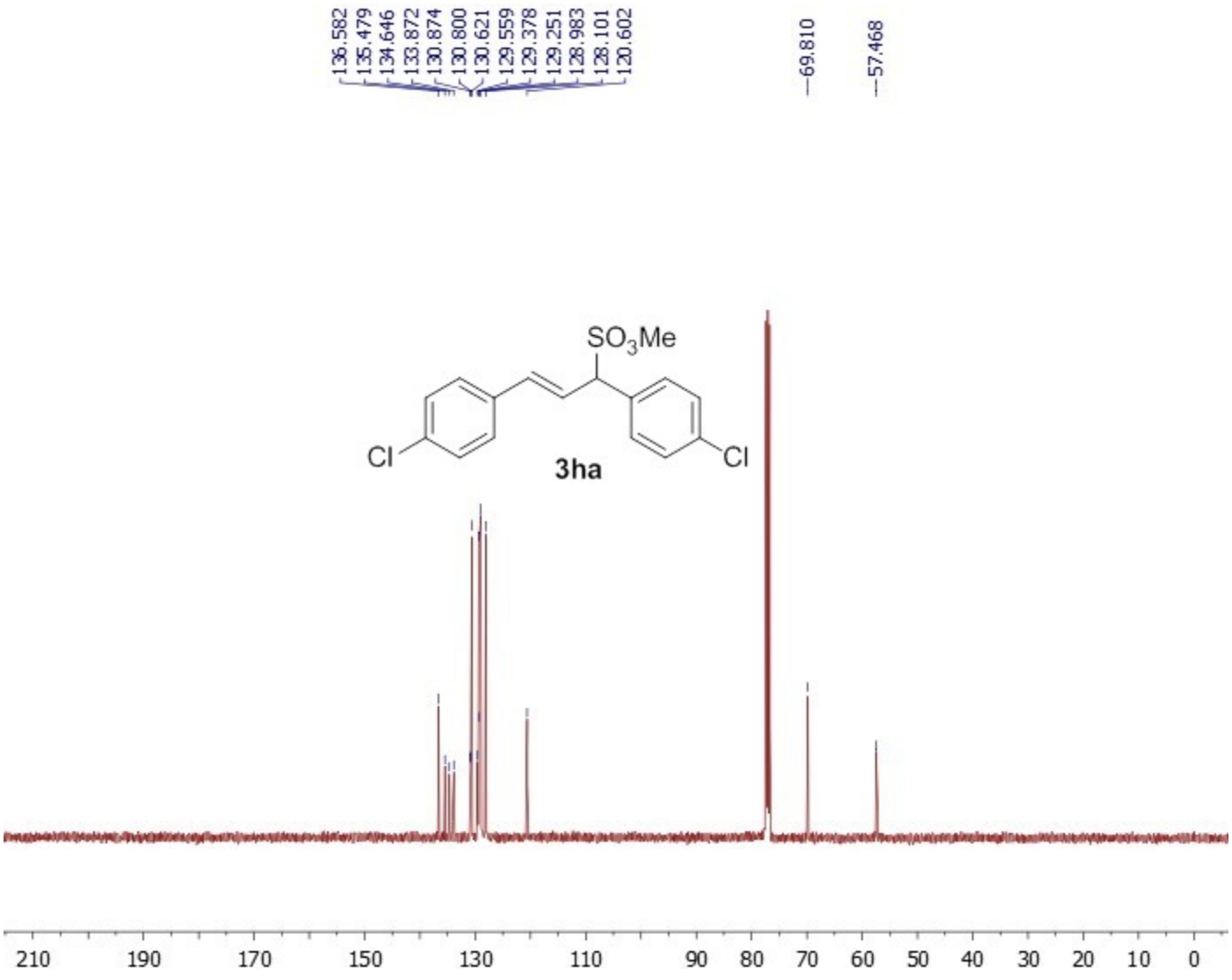
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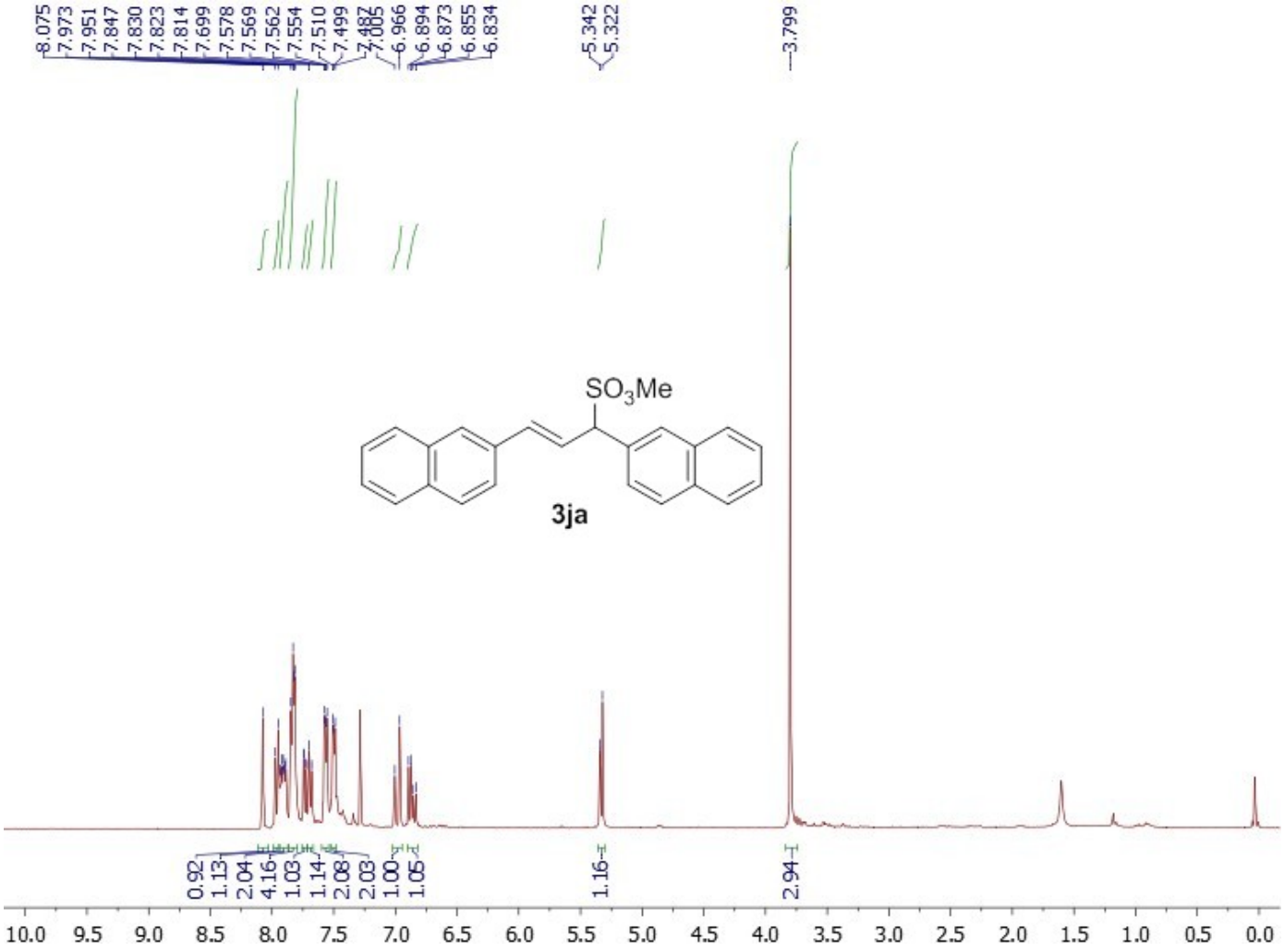
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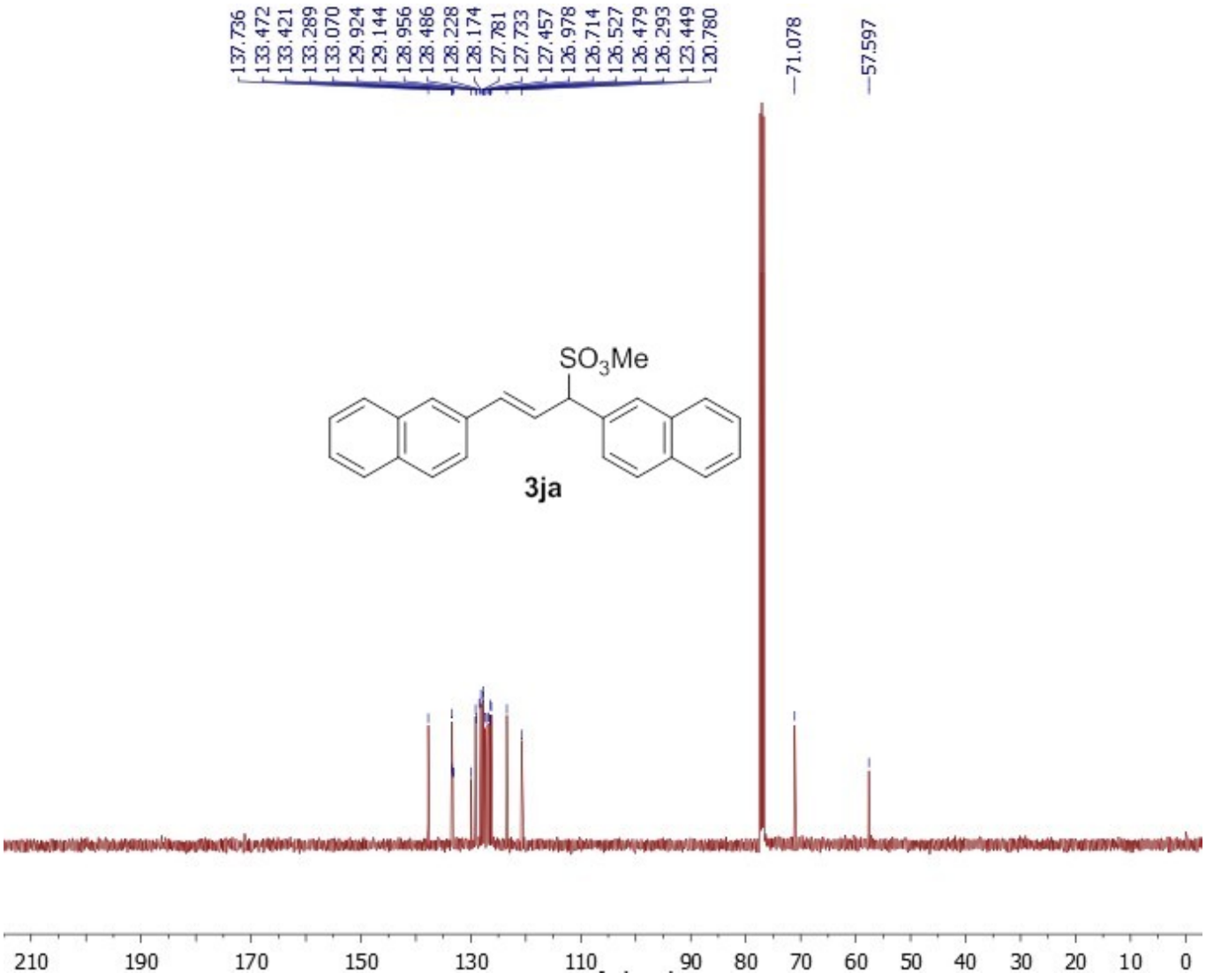
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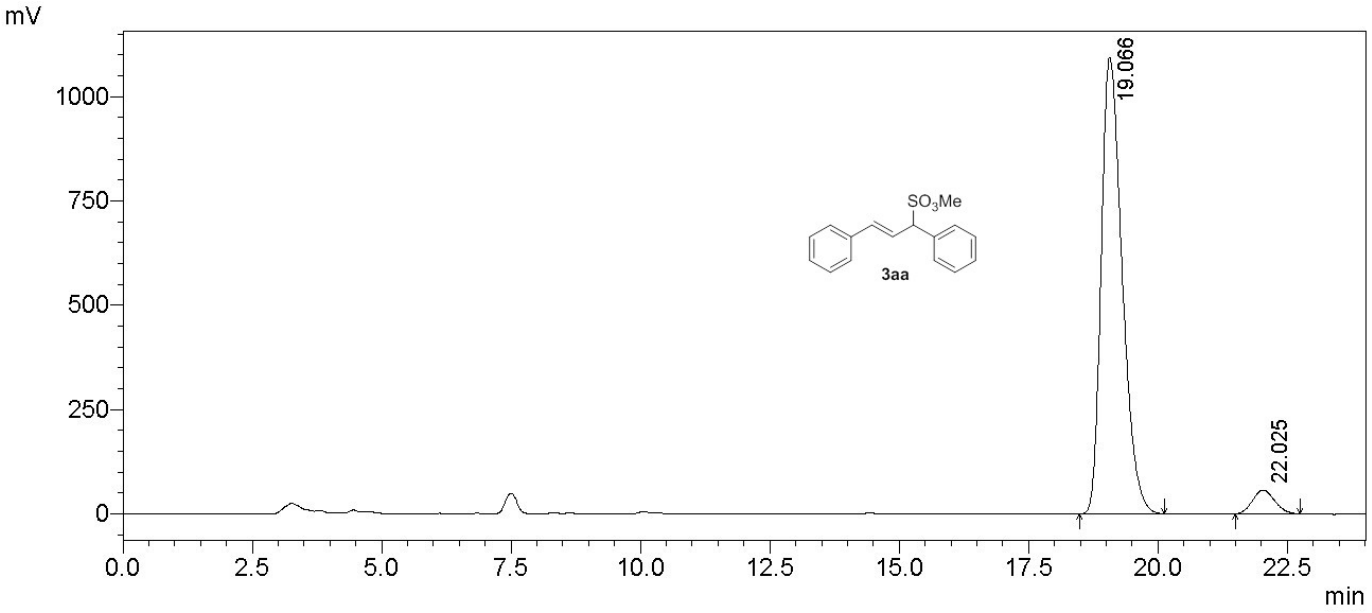
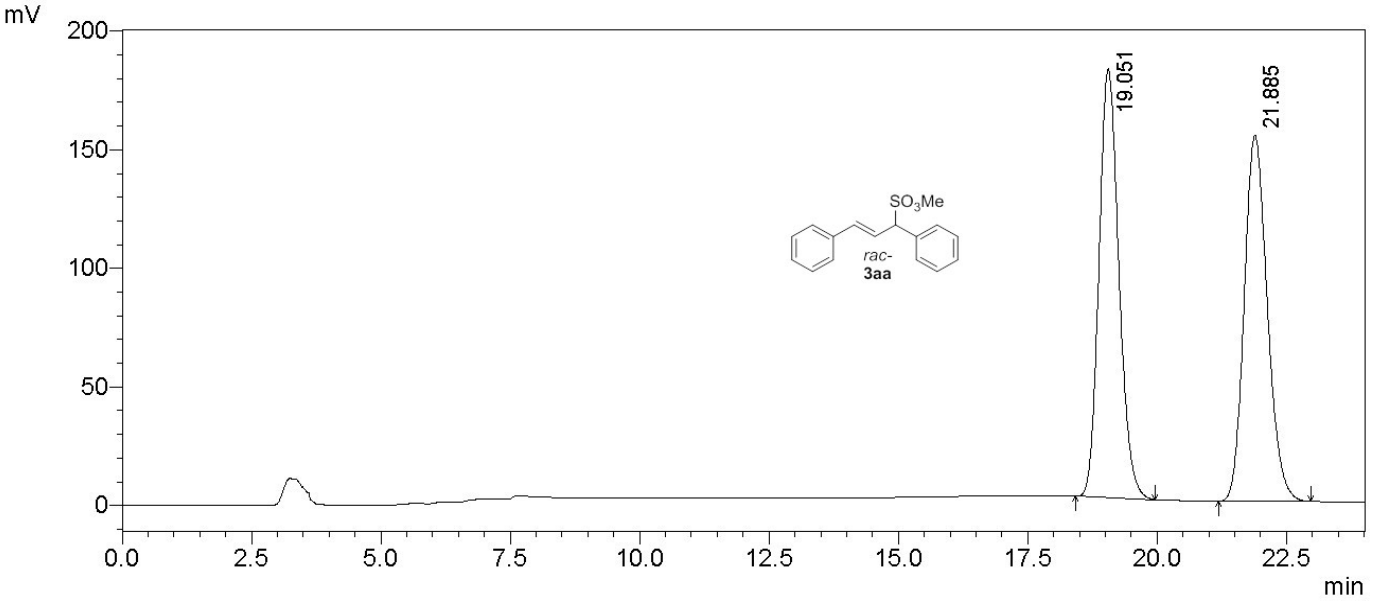
HPLC Chromatograms



