Supporting Information

Decarboxylative Allylation of Trifluoroethyl Sulfones and Approach to Difluoromethyl Compounds

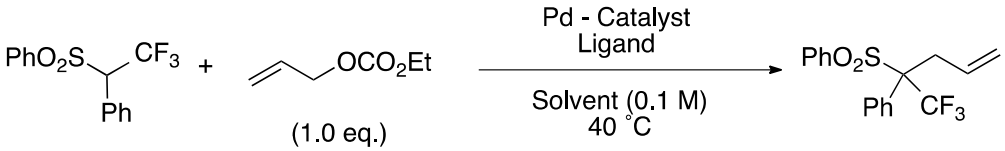
Norio Shibata,*,† Kazunobu Fukushi,† Tatsuya Furukawa,† Satoru Suzuki,† Etsuko Tokunaga† and Dominique Cahard‡

†*Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya, 466-8555, Japan.*

‡*UMR 6014 CNRS COBRA, Université et INSA de Rouen, 76821 Mont Saint Aignan, France.*

CONTENTS

Table S1. Optimization of Reaction conditions



Entry	Pd-Catalyst	(mol%)	Ligand	(mol%)	Solvent	Time (h)	Yield (%)
1	$Pd(OAc)_2$	5	Dppe	6	THF	24	N.R.
2	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	2.5	Dppe	6	THF	24	18
3	$Pd(dba)_2$	5	Dppe	6	THF	1	85
4	$Pd_2(dba)_3$	2.5	Dppe	6	THF	1	92
5	$Pd(PPh_3)_4$	5	-	-	THF	2	49
6	$Pd_2(dba)_3$	2.5	Dppp	6	THF	2	68
7	$Pd_2(dba)_3$	2.5	Dppf	6	THF	2	72
8	$Pd_2(dba)_3$	2.5	PPh_3	12	THF	1	62
9	$Pd_2(dba)_3$	2.5	PCy_3	12	THF	24	N.R.
10	$Pd_2(dba)_3$	2.5	$Pt Bu_3$	12	THF	24	N.R.
11	$Pd_2(dba)_3$	2.5	BIHEAP	6	THF	2	83
12	$Pd_2(dba)_3$	2.5	Dppe	6	CH_2Cl_2	24	Trace
13	$Pd_2(dba)_3$	2.5	Dppe	6	Toluene	12	84
14	$Pd_2(dba)_3$	2.5	Dppe	6	Dioxane	24	41
15	$Pd_2(dba)_3$	2.5	Dppe	6	DME	24	N.R.

Supplemental Methods

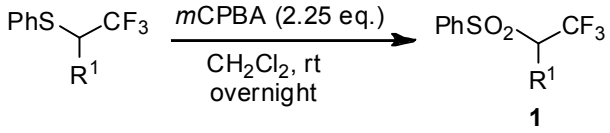
General information:

All reactions were performed in oven-dried glassware under positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels though a rubber septum. 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 $KMnO_4$ or *p*-anisaldehyde in ethanol/heat. Column chromatography was carried out on columns packed with silica gel (60N spherical neutral size 63-210 μm). The ^1H NMR (300 MHz), ^{19}F NMR (282 MHz), and ^{13}C NMR (150.9 MHz, 75.5 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker Avance 600 and a Varian

Mercury 300; chemical shifts (δ) are expressed in ppm downfield from internal TMS or $CHCl_3$. Mass spectra were recorded on a SHIMADZU DCMS-QP5050A and a SHIMADZU LCMS-2010EV. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer.

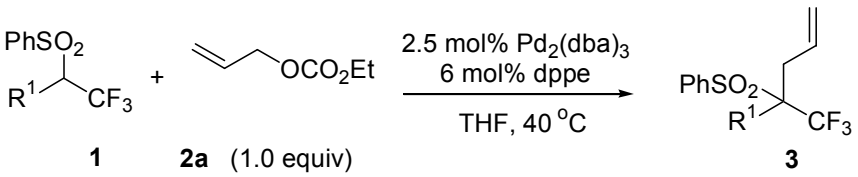
Preparation of α-trifluoromethyl phenylsulfones 1.

α-Trifluoromethyl phenylsulfones **1h** and **1m** are known compounds and they were prepared according to the reported procedure.[1] Other α-trifluoromethyl phenylsulfones **1** were prepared from corresponding α-trifluoromethyl sulfides (prepared according to the reported methods[2-3]) by *m*-CPBA oxidation.



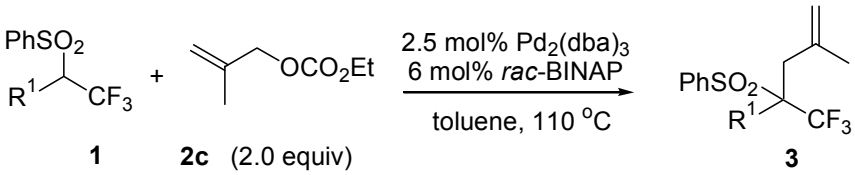
To a solution of α-trifluoromethyl phenylsulfides in CH_2Cl_2 (0.3 M), *m*CPBA (2.25 equiv) was added slowly at 0 °C and stirred at room temperature. The reaction was monitored by TLC with UV light and $KMnO_4$ staining until starting material was consumed. The resulting mixture was filtered with CH_2Cl_2. The filtrate was treated with aqueous sodium hydrogen carbonate and extracted with CH_2Cl_2 three times. The extract was washed with water and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography eluting with *n*-hexane/EtOAc to give compound **1**.

General procedure I: Palladium catalyzed decarboxylative allylation



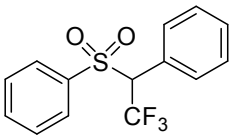
To a stirred solution of α-trifluoromethyl sulfone **1** (0.10 mmol), dppe (2.3 mg, 0.006 mmol) and $Pd_2(dba)_3$ (2.4 mg, 0.0025 mmol) in THF (1.0 ml) was added allyl ethyl carbonate (13.0 mg, 0.10 mmol) at room temperature. The solution was heated at 40 °C and the progress of the reaction monitored by TLC. After completion, the mixture was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane/benzene) after passing through a short column on silica gel (Et_2O) to give the compounds **3a-l**.

General procedure II: Palladium catalyzed decarboxylative allylation



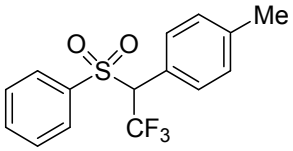
To a stirred solution of α-trifluoromethyl sulfone (0.10 mmol), *rac*-BINAP (3.7 mg, 0.006 mmol) and $Pd_2(dba)_3$ (2.4 mg, 0.0025 mmol) in toluene (1.0 ml) was added ethyl 2-methyl-2-propenyl carbonate (28.8 mg, 0.20 mmol) at room temperature. The solution was heated at 110 °C and the progress of the reaction monitored by TLC. After completion, the mixture was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc 9:1) after passing through a short column on silica gel (Et_2O) to give compounds **3m-o**.

