Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Reactions of allyl alcohols and boronic acids with trifluoromethanesulfonyl hypervalent iodonium ylide under copper-catalysis

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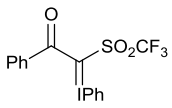
1. General information.

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum. All solvents were purified by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. All of the reaction products were purified by preparative thin-layer plates (PLC) carried out on 2.0 mm Merck silica gel (60-F254) or Column chromatography. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 mm. The ^{1}H NMR (300 MHz) and ^{19}F NMR (282 MHz) spectra (with Hexafluorobenzene (δ ppm -162.2) as an internal standard) as for solution in $CDCl_3$ were recorded on a Varian Mercury 300. ^{13}C NMR spectra for solution in $CDCl_3$ was recorded on a BRUKER 500 UltraShield^{TR} (125.8 MHz). Chemical shifts (δ) are expressed in ppm downfield from internal TMS or C_6F_6. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2010EV (ESI-MS and APCI-MS). Infrared spectra were recorded on JASCO FT/IR-200 or a JASCO FT/IR-4100 spectrometer.

Preparation of the $^{+}SCF_3$ reagent 1

The $^{+}SCF_3$ reagent **1**[1)] was prepared according to the referential procedure.



Reference: (1) Y. –D. Yang, A. Azuma, E. Tokunaga, M. Yamasaki, M. Shiro and N. Shibata, *J. Am. Chem. Soc.*, 2013, **135**, 8782.

2. Experimental details

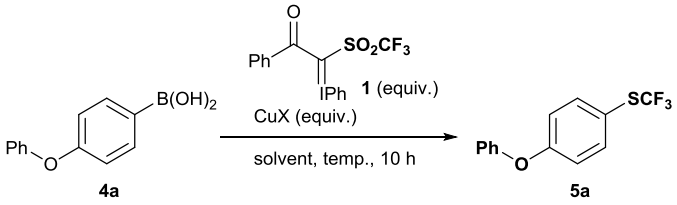
General procedure for synthesis of trifluoromethylsulfinyl derivatives.

A mixture of allyl alcohol **2a-n** (0.25 mmol), $^{+}SCF_3$-reagent **1** (0.50 mmol), CuF_2 (0.05 mmol) and DMAc (1.25 ml) was stirred under N_2 at room temperature for 24 h. Then, H_2O was added, and then extracted with AcOEt three times. The organic layer was washed with brine and dried over $MgSO_4$. Solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica-gel to give the $S(O)CF_3$-product **3a-n**.

General procedure for trifluoromethylthiolation of boronic acids.

To a mixture of boronic acid **4a-i** (0.25 mmol), $^{+}SCF_3$-reagent **1** (0.50 mmol) and DMAc (1.25 ml) under N_2 was added $Cu(OAc)_2$ (0.30 mmol). The reaction mixture was stirred at 80 °C for 10 h. After cooling at room temperature, H_2O was added, and then extracted with AcOEt three times. The organic layer was washed with brine and dried over $MgSO_4$. Solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica-gel to give the SCF_3-product **5a-i**.

Table 1S Optimization of trifluoromethythiolation reaction of boronic acid 4a with 1.[a]



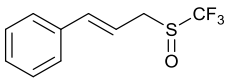
run	**1** (equiv.)	CuX (equiv.)	solvent	temp. (°C)	yield (%)[b]
1	2.0	CuF_2 (0.2)	DMAc	rt	0
2	2.0	CuF_2 (1.2)	DMAc	80	13
3	1.0	$Cu(OAc)_2$ (0.2)	DMAc	80	10
4	1.0	$Cu(OAc)_2$ (1.0)	DMAc	80	40
5	2.0	$Cu(OAc)_2$ (2.0)	DMAc	80	**47**

6	2.0	$Cu(OAc)_2$ (1.0)	DMAc	80	35
7	2.0	$Cu(OAc)_2$ (1.2)	DMAc	80	47
8	2.0	$Cu(OAc)_2$ (1.2)	DMAc	100	44
9	2.0	$Cu(OAc)_2$ (1.2)	DMAc	50	5
10	2.0	$Cu(OAc)_2$ (1.2)	NMP	80	0
11[c]	2.0	$Cu(OAc)_2$ (1.2)	DMAc	80	0
12	2.0	Cu (1.2)	DMAc	80	26
13	2.0	Cu(OAc) (1.2)	DMAc	80	44
14	2.0	CuTc[d] (1.2)	DMAc	80	39
15	2.0	CuCl (1.2)	DMAc	80	2
16	2.0	$CuCl_2$ (1.2)	DMAc	80	0
17	2.0	$Cu(OTf)_2$ (1.2)	DMAc	80	11
18	2.0	$Cu(OTFA)_2$[e]-xH_2O (1.2)	DMAc	80	1
19[f]	2.0	$Cu(OAc)_2$ (1.2)	DMAc	80	0
20[g]	2.0	$Cu(OAc)_2$ (1.2)	DMAc	80	0

[a]The reaction were carried out with **4a** (0.25 mmol), **1** and CuX in each solvent (1.25 ml). [b]^{19}F NMR yields with PhF (0.75 mmol) as an internal standard. [c]1,10-phenanthroline (0.25 mmol) was added. [d]CuTc: Cu-thiophene-2-carboxylate. [e]$Cu(OTFA)_2$: Cu-bis- trifluoroacetate. [f]AcONa (0.25 mmol) was added. [g]$PhCO_2Na$ (0.25 mmol) was added.

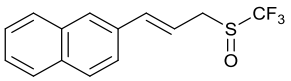
3. Products Spectra data

(E)-(3-((trifluoromethyl)sulfinyl)prop-1-en-1yl)benzene (3a)



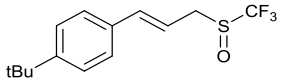
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.33 (m, 5H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.27-6.16 (m, 1H), 3.93-3.89 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). HRMS (ESI^+): m/z calcd. for [M+Na]; 257.0224 found 257.0230. White solid (41.6 mg, 71%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

2-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)naphthalene (3b)



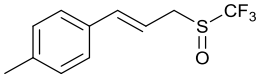
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83-7.78 (m, 4H), 7.60 (d, *J* = 8.4 Hz, 1H) 7.50 -7.49 (m, 2H), 6.96 (d, *J* = 15.6 Hz, 1H), 6.38-6.28 (m, 1H), 3.96 (br s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = - 72.6 (s, 3F). HRMS (ESI^+): m/z calcd. for [M+Na]; 307.0380 found 307.0358. White solid (44.1 mg, 62%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

***(E)*-1-(*tert*-butyl)-4-(3-((trifleoromethyl)sulfinyl)prop-1-en-1yl)benzene (3c)**



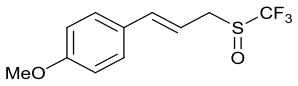
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (br s, 4H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.22-6.12 (m, 1H), 3.91 (d, *J* = 3.9 Hz, 2H), 1.32 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 152.1, 140.2, 132.7, 126.1 (q, *J* = 338.0 Hz), 126.5, 125.7, 112.4, 53.5 (d, *J* = 3.0 Hz), 34.7, 31.2. HRMS (ESI^+): m/z calcd. for [M+Na]; 313.0850 found 313.0847. ATR-FTIR: v= 3458, 2962, 2904, 2866, 1750, 1515, 1476, 1462, 1400, 1367, 1283, 1267, 1181, 1139, 1073, 968, 821, 570 cm^{-1}. mp: 42.5 ° C. White solid (61.7 mg, 85%)

1-methyl-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3d)



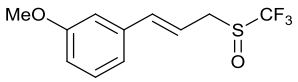
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 16.2 Hz, 1H), 6.15 (dt, *J* = 15.9Hz, 8.1Hz, 1H), 3.86 (m, 2H), 2.32 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). HRMS (ESI^+): m/z calcd. for [M+Na]; 271.0380 found 271.0377. White solid (37.9 mg, 61%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

1-methoxy-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3e)



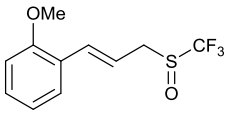
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.05 (dt, *J* = 15.4, 7.6 Hz, 1H), 3.89 (br s, 2H), 3.82 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). HRMS (ESI^+): m/z calcd. for [M+Na]; 287.0330 found 287.0333. White solid (29.7 mg, 45%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

1-methoxy-3-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3f)



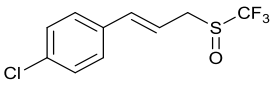
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7-26 (m, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.93 (s, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 15.9, 7.8 Hz, 1H), 3.91-3.89 (m, 2H), 3.83(s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). HRMS (ESI^+): m/z calcd. for [M+Na]; 287.0330 found 287.0316. White solid (33.0 mg, 50%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

***(E)*-1-methoxy-2-(3-((trifleoromethyl)sulfinyl)prop-1-en-1yl)benzene (3g)**



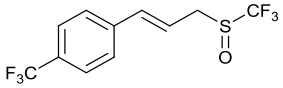
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.2Hz, 1H), 7.30-7.28 (m, 1H), 7.11 (d, *J* = 15.6Hz, 1H), 6.96-6.90 (m, 2H), 6.26 (dt, *J* = 15.6Hz, 7.5Hz, 1H), 3.93-3.92 (m, 2H), 3.86 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). HRMS (ESI^+): m/z calcd. for [M+Na]; 287.0330 found 287.0332. White solid (39.7 mg, 60%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

1-Chloro-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3h)



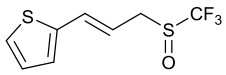
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (br s, 4H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.3, 7.5 Hz, 1H), 3.85 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.6 (s, 3F). HRMS (ESI^-): m/z calcd. for [M-H]; 266.9858 found 266.9864. White solid (50.4 mg, 75%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

1-(Trifluoromethyl)-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3i)



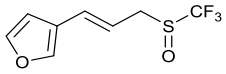
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 6.9 Hz, 2H), 7.50 (d, *J* = 6.9 Hz, 2H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.35-6.30 (m, 1H), 3.92 (br s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.2 (s, 3F), -72.5 (s, 3F). HRMS (ESI^-): m/z calcd. for [M-H]; 301.0122 found 301.0124. White solid (33.3 mg, 44%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

2-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)thiophene (3j)



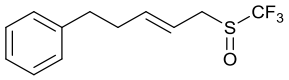
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06-7.00 (m, 3H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.08-6.00 (m, 1H), 3.88 (d, *J* = 6.0 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). HRMS (ESI^-): m/z calcd. for [M-H]; 262.9788 found 262.9789. White solid (18.0 mg, 30%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

3-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)furan (3k)



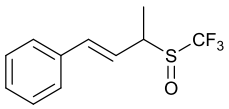
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (s, 1H), 7.39 (s, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.54 (s, 1H), 5.92 (dt, *J* = 15.9Hz, 7.5Hz, 1H), 3.86-3.84 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.7 (s, 3F). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 144.0, 141.7, 130.2, 125.3 (q, *J* = 402.9 Hz), 123.0, 112.8, 107.2, 53.3 (q, *J* = 4.5 Hz). HRMS (ESI^-): m/z calcd. for [M-H]; 247.0017 found 247.0021. ATR-FTIR: v= 3140, 2924, 2320, 1746, 1654, 1511, 1402, 1367, 1189, 1139, 1023, 964, 872, 791, 736, 601 cm^{-1}. Brown oil (39.2 mg, 70%).

1-((*E*)-5-(trifluoromethylsulfinyl)pent-3-enyl)benzene (3l)



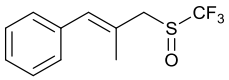
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7.27 (m, 2H), 7.21-7.16 (m, 3H), 6.01-5.96 (m, 1H), 5.54-5.49 (m, 1H), 3.67 (br s, 2H), 2.76-2.71 (m, 2H), 2.47-2.45 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.8 (s, 3F), -73.2 (s, 3F), 88% of *E* isomer, 12% of *Z* isomer. HRMS (ESI^-): m/z calcd. for [M+Na]; 285.0537 found 285.0537. Colorless oil (27.5 mg, 42%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

1-((*E*)-3-(trifluoromethylsulfinyl)but-1-enyl)benzene (3m)



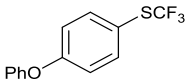
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49-7.32 (m, 5H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.26-6.21 (m, 0.4H), 6.12 (dd, 0.6H, *J* = 15.6, 8.7 Hz), 4.07-3.96 (1H, m), 1.66 (s, 1H), 1.64 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -68.6 (s, 3F), -68.8 (s, 3F, maindiastereomer), d.r. = 3/2. HRMS (ESI^+): m/z calcd. for [M-$SOCF_3$]; 131.0861 found 131.0880. Colorless oil (21.7 mg, 35%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

1-((*E*)-2-methyl-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3n)



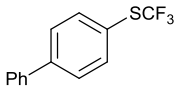
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 6.0 Hz, 2H), 7.30-7.27 (m, 3H), 6.68 (s, 1H), 3.82 (dd, *J* = 33.0, 12.3 Hz, 2H), 2.08 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -73.4 (s, 3F,). HRMS (ESI^+): m/z calcd. for [M+Na]; 271.0380 found 271.0377. White solid (9.3 mg, 15%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Maeno, N. Shibata and D. Cahard, *Org*. *Lett*., 2015, **17**, 1990.

4-Phenoxy-1-(trifluoromethylthio)benzene (5a)



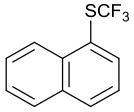
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 6.6 Hz, 1H), 7.08-6.98 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -44.0 (s, 3F). GC-MS (EI): 270 [M+]. Colorless oil (30.4 mg, 45%). The product was identified by comparison of the spectral data with the reported data. Reference: C. Chen, Y. Xie, L. Chu, R. –W. Wang, X. Zhang and F. –L. Quing, *Angew*. *Chem*. *Int*. *Ed*., 2012, **51**, 2492.

4-(Trifluoromethylthio)biphenyl (5b)



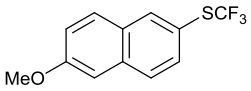
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 6.9 Hz, 2H), 7.64-7.58 (m, 4H), 7.47-7.40 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -43.2 (s, 3F). GC-MS (EI): 254 [M+]. White solid (15.9 mg, 25%). The product was identified by comparison of the spectral data with the reported data. Reference: Z. Wenig, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan and K. –W. Huang, *Angew*. *Chem*. *Int*. *Ed*., 2013, **52**, 1548.

1-(Trifluoromethylthio)naphthalene (5c)



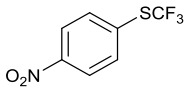
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 8.4 Hz, 1H), 8.03-7.86 (m, 3H), 7.66-7.49 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -42.7 (s, 3F). GC-MS (EI): 228 [M+]. Colorless oil (16.6 mg, 29%). The product was identified by comparison of the spectral data with the reported data. Reference: Z. Wenig, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan and K. –W. Huang, *Angew*. *Chem*. *Int*. *Ed*., 2013, **52**, 1548.

(6-Methoxynaphthalene-2-yl)(trifluoromethyl)sulfane (5d)



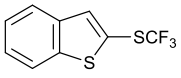
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.78-7.75 (m, 2H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.21 (dd, *J* = 8.5 Hz, 2.3Hz, 1H), 7.15-7.14 (m, 1H), 3.93 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -43.4 (s, 3F). GC-MS (EI): 258 [M+]. Colorless oil (23.9 mg, 38%). The product was identified by comparison of the spectral data with the reported data. Reference: X. Shao, X. Wang, T. Yang, L. Lu and Q. Shen, *Angew*. *Chem*. *Int*. *Ed*., 2013, **52**, 3457.

4-Nitro-1-(trifluoromethylthio)benzene (5e)



^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -41.8 (s, 3F). GC-MS (EI): 223 [M+]. Colorless oil (15.1 mg, 27%). The product was identified by comparison of the spectral data with the reported data. Reference: Z. Wenig, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan and K. –W. Huang, *Angew*. *Chem*. *Int*. *Ed*., 2013, **52**, 1548.

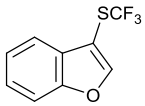
2-(Trifluoromethylthio)benzo[*b*]thiophene (5f)



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (br s, 2H), 7.68 (s, 1H), 7.41 (br s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -44.3 (s, 3F). GC-MS (EI): 234 [M+]. Colorless oil (7.1 mg, 12%). The product was identified by comparison of the spectral data

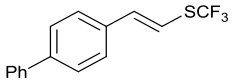
with the reported data. Reference: S, Alazet, L. Zimmer and T. Billard, *J*. *Fluorine Chem*., 2015, **171**, 78.

3-(Trifluoromethylthio)benzo[*b*]furan (5g)



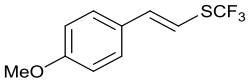
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.72 (br s, 1H), 7.57-7.55 (m, 1H), 7.40-7.38 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -43.6 (s, 3F). GC-MS (EI): 218 [M+]. Colorless oil (8.1 mg, 15%). The product was identified by comparison of the spectral data with the reported data.Reference: G. Teverovskiy, D. S. Surry and S. L. Buchwald, *Angew*. *Chem*. *Int*. *Ed*., 2011, **50**, 7312.

(*E*)-(4-phenylstyryl)(trifluoromethyl)sulfane (5h)



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61-7.56 (m, 4H), 7.48-7.34 (m, 5H), 7.04 (d, *J* = 15.3 Hz, 1H), 6.77 (d, *J* = 15.3 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -43.2 (s, 3F). GC-MS (EI): 280 [M+]. White solid (31.5 mg, 45%). The product was identified by comparison of the spectral data with the reported data. Reference: M. Rueping, N. Tolstoluzhsky and P. Nikolaienko, *Chem*. *Eur*. *J*., 2013, **19**, 14043.

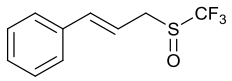
(*E*)-(4-methoxystyryl)(trifluoromethyl)sulfane (5i)

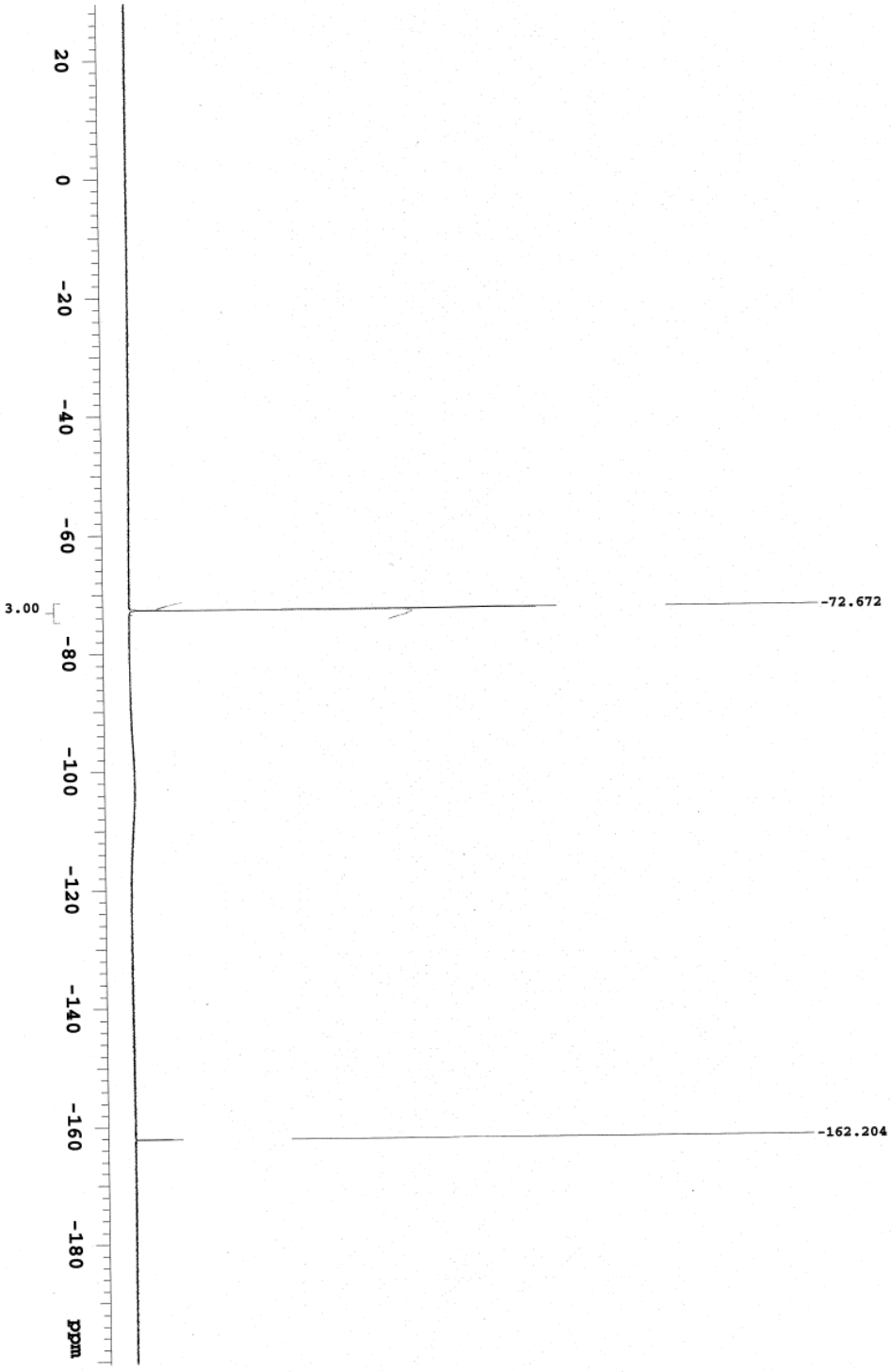


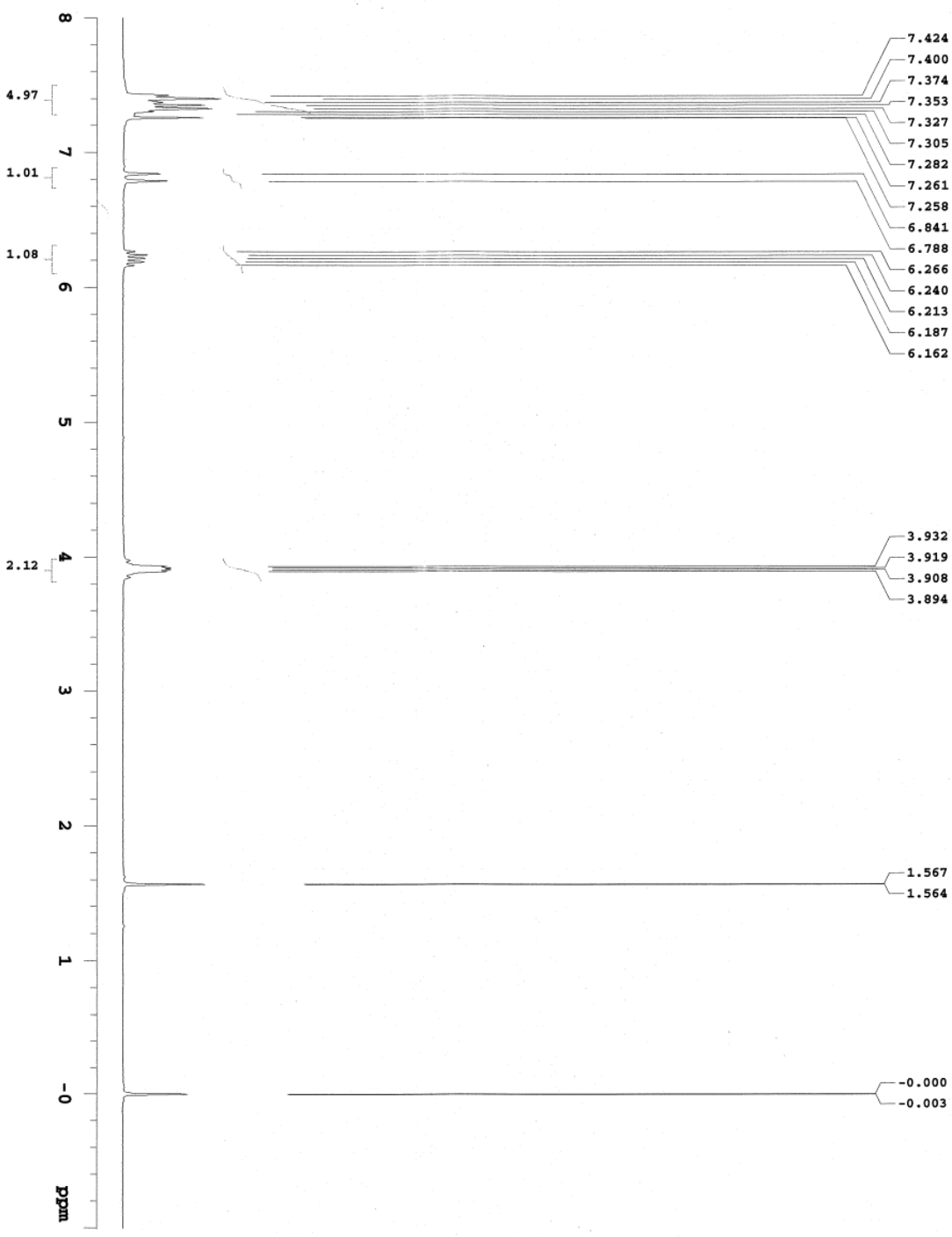
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 14.7 Hz, 1H), 6.88 (d, *J* = 6.6 Hz, 2H), 6.57 (d, *J* = 14.7 Hz, 1H), 3.83 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -43.6 (s, 3F). GC-MS (EI): 234 [M+]. Colorless oil (32.2 mg, 55%). The product was identified by comparison of the spectral data with the reported data. Reference: X. Shao, X. Wang, T. Yang, L. Lu and Q. Shen, *Angew*. *Chem*. *Int*. *Ed*., 2013, **52**, 3457.