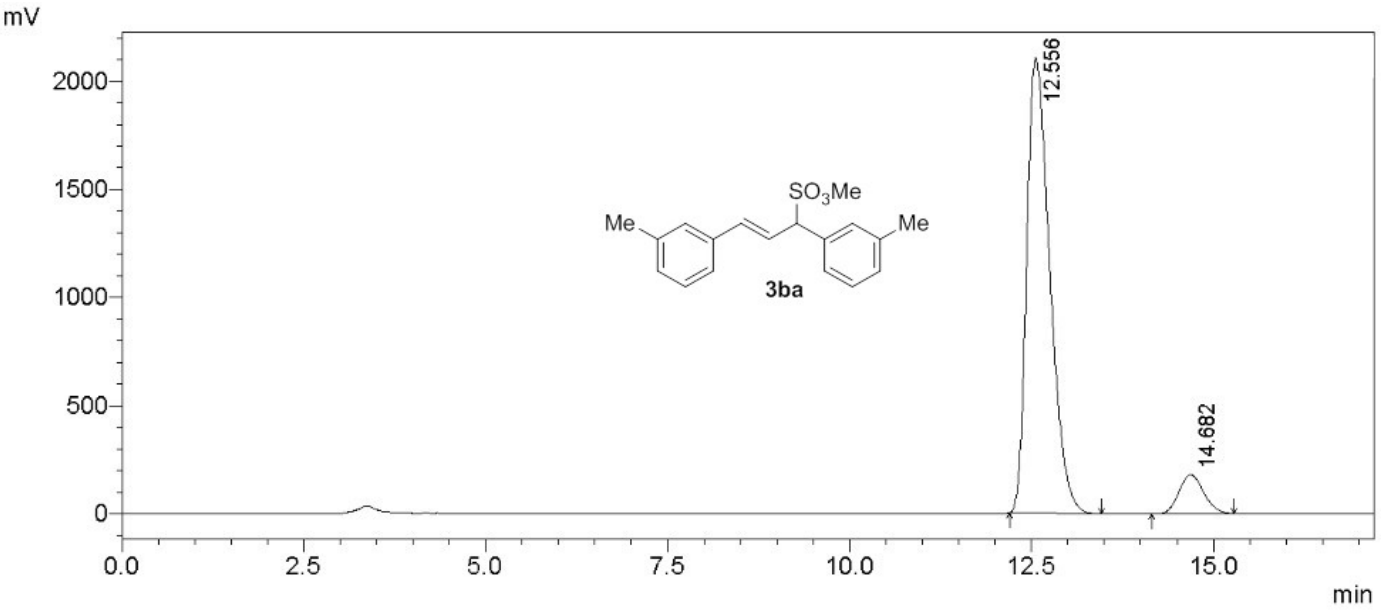
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	19.064	30828648	1107387	94.837
2	22.023	1678460	55778	5.163