(2,2,2-Trifluoro-1-phenylethylsulfonyl)benzene (1a)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.75 (q, *J* = 8.1 Hz, 1H), 7.26-7.48 (m, 7H), 7.61-7.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 72.2 (q, *J* = 28.8 Hz), 122.5 (q, *J* = 282.1 Hz), 125.8, 128.8, 128.9, 129.4, 130.2, 130.6, 134.5, 137.0; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –61.6 (d, *J* = 7.9 Hz, 3F); IR (KBr): 2954, 1447, 1332, 1257, 1150, 1114, 724, 594 cm^{-1}; MS (ESI): m/z 323 (M+Na$^+$); HRMS (ES+): calcd for $C_{14}H_{11}F_3NaO_2S$ (M+Na$^+$) 323.0330 found for 323.0336; white solid; Mp : 133-134 °C (*n*-hexane/acetone).

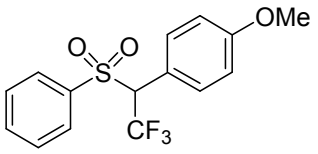
[2,2,2-Trifluoro-1-(4-methylphenyl)ethylsulfonyl]benzene (1b)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H), 4.72 (q, *J* = 8.4 Hz, 1H), 7.13-7.21 (m, 4H), 7.44-7.49 (m, 2H), 7.62-7.70 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.2, 72.5 (q, *J* = 28.8 Hz), 122.53 (q, *J* = 281.8 Hz), 125.56, 128.9, 129.4, 129.5, 130.5, 134.4, 137.2, 140.4; ^{19}F NMR

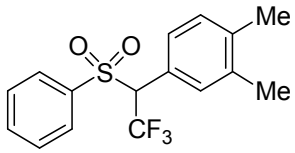
($CDCl_3$, 282 MHz): δ –61.8 (d, J = 9.0 Hz, 3F); IR (KBr): 3071, 2957, 1611, 1512, 1448, 1153, 860, 726, 603 cm^{-1}; MS (ESI): m/z 337 ($M+Na^+$); HRMS (ES+): calcd for $C_{15}H_{13}F_3NaO_2S$ ($M+Na^+$) 337.0486 found for 337.0493; white solid; Mp: 171–172 °C (*n*-hexane/acetone).

[2,2,2-Trifluoro-1-(4-methoxylphenyl)ethylsulfonyl]benzene (1c)



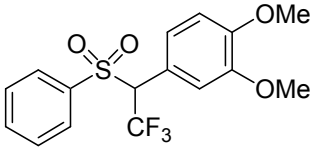
^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (s, 3H), 4.71 (q, J = 8.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.21-7.26 (m, 2H), 7.45-7.50 (m, 2H), 7.62-7.70 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 55.3, 72.1 (q, J = 28.8 Hz), 114.2, 117.4, 122.5 (q, J = 281.8 Hz), 128.9, 129.4, 131.9, 134.4, 137.2, 160.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –61.9 (d, J = 7.9 Hz, 3F); IR (KBr): 3433, 3029, 2957, 1611, 1515, 1155, 1021, 891, 605 cm^{-1}; MS (ESI): m/z 353 ($M+Na^+$); HRMS (ES+): calcd for $C_{15}H_{13}F_3NaO_3S$ ($M+Na^+$) 353.0435 found for 353.0443; white solid; Mp: 132–133 °C (*n*-hexane/acetone)

[2,2,2-Trifluoro-1-(3,4-dimethylphenyl)ethylsulfonyl]benzene (1d)



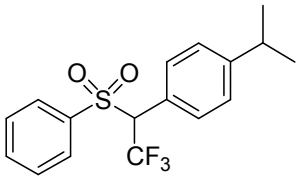
^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.22 (s, 3H), 2.26 (s, 3H), 4.68 (q, J = 8.7 Hz, 1H), 7.01-7.11 (m, 3H), 7.45-7.50 (m, 2H), 7.62-7.73 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 19.6, 19.7, 72.7 (q, J = 27.9 Hz), 120.7, 122.6 (q, J = 281.8 Hz), 122.8, 128.0, 128.8, 129.5, 130.0, 131.7, 134.4, 137.3, 139.1; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –61.8 (d, J = 7.9 Hz, 3F); IR (KBr): 3432, 3073, 2954, 1905, 1448, 1235, 1154, 946 cm^{-1}; MS (ESI): m/z 351 ($M+Na^+$); HRMS (ES+): calcd for $C_{16}H_{15}F_3NaO_2S$ ($M+Na^+$) 351.0643 found for 351.0640; white solid; Mp: 128–129 °C (*n*-hexane/acetone).

[2,2,2-Trifluoro-1-(3,4-dimethoxyphenyl)ethylsulfonyl]benzene (1e)



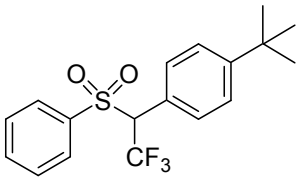
^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.78 (s, 3H), 3.89 (s, 3H), 4.70 (q, J = 8.1 Hz, 1H), 6.78-6.85 (m, 3H), 7.32-7.50 (m, 2H), 7.62-7.70 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 55.8, 72.7 (q, J = 28.8 Hz), 110.9, 112.8, 117.7, 122.6 (q, J = 281.8 Hz), 124.1, 128.9, 129.5, 134.4, 137.2, 149.0, 150.6 (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –61.8 (d, J = 7.9 Hz, 3F); IR (KBr): 3072, 2963, 1603, 1520, 1154, 1019, 956 cm^{-1}; MS (ESI): m/z 383 (M+Na^{+}); HRMS (ES+): calcd for $C_{16}H_{15}F_3NaO_4S$ (M+Na^{+}) 383.0541 found for 382.0541; white solid; Mp: 91–92 °C (*n*-hexane/acetone).

{2,2,2-Trifluoro-1-[4-(1-methylethyl)phenyl]ethylsulfonyl}benzene (1f)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (s, 3H), 1.25 (s, 3H), 2.86-2.95 (m, 1H), 4.73 (q, J = 6.6 Hz, 1H), 7.17-7.24 (m, 4H), 7.42-7.47 (m, 2H), 7.60-7.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 23.65, 23.70, 33.8, 72.9 (d, J = 30.2 Hz), 122.6 (q, J = 286.0 Hz), 122.9, 126.9, 128.8, 129.4, 130.6, 134.4, 137.3, 151.3; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –61.8 (d, J = 8.7 Hz, 3F); IR (KBr): 3047, 2956, 1448, 1334, 1257, 1154, 1055, 896, 585 cm^{-1}; MS (ESI): m/z 365 (M+Na^{+}); HRMS (ES+): calcd for $C_{17}H_{17}F_3NaO_2S$ (M+Na^{+}) 365.0799 found for 365.0798; yellow solid; Mp: 134–135 °C (*n*-hexane/EtOAc).