Copies of ^{19}F NMR and ^{1}H NMR

***(E)*-(3-((trifluoromethyl)sulfinyl)prop-1-en-1yl)benzene (3a)**

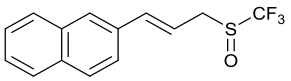


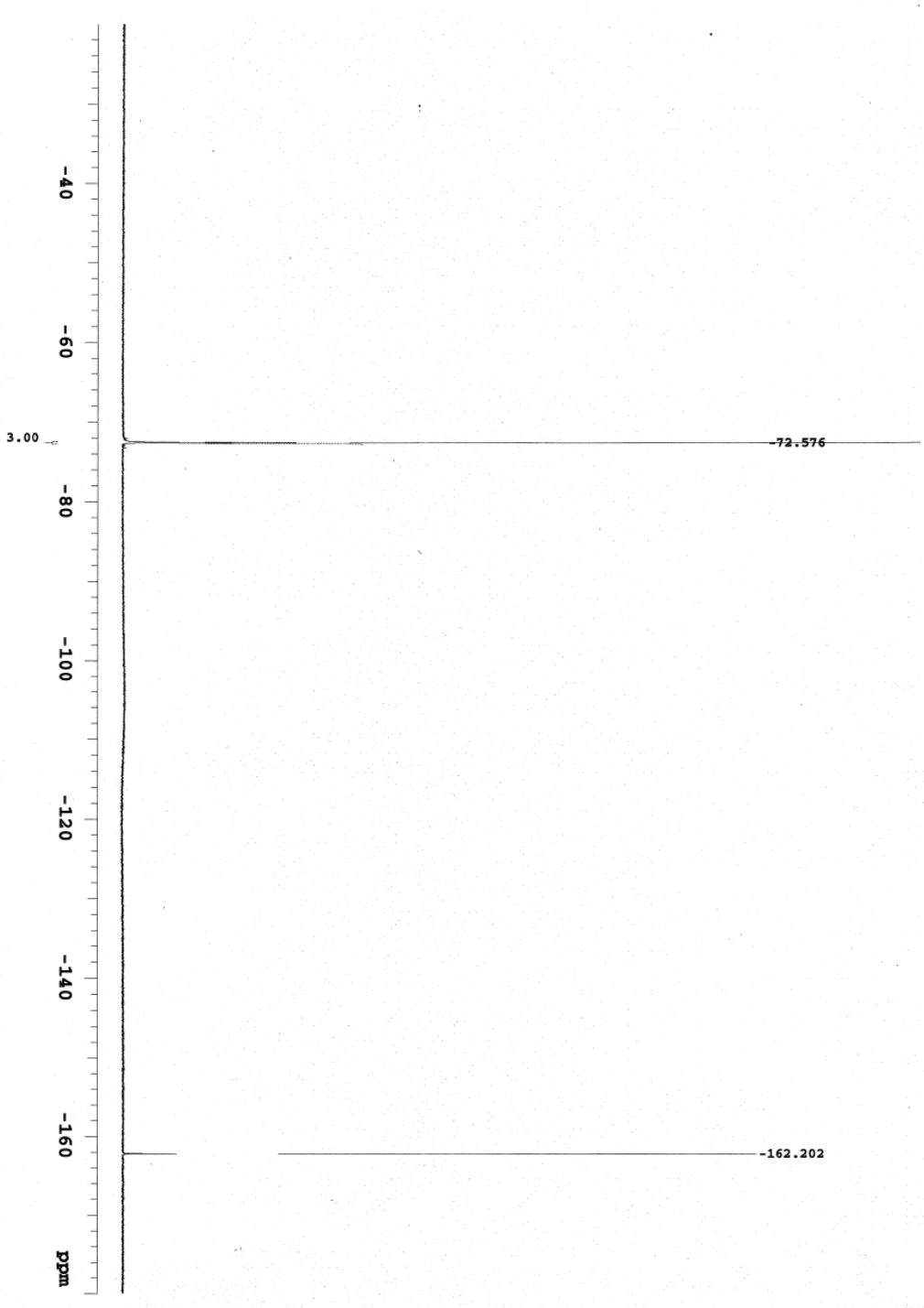


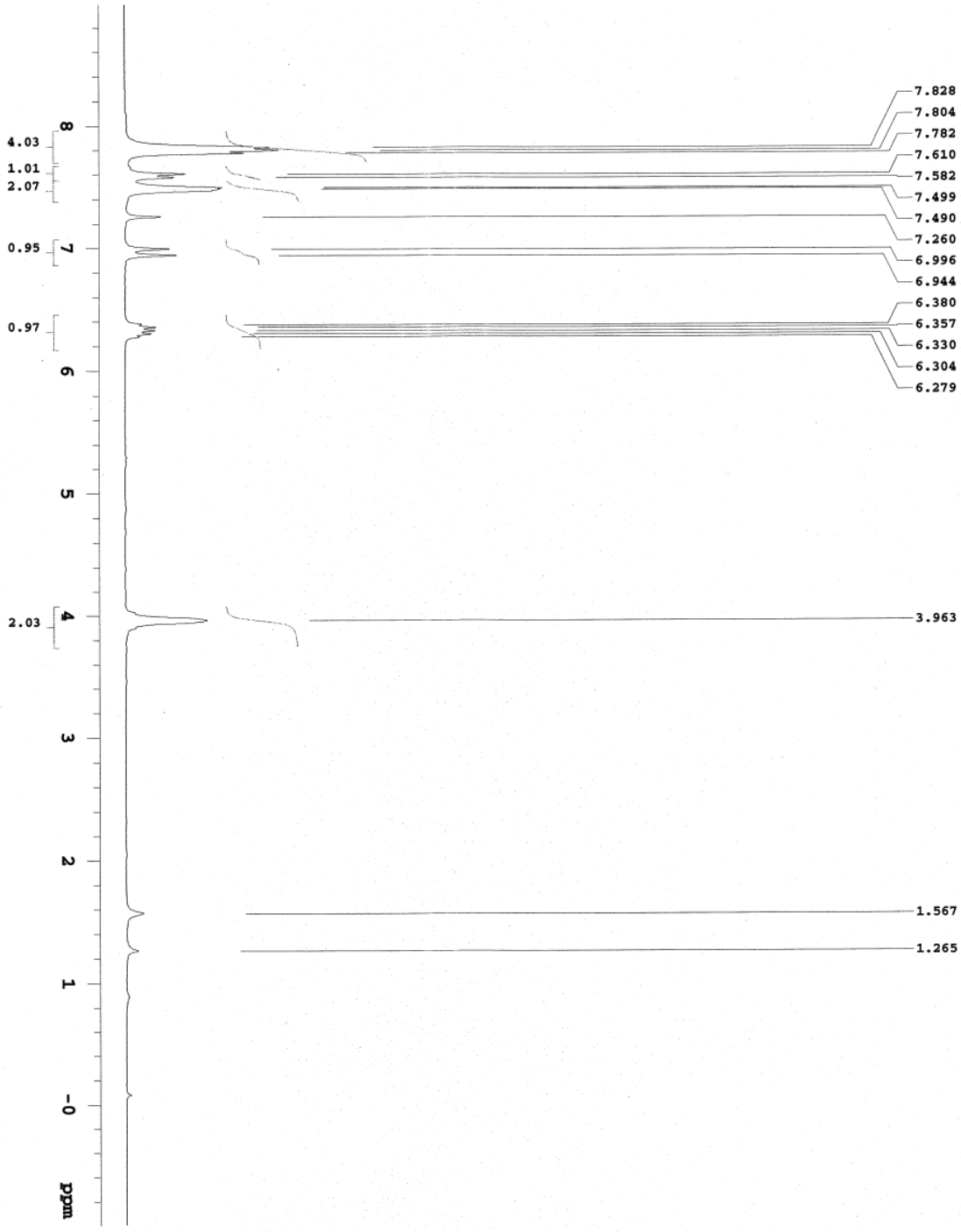

7.424
7.400
7.374
7.353
7.327
7.305
7.282
7.261
7.258
6.841
6.788
6.266
6.240
6.213
6.187
6.162
3.932
3.919
3.908
3.894
1.567
1.564
-0.000
-0.003
4.97
1.01
1.08
2.12
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

2-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)naphthalene (3b)

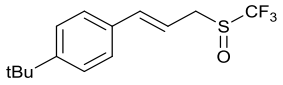


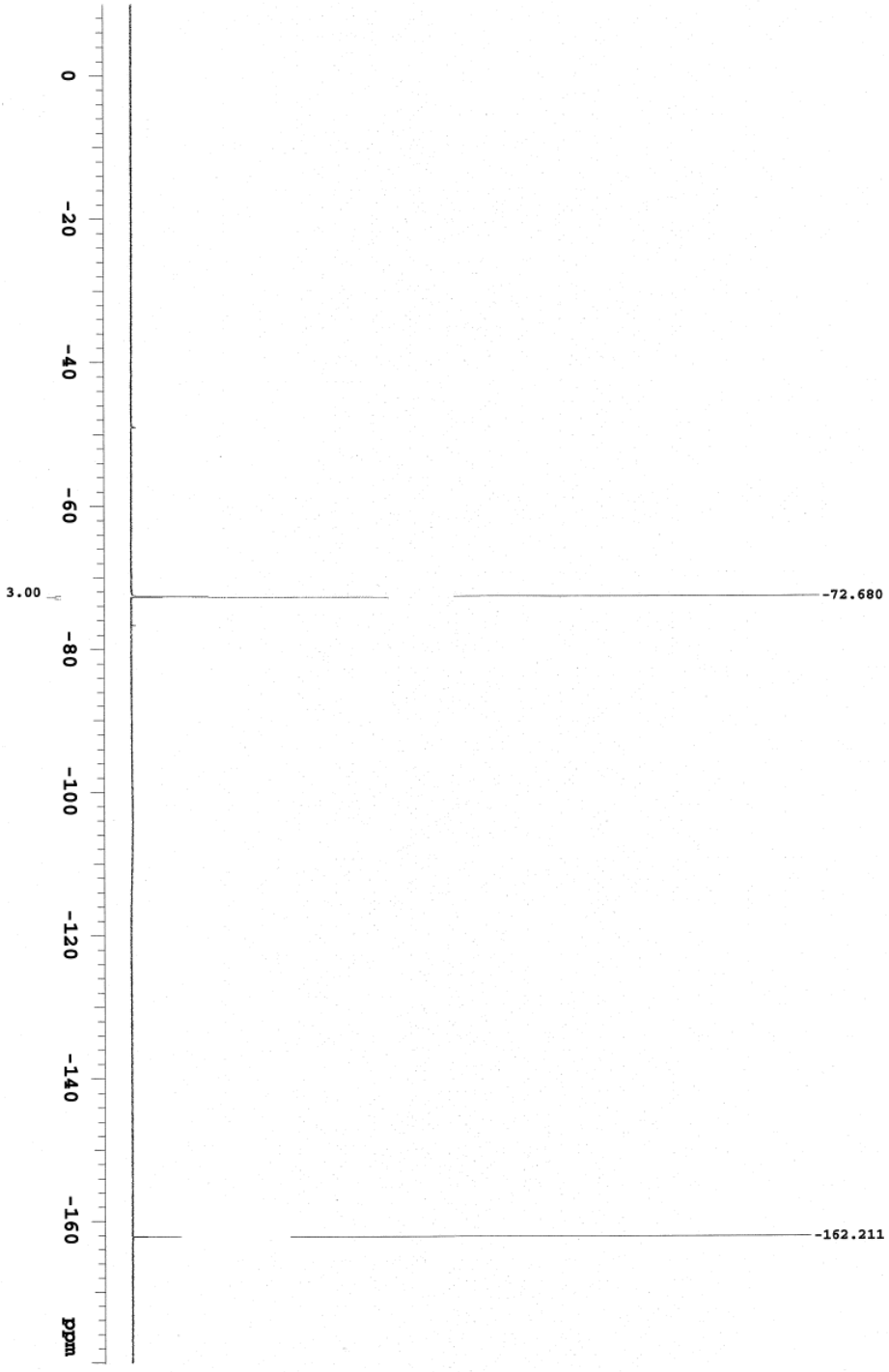


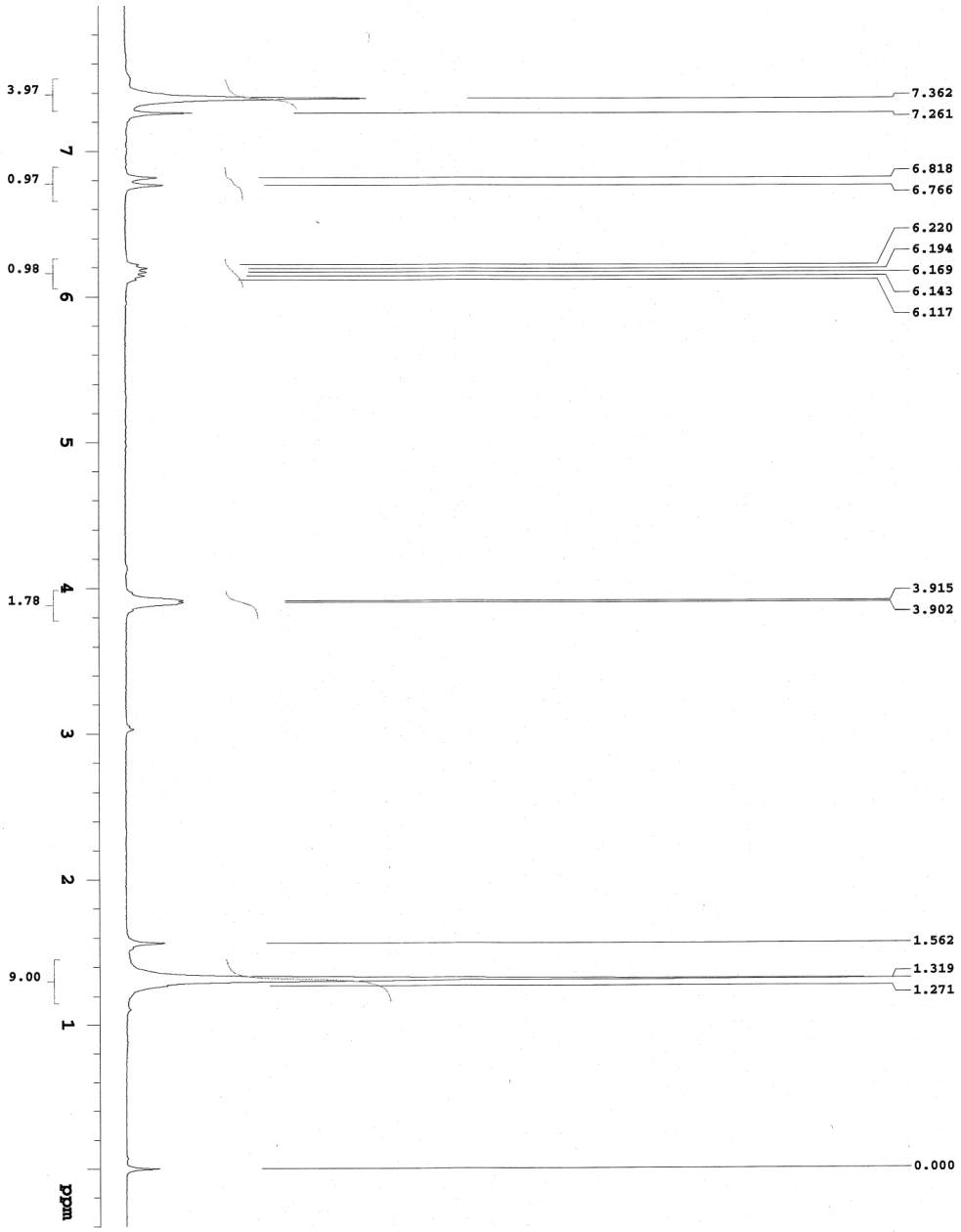

7.828
7.804
7.782
7.610
7.582
7.499
7.490
7.260
6.996
6.944
6.380
6.357
6.330
6.304
6.279
3.963
1.567
1.265
4.03
1.01
2.07
0.95
0.97
2.03
8
7
6
5
4
3
2
1
-0
ppm

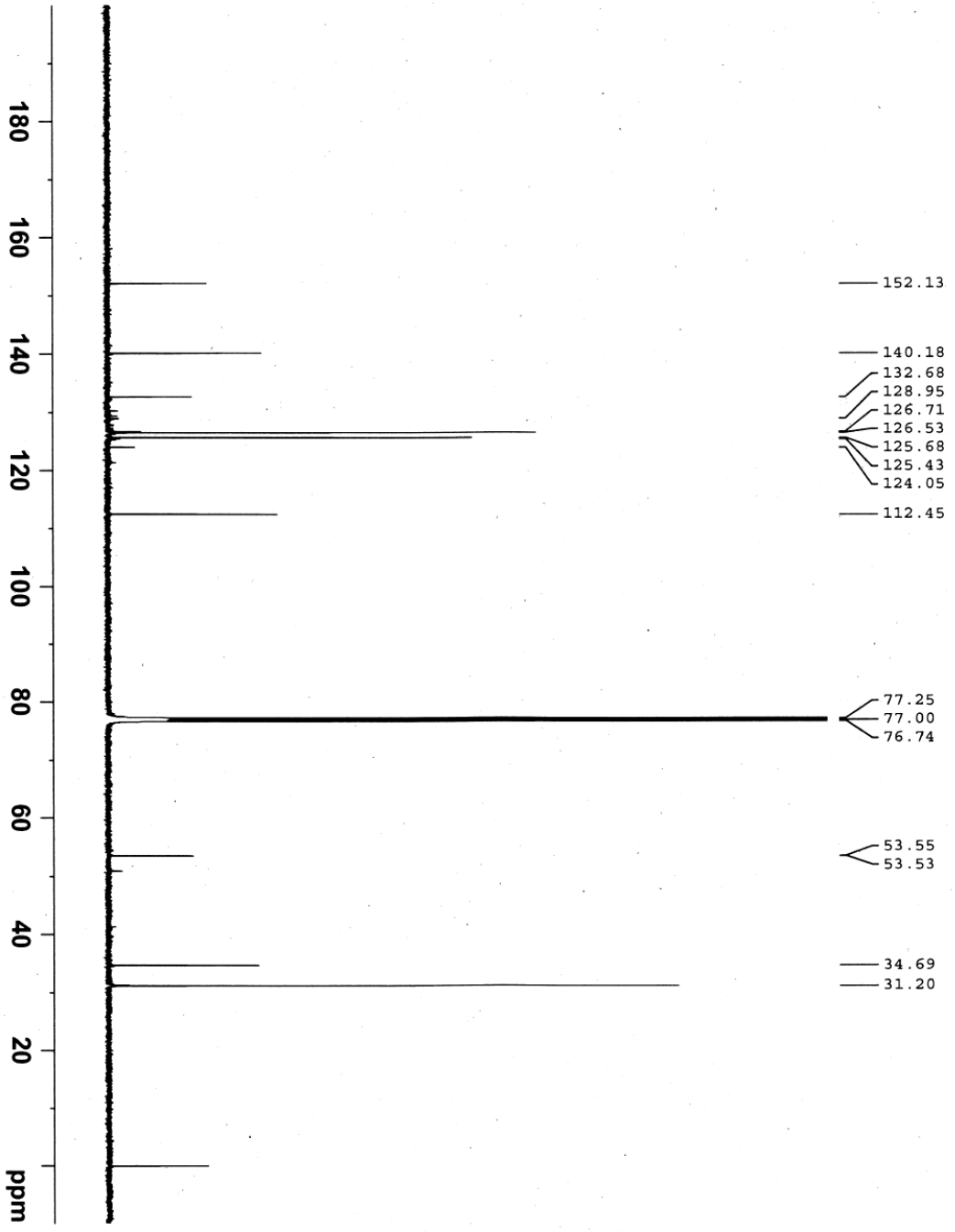
Copies of ^{19}F NMR, ^{1}H NMR and ^{13}C NMR

***(E)*-1-(*tert*-butyl)-4-(3-((trifleoromethyl)sulfinyl)prop-1-en-1yl)benzene (3c)**



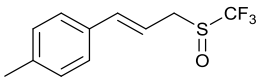


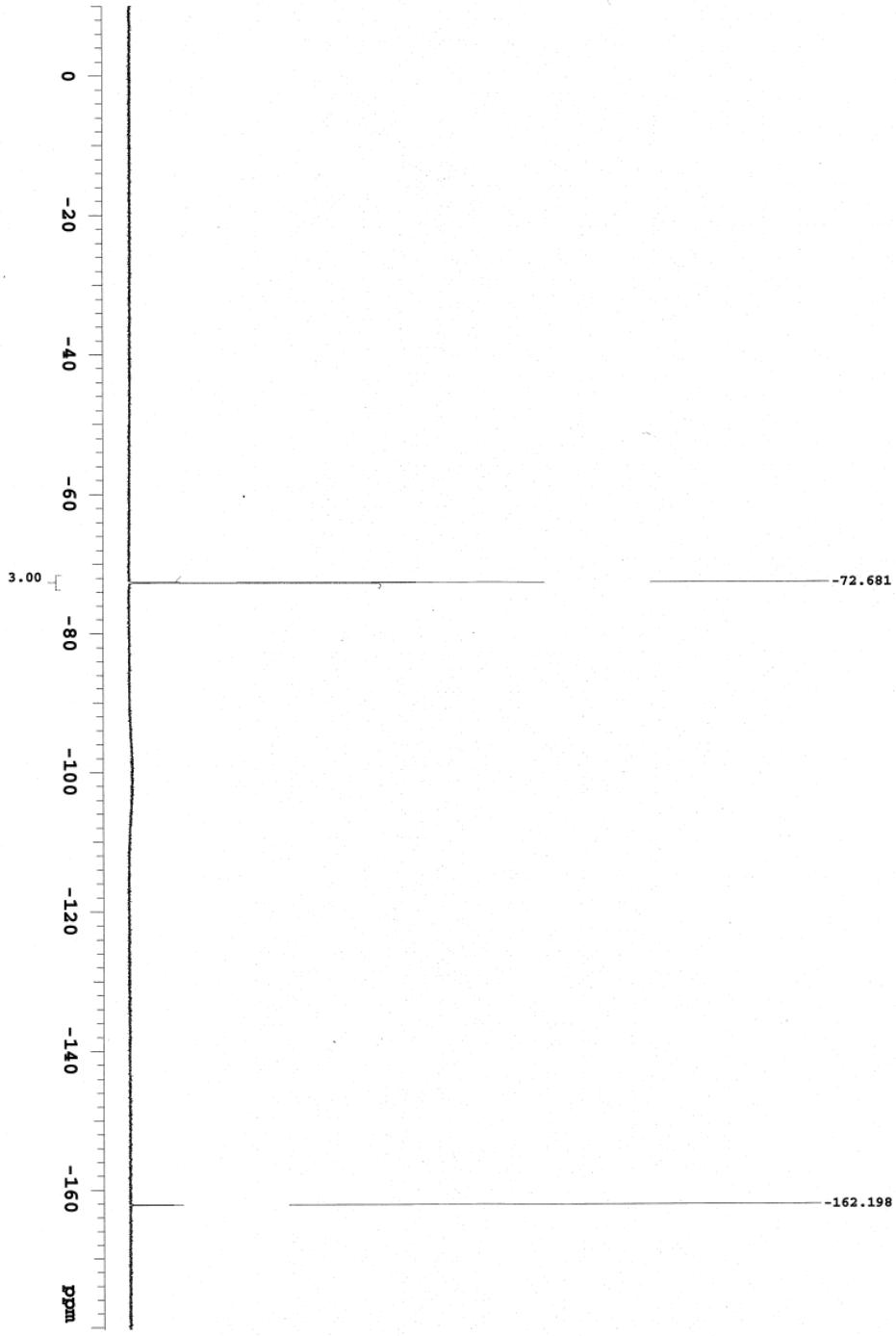

3.97
0.97
0.98
1.78
9.00
7
6
5
4
3
2
1
ppm
7.362
7.261
6.818
6.766
6.220
6.194
6.169
6.143
6.117
3.915
3.902
1.562
1.319
1.271
0.000

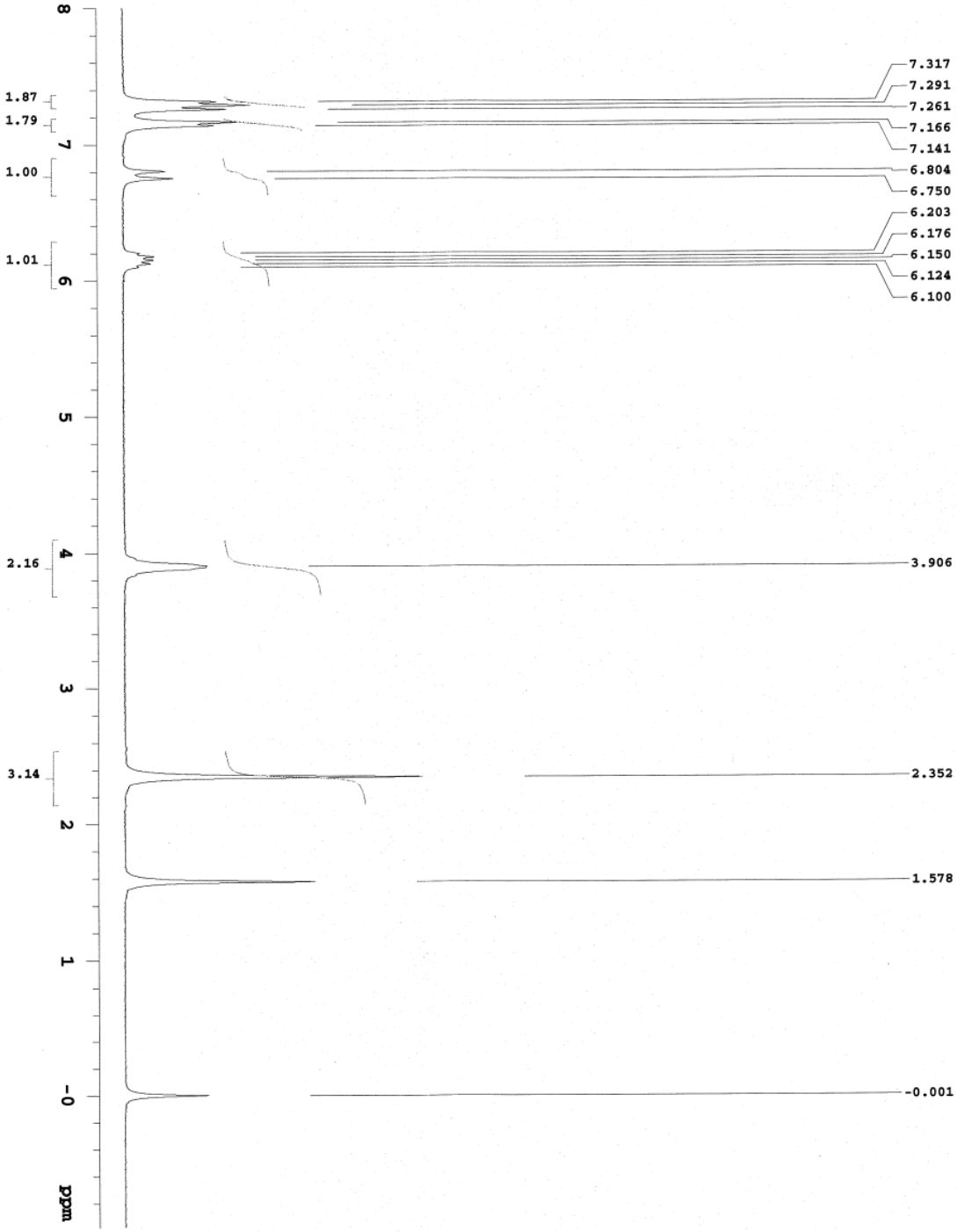

180
160
140
120
100
80
60
40
20
ppm
152.13
140.18
132.68
128.95
126.71
126.53
125.68
125.43
124.05
112.45
77.25
77.00
76.74
53.55
53.53
34.69
31.20

Copies of ^{19}F NMR and ^{1}H NMR

1-methyl-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3d)