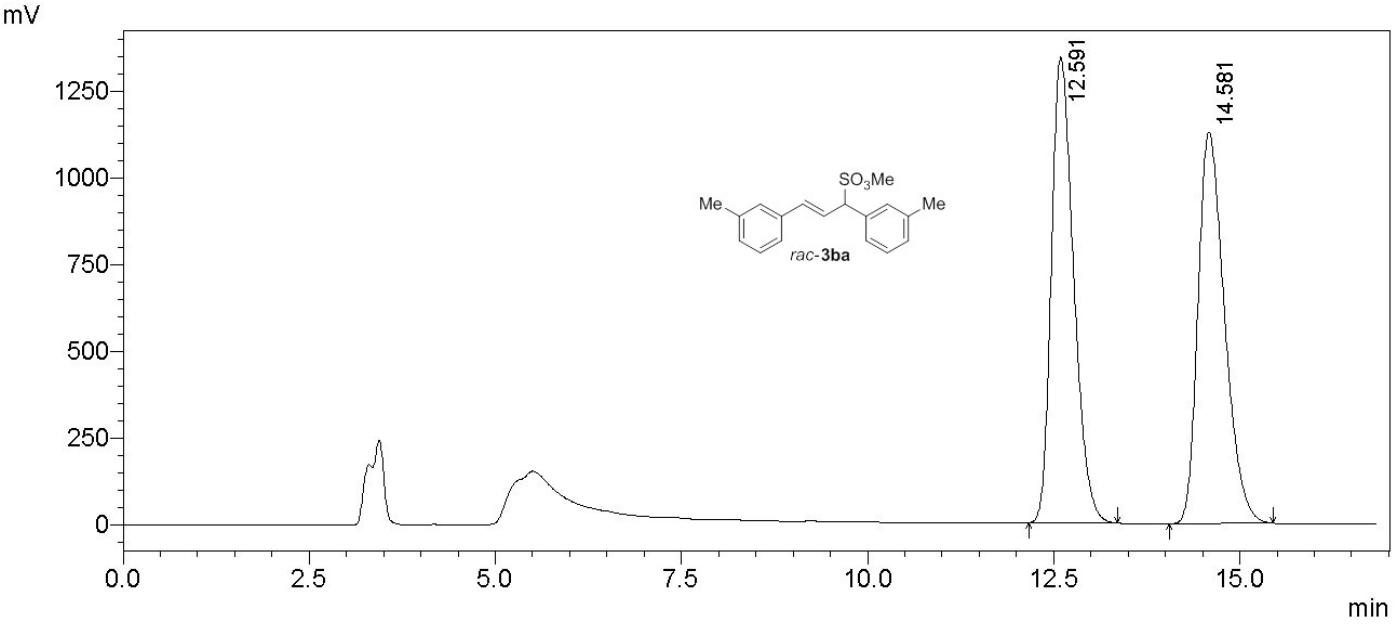
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	19.051	4837571	180731	50.231
2	21.885	4793150	154476	49.769



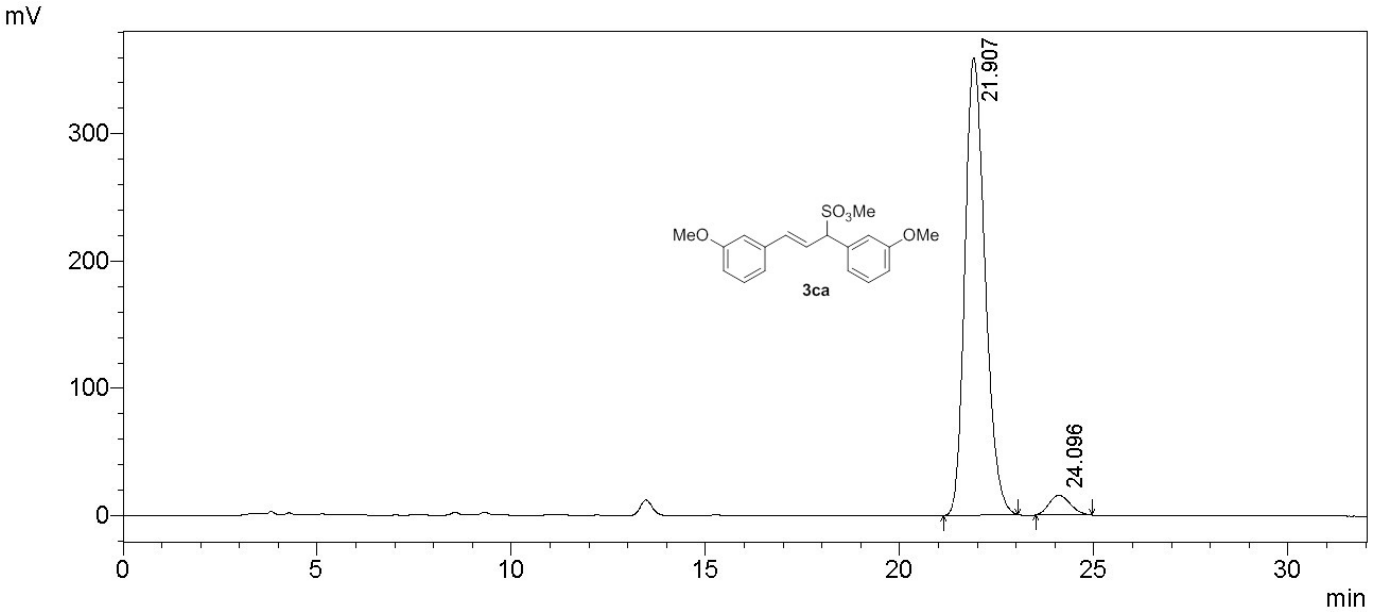
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	12.556	46388284	2103829	91.460
2	14.682	4331489	181747	8.540