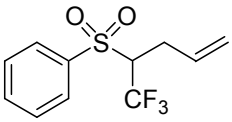
{2,2,2-Trifluoro-1-[4-(1,1-dimethylethyl)phenyl]ethylsulfonyl}benzene (1g)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (s, 9H), 4.74 (q, J = 8.4 Hz, 1H), 7.22-7.33 (m, 3H), 7.36-7.47 (m, 4H), 7.60-7.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): 31.1, 34.7, 72.9 (q, J = 28.2 Hz), 122.56, 122.59 (q, J = 282.1 Hz), 125.8, 128.8, 129.4, 130.3, 134.4, 137.3, 153.5; ^{19}F

NMR ($CDCl_3$, 282 MHz): δ –61.8 (d, J = 7.9 Hz, 3F); IR (KBr): 3047, 2956, 1448, 1334, 1257, 1154, 1055, 896, 585 cm^{-1}; MS (ESI): m/z 379 ($M+Na^+$); HRMS (ES+): calcd for $C_{18}H_{19}F_3NaO_2S$ ($M+Na^+$) 379.0956 found for 379.0954; yellow solid; Mp: 106-107 °C (*n*-hexane/EtOAc).

(1,1,1-Trifluoropent-4-en-2-ylsulfonyl)benzene (1j)

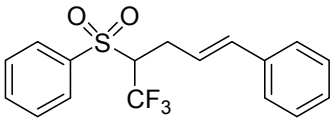


To a stirred solution of **1m** (22.4 mg, 0.1 mmol), dppf (3.3 mg, 0.006 mmol) and $Pd_2(dba)_3$ (2.4 mg, 0.0025 mmol) in THF (1.0 ml) was added allyl ethyl carbonate (13.0 mg 0.1 mmol) at room temperature. The solution was heated at 40 °C and the progress of the reaction was monitored by TLC. The, the mixture was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane/benzene 1:1) after passing through a short column on silica gel (Et_2O). **1j** Was obtained as yellow oil (15.4 mg, 58%).

^1H NMR ($CDCl_3$, 300 MHz): δ 2.66-2.82 (m, 1H), 2.95-3.04 (m, 1H), 3.67-3.78 (m, 1H), 5.16 (dd, J = 10.2, 1.2 Hz, 1H), 5.23 (d, J = 0.9 Hz, 1H), 5.79-5.93 (m, 1H), 7.58-7.66 (m, 2H), 7.70-7.75 (m, 1H), 7.95 (d, J = 7.8, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 28.6 (q, J = 1.5 Hz), 67.2 (q, J = 27.2 Hz), 119.2, 122.3 (q, J = 282.2 Hz), 129.1, 129.3, 132.0, 134.6, 137.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.2 (d, J = 7.7 Hz, 3F); IR (NaCl): 3072, 2948, 1585, 1449, 1335, 1123, 927, 756 cm^{-1}; MS (ESI): m/z 287 ($M+Na^+$); HRMS (ES+): calcd for $C_{11}H_{11}F_3NaO_2S$ ($M+Na^+$) 287.0330 found for 287.0327.

Lit[1a]; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.62-3.10 (m, 2H), 3.63-3.81 (m, 1H), 5.13-5.26 (m, 2H), 5.75-6.00 (m, 1H), 7.56-8.00 (m, 5H).

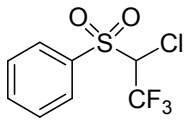
(1,1,1-Trifluoro-5-phenyl-pent-4-en-2-ylsulfonyl)benzene (1k)



To a stirred solution of **1m** (22.4 g, 0.1 mmol), dppf (3.3 mg, 0.006 mmol) and $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) in THF (1.0 ml) was added cinnamyl ethyl carbonate (20.6 mg, 0.1 mmol) at room temperature. The solution was heated at 60 °C and the progress of the reaction was monitored by TLC. Then, the mixture was evaporated under reduced pressure, and the residue was purified by

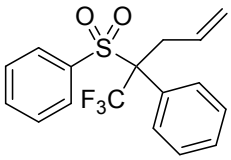
flash column chromatography on silica gel (*n*-hexane/Et_2O 95:5) after passing through a short column on silica gel (Et_2O). **1k** was obtained as yellow oil (17.7 mg, 52%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.83-2.93 (m, 1H), 3.11-3.21 (m, 1H), 3.76-3.83 (m, 1H), 6.14-6.24 (m, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 7.26-7.33 (m, 5H), 7.57-7.62 (m, 2H), 7.70-7.74 (m, 1H), 7.97 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.0 (d, *J* = 1.1 Hz), 67.4 (q, *J* = 26.5 Hz), 123.0 (q, *J* = 281.8 Hz), 123.1, 126.3, 127.8, 128.5, 129.1, 129.3, 134.2, 134.6, 136.3, 137.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.1 (d, *J* = 7.9 Hz, 3F); IR (NaCl): 3062, 2944, 2321, 1968, 1736, 1448, 1150, 967 cm^{-1}; MS (ESI): m/z 363 (M+Na$^+$); HRMS (ES+): calcd for $C_{17}H_{15}F_3NaO_2S$ (M+Na$^+$) 363.0643 found for 363.0644.

(2,2,2-Trifluoro-1-chloroethylsulfonyl)benzene (1l)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.04-5.10 (m, 1H), 7.64-7.67 (m, 2H), 7.77-7.82 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 70.0 (q, *J* = 33.7 Hz), 120.6 (q, *J* = 282.1 Hz), 129.3, 130.3, 134.5, 135.6; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –67.5 (d, *J* = 5.9 Hz, 3F); IR (NaCl): 2966, 1350, 1306, 1252, 684, 591 cm^{-1}; MS (ESI): m/z 281 (M+Na$^+$); HRMS (ES+): calcd for $C_8H_6ClF_3NaO_2S$ (M+Na$^+$) 280.9627 found for 280.9635; yellow oil.

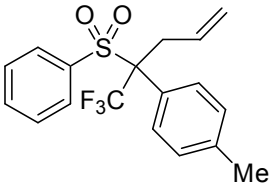
(1,1,1-Trifluoro-2-phenylpent-4-en-2-ylsulfonyl)benzene (3a)



The general procedure **I** was applied, using **1a** (30.0 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The obtained crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3a** as a white solid (31.3 mg, 92%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.34 (dd, *J* = 15.3, 7.8 Hz, 1H), 3.68-3.75 (m, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 5.30 (dd, *J* = 16.6, 1.2 Hz, 1H), 5.51-5.62 (m, 1H), 7.26-7.58 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 32.7 (d, *J* = 2.2 Hz), 77.7 (q, *J* = 23.8 Hz), 120.4, 124.5 (q, *J* = 287.1 Hz), 128.0, 128.2, 128.4, 129.6, 129.95, 129,98 130.6, 134.1, 135.7; ^{19}F NMR ($CDCl_3$, 282 MHz): δ

–59.0 (s, 3F); IR (KBr): 3071, 1642, 1327, 1150, 694, 596 cm^{-1}; MS (ESI): m/z 363 ($M+Na^+$); HRMS (ES+): calcd for $C_{17}H_{15}F_3NaO_2S$ ($M+Na^+$) 363.0643 found for 363.0638; white solid; Mp: 94-95 °C (*n*-hexane/acetone).