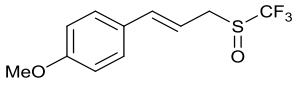


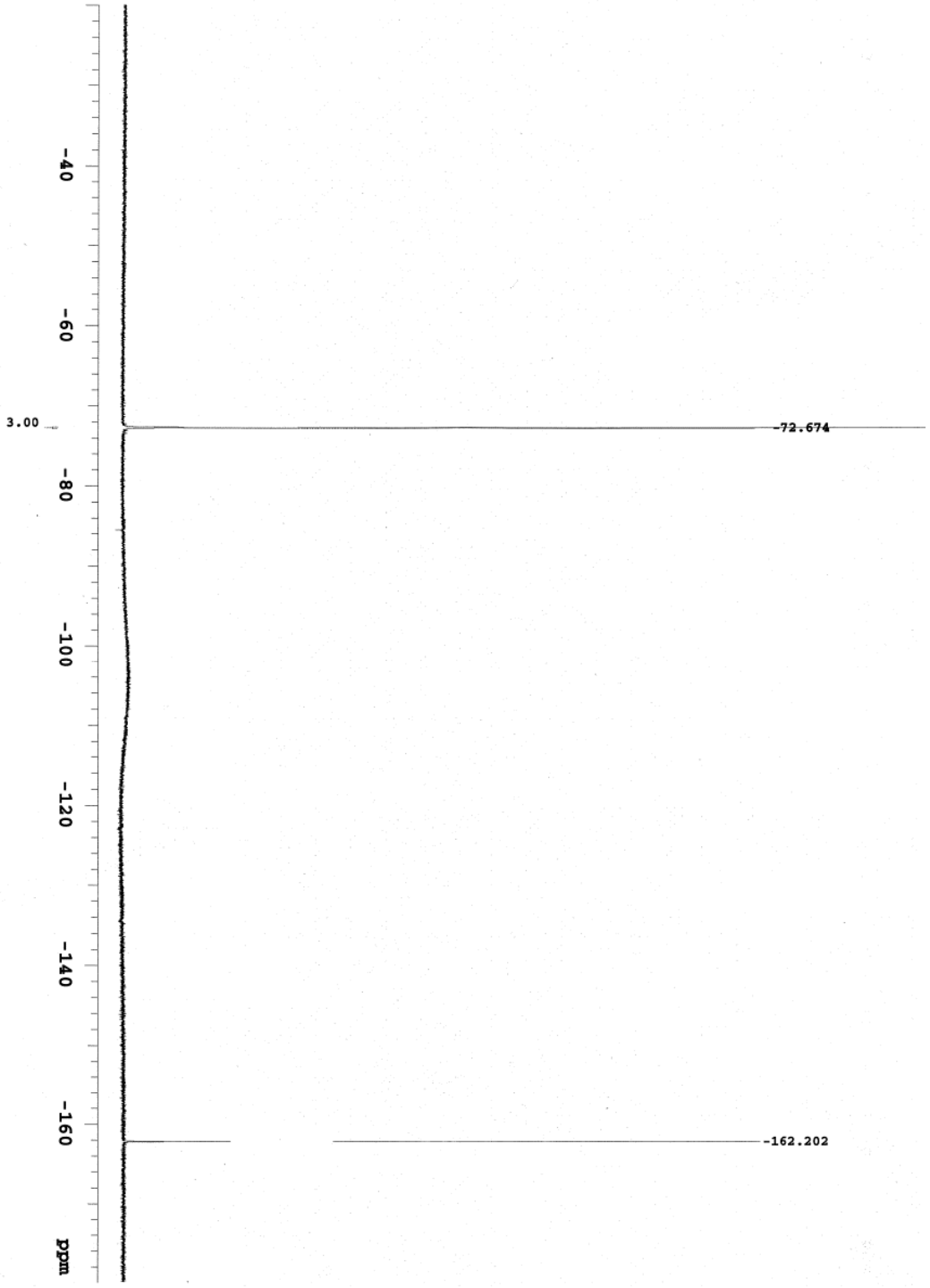


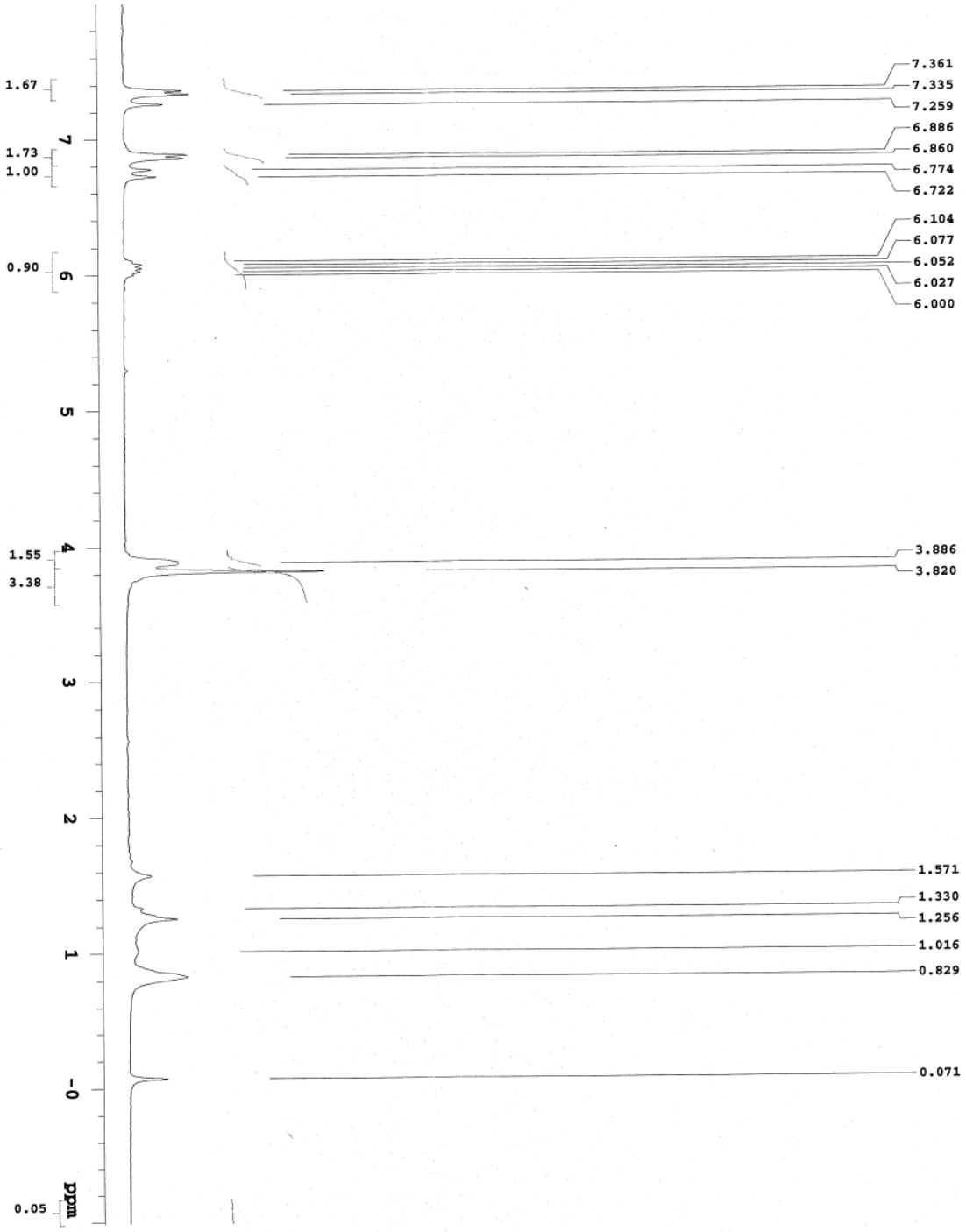

7.317
7.291
7.261
7.166
7.141
6.804
6.750
6.203
6.176
6.150
6.124
6.100
3.906
2.352
1.578
-0.001
1.87
1.79
1.00
1.01
2.16
3.14
8
7
6
5
4
3
2
1
0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

1-methoxy-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3e)

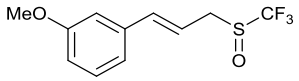


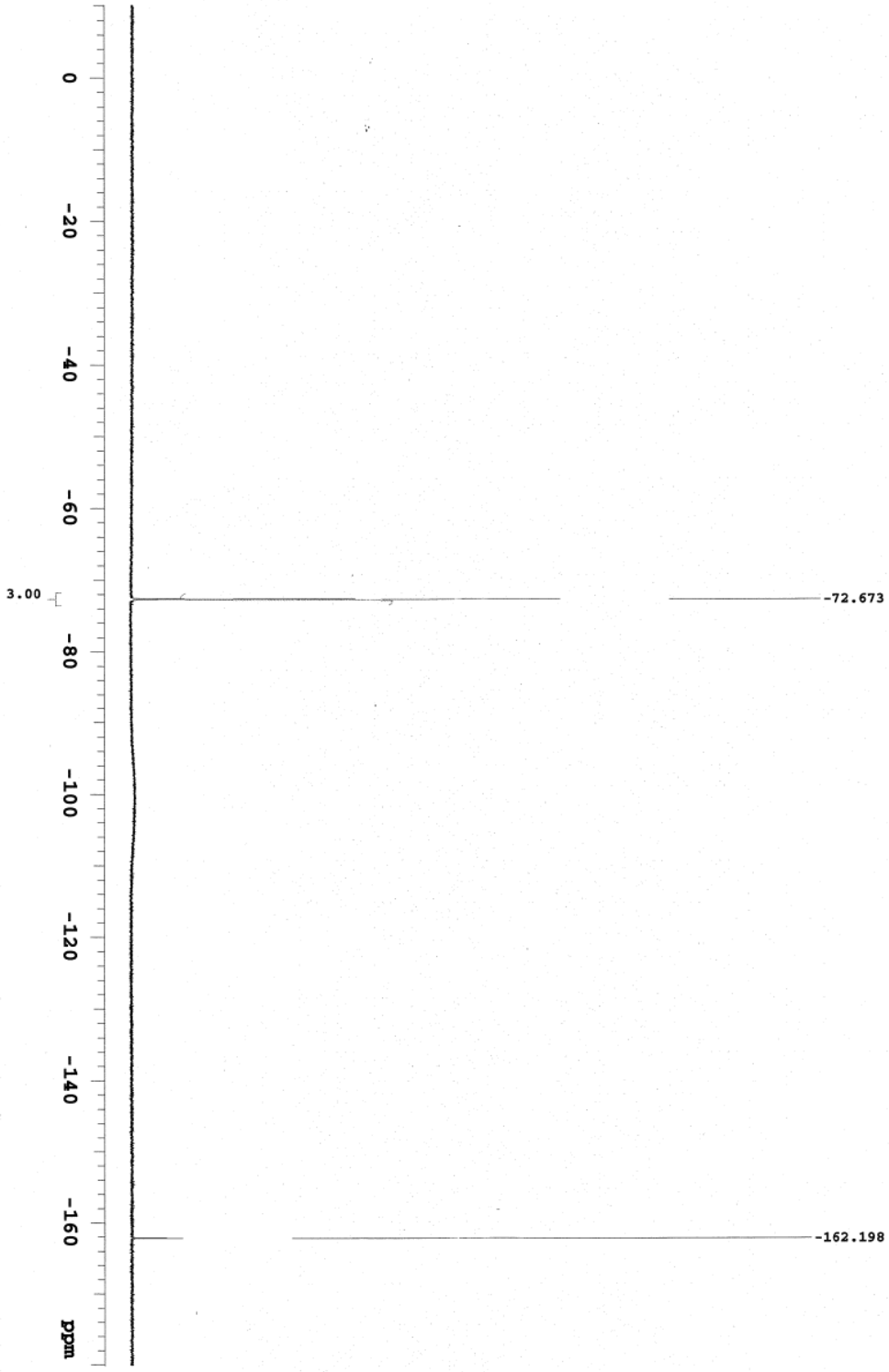


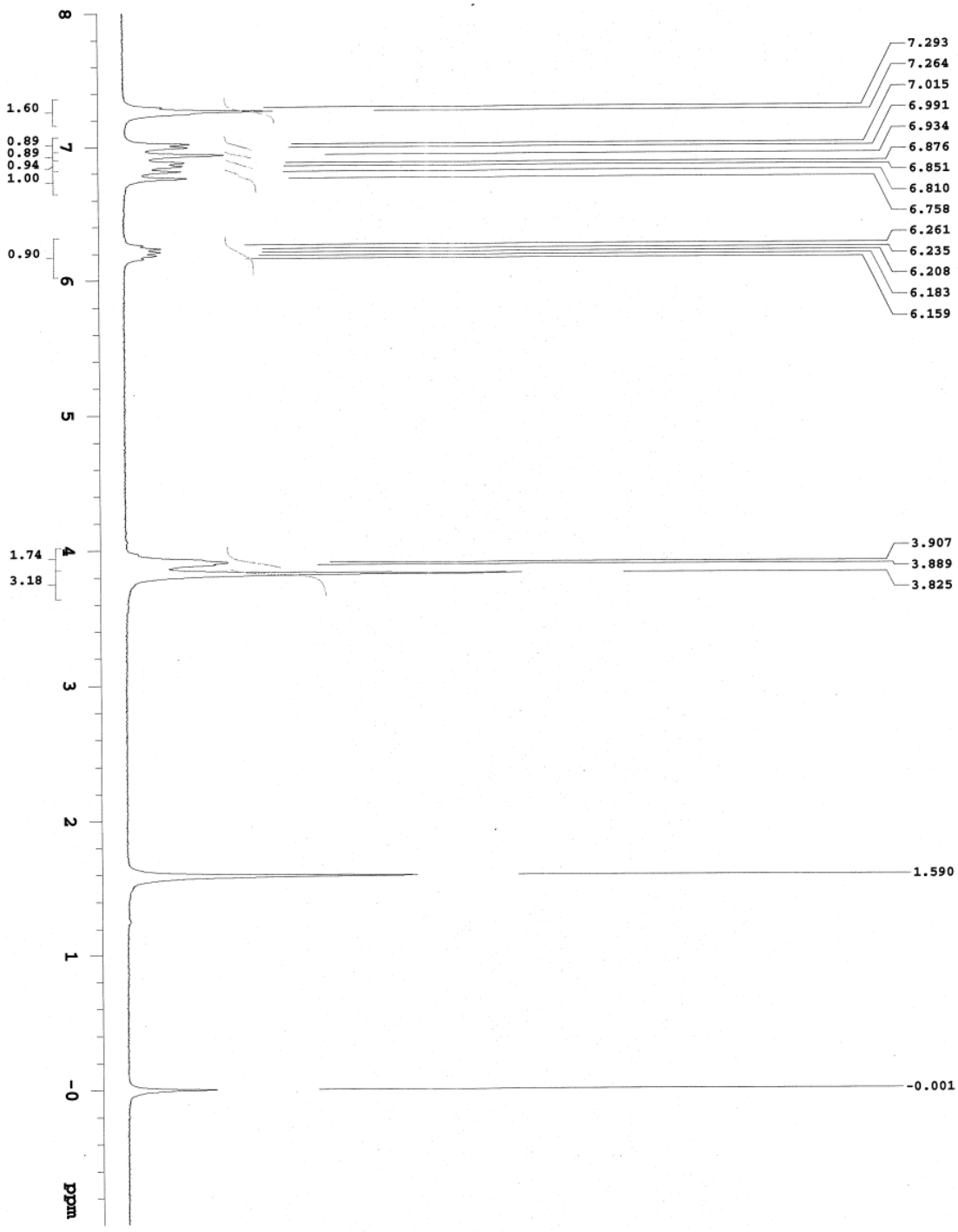

7.361
7.335
7.259
6.886
6.860
6.774
6.722
6.104
6.077
6.052
6.027
6.000
3.886
3.820
1.571
1.330
1.256
1.016
0.829
0.071
1.67
1.73
1.00
0.90
1.55
3.38
0.05
ppm

Copies of ^{19}F NMR and ^{1}H NMR

1-methoxy-3-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3f)

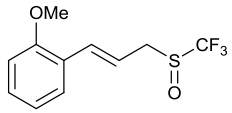


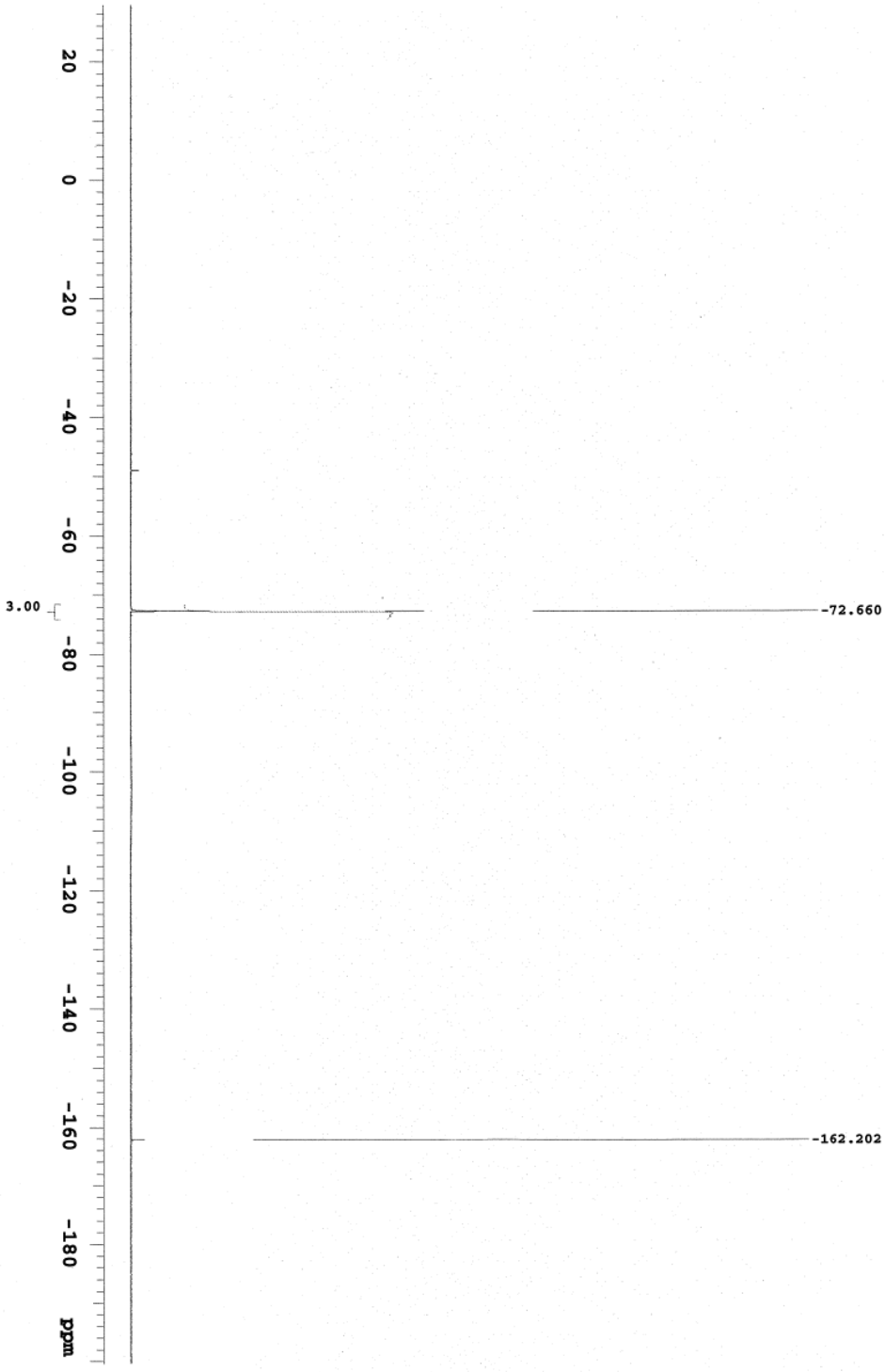


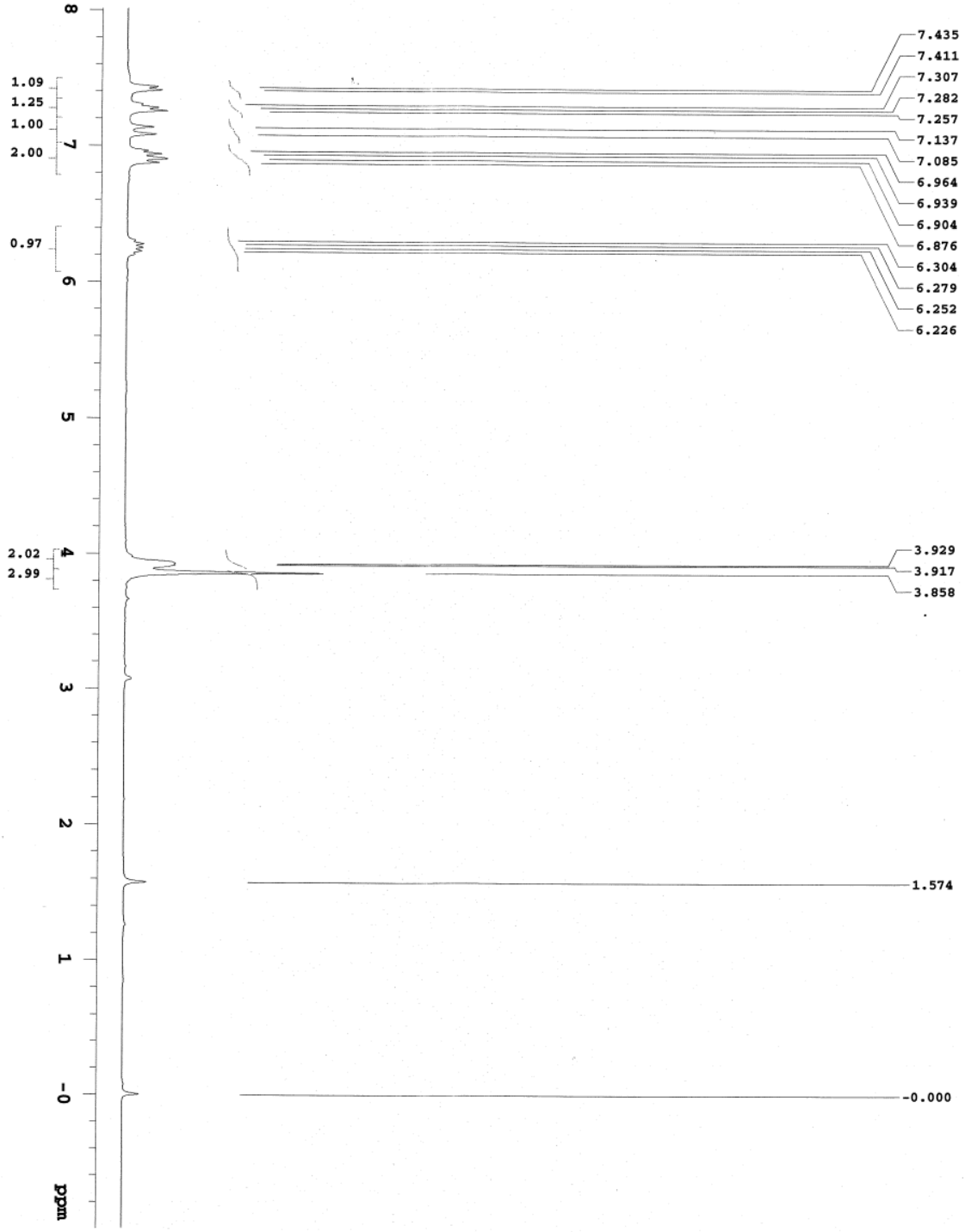

7.293
7.264
7.015
6.991
6.934
6.876
6.851
6.810
6.758
6.261
6.235
6.208
6.183
6.159
3.907
3.889
3.825
1.590
-0.001
1.60
0.89
0.89
0.94
1.00
0.90
1.74
3.18
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