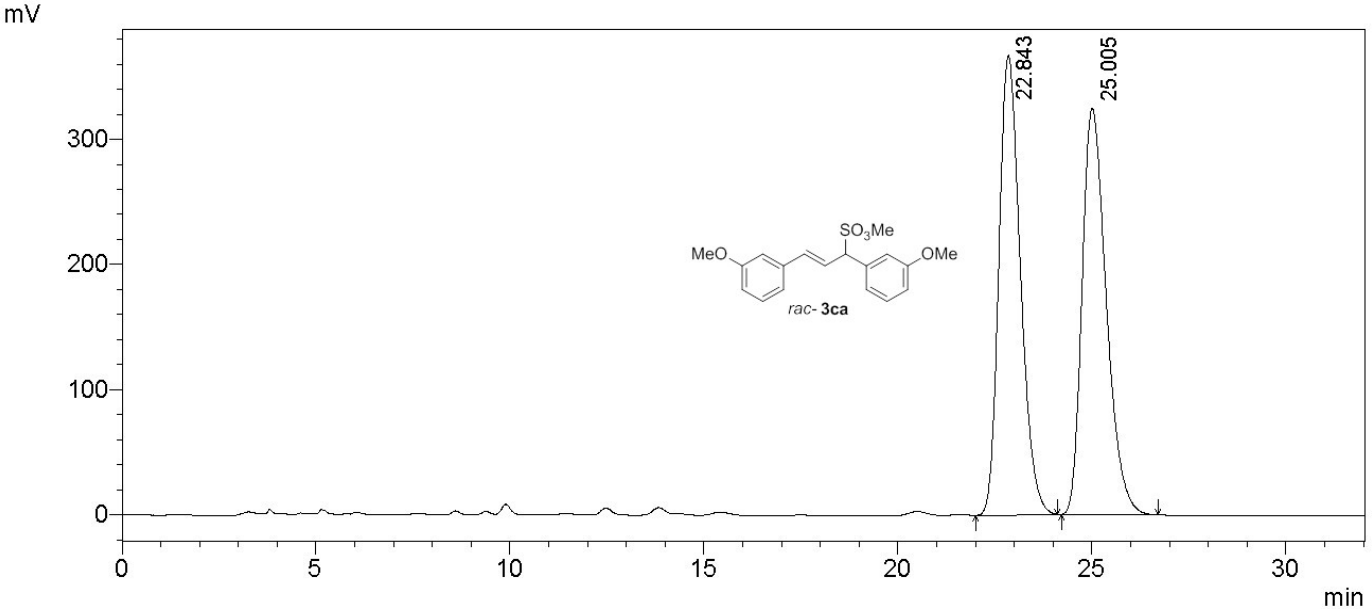
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	12.591	27976500	1340782	49.987
2	14.581	27991555	1126834	50.013



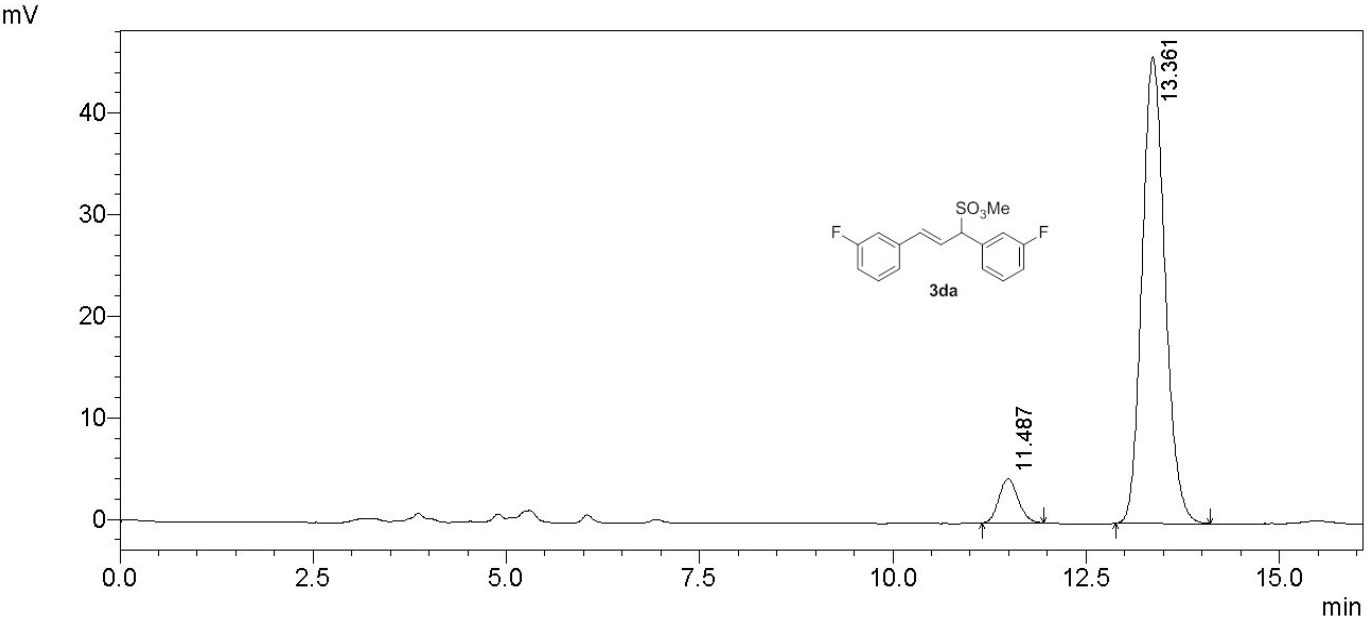
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	21.907	12973251	359582	95.653
2	24.096	589520	15562	4.347



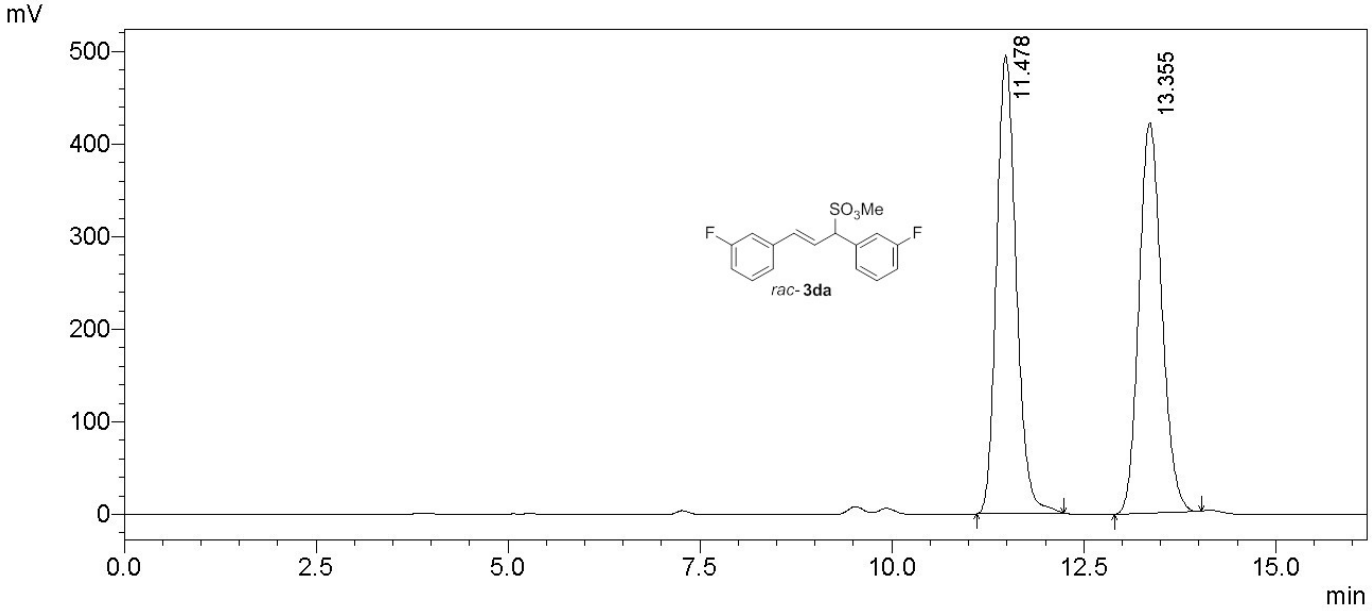
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	22.843	14148508	367192	50.111
2	25.005	14085799	324738	49.889