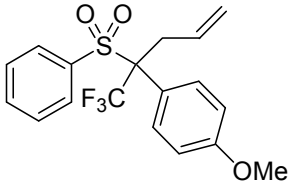
[1,1,1-Trifluoro-2-(4-methylphenyl)pent-4-ene-2-ylsulfonyl]benzene (3b)



The general procedure **I** was applied, using **1b** (32.0 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3b** as a white solid (32.2 mg, 91%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.37 (s, 3H), 3.29 (dd, *J* = 15.3 Hz, 8.1 Hz 2H), 3.67 (d, *J* = 11.4 Hz, 1H), 5.17 (d, *J* = 9.9 Hz, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.51-5.62 (m, 1H), 7.12-7.14 (m, 2H), 7.26-7.79 (m, 6H), 7.54-7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.1, 32.8 (d, *J* = 1.2 Hz), 77.6 (q, *J* = 24.6 Hz), 120.3, 124.5 (q, *J* = 286.9 Hz), 124.7, 128.2, 129.1, 129.8, 129.9, 130.7, 134.1, 135.8, 139.8; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –59.1 (s, 3F); IR (KBr): 3072, 2979, 2351, 1641, 1447, 1307, 1153, 931 cm^{-1}; MS (ESI): m/z 377 ($M+Na^+$); HRMS (ES+): calcd for $C_{18}H_{17}F_3NaO_2S$ ($M+Na^+$) 377.0799 found for 377.0797; white solid; Mp: 80-81 °C (*n*-hexane/acetone).

[1,1,1-Trifluoro-2-(4-methoxylphenyl)pent-4-ene-2-ylsulfonyl]benzene (3c)

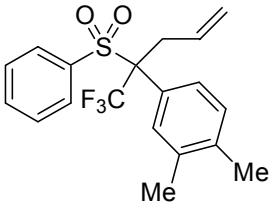


The general procedure **I** was applied, using **1c** (33.0 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3c** as colorless oil (36.5 mg, 98%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.30 (dd, *J* = 15.3, 8.1 Hz, 1H), 3.64 (ddd, *J* = 15.3, 3.9, 1.8 Hz, 1H), 3.83 (s, 3H), 5.13 (d, *J* = 9.9 Hz, 1H), 5.28 (dd, *J* = 16.8, 0.9 Hz, 1H), 6.81-6.87 (m, 2H),

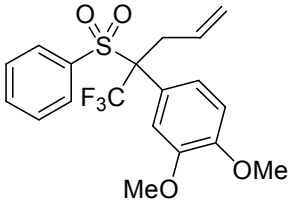
7.30-7.40 (m, 6H), 7.54-7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 32.9, 55.3, 113.7, 119.5, 120.2, 124.5 (q, J = 286.5 Hz), 128.2, 128.9, 129.8, 130.6, 131.40, 131.43, 134.04, 135.9, 160.4 (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –59.2 (s, 3F); IR (NaCl): 3436, 3073, 2937, 1611, 1517, 1159, 979, 869 cm^{-1}; MS (ESI): m/z 393 (M+Na$^+$); HRMS (ES+): calcd for $C_{18}H_{17}F_3NaO_3S$ (M+Na$^+$) 393.0748 found for 393.0743.

[1,1,1-Trifluoro-2-(3,4-dimethylphenyl)pent-4-ene-2-ylsulfonyl]benzene (3d)



The general procedure **I** was applied, using **1d** (32.8 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The obtained crude product was purified by chromatography (*n*-hexane/benzene 3:7) affording pure **3d** was obtained as colorless oil (35.8 mg, 97%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.19 (s, 3H), 2.27 (s, 3H), 3.28 (dd, J = 15.3, 8.7 Hz, 1H), 3.68 (ddd, J = 15.0, 3.6, 2.1 Hz, 1H), 5.12 (d, J = 9.9 Hz, 1H), 5.29 (d, J = 16.8 Hz, 1H), 5.53-5.66 (m, 1H), 7.06-7.12 (m, 3H), 7.21-7.37 (m, 4H), 7.40-7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 19.4, 19.9, 32.7, 77.4 (q, J = 23.6 Hz), 120.1, 124.5 (q, J = 282.9 Hz), 124.9, 127.5, 128.1, 129.6, 129.9, 130.8, 131.1, 134.0, 135.9, 136.7, 138.5; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –58.9 (s, 3F); IR (NaCl): 3073, 2979, 2923, 1148, 1165, 1081, 980, 756 cm^{-1}; MS (ESI): m/z 391 (M+Na$^+$); HRMS (ES+): calcd for $C_{19}H_{19}F_3NaO_2S$ (M+Na$^+$) 391.0956 found for 391.0959.

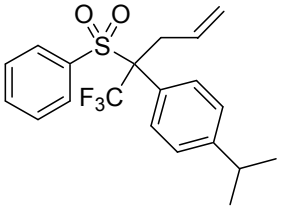
[1,1,1-Trifluoro-2-(3,4-dimethoxyphenyl)pent-4-ene-2-ylsulfonyl]benzene (3e)



The general procedure **I** was applied, using **1e** (36.0 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 mL) at 40 °C for 2 h. The crude product was purified by chromatography (benzene) to afford pure **3e**

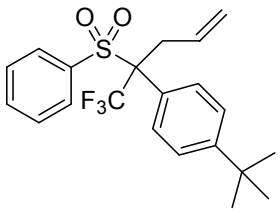
as a white solid (37.4 mg, 93%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.32 (dd, *J* = 15.3, 7.8 Hz, 1H), 3.62-3.68 (m, 4H), 3.90 (s, 3H), 5.15 (d, *J* = 9.9 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 5.58-5.63 (m, 1H), 6.79-6.98 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 7.32-7.40 (m, 4H), 7.54-7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 32.8 (d, *J* = 2.3 Hz), 55.8, 55.9, 110.5, 113.1, 119.8, 120.3, 123.2, 124.5 (q, *J* = 279.5 Hz), 128.2, 129.8, 130.7, 134.0, 135.9, 148.4, 150.0 (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –59.0 (s, 3F); IR (KBr): 3089, 2938, 1604, 1247, 1152, 985 cm^{-1}; MS (ESI): m/z 423 (M+Na$^+$); HRMS (ES+): calcd for $C_{19}H_{19}F_3NaO_4S$ (M+Na$^+$) 423.0854 found for 423.0851; white solid; Mp: 90-91 °C (*n*-hexane/acetone).

{1,1,1-Trifluoro-2-[4-(1-methylethyl)phenyl]pent-4-ene-2-ylsulfonyl}benzene (3f)



The general procedure **I** was applied, using **1f** (34.2 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3f** as colorless oil (34.5 mg, 90%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24 (s, 3H), 1.28 (s, 3H), 2.86-2.93 (m, 1H), 3.31 (dd, *J* = 15.3, 8.1 Hz, 1H), 3.71 (ddd, *J* = 15.0, 3.9, 1.8 Hz, 1H), 5.12 (d, *J* = 9.9 Hz, 1H), 5.30 (d, *J* = 16.5 Hz, 1H), 5.59-5.62 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.26-7.36 (m, 6H), 7.50-7.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 23.8, 23.9, 32.7 (d, *J* = 7.0 Hz), 33.7, 120.2, 124.6 (q, *J* = 286.7 Hz), 125.1, 126.5, 128.2, 129.85, 129.90, 130.6, 134.0, 135.9, 150.8 (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –59.1 (s, 3F); IR (NaCl): 3072, 2962, 1641, 1448, 1081, 925, 599 cm^{-1}; MS (ESI): m/z 405 (M+Na$^+$); HRMS (ES+): calcd for $C_{20}H_{21}F_3NaO_2S$ (M+Na$^+$) 405.1112 found for 405.1121.