***(E)*-1-methoxy-2-(3-((trifleoromethyl)sulfinyl)prop-1-en-1yl)benzene (3g)**

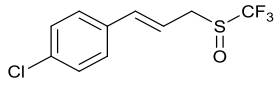


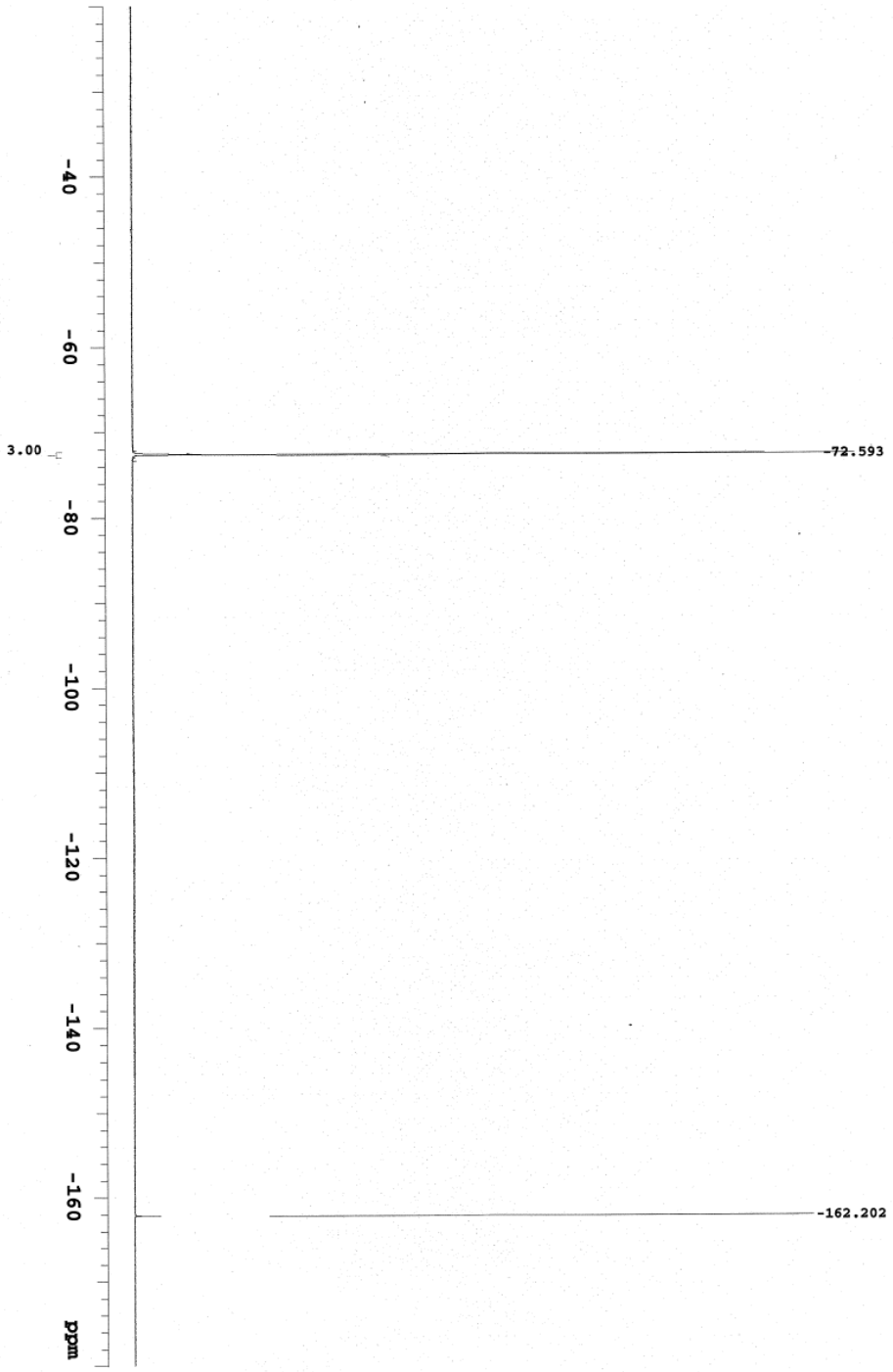


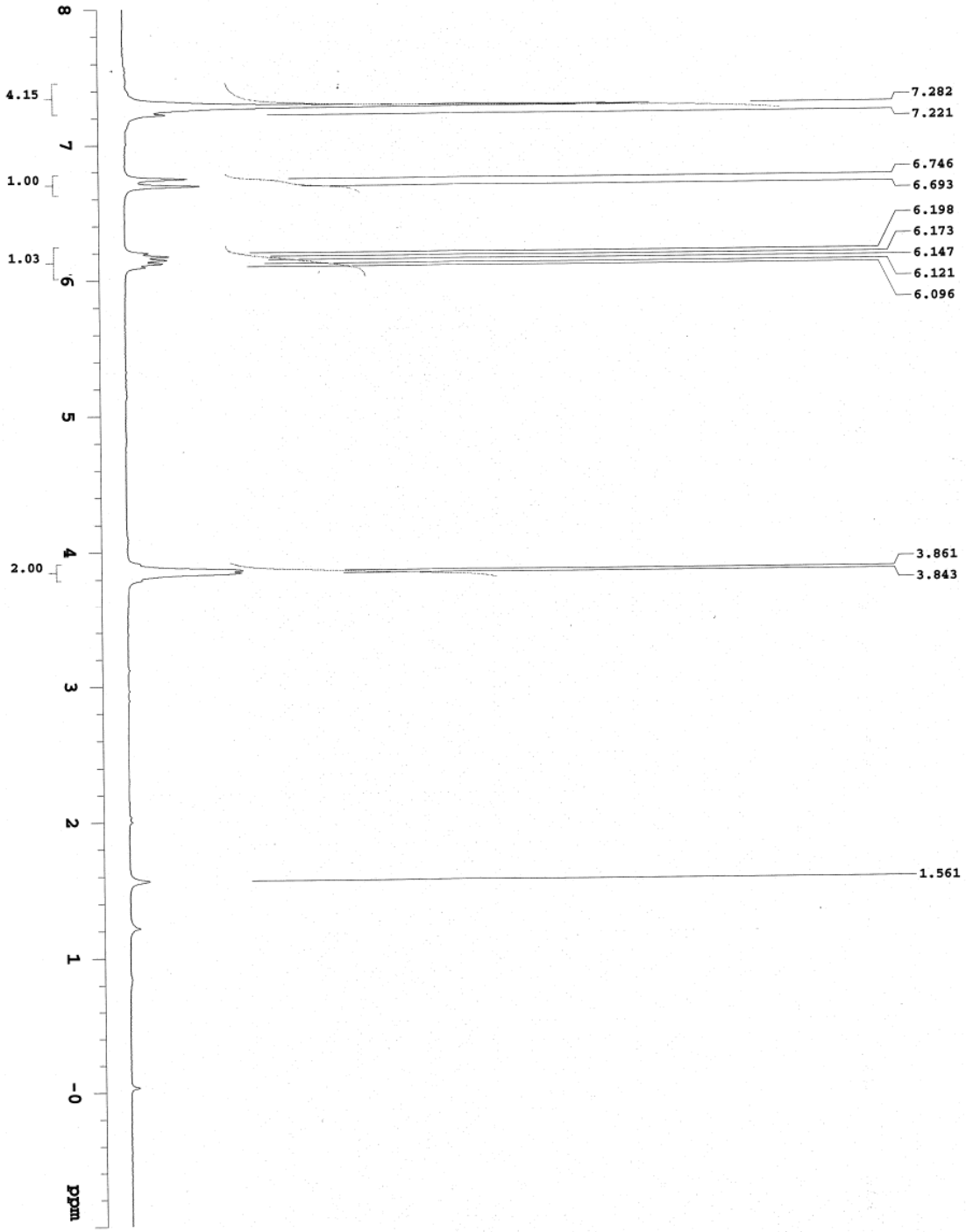

7.435
7.411
7.307
7.282
7.257
7.137
7.085
6.964
6.939
6.904
6.876
6.304
6.279
6.252
6.226
3.929
3.917
3.858
1.574
-0.000
1.09
1.25
1.00
2.00
0.97
2.02
2.99
8
7
6
5
4
3
2
1
0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

1-Chloro-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3h)

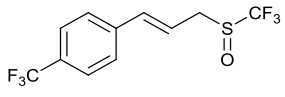


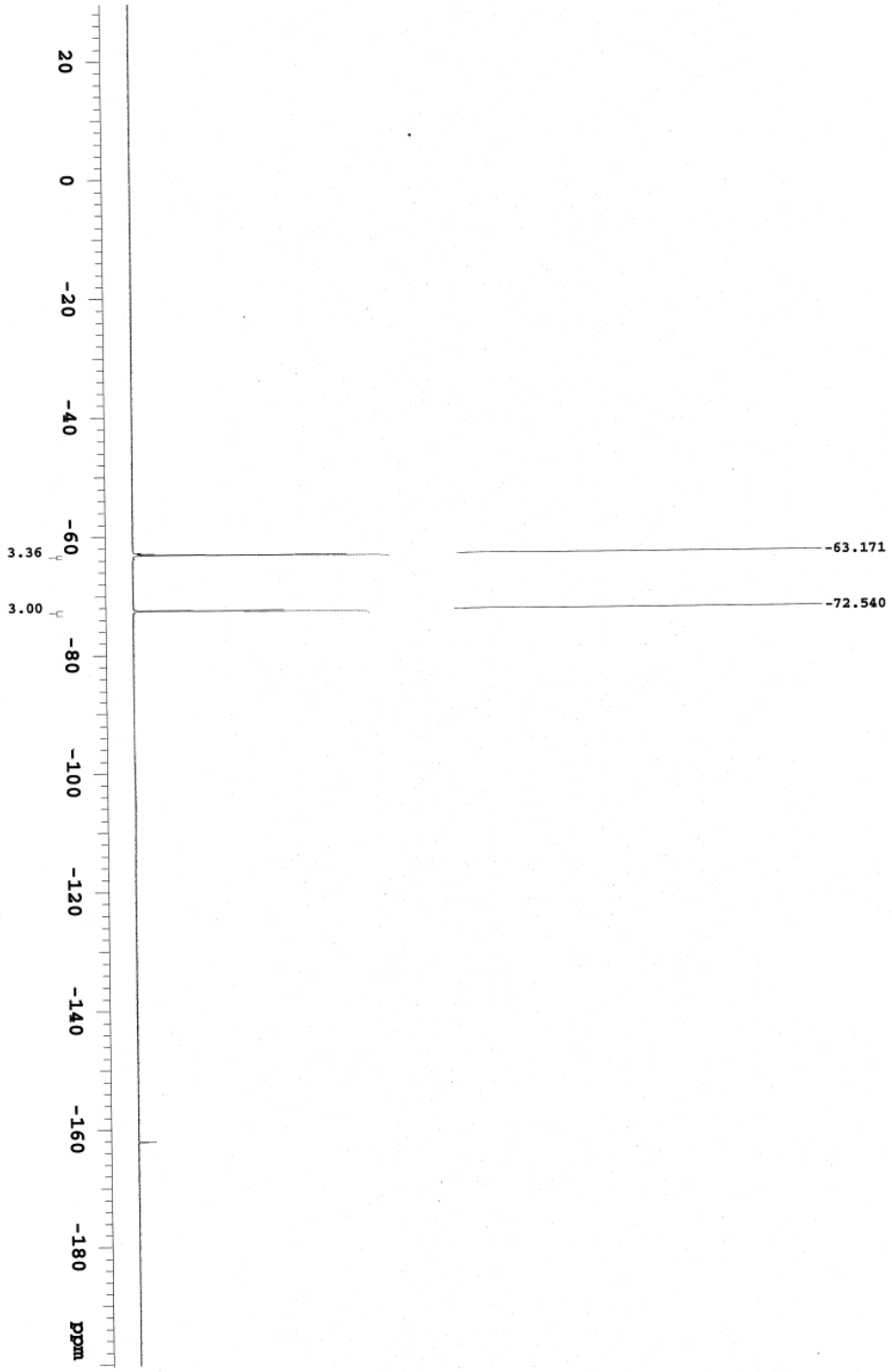


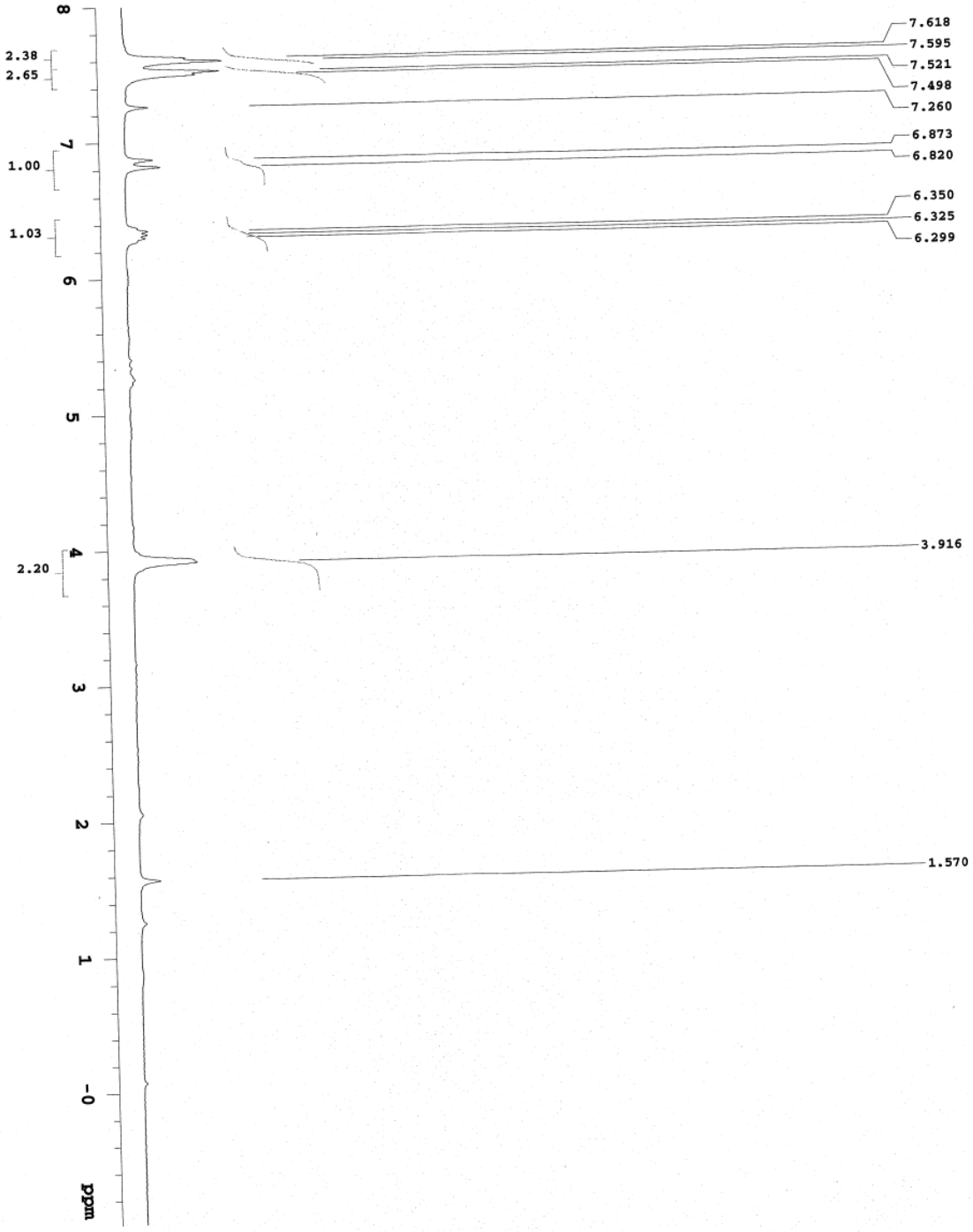

4.15
1.00
1.03
2.00
8
7
6
5
4
3
2
1
0
ppm
7.282
7.221
6.746
6.693
6.198
6.173
6.147
6.121
6.096
3.861
3.843
1.561

Copies of ^{19}F NMR and ^{1}H NMR

1-(Trifluoromethyl)-4-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3i)

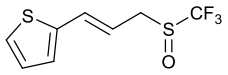


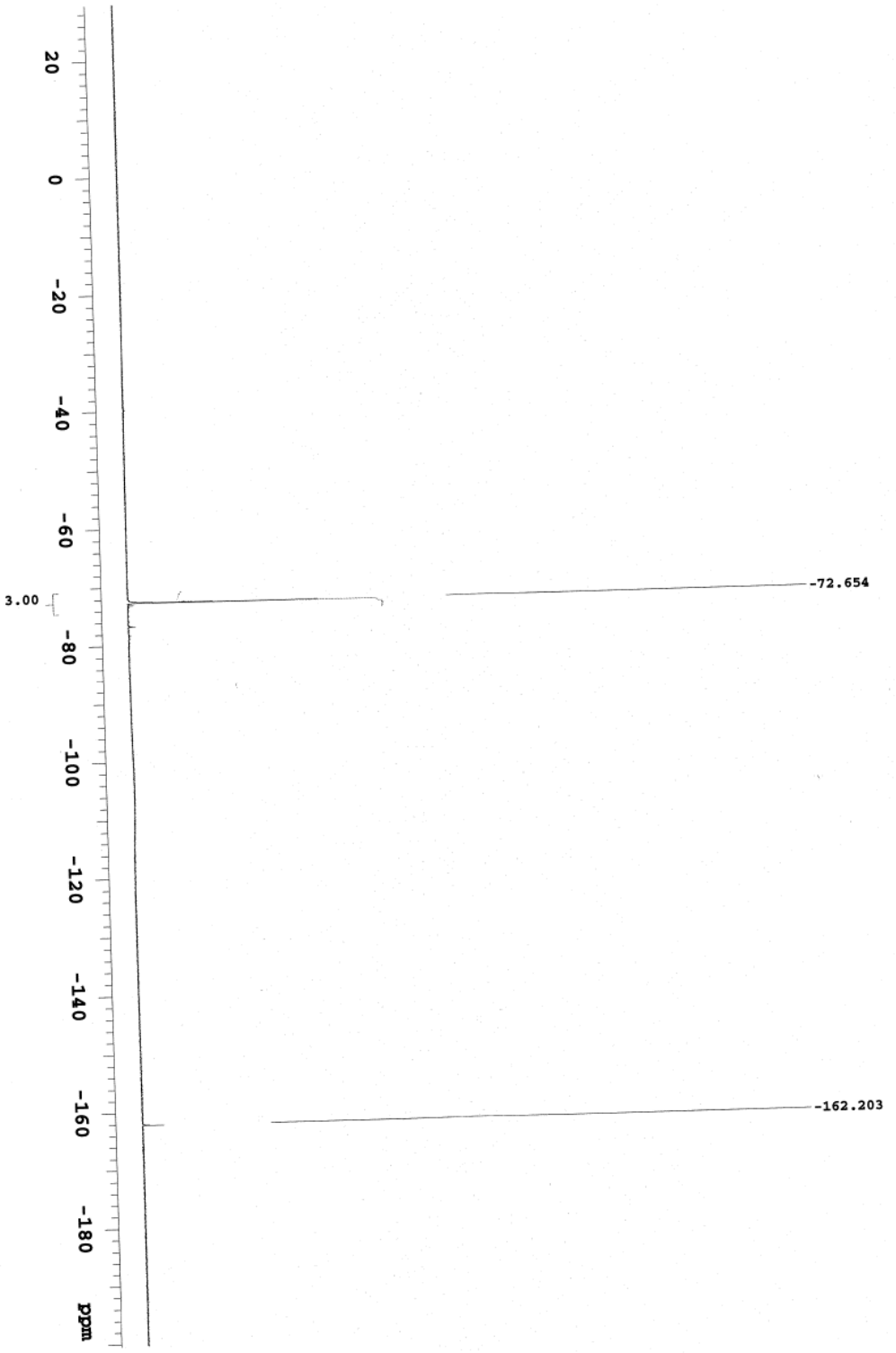


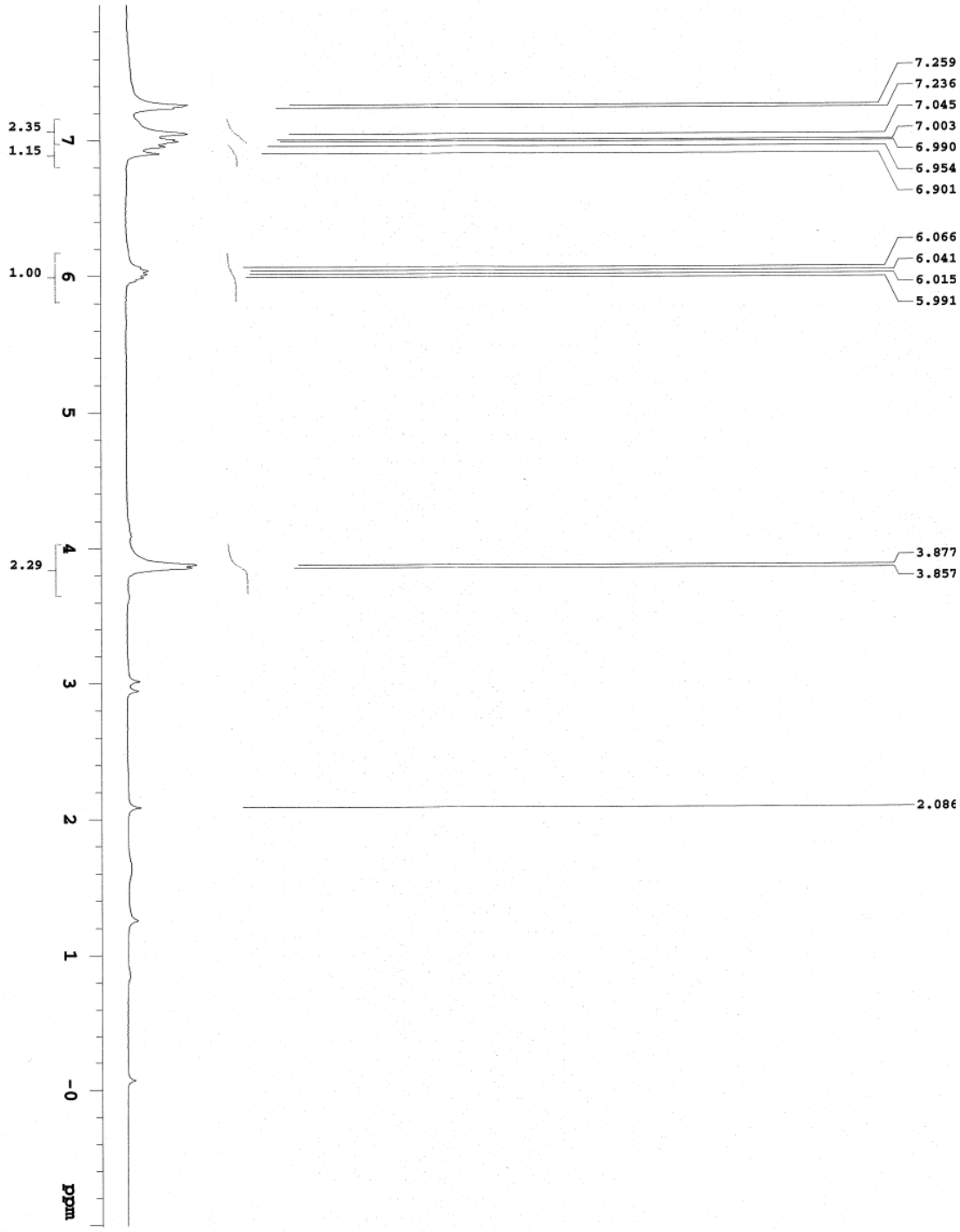

7.618
7.595
7.521
7.498
7.260
6.873
6.820
6.350
6.325
6.299
3.916
1.570
2.38
2.65
1.00
1.03
2.20
8
7
6
5
4
3
2
1
0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

2-((*E*)-3-(trifluoromethylsulfinyl)prop-1-enyl)thiophene (3j)

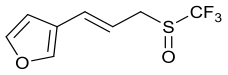


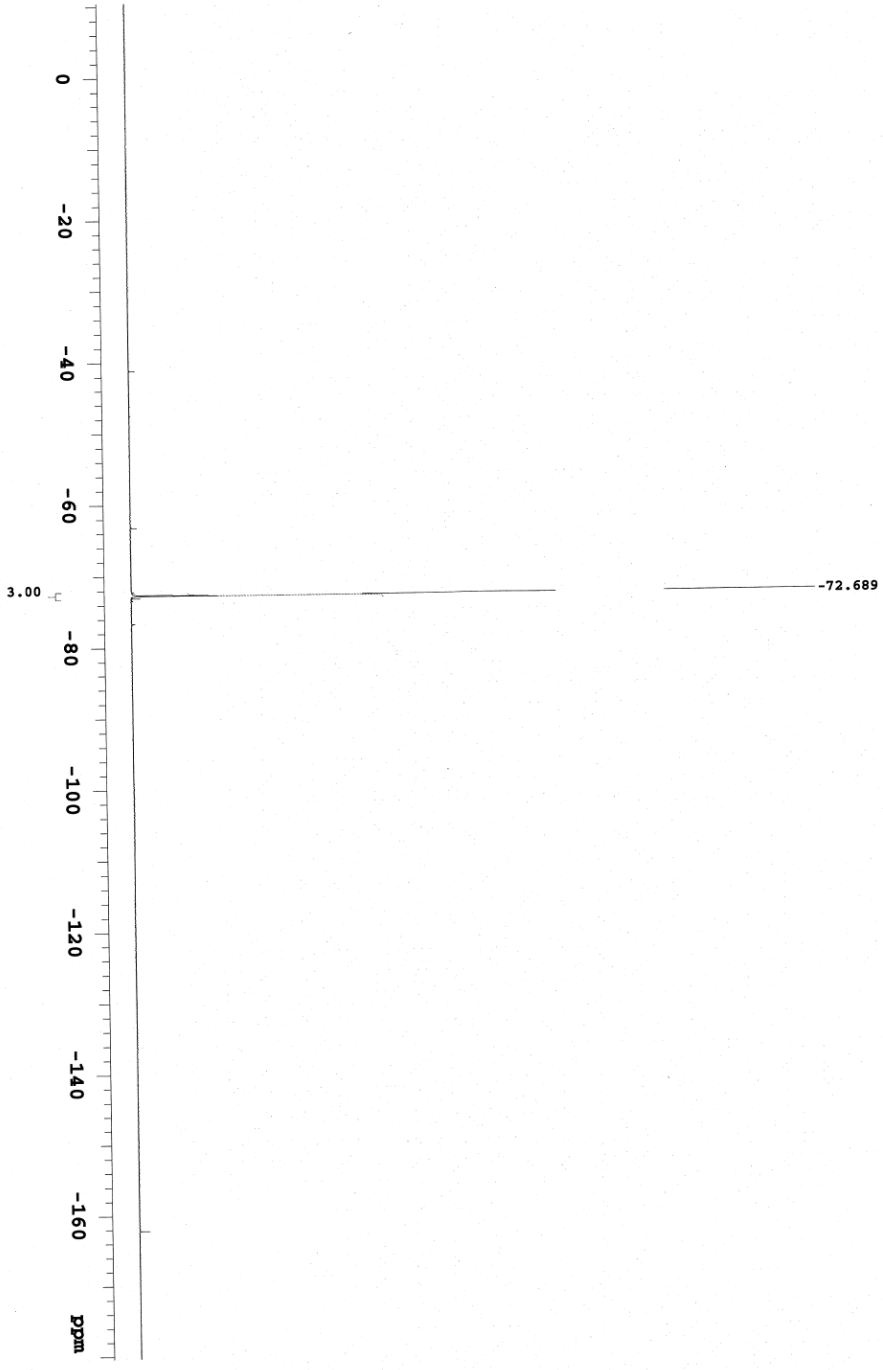


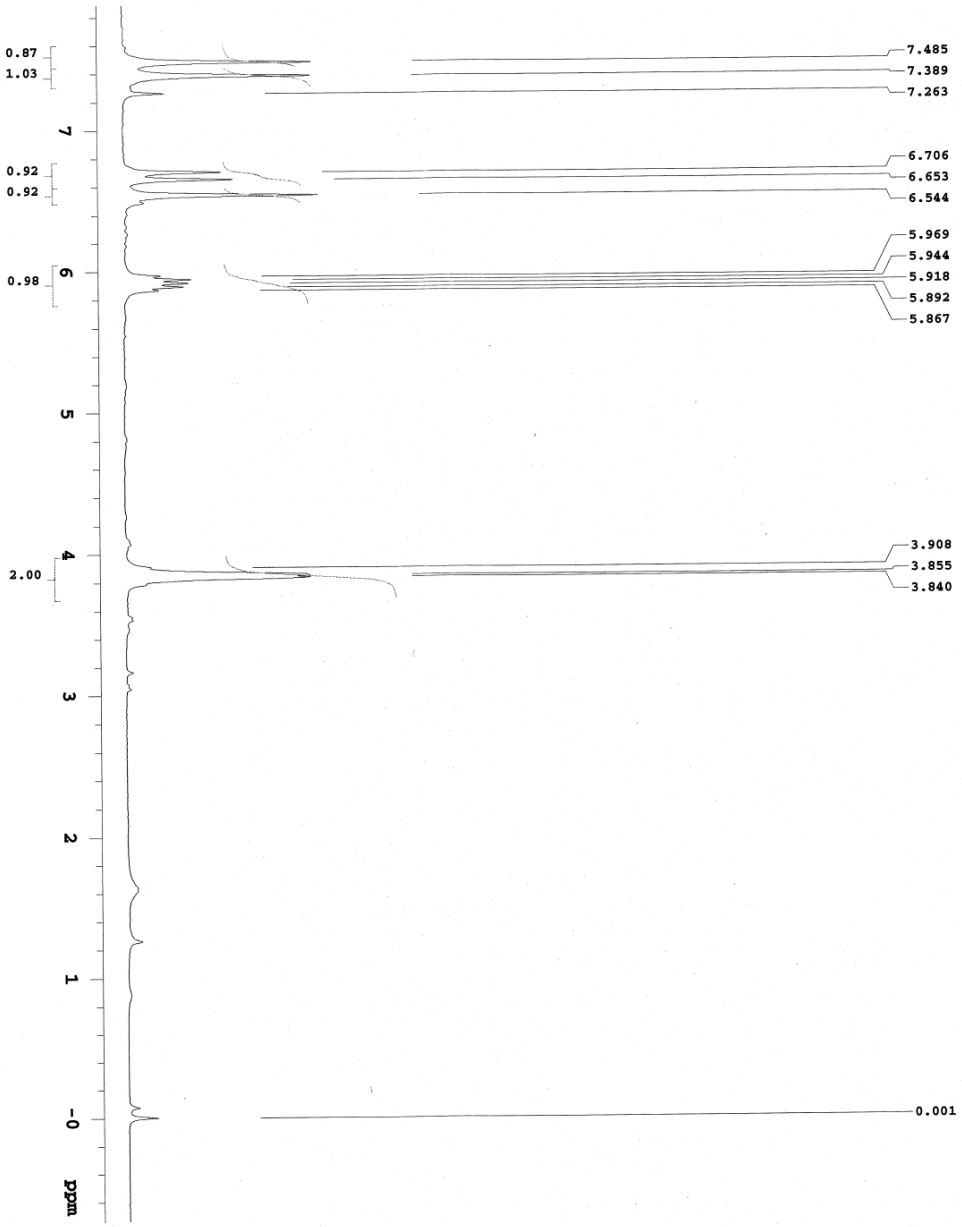

7.259
7.236
7.045
7.003
6.990
6.954
6.901
6.066
6.041
6.015
5.991
3.877
3.857
2.086
2.35
1.15
1.00
2.29
7
6
5
4
3
2
1
-0
ppm