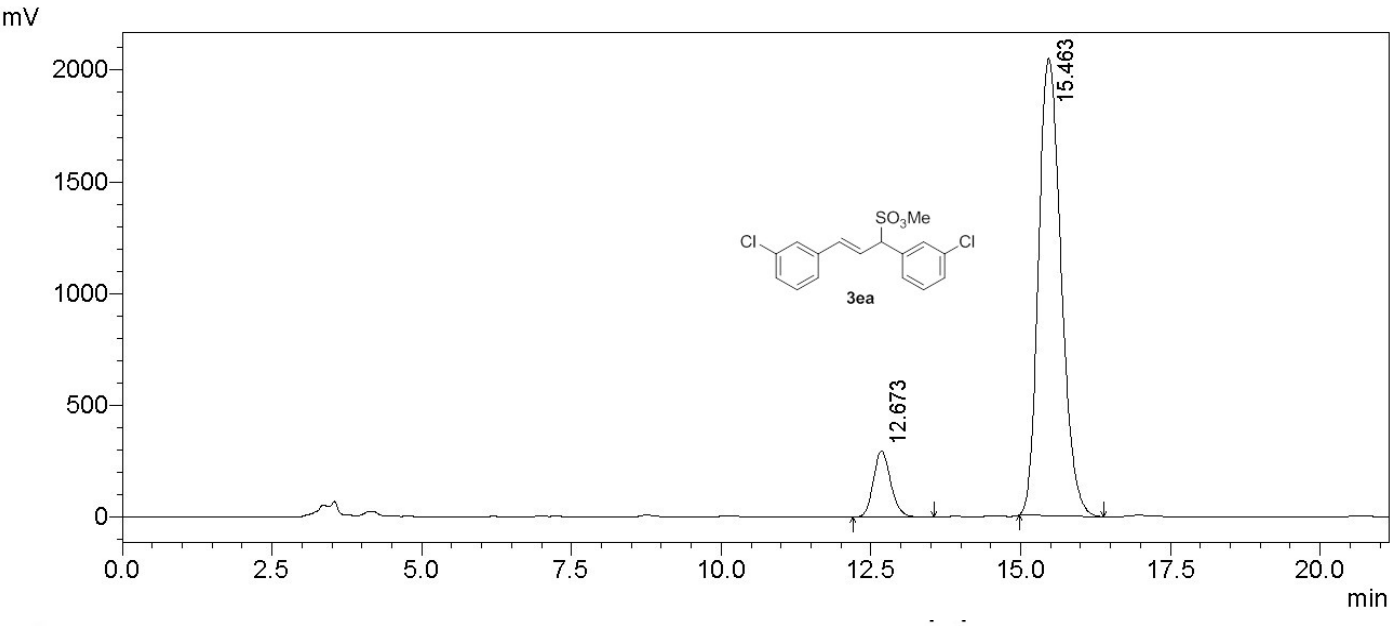
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	11.487	75027	4336	7.338
2	13.361	947426	45903	92.662



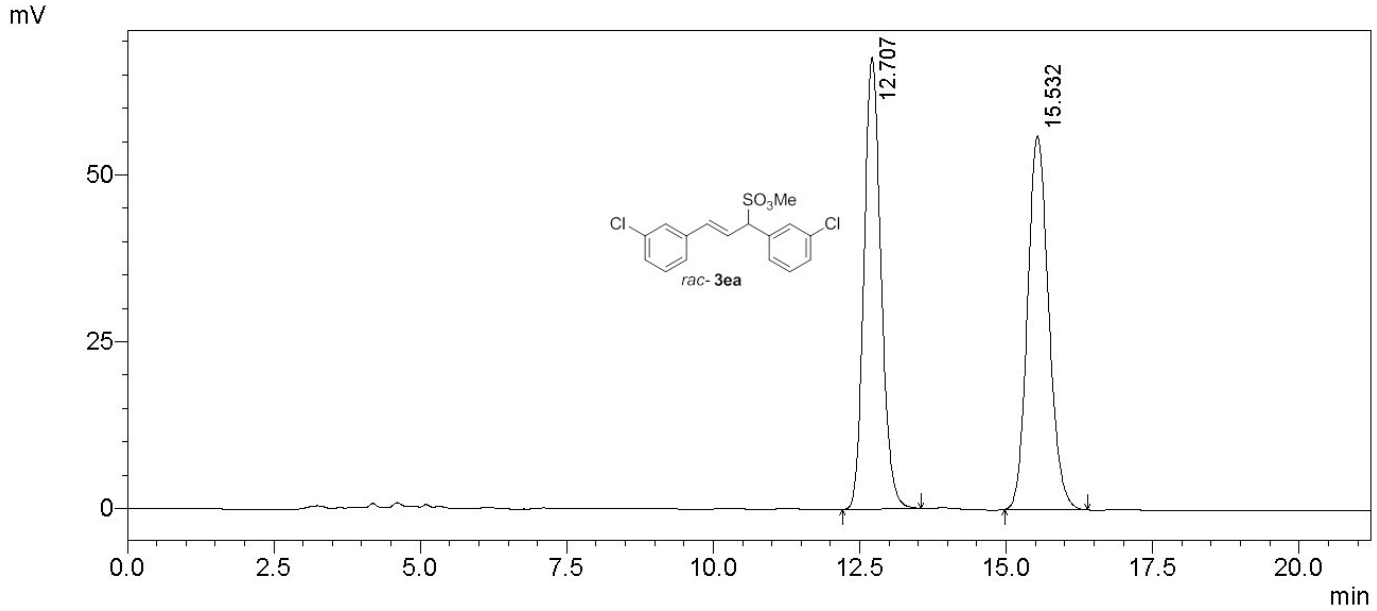
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	11.478	8822139	494831	50.417
2	13.355	8676344	421429	49.583



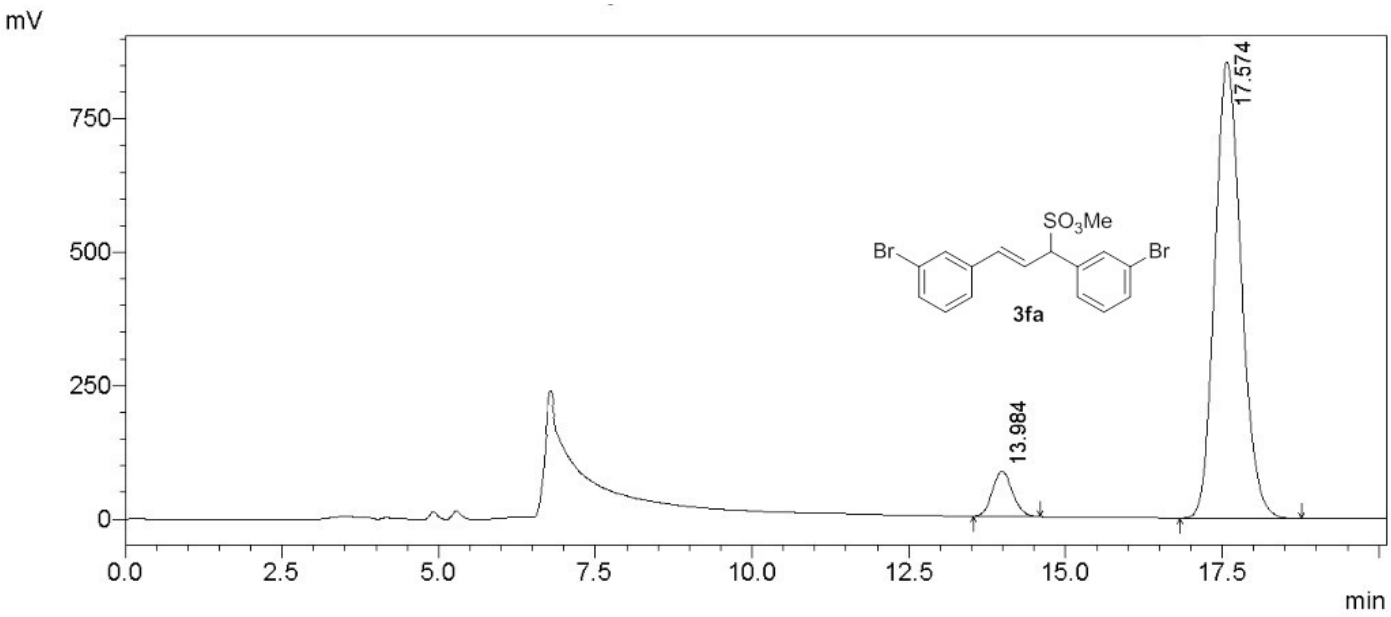
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	12.672	3457952	171066	9.701
2	15.461	32187602	1258026	90.299