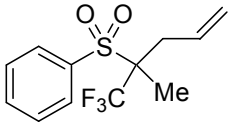
{1,1,1-Trifluoro-2-[4-(1,1-dimethylethyl)phenyl]pent-4-ene-2-ylsulfonyl}benzene (3g)



The general procedure **I** was applied, using **1g** (35.6 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3g** as colorless oil (39.4 mg, 99%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (s, 9H), 3.31 (dd, *J* = 15.3, 8.4 Hz, 1H), 3.69-3.75 (m, 1H), 5.12 (d, *J* = 9.9 Hz, 1H), 5.30 (d, *J* = 16.8, 1H), 5.42-5.65 (m, 1H), 7.24-7.55 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 31.1, 32.7 (d, *J* = 2.2 Hz), 34.6, 77.8 (q, *J* = 23.8 Hz), 120.2, 124.5 (q, *J* = 286.5 Hz), 124.8, 128.0, 129.65, 129.68, 130.6, 133.9, 133.9, 136.0, 153.1; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –59.1 (s, 3F); IR (NaCl): 3069, 2964, 2870, 1449, 1329, 1167, 924, 687 cm^{-1}; MS (ESI): m/z 419 (M+Na$^+$): HRMS (ES+): calcd for $C_{21}H_{23}F_3NaO_2S$ (M+Na$^+$) 419.1269 found for 419.1270.

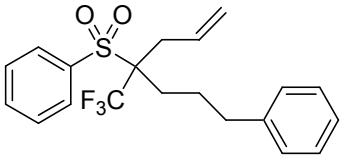
(1,1,1-Trifluoro-2-methylpent-4-en-2-ylsulfonyl)benzene (3h)



The general procedure **I** was applied, using **1h** (47.6 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), dppe (4.8 mg, 0.012 mmol), allyl ethyl carbonate (26.0 mg, 0.2 mmol) in THF (2.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 2:8) to afford pure **3h** as yellow oil (50.5 mg, 91%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (s, 3H), 2.73-2.88 (m, 2H), 5.19-5.24 (m, 2H), 5.79-5.91 (m, 1H), 7.56-7.61 (m, 2H), 7.69-7.74 (m, 1H), 7.94 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.7 (d, *J* = 1.7 Hz), 34.9 (d, *J* = 1.1 Hz), 69.6 (q, *J* = 24.8 Hz), 120.9, 124.7 (q, *J* = 284.6 Hz), 128.9, 130.1, 130.6, 134.5, 136.2; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –68.2 (s,3F); IR (NaCl): 3073, 2929, 1642, 1329, 1150, 928, 731 cm^{-1}; MS (ESI): m/z 301 (M+Na$^+$); HRMS (ES+): calcd for $C_{12}H_{13}F_3NaO_2S$ (M+Na$^+$) 301.0486 found for 301.0487.

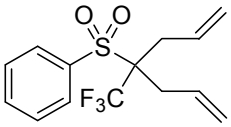
(4-Trifluoromethyl-1-phenyl hept-6-ene-4-ylsulfonyl)benzene (3i)



The general procedure **I** was applied, using **1i** (34.2 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3i** as yellow oil (35.4 mg, 93%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88-2.17 (m, 4H), 2.60-3.03 (m, 4H), 5.15-5.20 (m, 2H), 5.88-5.92 (m, 1H), 7.15-7.32 (m, 5H), 7.51-7.61 (m, 2H), 7.66-7.70 (m, 1H), 7.86 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.0, 28.2, 33.2, 36.1, 72.9 (q, J = 23.7 Hz), 120.5, 122.3, 124.7 (q, J = 285.8 Hz), 126.1, 126.5, 127.8, 128.4, 128.5, 128.9, 130.0, 130.4, 134.4, 135.2, 136.8, 140.0; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.8 (s, 3F); IR (NaCl): 3084, 2927, 1742, 1148, 927, 594 cm^{-1}; MS (ESI): m/z 405 (M+Na$^+$); HRMS (ES+): calcd for $C_{20}H_{21}F_3NaO_2S$ (M+Na$^+$) 405.1112 found for 405.1104.

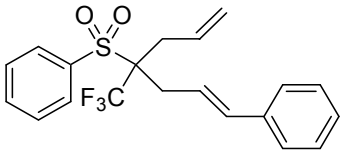
(4-Trifluoromethylhepta-1,6-diene-4-ylsulfonyl)benzene (3j)



The general procedure **I** was applied, using **1j** (26.6 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3j** as yellow oil (27.4 mg, 90%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.77 (dd, J = 15.3, 7.2 Hz, 2H), 2.91 (dd, J = 15.3, 7.2 Hz, 2H), 5.19-5.25 (m, 4H), 5.88-6.01 (m, 2H), 7.56-7.61 (m, 2H), 7.68-7.93 (m, 1H), 7.95 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 33.3 (q, J = 1.1 Hz), 72.8 (q, J = 23.2 Hz), 120.7, 124.4 (q, J = 286.0 Hz), 128.9, 130.0, 130.6, 134.5, 136.7; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.7 (s, 3F); IR (NaCl): 3083, 2985, 1641, 1330, 1167, 733, 689 cm^{-1}; MS (ESI): m/z 327 (M+Na$^+$); HRMS (ES+): calcd for $C_{14}H_{15}F_3NaO_2S$ (M+Na$^+$) 327.0643 found for 327.0639.

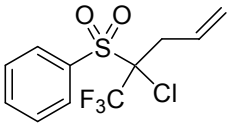
(4-Trifluoromethyl-1-phenylhept-1,6-diene-4-ylsulfonyl)benzene (3k)



The general procedure **I** was applied, using **1k** (34.0 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 3:7) to afford pure **3k** as yellow oil (36.7 mg, 97%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.78-3.10 (m, 4H), 5.20-5.30 (m, 2H), 5.96-6.02 (m, 1H), 6.21-6.31 (m, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 7.29-7.33 (m, 5H), 7.55-7.61 (m, 2H), 7.69-7.74 (m, 1H), 7.96 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 32.7, 33.6, 72.9 (q, *J* = 23.1 Hz), 120.8, 121.3, 124.5 (q, *J* = 286.4 Hz), 126.3, 127.7, 128.6, 128.9, 130.0, 130.7, 134.5, 135.4, 136.6, 136.7; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.6 (s, 3F); IR (NaCl): 3081, 2959, 1725, 1329, 1149, 927, 598 cm^{-1}; MS (ESI): m/z 403 (M+Na$^+$); HRMS (ES+): calcd for $C_{20}H_{19}F_3NaO_2S$ (M+Na$^+$) 403.0956 found for 403.0954.