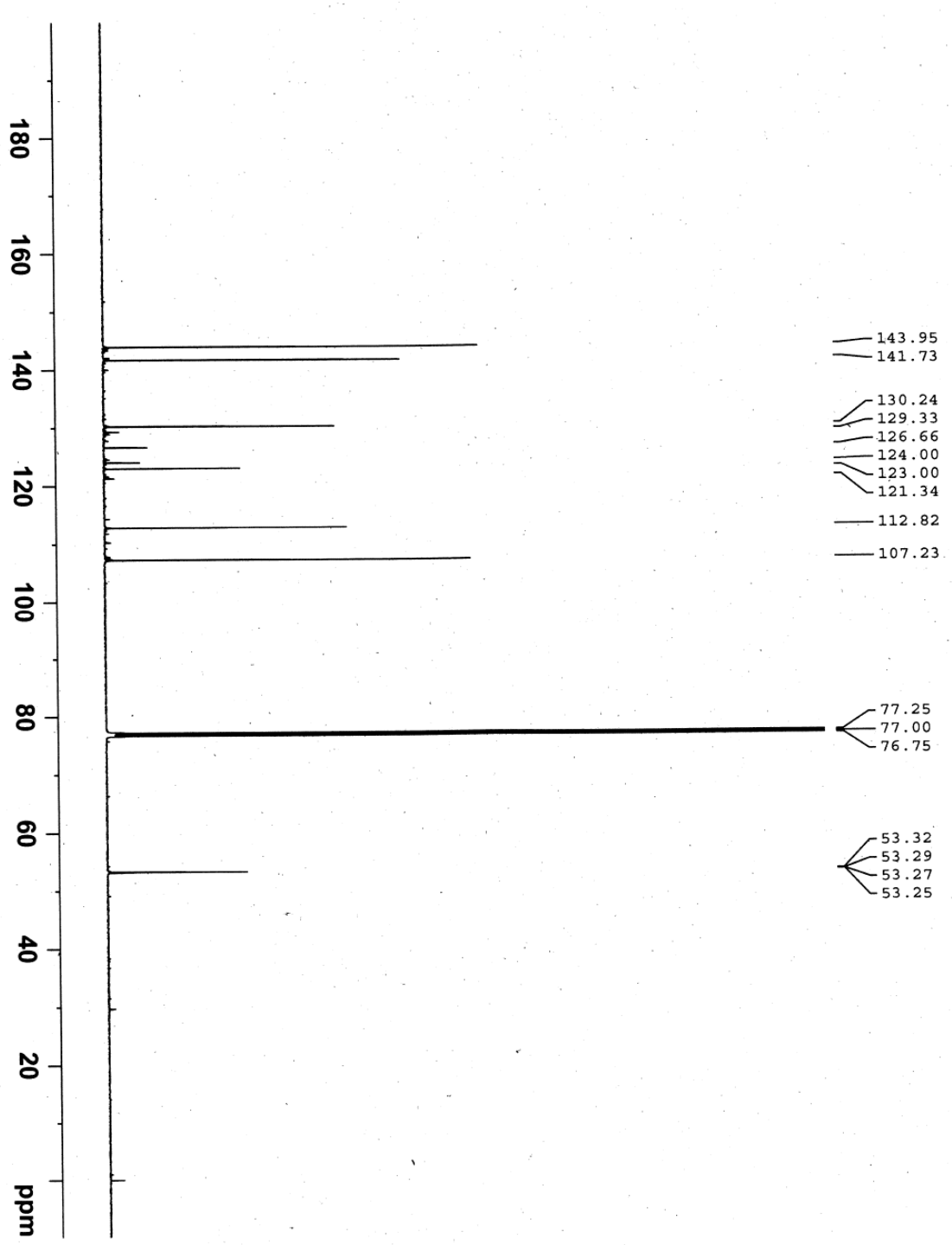
Copies of ^{19}F NMR, ^{1}H NMR and ^{13}C NMR

3-((*E*)-3-(Trifluoromethylsulfinyl)prop-1-enyl)furan (3k)



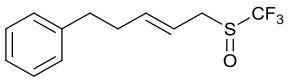


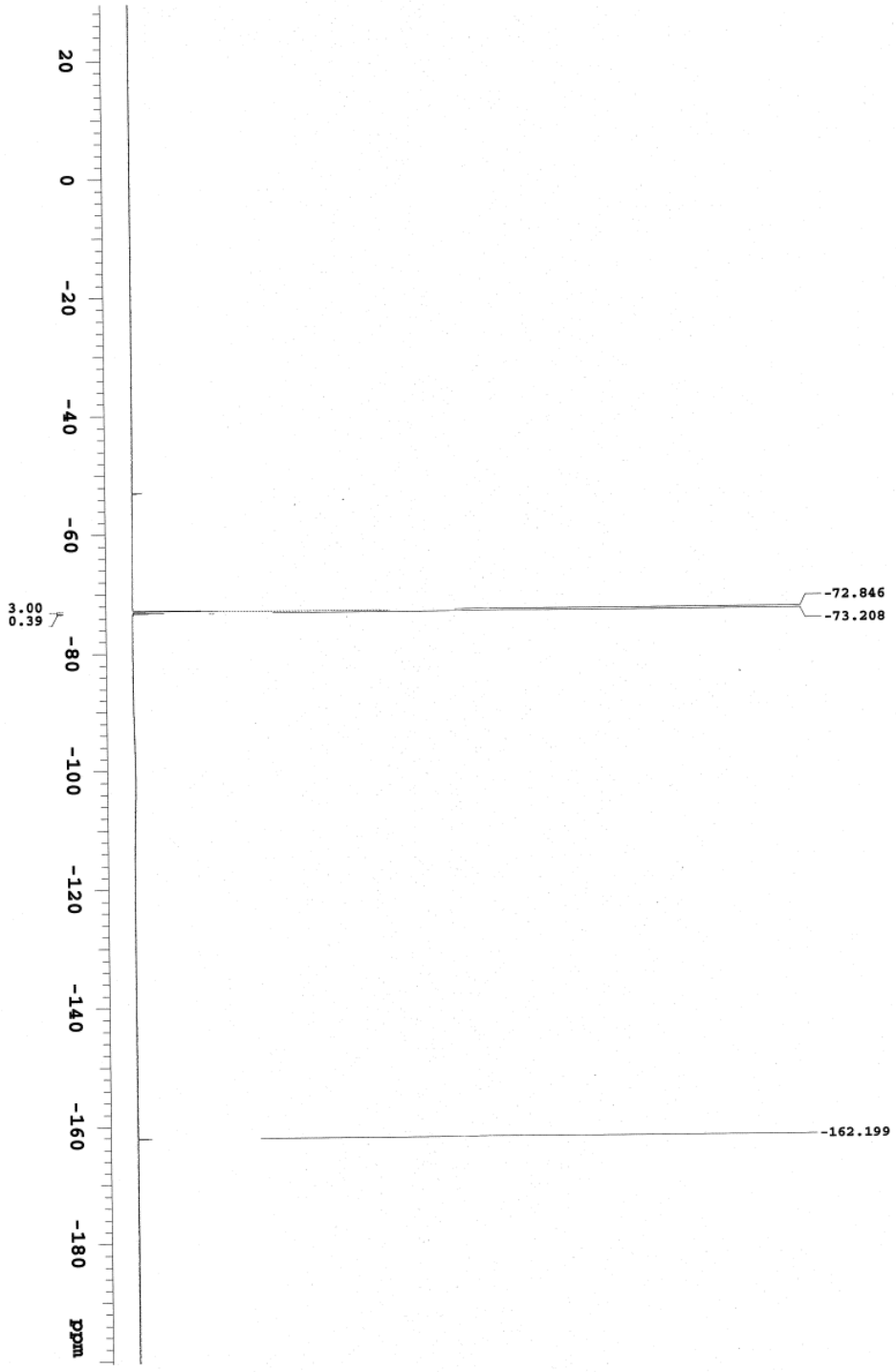

0.87
1.03
0.92
0.92
0.98
2.00
7.485
7.389
7.263
6.706
6.653
6.544
5.969
5.944
5.918
5.892
5.867
3.908
3.855
3.840
0.001
ppm

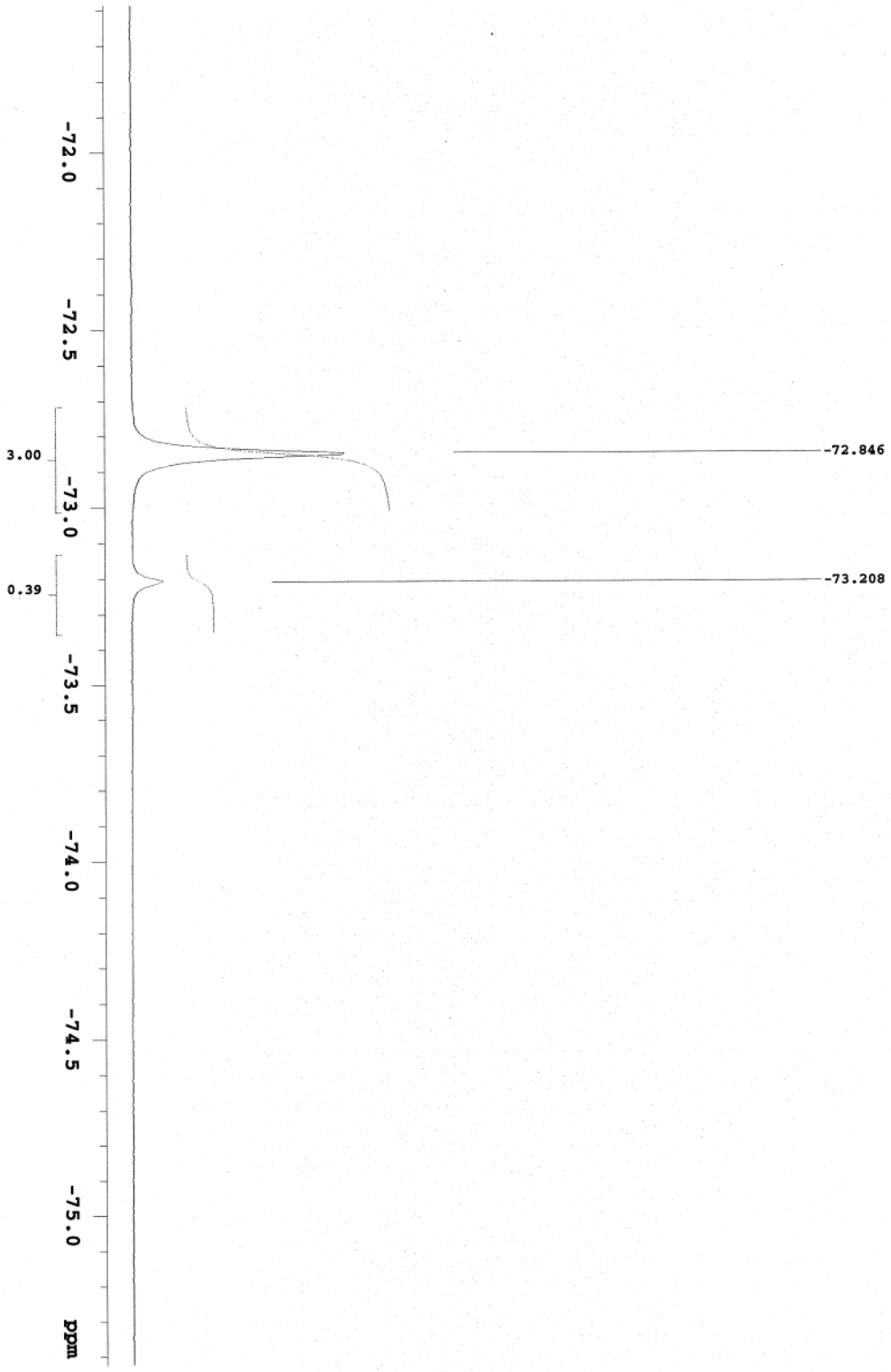

180
160
140
120
100
80
60
40
20
ppm
143.95
141.73
130.24
129.33
126.66
124.00
123.00
121.34
112.82
107.23
77.25
77.00
76.75
53.32
53.29
53.27
53.25

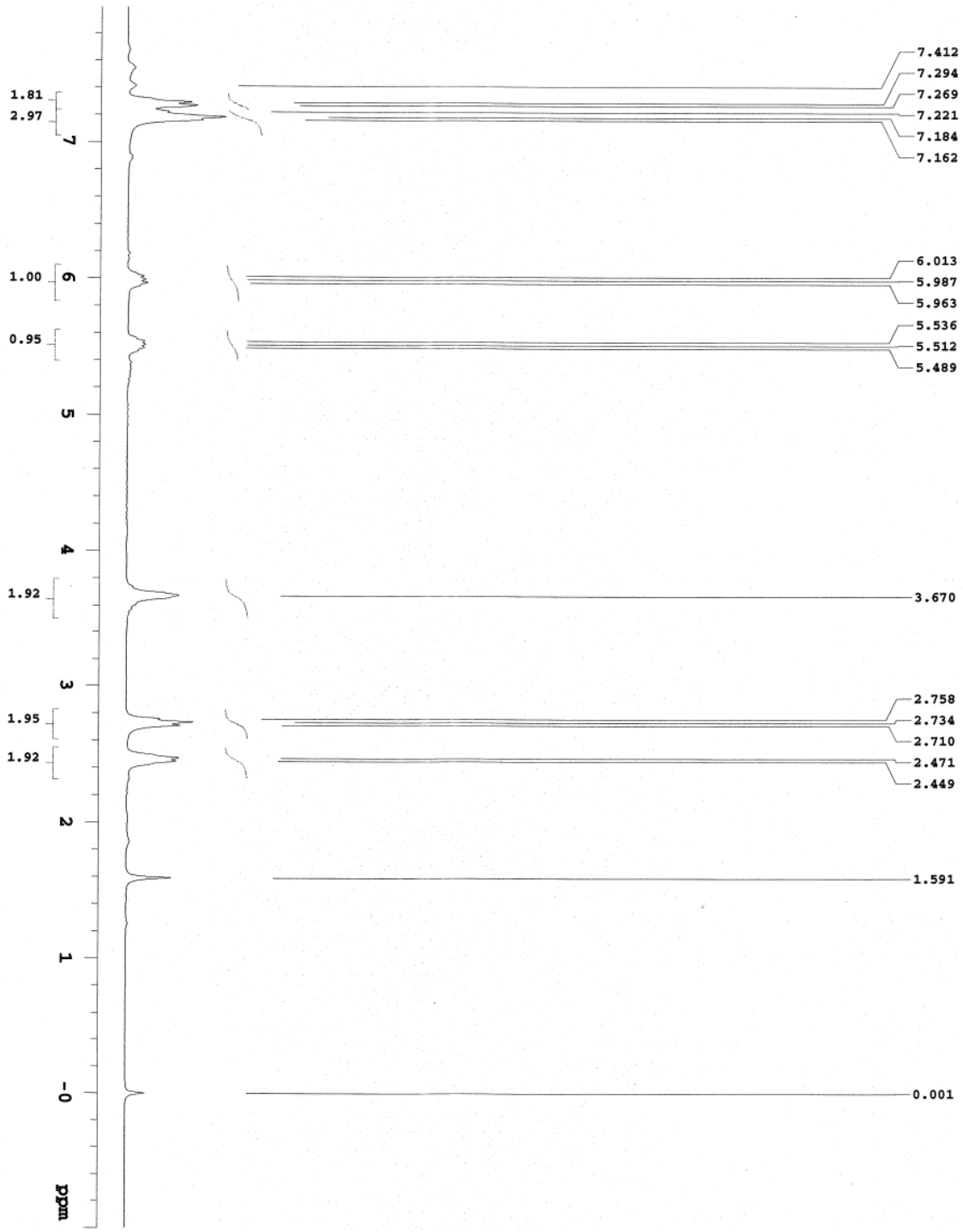
Copies of ^{19}F NMR and ^{1}H NMR

1-((*E*)-5-(trifluoromethylsulfinyl)pent-3-enyl)benzene (3l)



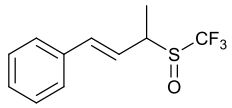


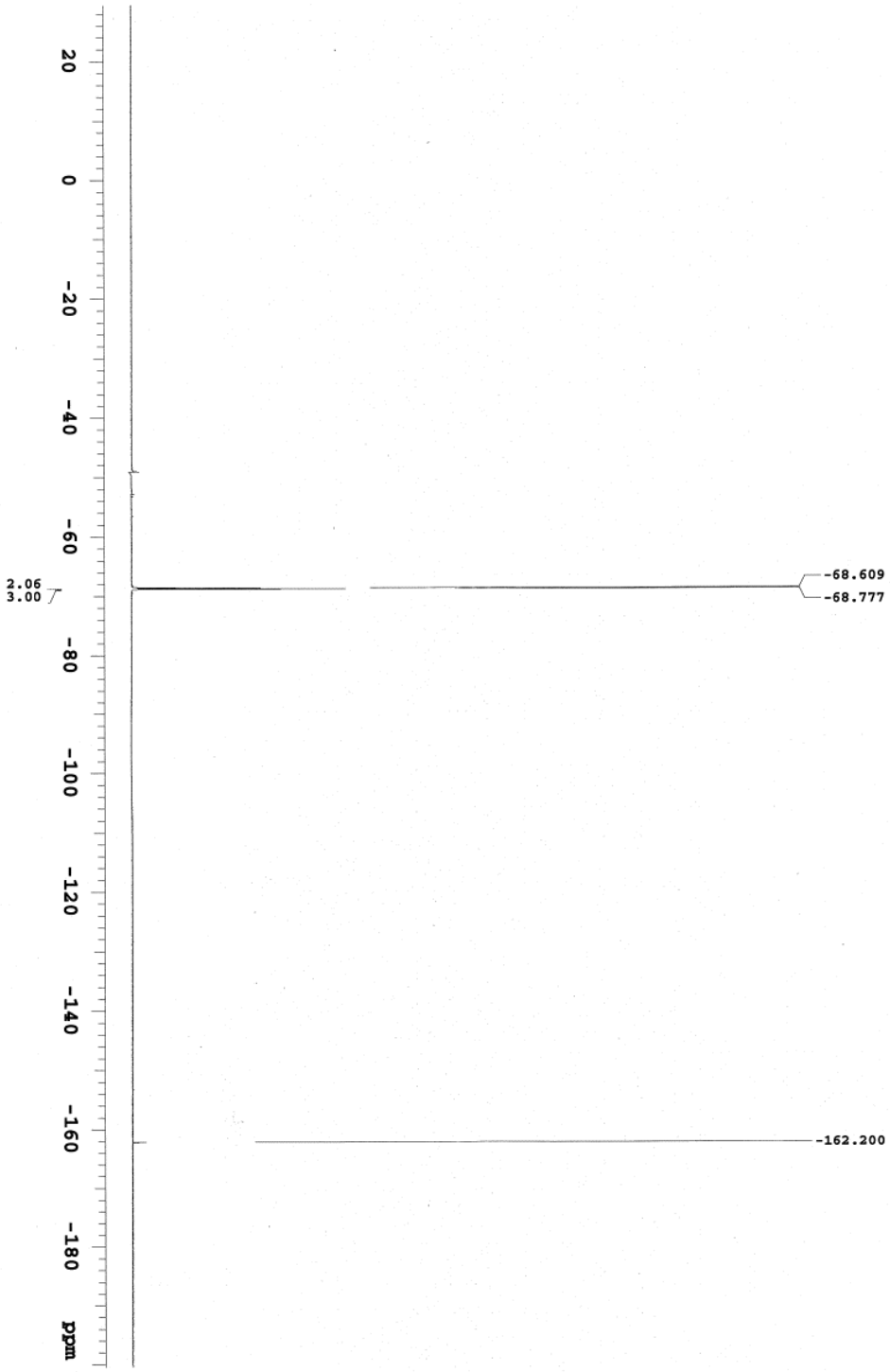

-72.0
-72.5
3.00
-73.0
0.39
-73.5
-74.0
-74.5
-75.0
ppm
-72.846
-73.208

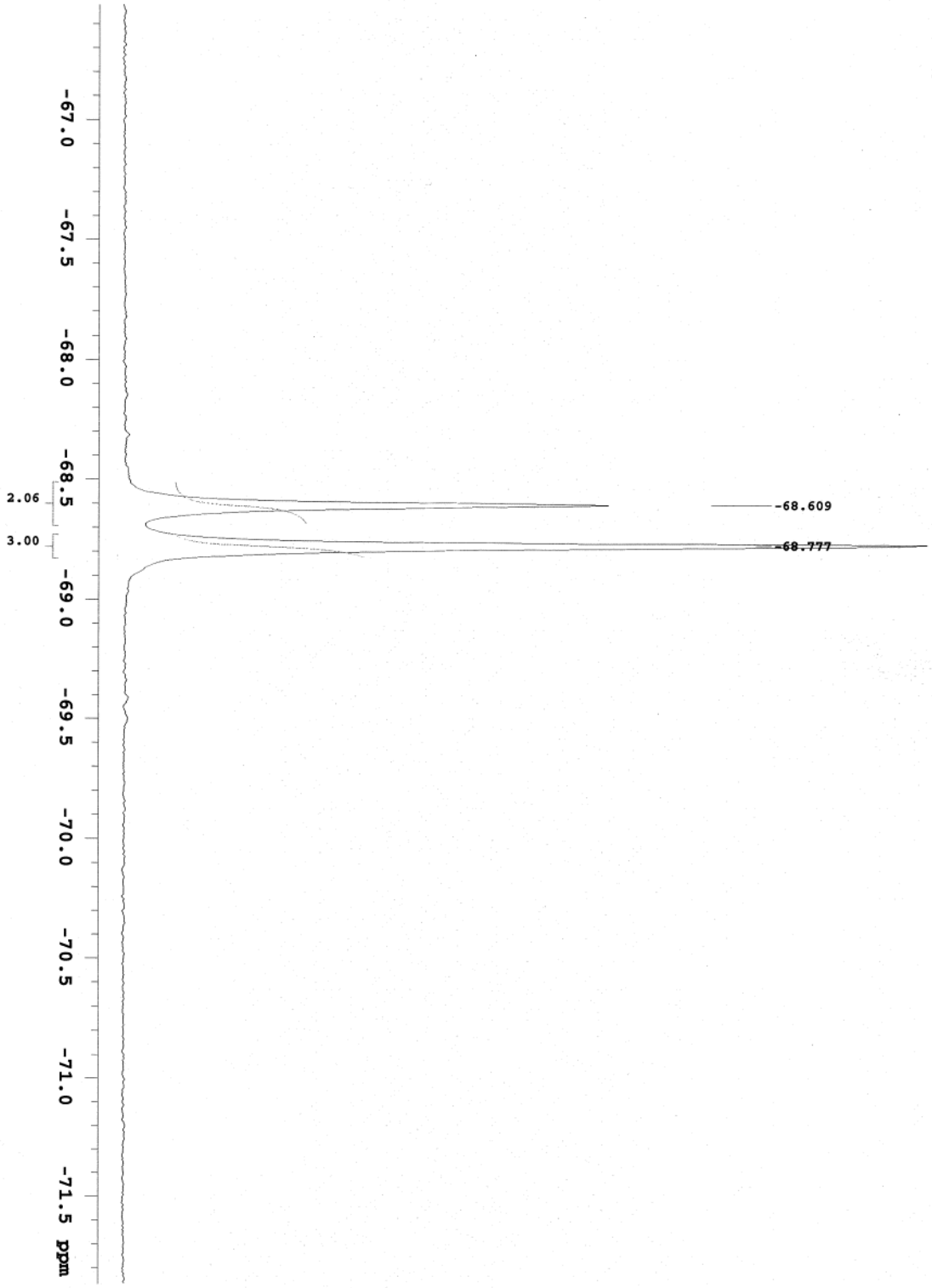

7.412
7.294
7.269
7.221
7.184
7.162
6.013
5.987
5.963
5.536
5.512
5.489
3.670
2.758
2.734
2.710
2.471
2.449
1.591
0.001
1.81
2.97
1.00
0.95
1.92
1.95
1.92
7
6
5
4
3
2
1
0
ppm