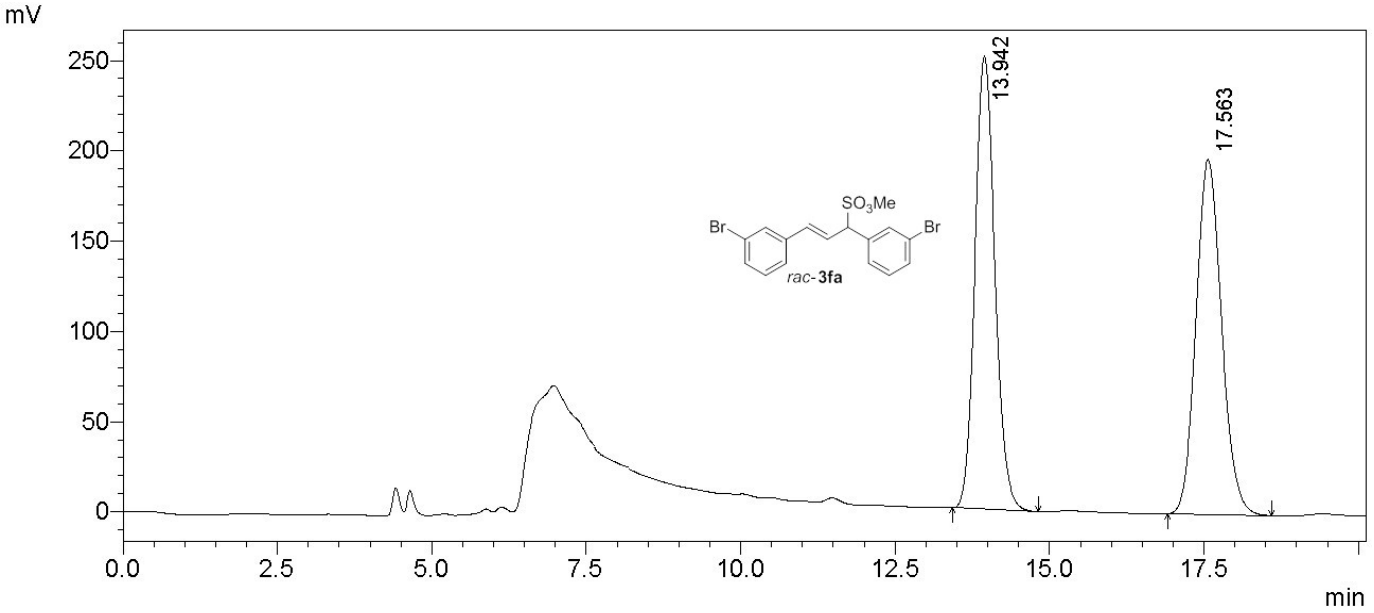
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	12.707	1370937	67832	49.325
2	15.532	1408480	56066	50.675



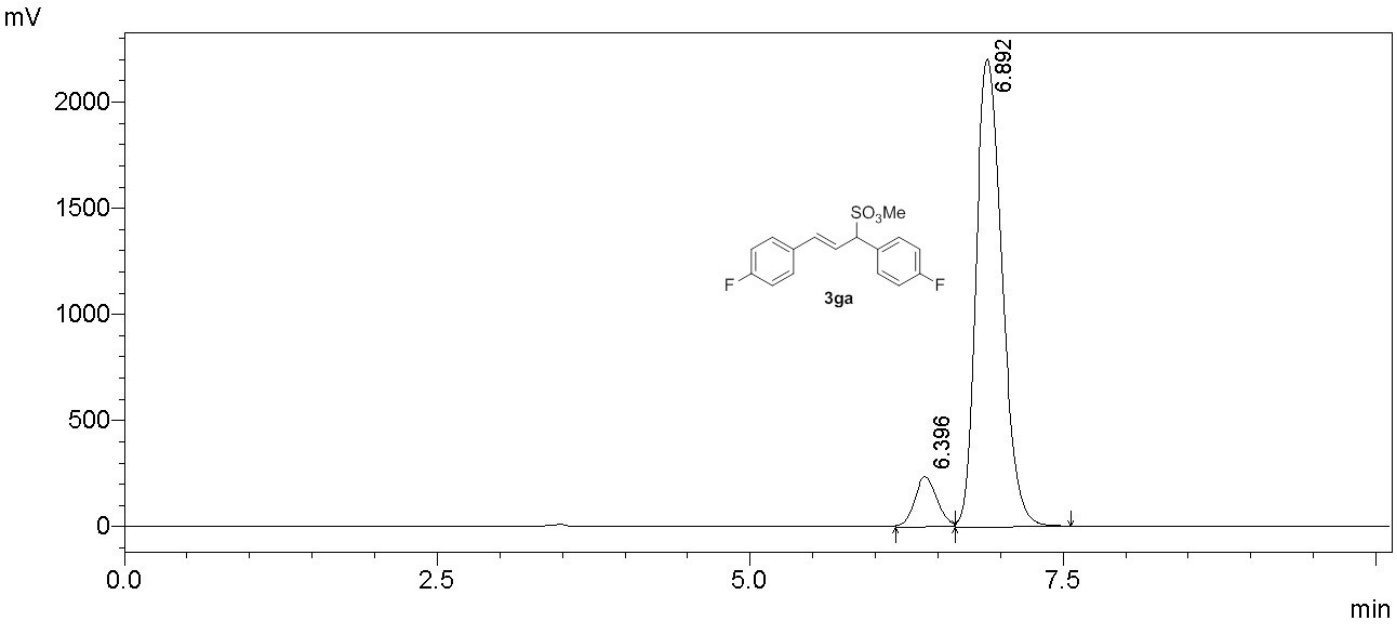
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	13.984	1886598	84400	7.007
2	17.574	25036566	855459	92.993



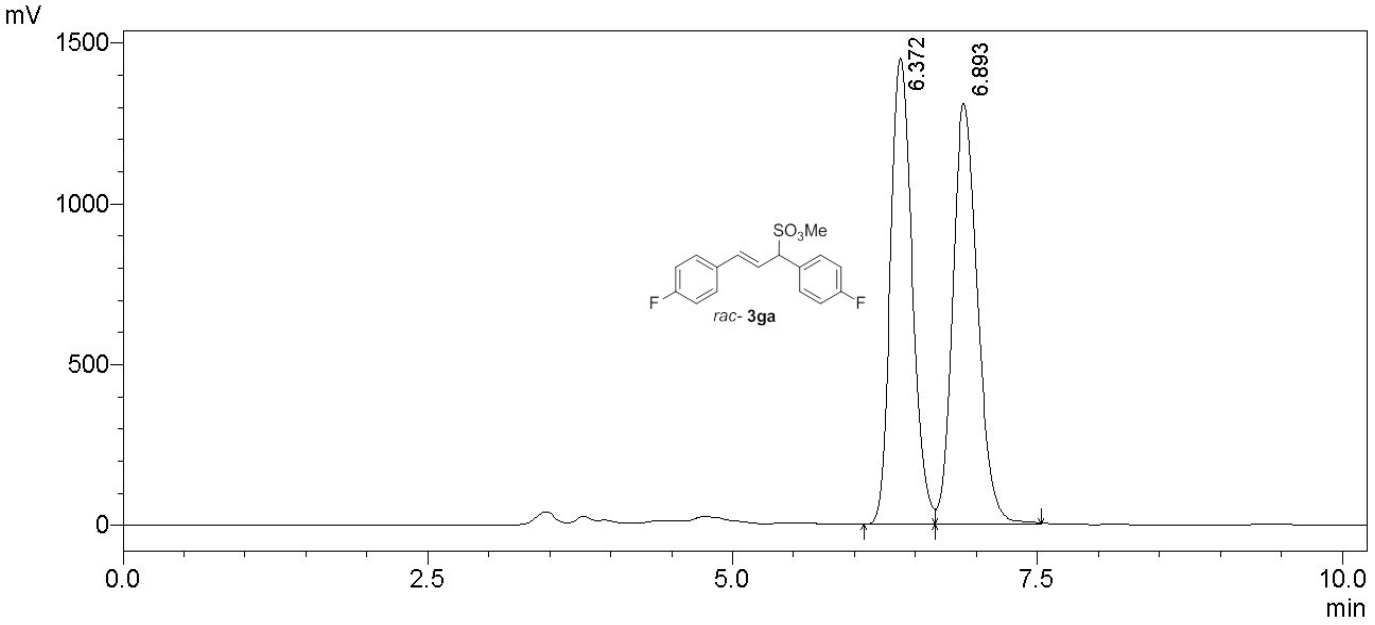
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	13.942	5643868	250839	49.874
2	17.563	5672338	196607	50.126