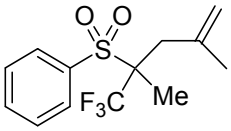
(1,1,1-Trifluoro-2-chloropent-4-en-2-ylsulfonyl)benzene (3l)



The general procedure **I** was applied, using **1l** (25.9 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), dppe (2.4 mg, 0.006 mmol), allyl ethyl carbonate (13.0 mg, 0.1 mmol) in THF (1.0 ml) at 40 °C for 1 h. The crude product was purified by chromatography (*n*-hexane/benzene 2:8) to afford pure **3l** as yellow oil (28.5 mg, 95%).

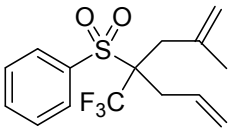
^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.20 (d, *J* = 7.2 Hz, 2H), 5.29-5.34 (m, 2H), 5.85-5.97 (m, 1H), 7.58-7.63 (m, 2H), 7.73-7.78 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 36.7, 83.8 (q, *J* = 28.8 Hz), 121.7, 122.1 (q, *J* = 285.5 Hz), 128.3, 128.9, 131.5, 134.5, 135.3; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –67.8 (s, 3F); IR (NaCl): 3085, 2927, 1643, 1583, 1156, 931, 593 cm^{-1}; MS (ESI): m/z 321 (M+Na$^+$); HRMS (ES+): calcd for $C_{11}H_{10}ClF_3NaO_2S$ (M+Na$^+$); MS (ES+): calcd for [M+Na] 320.9940 found for 320.9938.

(1,1,1-Trifluoro-2,4-dimethylpent-4-en-2-ylsulfonyl)benzene (3m)



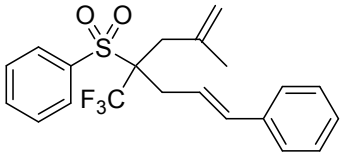
The general procedure **II** was applied, using **1h** (23.8 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), *rac*-BINAP (3.7 mg, 0.006 mmol), ethyl 2-methyl-2-propenyl carbonate (28.8 mg, 0.20 mmol) in toluene (1.0 ml) at 110 °C for 8 h. **3m** Was obtained as yellow oil (27.7 mg, 95%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.63 (s, 3H), 1.83 (s, 3H), 2.75 (d, J = 13.8 Hz, 1H), 2.89 (d, J = 13.8 Hz, 1H), 4.98 (d, J = 49.5 Hz, 2H), 7.58-7.61 (m, 2H), 7.67-7.73 (m, 1H), 7.94 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.9 (d, J = 1.7 Hz), 24.2 (d, J = 1.7 Hz), 37.0, 70.9 (q, J = 24.9 Hz), 118.9, 124.8 (q, J = 284.9 Hz), 128.9, 130.7, 134.4, 136.3, 137.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –67.5 (s, 3F); IR (NaCl): 3069, 2923, 1690, 1585, 1448, 1325, 1149, 906, 722, 689 cm^{-1}; MS (ESI): m/z 315 (M+Na$^+$); HRMS (ES+): calcd for $C_{13}H_{15}F_3NaO_2S$ (M+Na$^+$) 315.0643 found for 315.0638.

4-(Trifluoromethyl)-2-methylhepta-1,6-dien-4-ylsulfonylbenzene (3n)



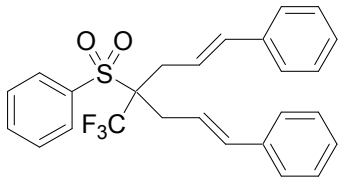
The general procedure **II** was applied, using **1j** (26.4 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), *rac*-BINAP (3.7 mg, 0.006 mmol), ethyl 2-methyl-2-propenyl carbonate (28.8 mg, 0.20 mmol) in toluene (1.0 ml) at 110 °C for 8 h. **3n** Was obtained as yellow oil (24.6 mg, 77%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.84 (s, 3H), 2.72-3.00 (m, 4H), 5.00 (d, J = 30.6 Hz, 2H), 5.19-5.26 (m, 2H), 6.02-6.16 (m, 1H), 7.55-7.61 (m, 2H), 7.68-7.93 (m, 1H), 7.95 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 24.2 (d, J = 1.6 Hz), 33.1 (d, J = 1.6 Hz), 36.2, 73.9 (q, J = 23.3 Hz), 119.2, 120.2, 124.4 (q, J = 285.5 Hz), 128.9, 130.6, 130.7, 134.5, 137.0, 137.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.0 (s, 3F); IR (NaCl): 3082, 2961, 1643, 1448, 1329, 1150, 909, 722, 689 cm^{-1}; MS (ESI): m/z 341 (M+Na$^+$); HRMS (ES+): calcd for $C_{15}H_{17}F_3NaO_2S$ (M+Na$^+$) 341.0799 found for 341.0795.

(4-Trifluoromethyl-6-methyl-1-phenylhept-1,6-diene-4-ylsulfonyl)benzene (3o)



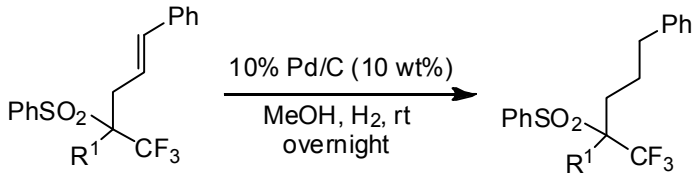
The general procedure **II** was applied, using **1k** (34.2 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), *rac*-BINAP (3.7 mg, 0.006 mmol), ethyl 2-methyl-2-propenyl carbonate (28.8 mg, 0.20 mmol) in toluene (1.0 ml) at 110 °C for 8 h. **3o** Was obtained as yellow oil (38.7 mg, 98%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.87 (s, 3H), 2.76-3.15 (m, 4H), 5.03 (d, *J* = 29.4 Hz, 2H), 6.34-6.54 (m, 2H), 7.22-7.38 (m, 5H), 7.53-7.58 (m, 2H), 7.63-7.71 (m, 1H), 7.95 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 24.6 (d, *J* = 1.6 Hz), 33.0, 36.4, 74.1 (q, *J* = 23.2 Hz), 119.4, 122.0, 124.7 (q, *J* = 285.8 Hz), 126.4, 127.7, 128.6, 128.9, 130.8, 134.4, 135.0, 136.8, 137.1, 138.0; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –63.8 (s, 3F); IR (NaCl): 3062, 2925, 1644, 1328, 1047, 909, 734 cm^{-1}; MS (ESI): m/z 417 (M+Na$^+$); HRMS (ES+): calcd for $C_{21}H_{21}F_3NaO_2S$ (M+Na$^+$) 417.1112 found for 417.1112.