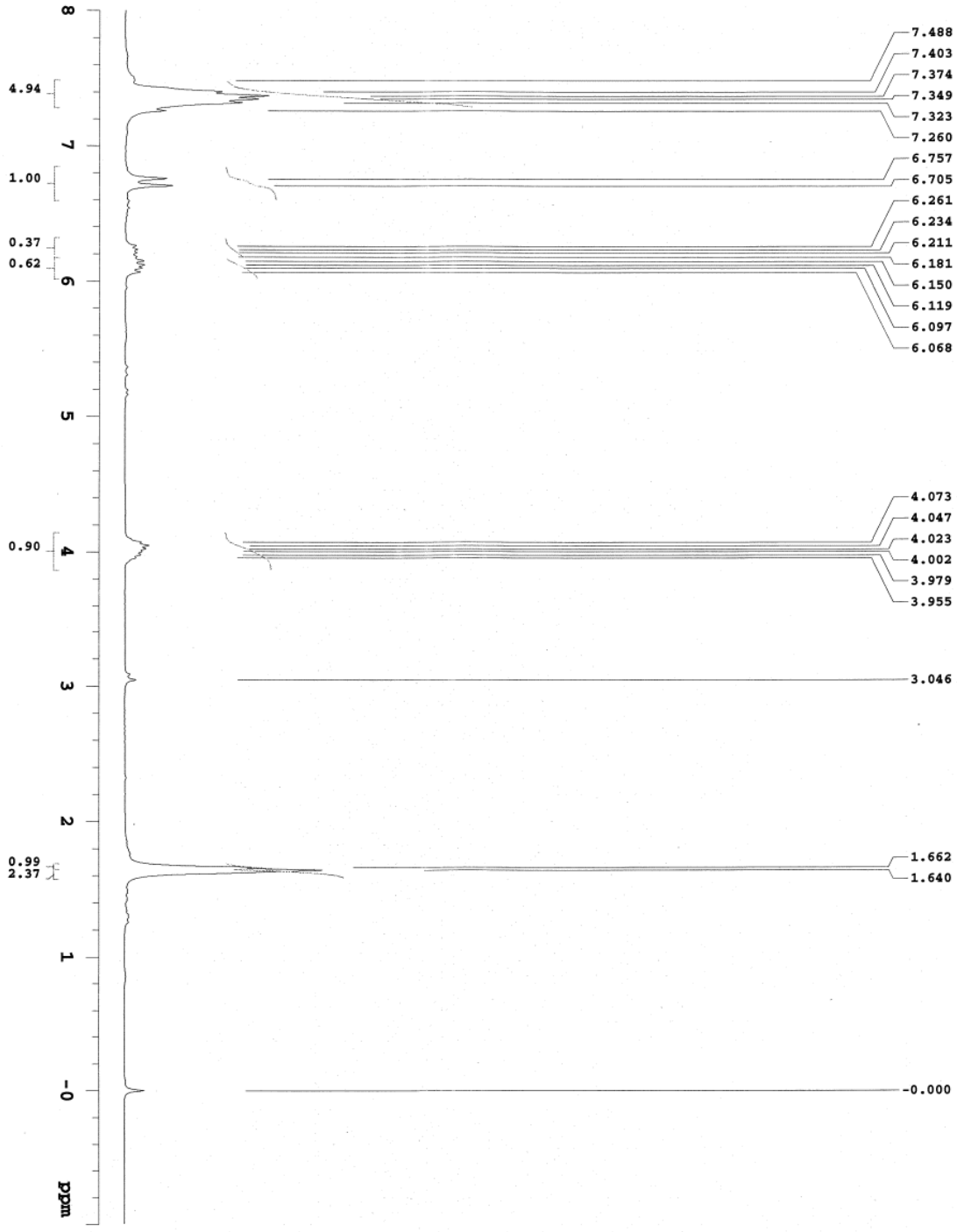
Copies of ^{19}F NMR and ^{1}H NMR

1-((*E*)-3-(trifluoromethylsulfinyl)but-1-enyl)benzene (3m)



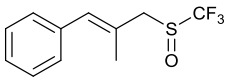


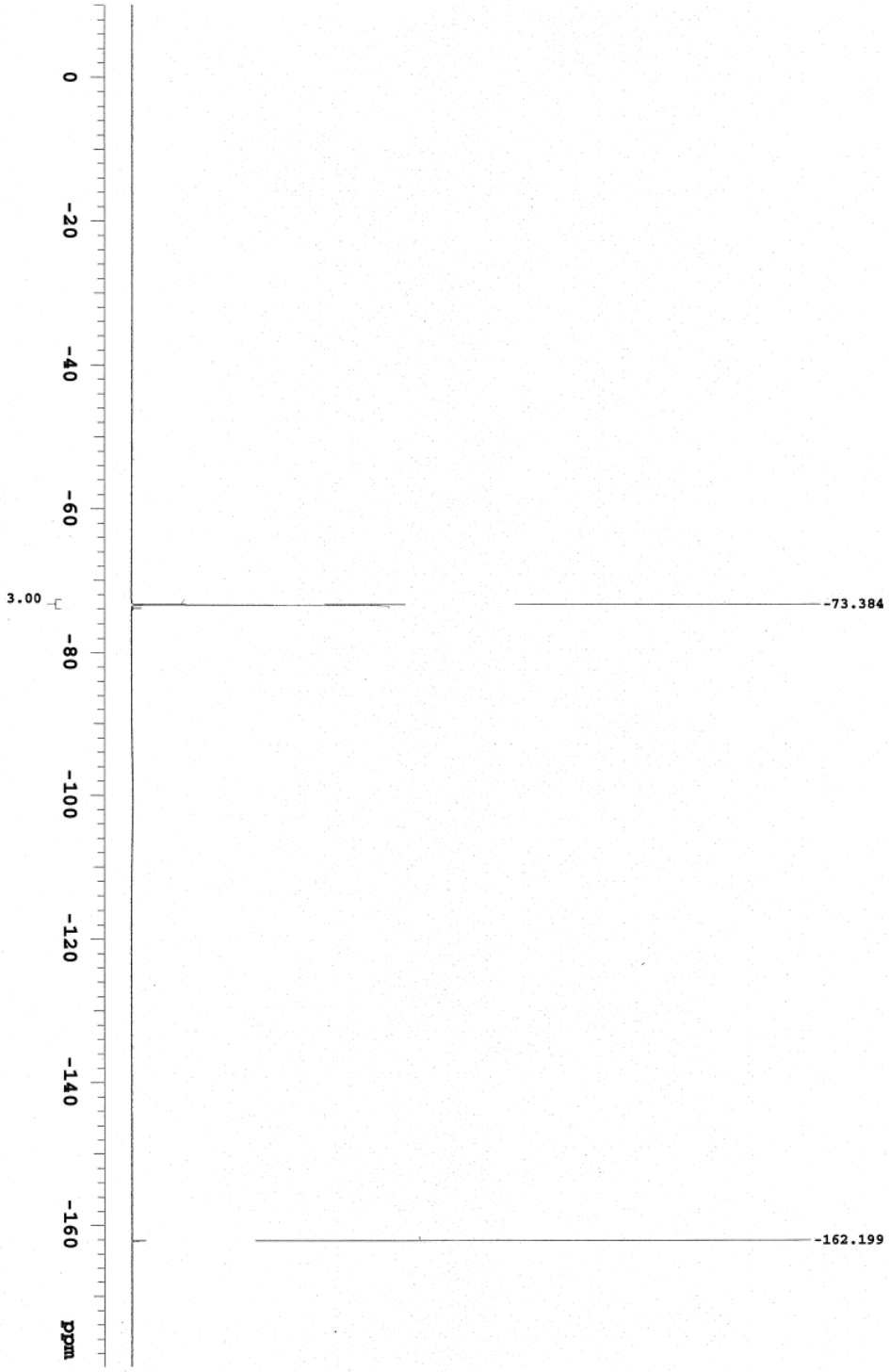

-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0
-71.5
ppm
2.06
3.00
-68.609
-68.777

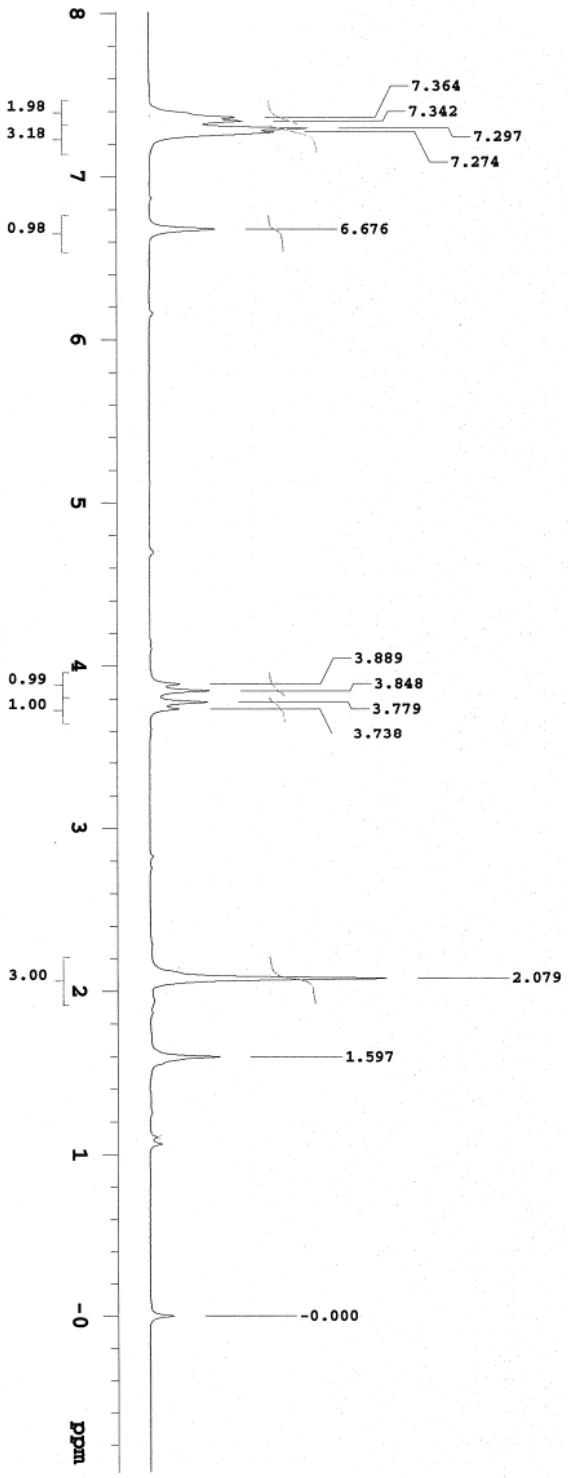

8
7
6
5
4
3
2
1
-0
ppm
4.94
1.00
0.37
0.62
0.90
0.99
2.37
7.488
7.403
7.374
7.349
7.323
7.260
6.757
6.705
6.261
6.234
6.211
6.181
6.150
6.119
6.097
6.068
4.073
4.047
4.023
4.002
3.979
3.955
3.046
1.662
1.640
-0.000

Copies of ^{19}F NMR and ^{1}H NMR

1-((*E*)-2-methyl-3-(trifluoromethylsulfinyl)prop-1-enyl)benzene (3n)

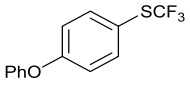


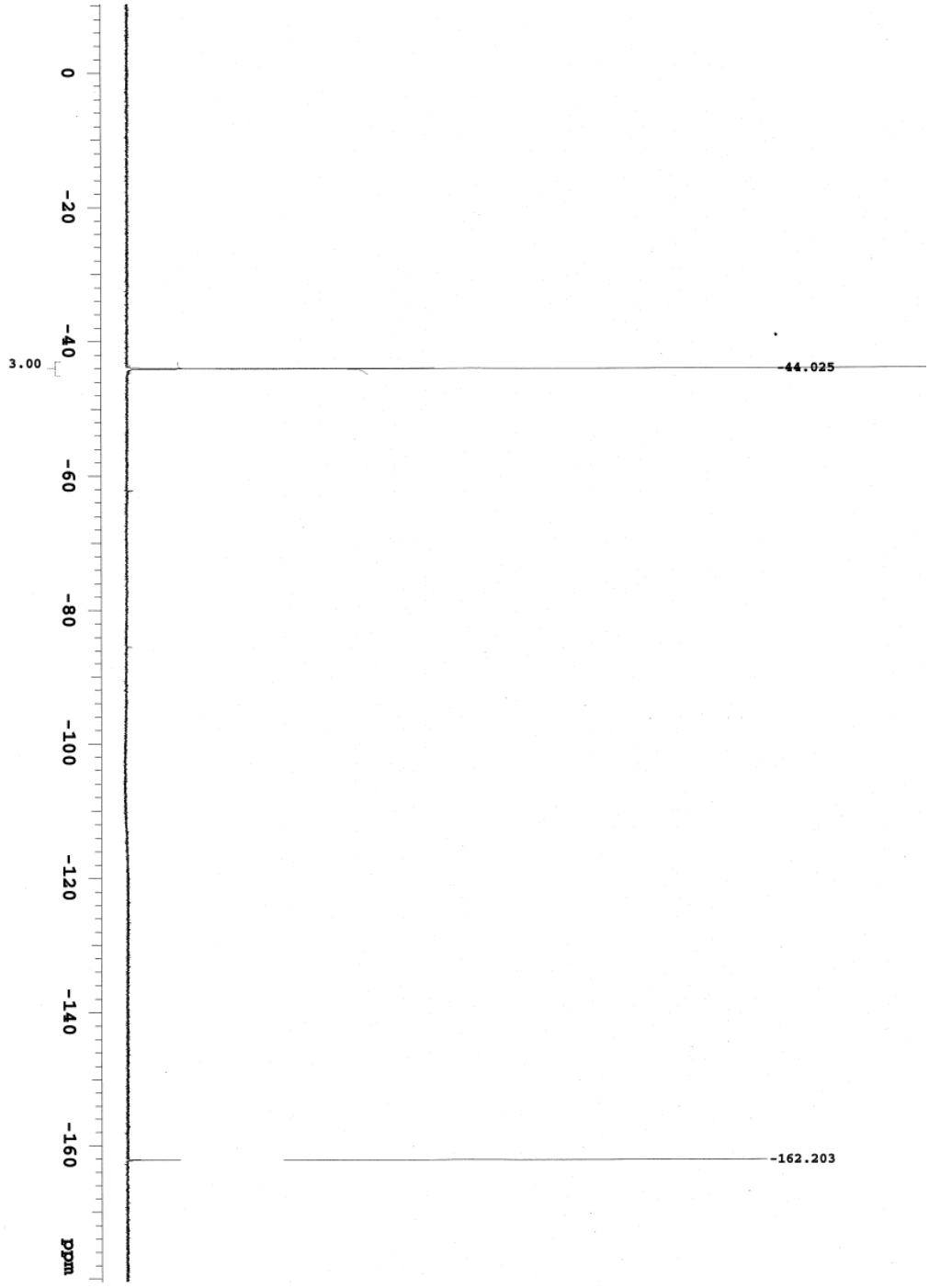


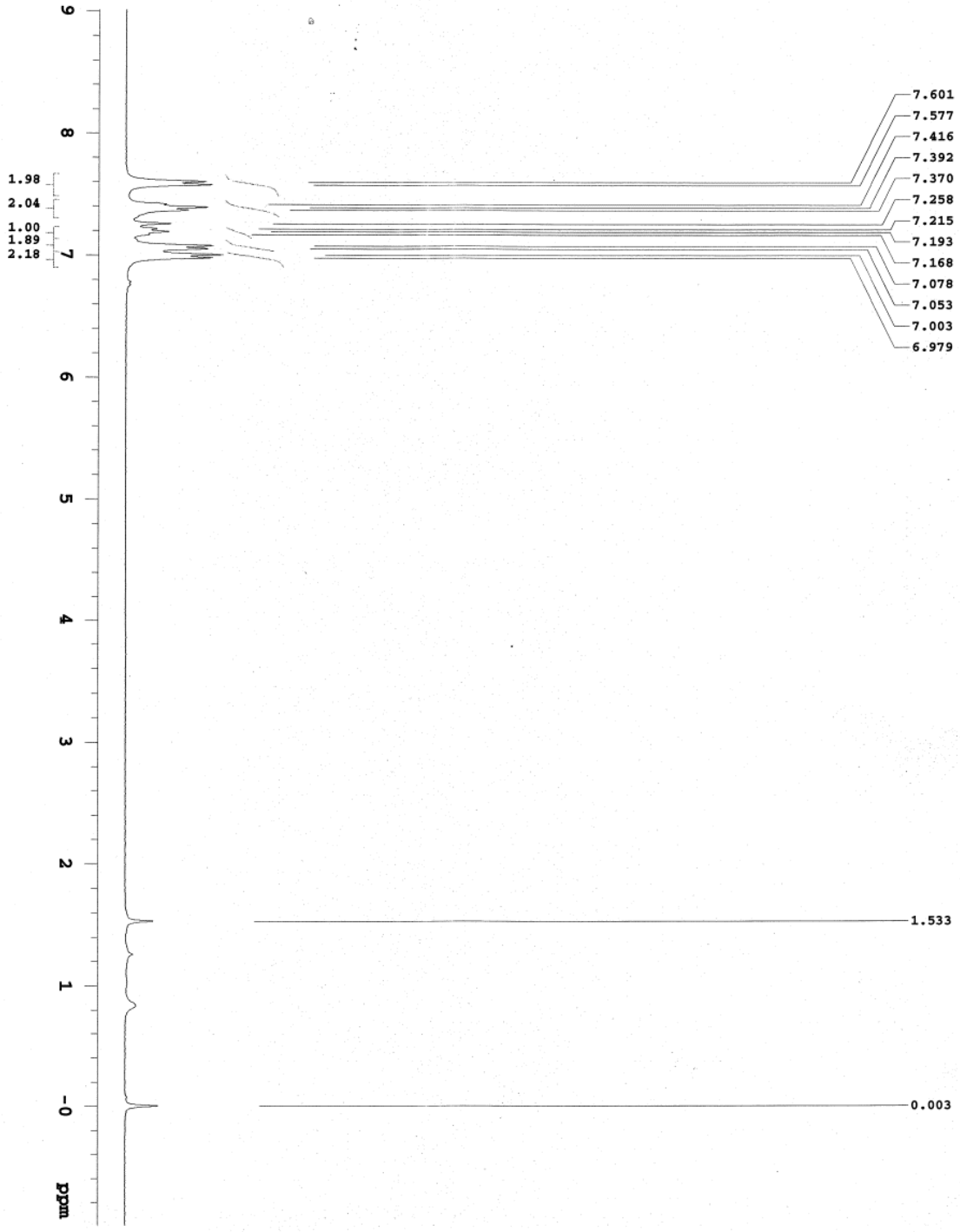

7.364
7.342
7.297
7.274
6.676
3.889
3.848
3.779
3.738
2.079
1.597
-0.000
1.98
3.18
0.98
0.99
1.00
3.00
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

4-Phenoxy-1-(trifluoromethylthio)benzene (5a)

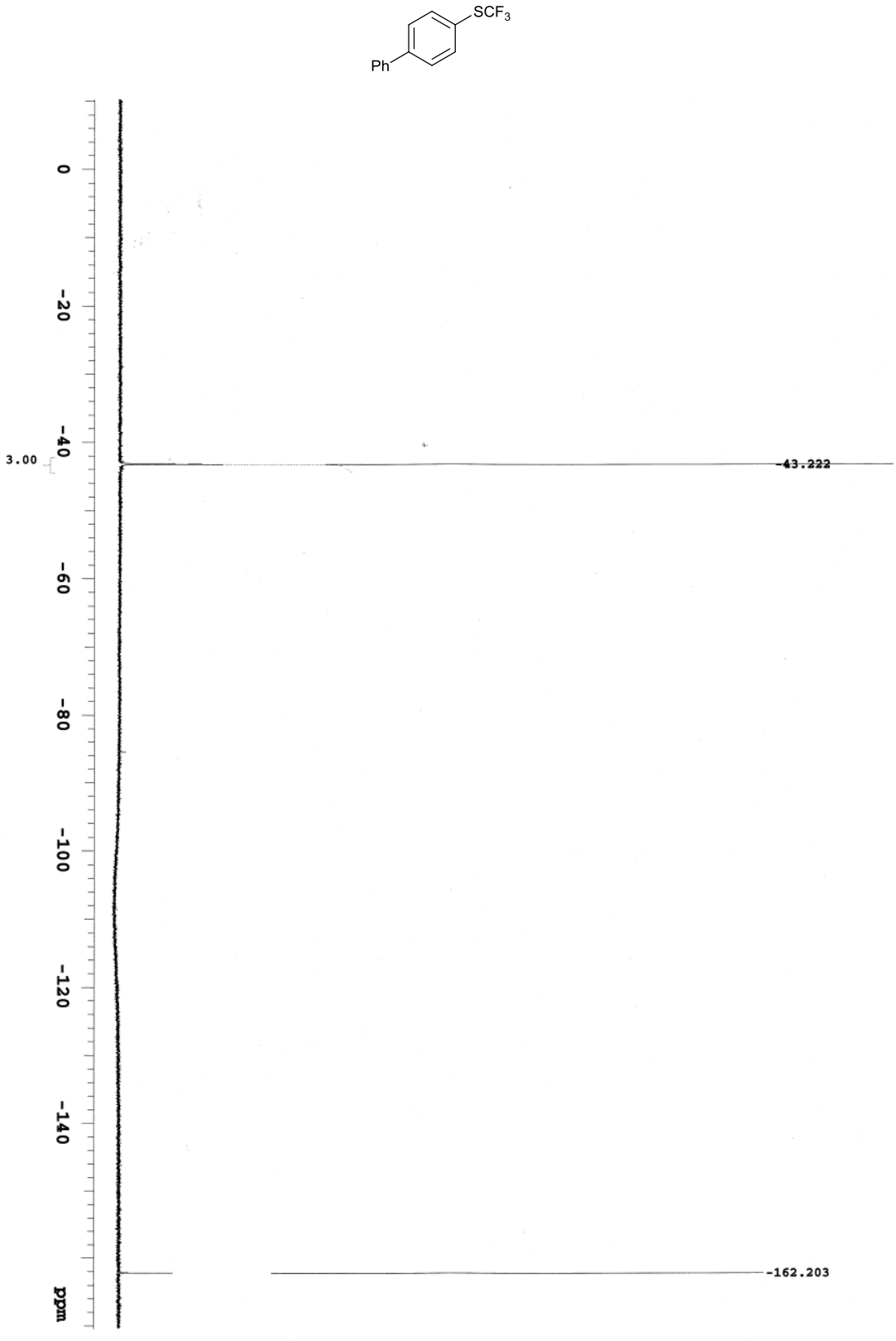


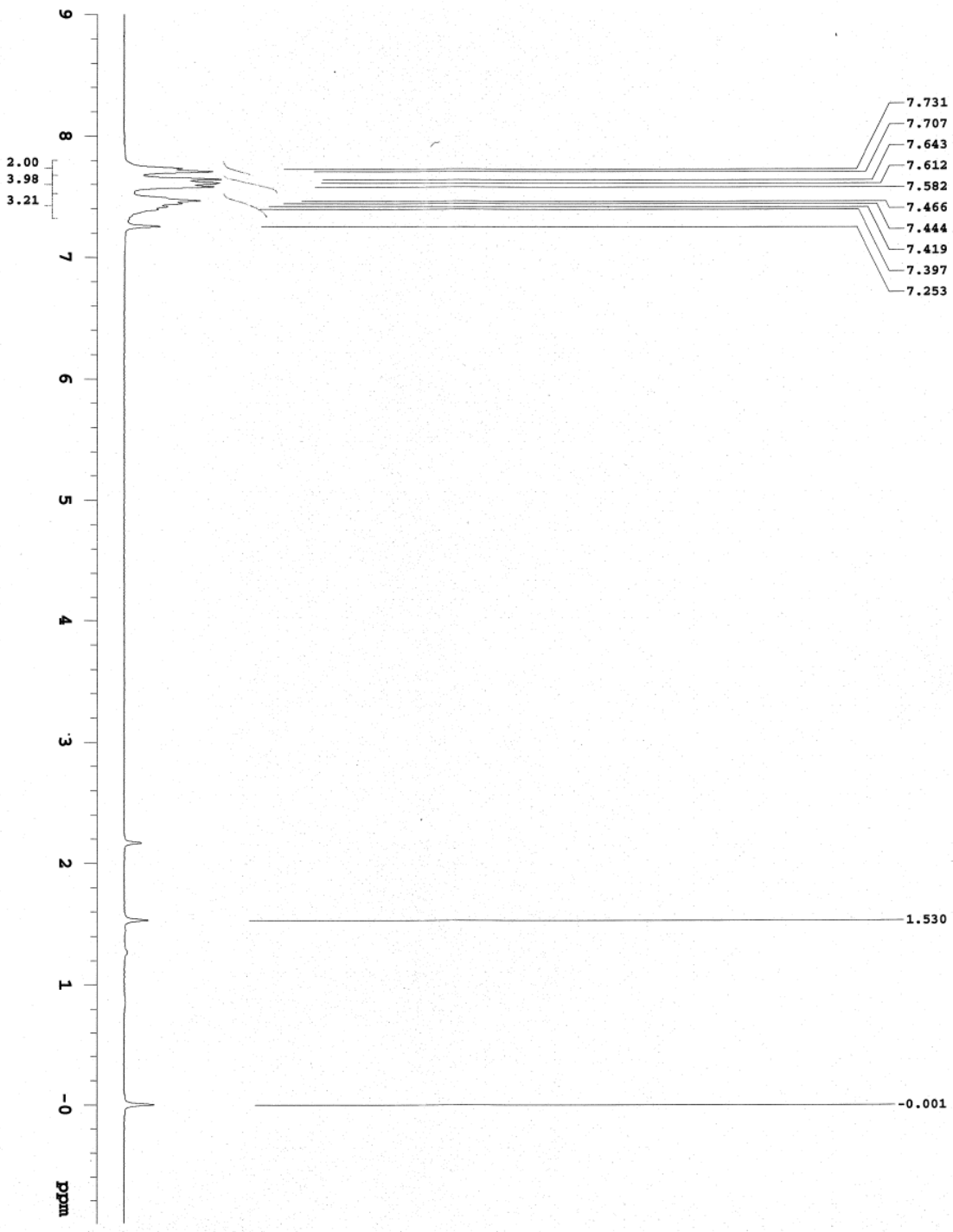



1.98
2.04
1.00
1.89
2.18
7.601
7.577
7.416
7.392
7.370
7.258
7.215
7.193
7.168
7.078
7.053
7.003
6.979
1.533
0.003
ppm

Copies of ^{19}F NMR and ^{1}H NMR

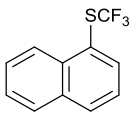
4-(Trifluoromethylthio)biphenyl (5b)