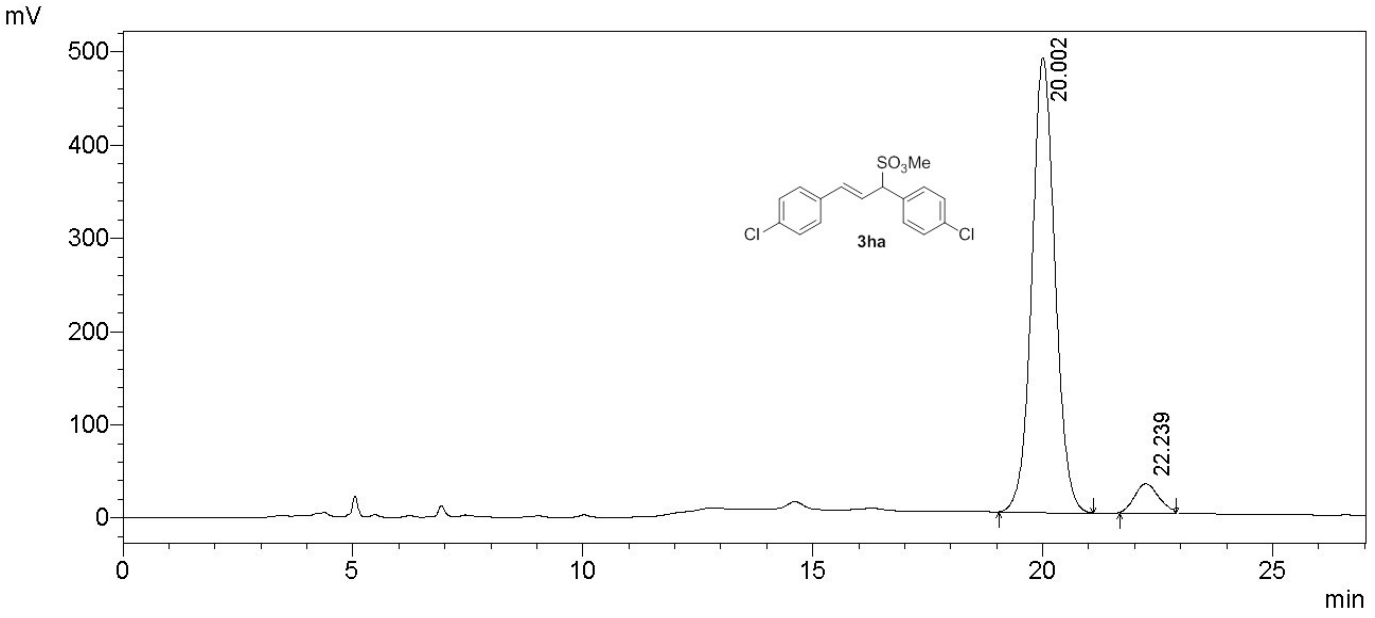
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	6.396	2963845	235886	8.508
2	6.892	31871625	2201034	91.492



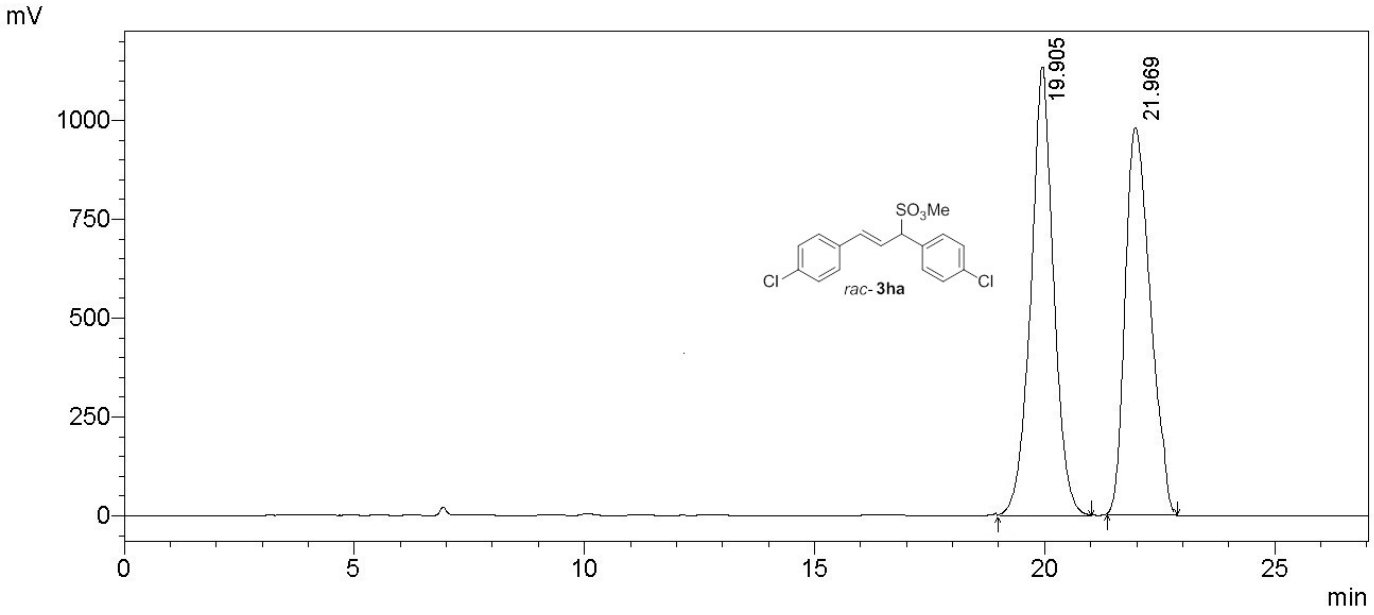
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	6.372	17950835	1450828	49.275
2	6.893	18479010	1308786	50.725



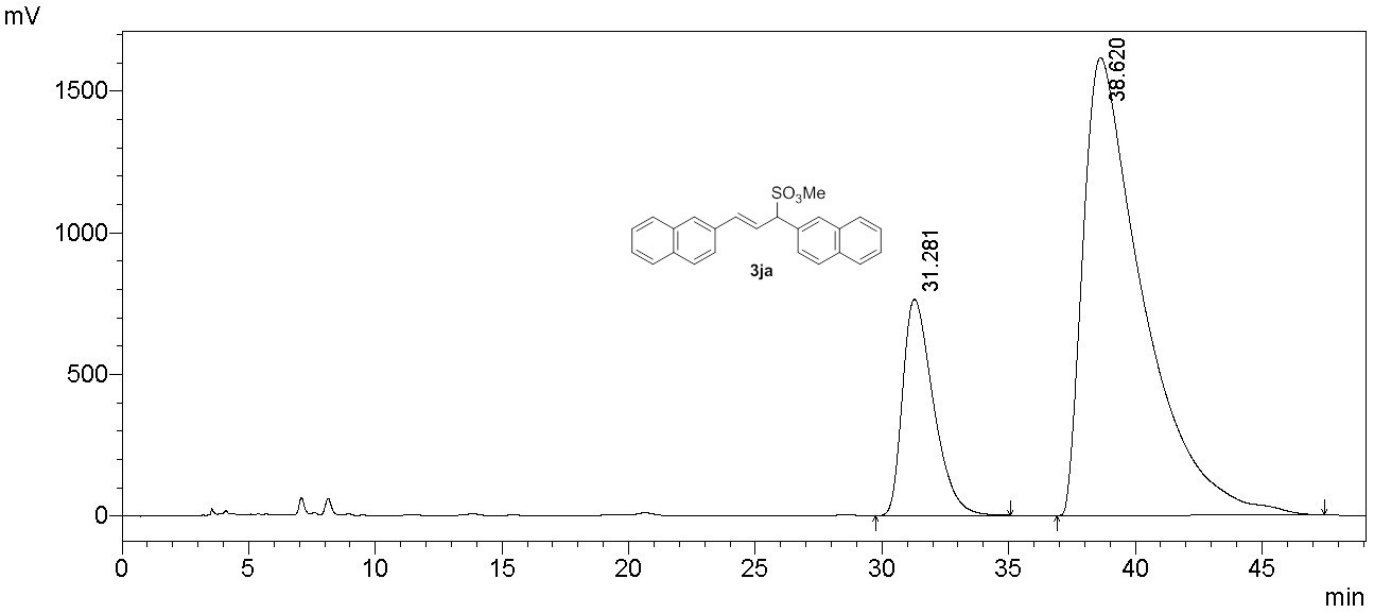
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	20.002	17089598	487885	93.366
2	22.239	1214347	31891	6.634