(4-Trifluoromethyl-1,7-diphenylhept-1,6-diene-4-ylsulfonyl)benzene (3p)



To a stirred solution of **1k** (34.0 mg, 0.1 mmol), dppf (3.3 mg, 0.006 mmol) and $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) in THF (1.0 ml) was added cinnamyl ethyl carbonate (41.2 mg, 0.2 mmol) at room temperature. The solution was heated at 60 °C and the progress of the reaction was monitored by TLC. Then, the mixture was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane/Et_2O 95:5) after passing through a short column on silica gel (Et_2O). **3p** was obtained as colorless oil (43.7 mg, 96%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.98 (dd, *J* = 15.0, 7.2 Hz, 2H), 3.10 (dd, *J* = 15.0, 7.2 Hz, 2H), 6.30 (dt, *J* = 15.0, 7.2 Hz, 2H), 6.53 (d, *J* = 15.6 Hz, 2H), 7.24-7.36 (m, 10H), 7.55-7.60 (m, 2H), 7.68-7.73 (m, 1H), 7.98 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ33.1, 73.4 (q, *J* = 23.2 Hz), 121.4, 124.6 (q, *J* = 286.5 Hz), 126.4, 127.8, 128.6, 129.0, 130.7, 134.6, 135.6, 136.6, 136.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.5 (s, 3F); IR (NaCl): 3084, 2924, 1599, 1328, 1313, 1149, 1079, 968, 728, 689 cm^{-1}; MS (ESI): m/z 479 (M+Na$^+$).

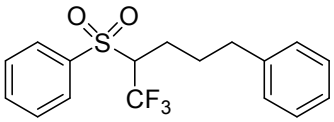
Reduction of olefin



1e, 3k **1i, 5**

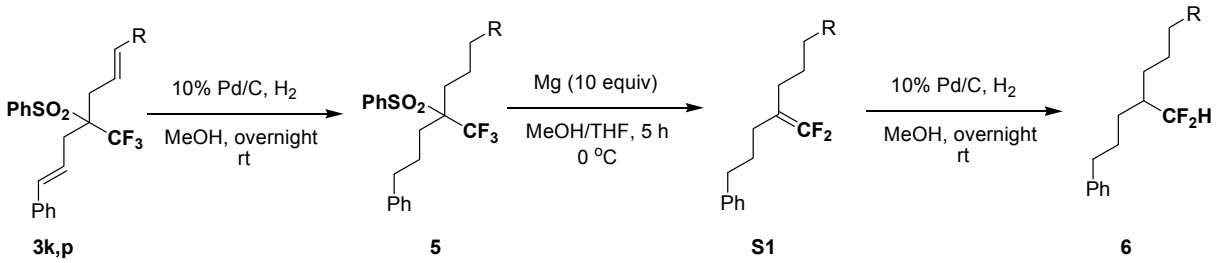
To a solution of **1k** or **3k** in MeOH (0.1 M), 10% Pd/C (10 wt%) was added. The reaction mixture was stirred at room temperature overnight under H_2 atomosphere . The resulting mixture was filtered on celite with elution by MeOH. After evaporation of the solvent, the crude product was purified by column chromatography eluting with *n*-hexane/EtOAc to give the compounds **1i** or **5**.

(1,1,1-Trifluoro-5-phenyl-2-pentylsulfonyl)benzene (1i)

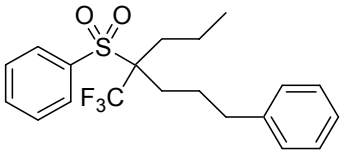


The reduction was performed, using 10% Pd/C (13.6 mg), **1e** (136.1 mg, 0.4 mmol) in MeOH (3.0 ml) at room temperature for 6 h. **1i** was obtained as yellow oil (139.0 mg, quant.).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88-2.03 (m, 3H), 2.16-2.29 (m, 1H), 2.64-2.69 (m, 2H), 3.57-3.66 (m, 1H), 7.15-7.32 (m, 5H), 7.54-7.59 (m, 2H), 7.67-7.72 (m, 1H), 7.87 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 23.9, 29.0, 35.3, 67.2 (q, J = 27.1 Hz), 123.2 (q, J = 281.2 Hz), 126.1, 128.3, 128.4, 129.0, 129.2, 134.5, 137.8, 140.7; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.6 (d, J = 7.9 Hz, 3F); IR (NaCl): 3063, 2938, 1744, 1449, 1153, 912, 752 cm^{-1}; MS (ESI): m/z 365 (M+Na$^+$); HRMS (ES+): calcd for $C_{17}H_{17}F_3O_2NaS$ (M+Na$^+$) 365.0799 found for 365.0798.

Synthesis of Difluoromethyl Compound

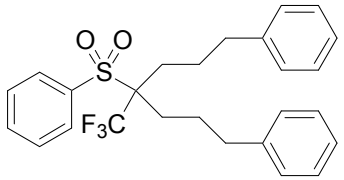


(4-trifluoromethyl-1-phenyl-4-heptylsulfonyl)benzene (5a)



The reduction was performed; using 10% Pd/C (26.0 mg), **3k** (225.8 mg, 0.34 mmol) in MeOH (6.0 ml) at room temperature for 33 h. **5a** was obtained as yellow oil (198.9 mg, 88%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.38-1.60 (m, 2H), 1,78-2.27 (m, 6H), 2.65 (t, *J* = 7.2 Hz, 2H), 7.17-7.33 (m, 5H), 7.50-7.55 (m, 2H), 7.64-7.69 (m, 1H), 7.84 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 14.6, 16.9, 25.2, 27.9, 30.4, 36.1, 73.6 (q, *J* = 24.1 Hz), 124.9 (q, *J* = 285.2 Hz), 126.1, 128.42, 128.44, 128.8, 130.3, 134.2, 137.1, 141.0; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –65.0 (s, 3F); IR (NaCl): 3064, 2972, 2252, 1603, 1449, 1326, 1147, 911, 724 cm^{-1}; MS (ESI): m/z 407 (M+Na^{+}); HRMS (ES+): calcd for $C_{20}H_{23}F_3O_2NaS$ (M+Na^{+}) 407.1269 found for 407.1265.

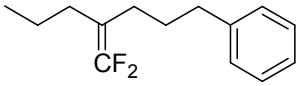
(4-Trifluoromethyl-1,7-diphenyl-4-heptylsulfonyl)benzene (5b)



The reduction was performed; using 10% Pd/C (30.2 mg), **3p** (301.9 mg, 0.66 mmol) in MeOH (7.0 ml) at room temperature for 12 h. **5b** was obtained as a white solid (256.5 mg, 84%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.70-2.15 (m, 8H), 2.61 (t, *J* = 7.2 Hz, 4H), 7.13-7.32 (m, 5H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 25.0, 27.8, 36.1, 73.5 (q, *J* = 23.8 Hz), 124.8 (q, *J* = 286.0 Hz), 126.1, 128.43, 128.45, 130.3, 134.2, 137.0, 137.0 141.9; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.9 (s, 3F); IR

(KBr): 3028, 2946, 1964, 1602, 1496, 1447, 1328, 1053, 952, 722 cm^{-1}; MS (ESI): m/z 483 ($M+Na^+$); white solid; Mp: 75-76 °C (*n*-hexane/acetone).