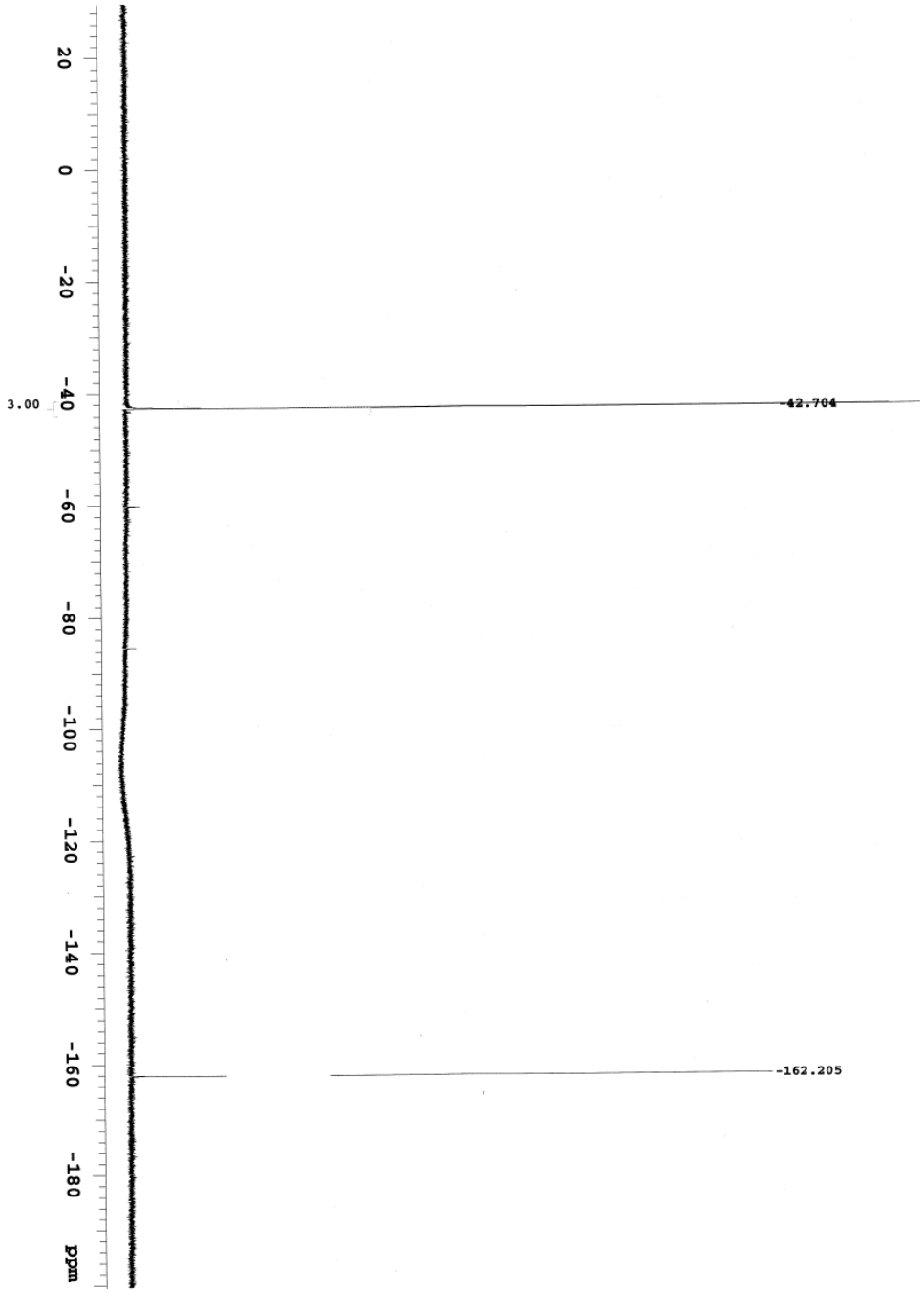


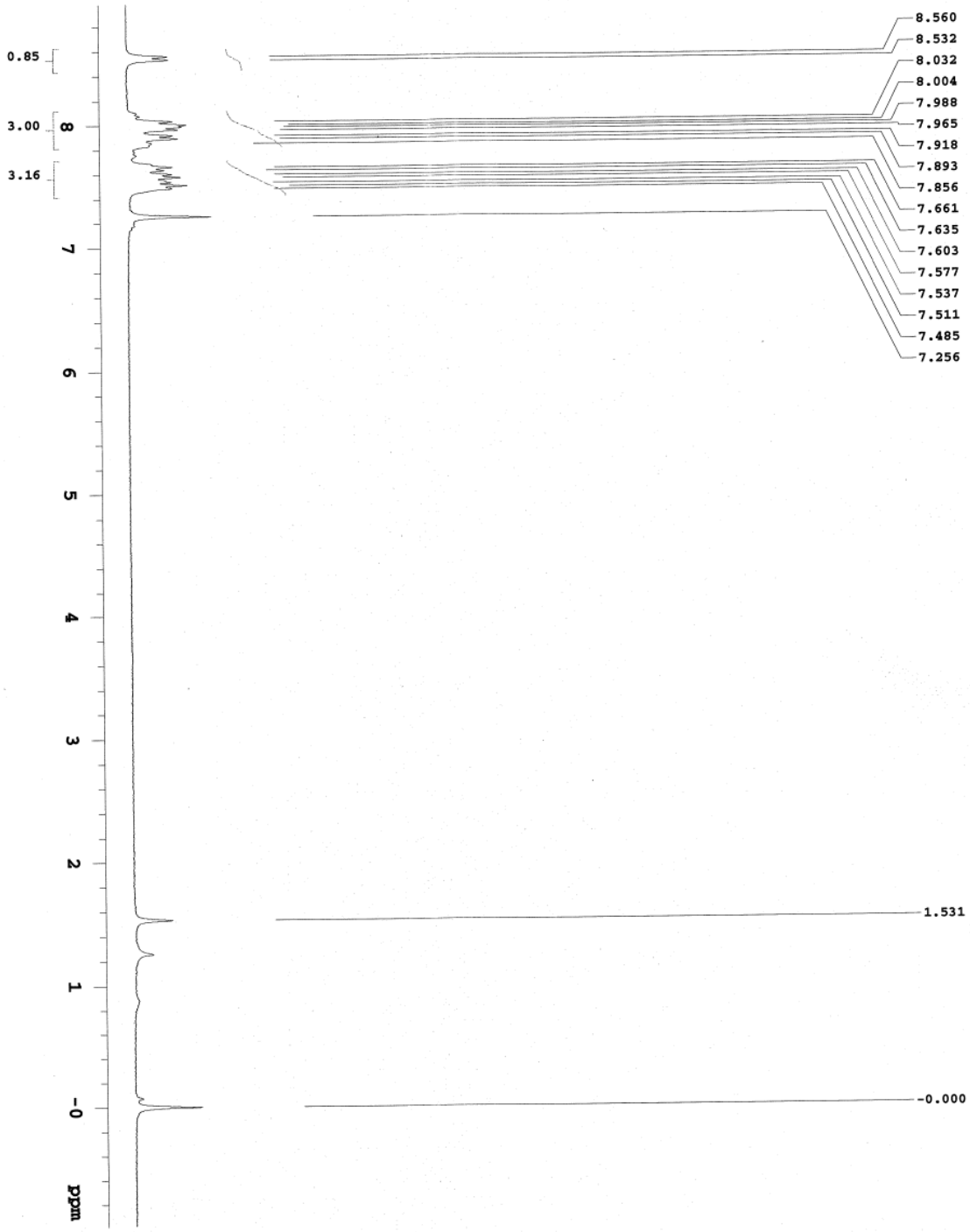

2.00
3.98
3.21
7.731
7.707
7.643
7.612
7.582
7.466
7.444
7.419
7.397
7.253
1.530
-0.001
ppm

Copies of ^{19}F NMR and ^{1}H NMR

1-(Trifluoromethylthio)naphthalene (5c)

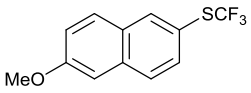


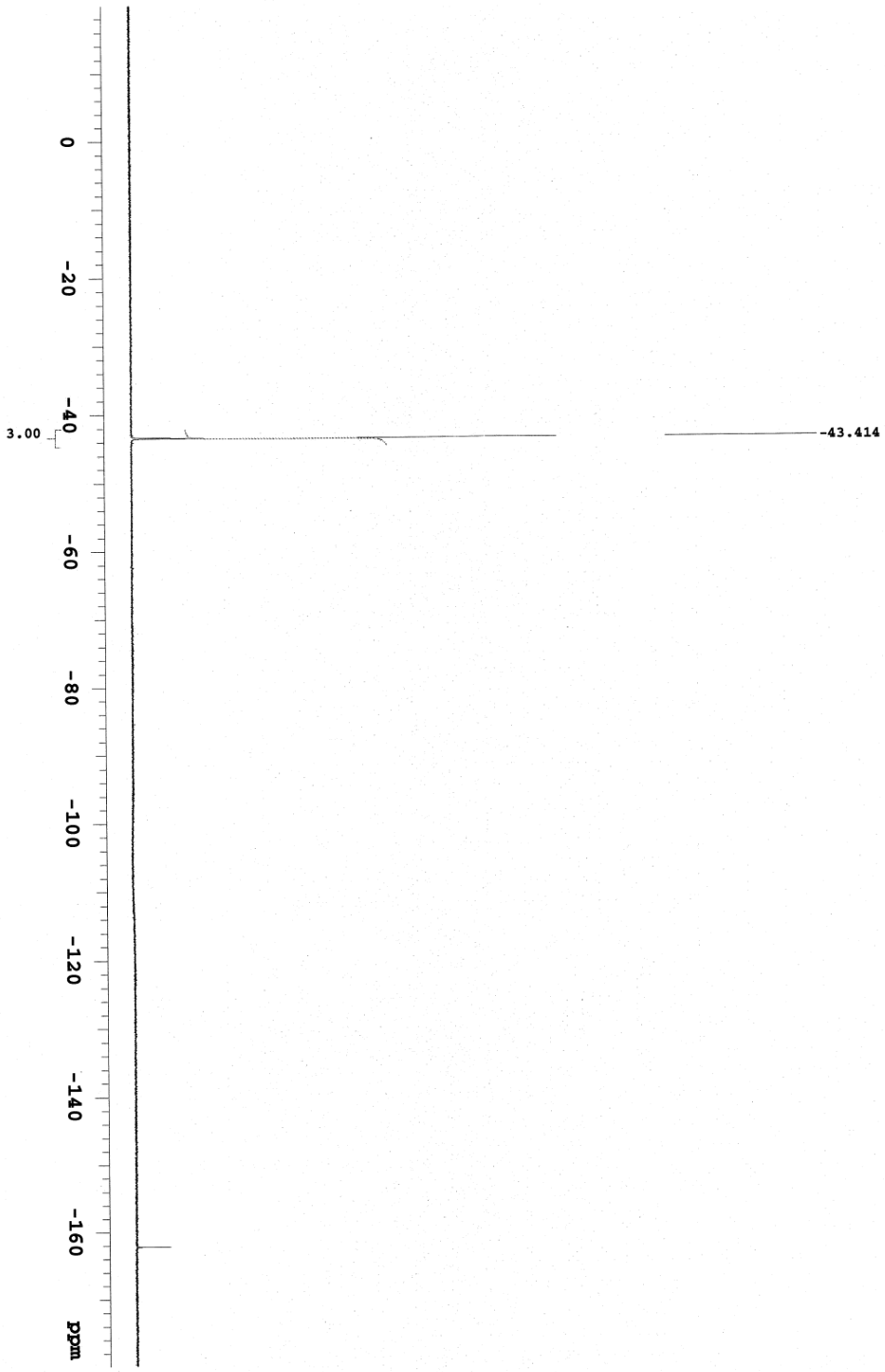


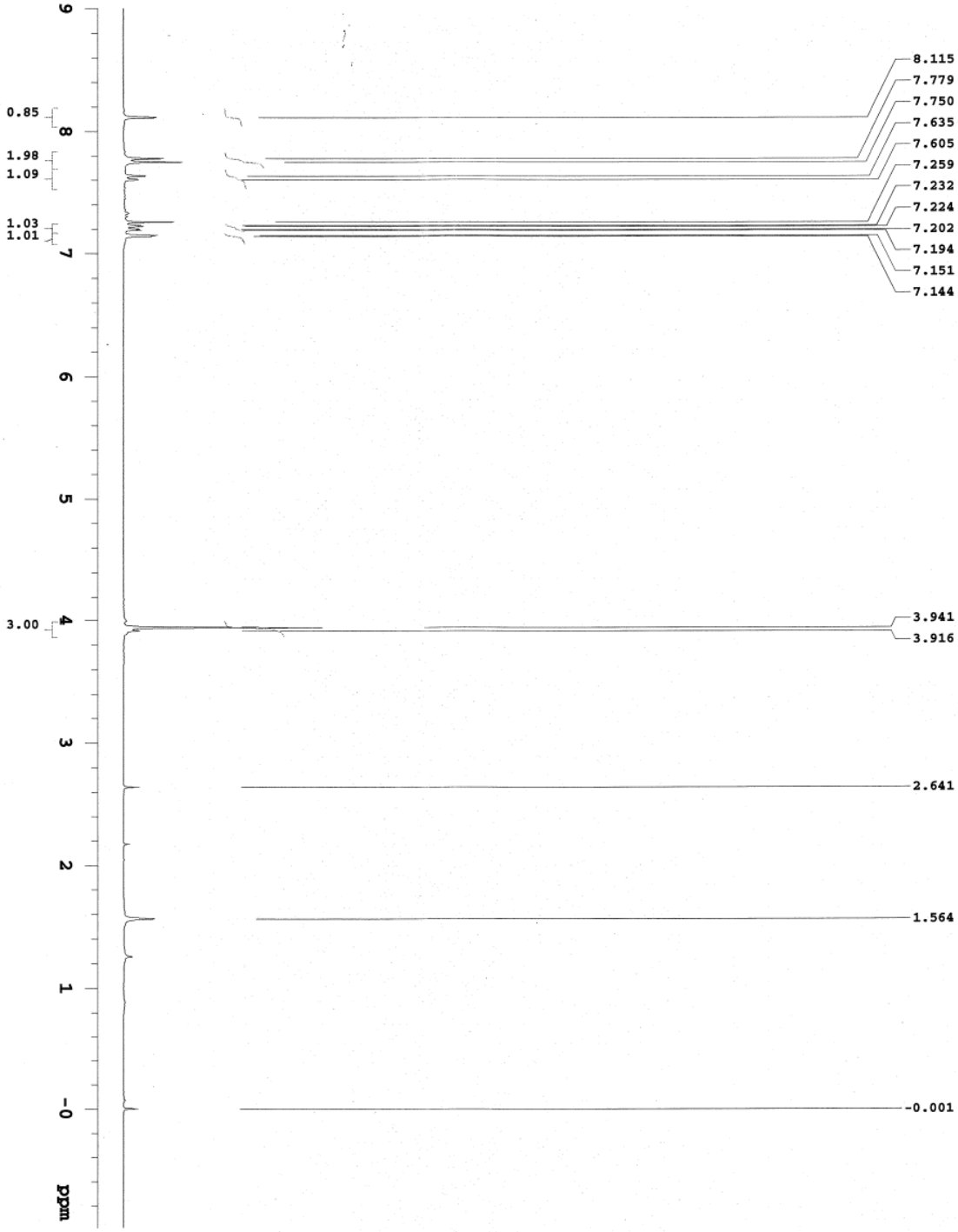

8.560
8.532
8.032
8.004
7.988
7.965
7.918
7.893
7.856
7.661
7.635
7.603
7.577
7.537
7.511
7.485
7.256
1.531
-0.000
0.85
3.00
3.16
ppm

Copies of ^{19}F NMR and ^{1}H NMR

(6-Methoxynaphthalene-2-yl)(trifluoromethyl)sulfane (5d)

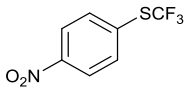


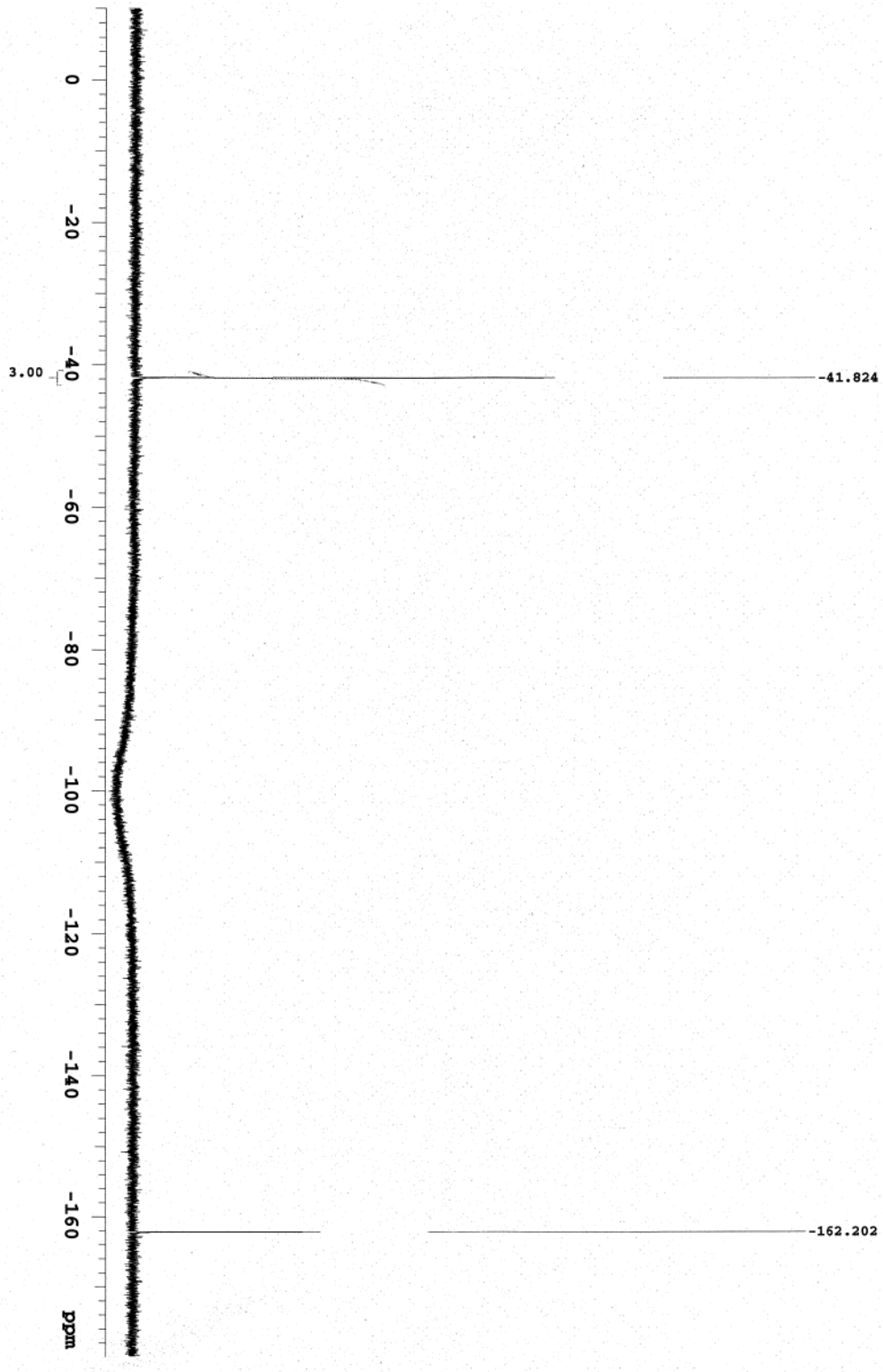


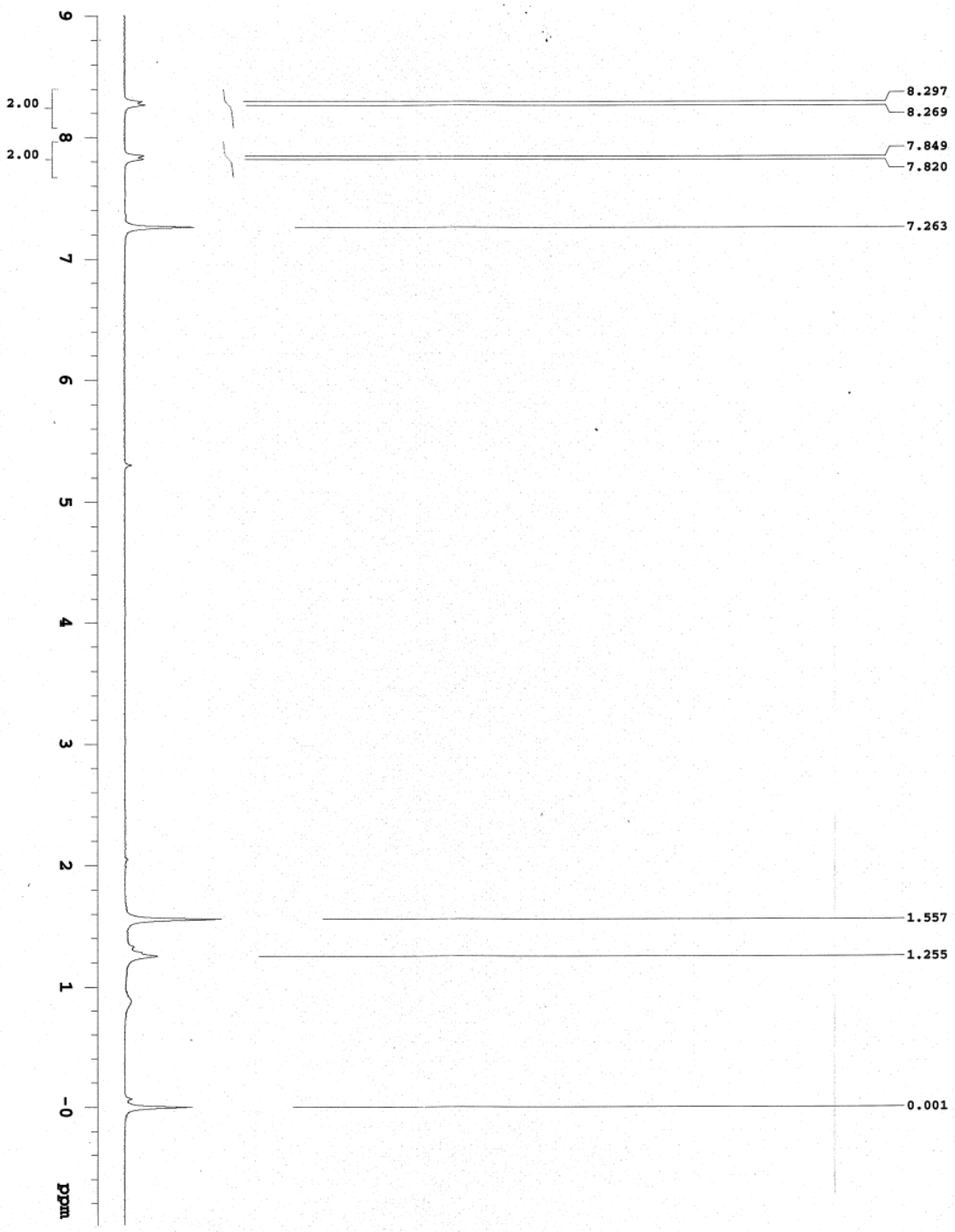

8.115
7.779
7.750
7.635
7.605
7.259
7.232
7.224
7.202
7.194
7.151
7.144
3.941
3.916
2.641
1.564
-0.001
0.85
1.98
1.09
1.03
1.01
3.00
9
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

4-Nitro-1-(trifluoromethylthio)benzene (5e)

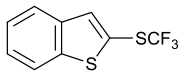


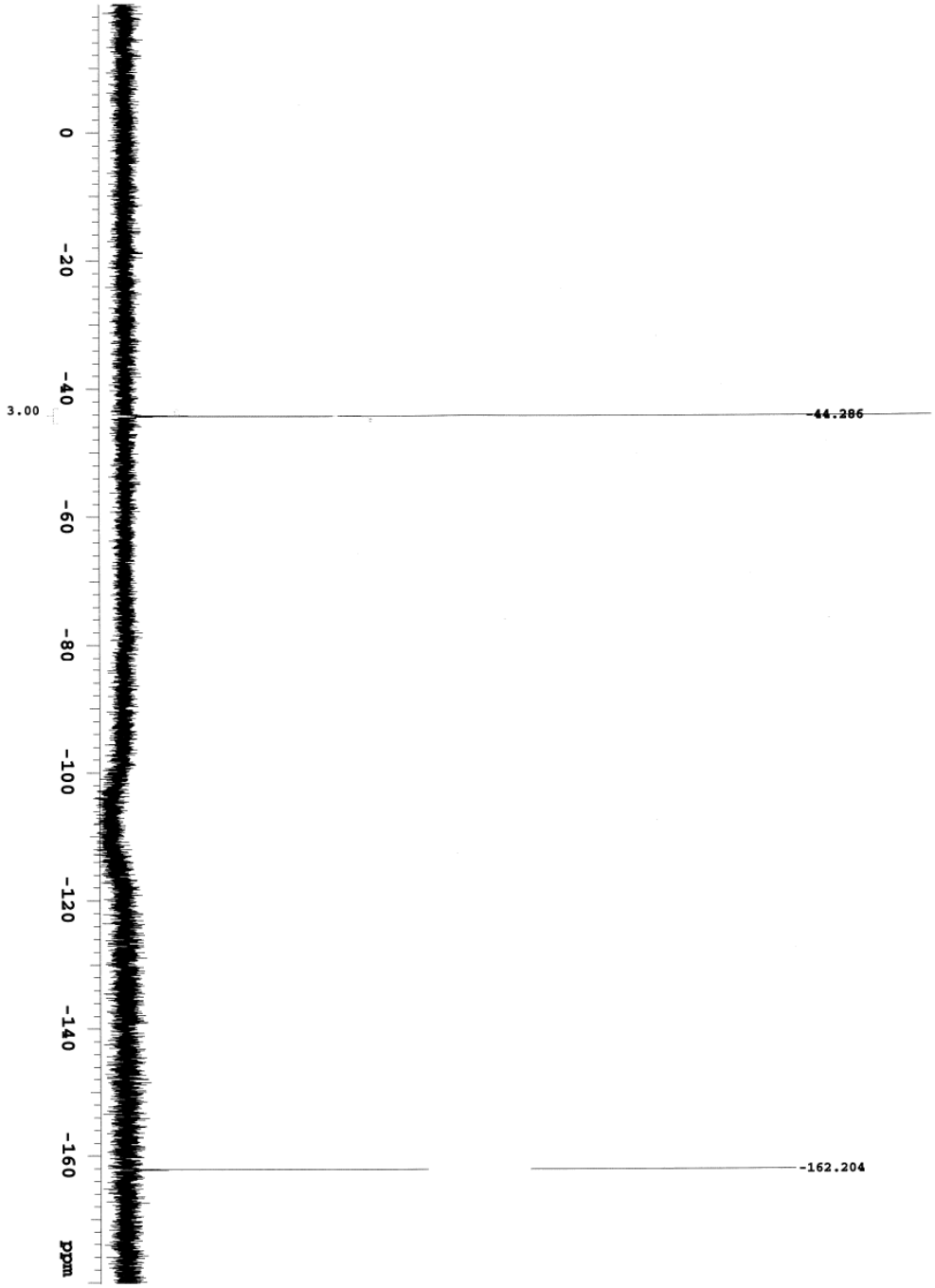


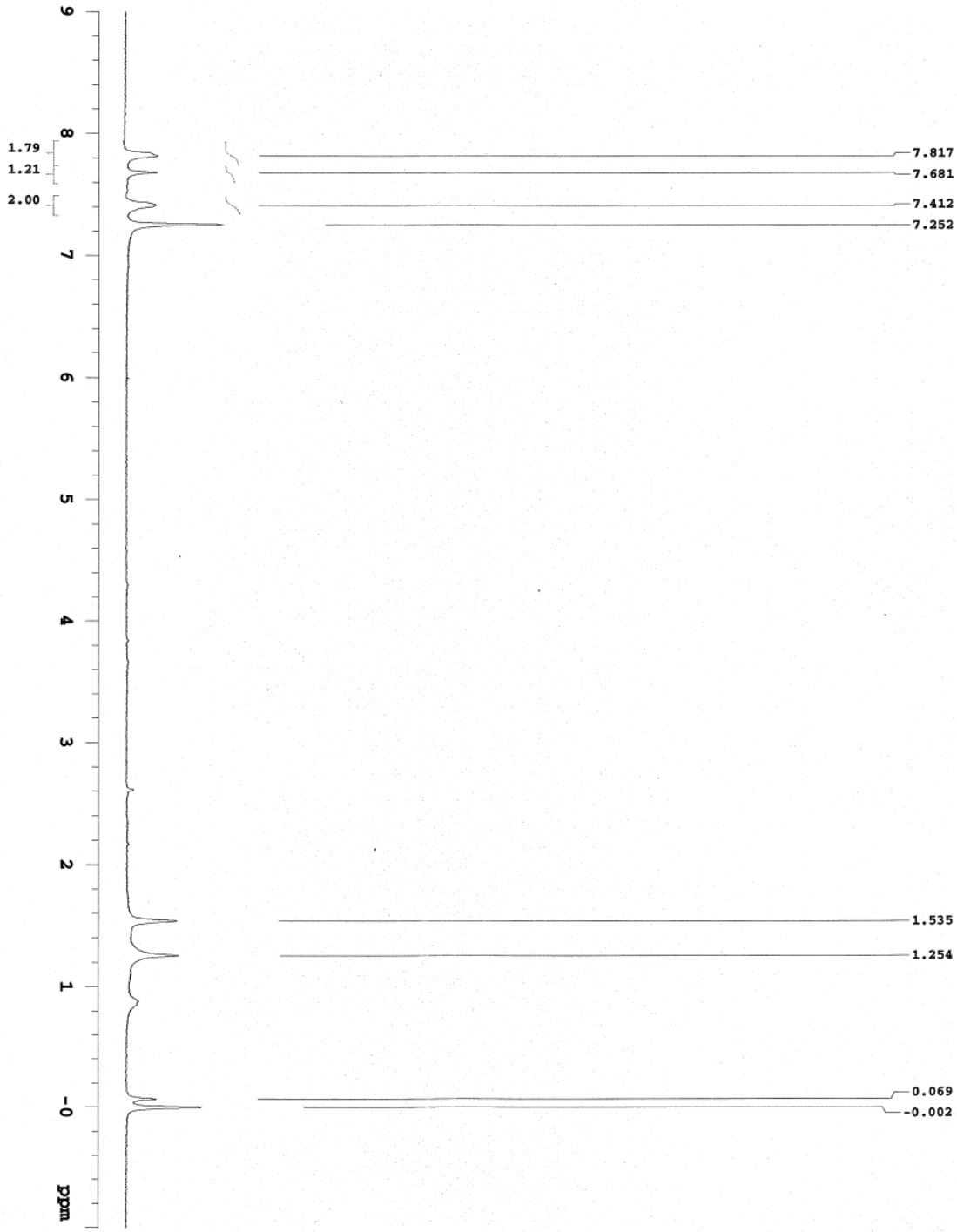

9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.00
8.297
8.269
7.849
7.820
7.263
1.557
1.255
0.001