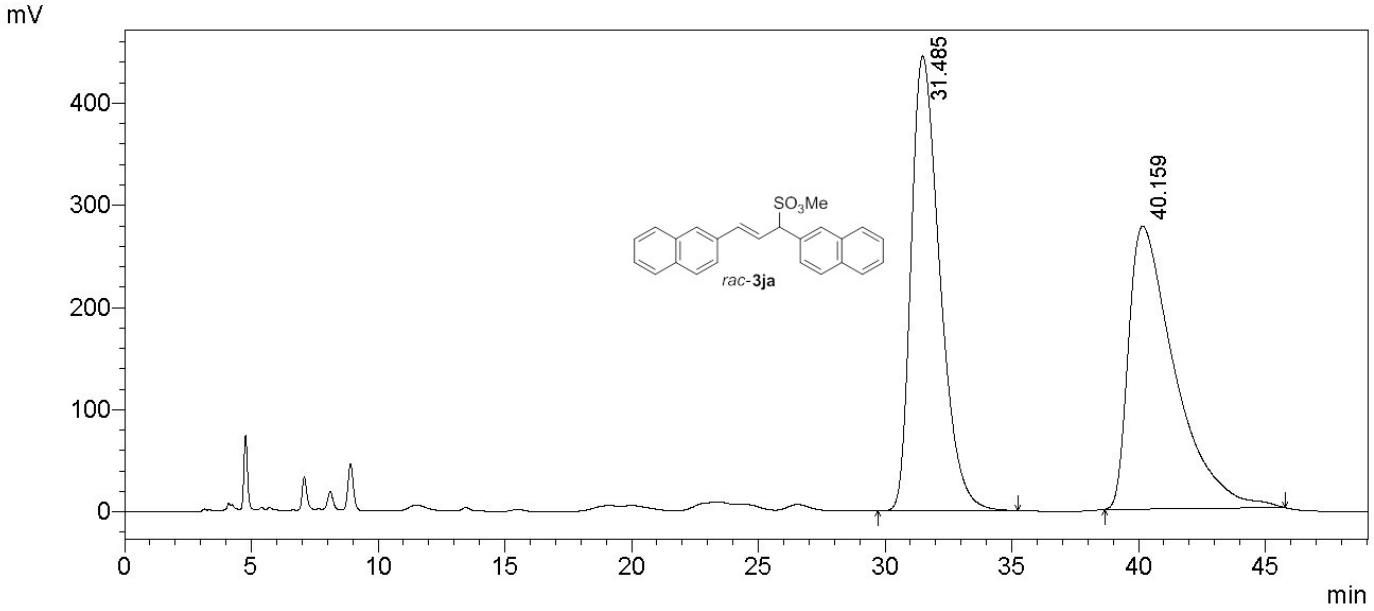
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	19.905	42138121	1158825	50.290
2	21.969	41651323	979151	49.710



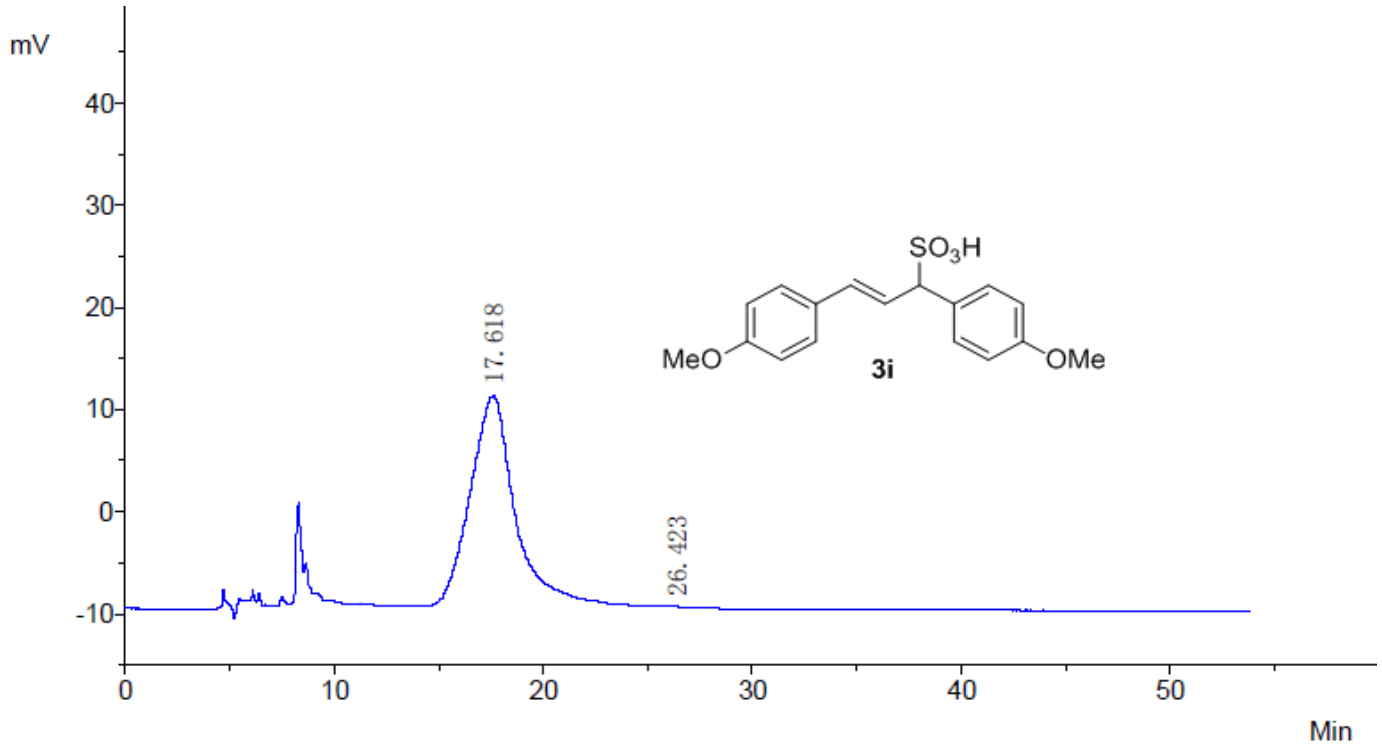
Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	31.281	64603677	763115	19.604
2	38.620	264942984	1616131	80.396

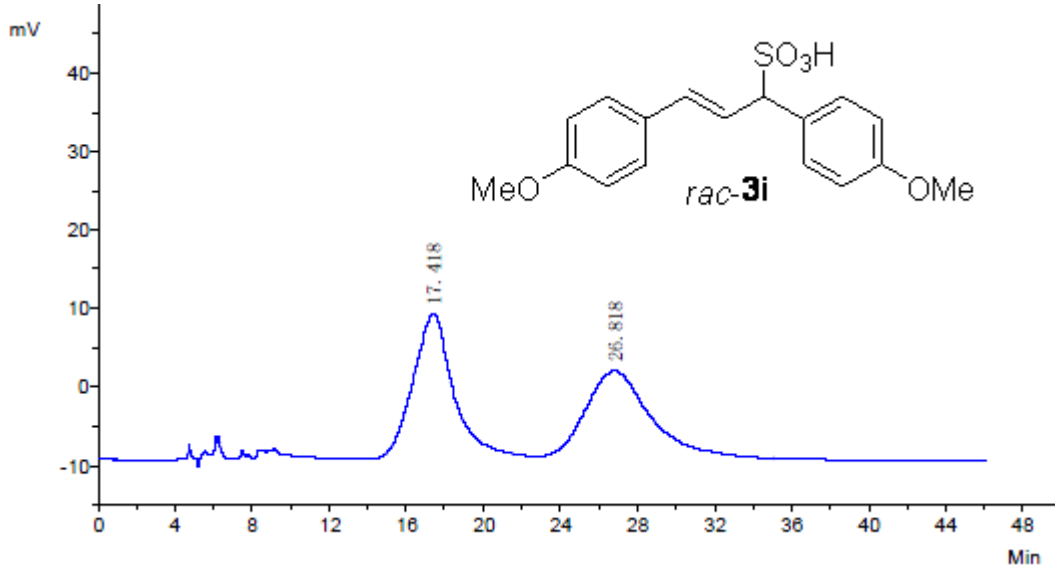


Ch1 254nm

Peak#	R.Time	Area	Height	Conc.%
1	31.485	35055340	445168	49.949
2	40.159	35127491	276988	50.051



Peak#	R. Time	Area	Height	Conc.%
1	17.618	20808.8	3184771.5	98.9026
2	26.423	128.8	35336.1	1.0974



Peak#	R. Time	Area	Height	Conc.%
1	17.418	18385.6	2656366.0	50.6169
2	26.818	10987.6	2591617.9	49.3831