Copies of ^{19}F NMR and ^{1}H NMR

2-(Trifluoromethylthio)benzo[*b*]thiophene (5f)

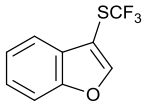


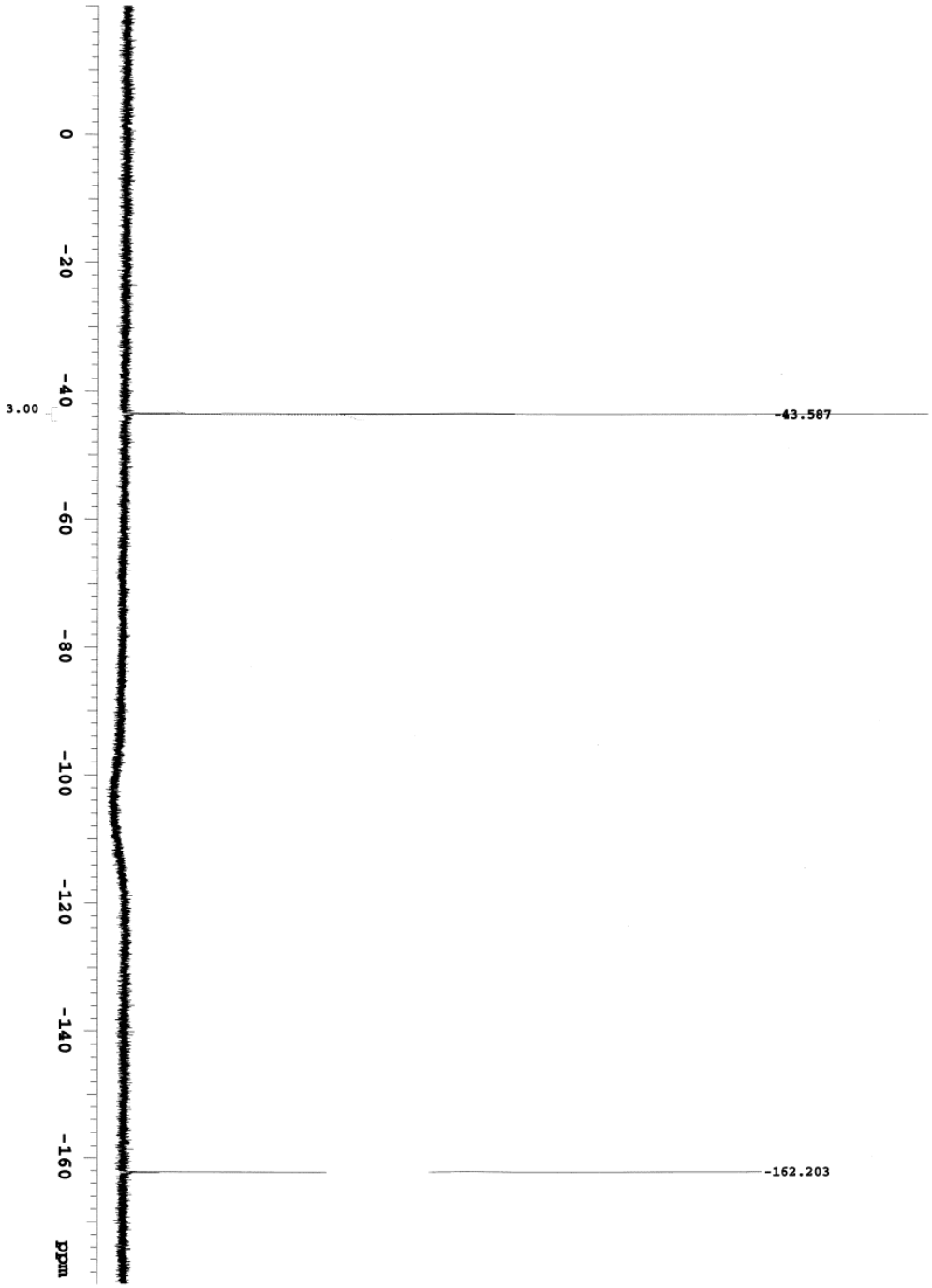


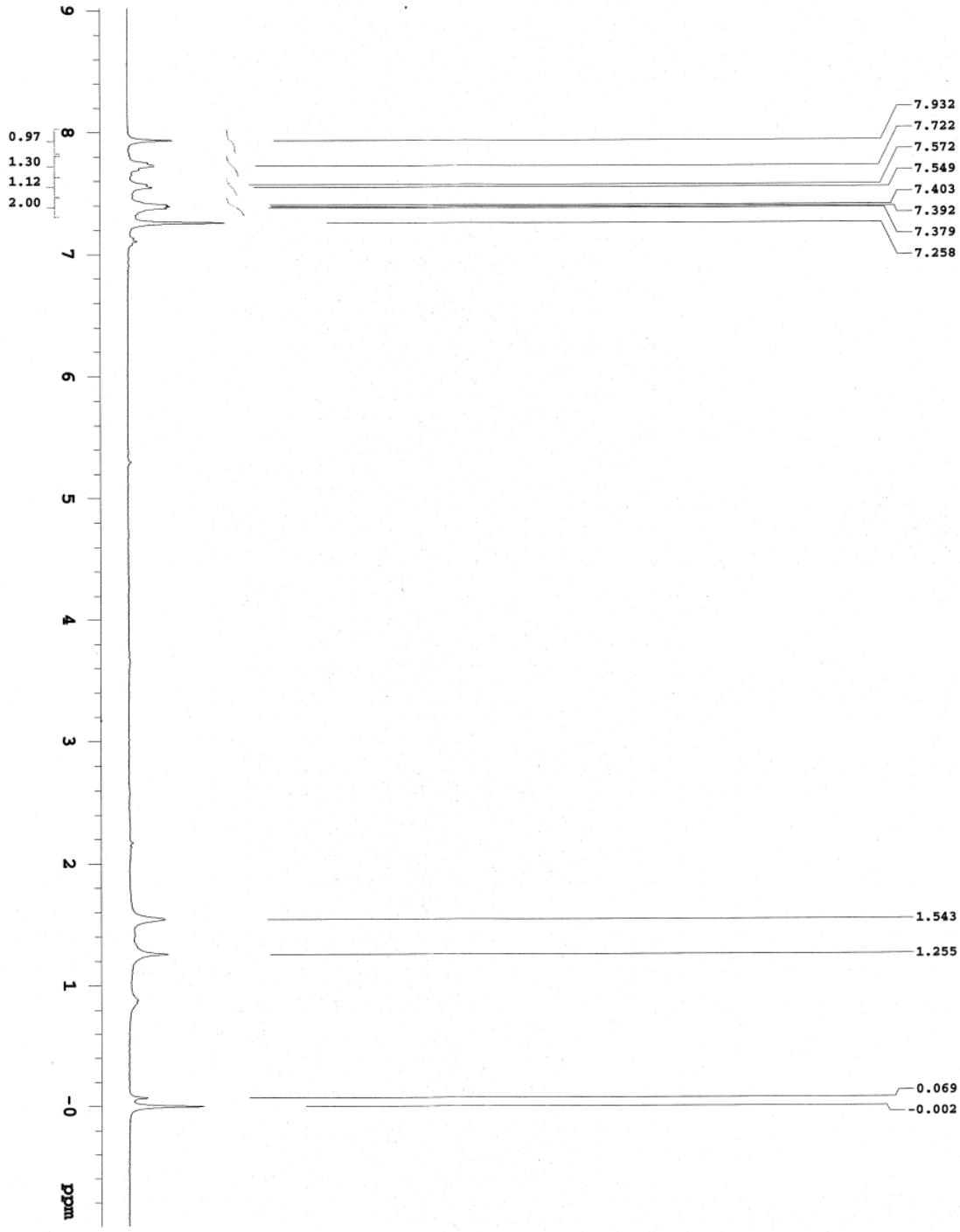

1.79
1.21
2.00
7.817
7.681
7.412
7.252
1.535
1.254
0.069
-0.002
9
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

3-(Trifluoromethylthio)benzo[*b*]furan (5g)

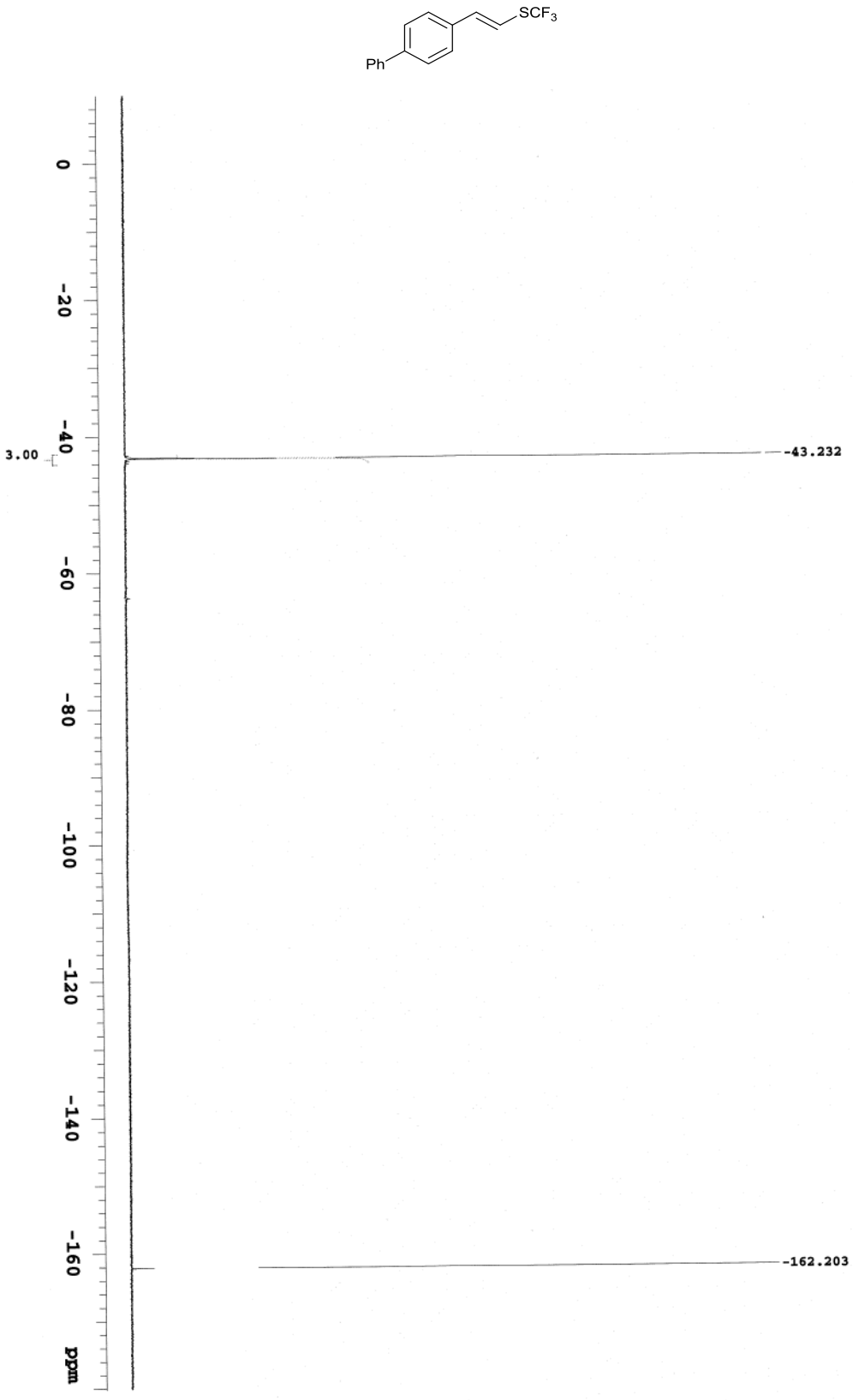


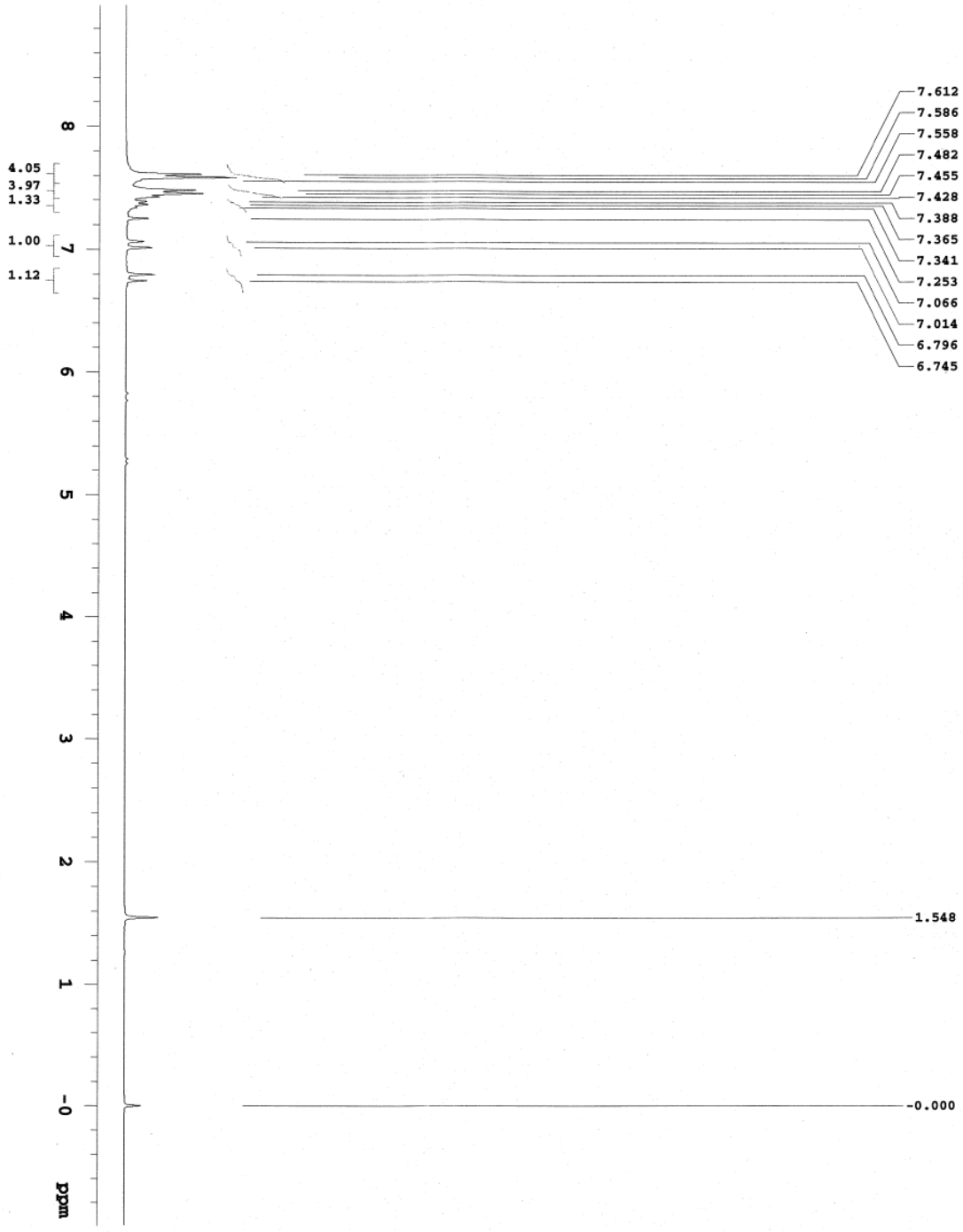



0.97
1.30
1.12
2.00
7.932
7.722
7.572
7.549
7.403
7.392
7.379
7.258
1.543
1.255
0.069
-0.002
9
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

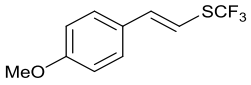
(*E*)-(4-phenylstyryl)(trifluoromethyl)sulfane (5h)

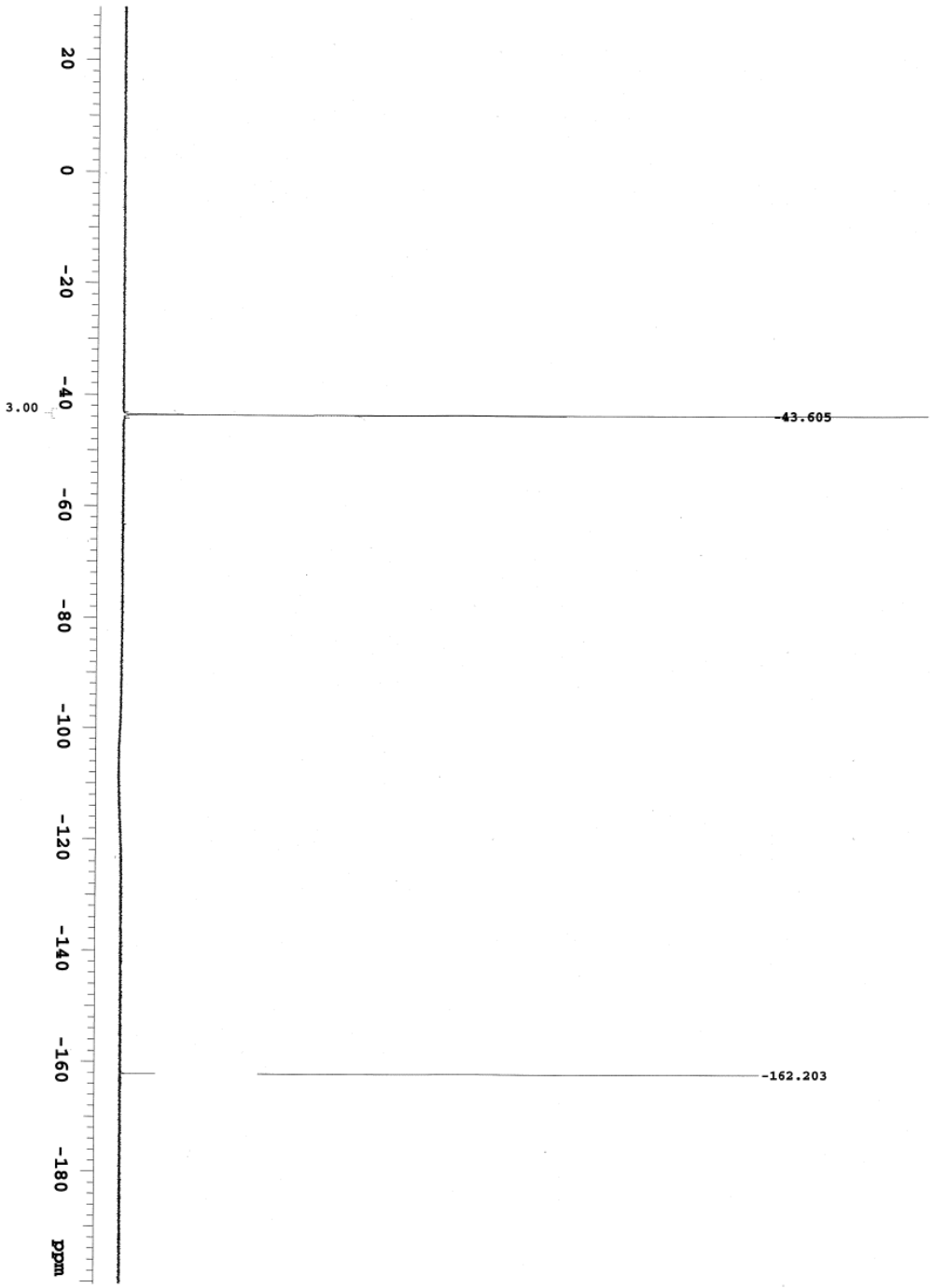


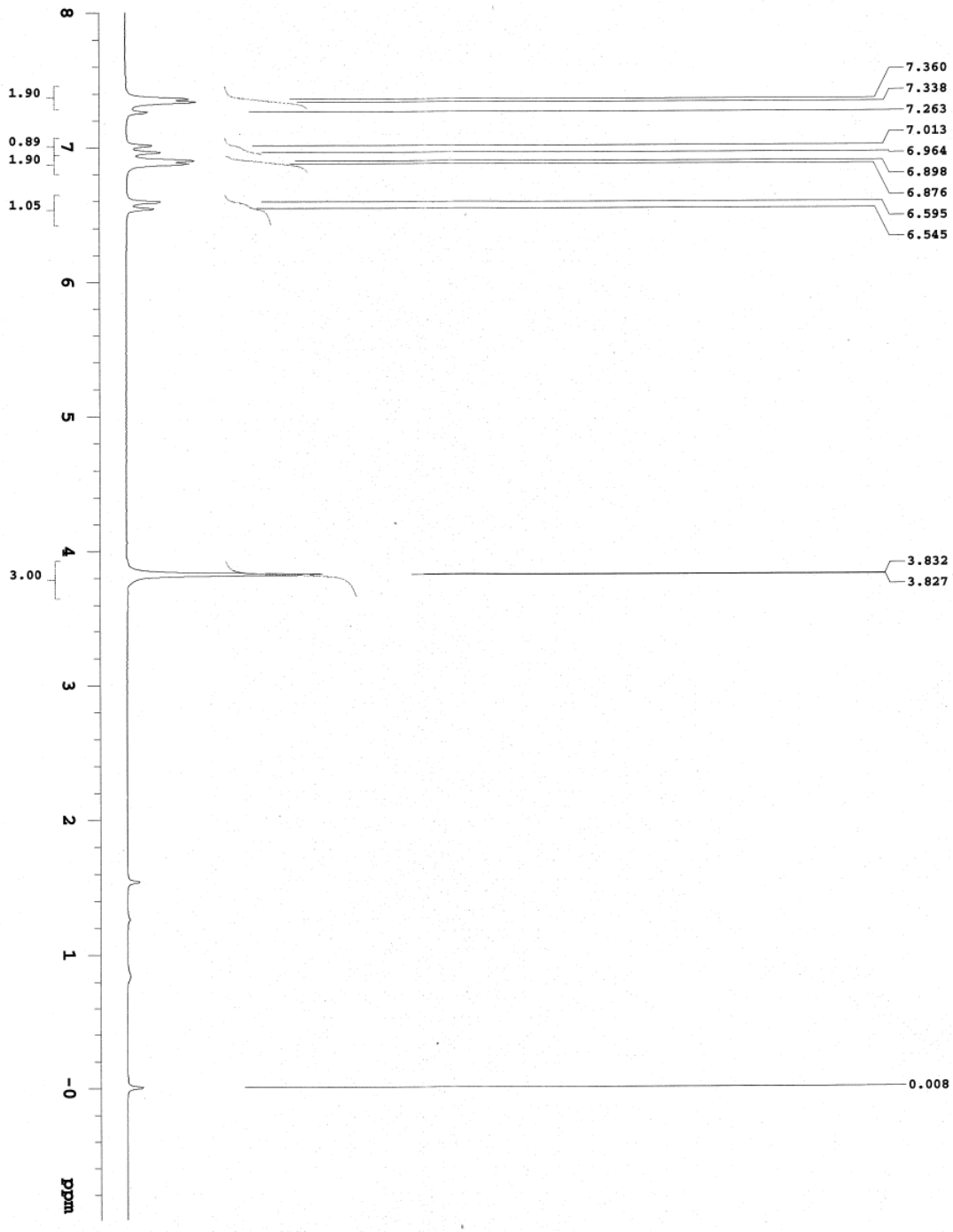

7.612
7.586
7.558
7.482
7.455
7.428
7.388
7.365
7.341
7.253
7.066
7.014
6.796
6.745
4.05
3.97
1.33
1.00
1.12
1.548
-0.000
8
7
6
5
4
3
2
1
-0
ppm

Copies of ^{19}F NMR and ^{1}H NMR

(*E*)-(4-methoxystyryl)(trifluoromethyl)sulfane (5i)






1.90
0.89
1.90
1.05
3.00
7.360
7.338
7.263
7.013
6.964
6.898
6.876
6.595
6.545
3.832
3.827
0.008
8
7
6
5
4
3
2
1
-0
ppm