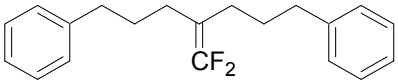
1-{4-(Difluoromethylene)heptyl}benzene (S1a)



A test tube containing Mg (126.4 mg, 5.2 mmol, 10 eq.) was heated for drying under N_2 atmosphere. The test tube was cooled at 0 °C, and then MeOH (5.2 mL) and a solution of **5a** (198.9 mg, 0.52 mmol) in THF (1.6 mL) were added. The reaction mixture was stirred at 0 °C for 5 h. The reaction was quenched with saturated NH_4Cl aqueous solution and extracted with CH_2Cl_2 for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 9:1) to give the desired difluoromethylene compound **S1a** as yellow oil (93.0 mg, 83%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.33-1.46 (m, 2H), 1,66-1.76 (m, 2H), 1.91-2.04 (m, 4H), 2.59 (t, *J* = 7.8 Hz, 2H), 7.13-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 13.5, 20.6 (t, *J* = 2.3 Hz), 25.7, 27.9, 29.3 (t, *J* = 2.3 Hz), 35.5, 88.4 (t, *J* = 16.8 Hz), 125.8, 128.3, 142.1, 153.5 (t, *J* = 283.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –96.5 (d, *J* = 10.7 Hz, 2F); IR (NaCl): 3030, 2960, 2864, 2320, 1747, 1494, 747 cm^{-1}; MS (EI): m/z 224 (M^+); HRMS (EI): calcd for $C_{14}H_{18}F_2$ (M^+) 224.1377 found for 224.1398.

1-{4-(Difluoromethylene)-7-phenylheptyl}benzene (S1b)

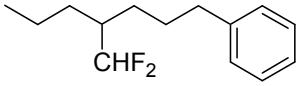


A test tube containing Mg (39.3 mg, 1.6 mmol, 10 eq.) was heated for drying under N_2 atmosphere. The test tube was cooled at 0 °C, and then MeOH (2.0 ml) and a solution of **5b** (74.6 mg, 0.16 mmol) in THF (0.6 ml) were added. The reaction mixture was stirred at 0 °C for 4 h. The reaction was quenched with saturated NH_4Cl aqueous solution and extracted with CH_2Cl_2 for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane) to give the desired difluoromethylene compound **S1b** as colorless oil (40.8 mg, 84%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.64-1.75 (m, 4H), 1.99-2.03 (m, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 7.15-7.31 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.6, 29.1 (t, *J* = 2.3 Hz), 35.4, 88.3 (t, *J* =

16.6 Hz), 125.8, 128.3, 142.0, 153.4 (t, J = 283.8 Hz) (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –95.9 (s, 2F); IR (NaCl): 3026, 2982, 2857, 1741, 1640, 1495, 928, 731 cm^{-1}; MS (EI): m/z 300 (M^+); HRMS (EI): calcd for $C_{20}H_{22}F_2$ (M^+) 300.1690 found for 300.1688.

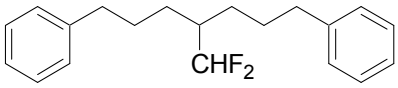
1-(4-(difluoromethyl)heptyl)benzene (6a)



10% Pd/C (2.3 mg) was added to a solution of the difluoromethylene compound **S1a** (22.4 mg, 0.10 mmol) in MeOH (1.0 mL). The reaction mixture was stirred at room temperature overnight under H_2 atmosphere. After celite filtration, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane) to give **6a** as yellow oil (21.7 mg, 96%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (t, J = 7.2 Hz, 3H), 1.23-1.85 (m, 9H), 2.61 (t, J = 7.8 Hz, 2H), 5.69 (td, J = 57.0, 3.6 Hz, 1H), 7.16-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.3, 20.0, 27.4 (t, J = 17.4 Hz), 28.8, 30.0 (t, J = 17.4 Hz), 36.1, 41.8 (t, J = 74.7 Hz), 119.0 (t, J = 242.4 Hz), 125.1, 128.3, 142.1 (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –122.5 (ddd, J = 270.2, 56.4 15.8 Hz, 1F), –123.6 (ddd, J = 270.2, 56.4 15.8 Hz, 1F); IR (NaCl): 3027, 2936, 2871, 1496, 1455, 1089, 747 cm^{-1}; MS (EI): m/z 226 (M^+); HRMS (EI): calcd for $C_{14}H_{20}F_2$ (M^+) 226.1533 found for 226.1562.

1-{4-(difluoromethyl)-1-phenylheptyl}benzene (6b)

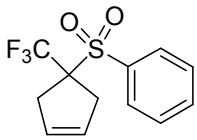


10% Pd/C (4.5 mg) was added to a solution of the difluoromethylene compound **S1b** (44.6 mg, 0.15 mmol) in MeOH (2.0 ml). The reaction mixture was stirred at room temperature overnight under H_2 atmosphere. After celite filtration, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane) to give **6b** as colorless oil (38.0 mg, 85%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32-1.85 (m, 9H), 2.60 (t, J = 7.5 Hz, 4H), 5.69 (td, J = 57.0, 3.3 Hz, 1H), 7.14-7.31 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 27.4 (t, J = 4.5 Hz), 28.6, 36.1, 41.9 (t, J = 18.3 Hz), 118.9 (t, J = 242.3 Hz), 125.8, 128.3, 142.0 (one carbon atom resonance was not detected); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –123.0 (dd, J = 57.3 15.8 Hz, 2F); IR (NaCl):

3026, 2938, 2862, 1495, 1454, 1392, 1127, 1081, 748, 699 cm^{-1}; MS (EI): m/z 300 (M^+); HRMS (EI): calcd for $C_{20}H_{24}F_2$ (M^+) 302.1846 found for 302.1848.

(4-Trifluoromethyl-cyclopent-1-ene-4-ylsulfonyl)benzene (4)



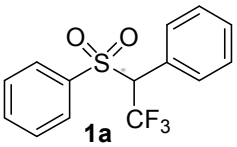
A solution of **3j** (30.4 mg, 0.10 mmol) and Grubbs' I catalyst (0.4 mg, 0.005 mmol, 5 mol%) in CH_2Cl_2 (1.0 ml) was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc 8:2) to give the **6** as a black solid (26.3 mg, 95 %).
^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.87 (dd, *J* = 15.9, 2.7 Hz, 2H), 3.36 (d, *J* = 16.5 Hz, 2H), 5.67 (s, 2H), 7.56-7.61 (m, 2H), 7.68-7.74 (m, 1H), 7.97 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 37.5 (d, *J* = 1.7 Hz), 74.2 (q, *J* = 26.0 Hz), 123.4 (q, *J* = 282.2 Hz), 127.4, 129.0, 130.3, 134.5, 136.4; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –70.3 (s, 3F); IR (KBr): 3073, 2938, 2867, 1584, 1313, 1159, 757, 594 cm^{-1}; MS (ESI): m/z 299 ($M+Na^+$); HRMS (ES+): calcd for $C_{12}H_{11}F_3NaO_2S$ ($M+Na^+$) 299.0330 found for 299.0336; black solid; Mp: 87-88 °C (*n*-hexane/acetone).

Supplemental References

[1] a) Uneyama, K.; Momota, M. *Bull. Chem. Soc. Jpn*. **1989**, *62*, 3378-3379. b) Feiring, A, E.; *J. Org. Chem*, **1980**, *45*, 1958-1961.

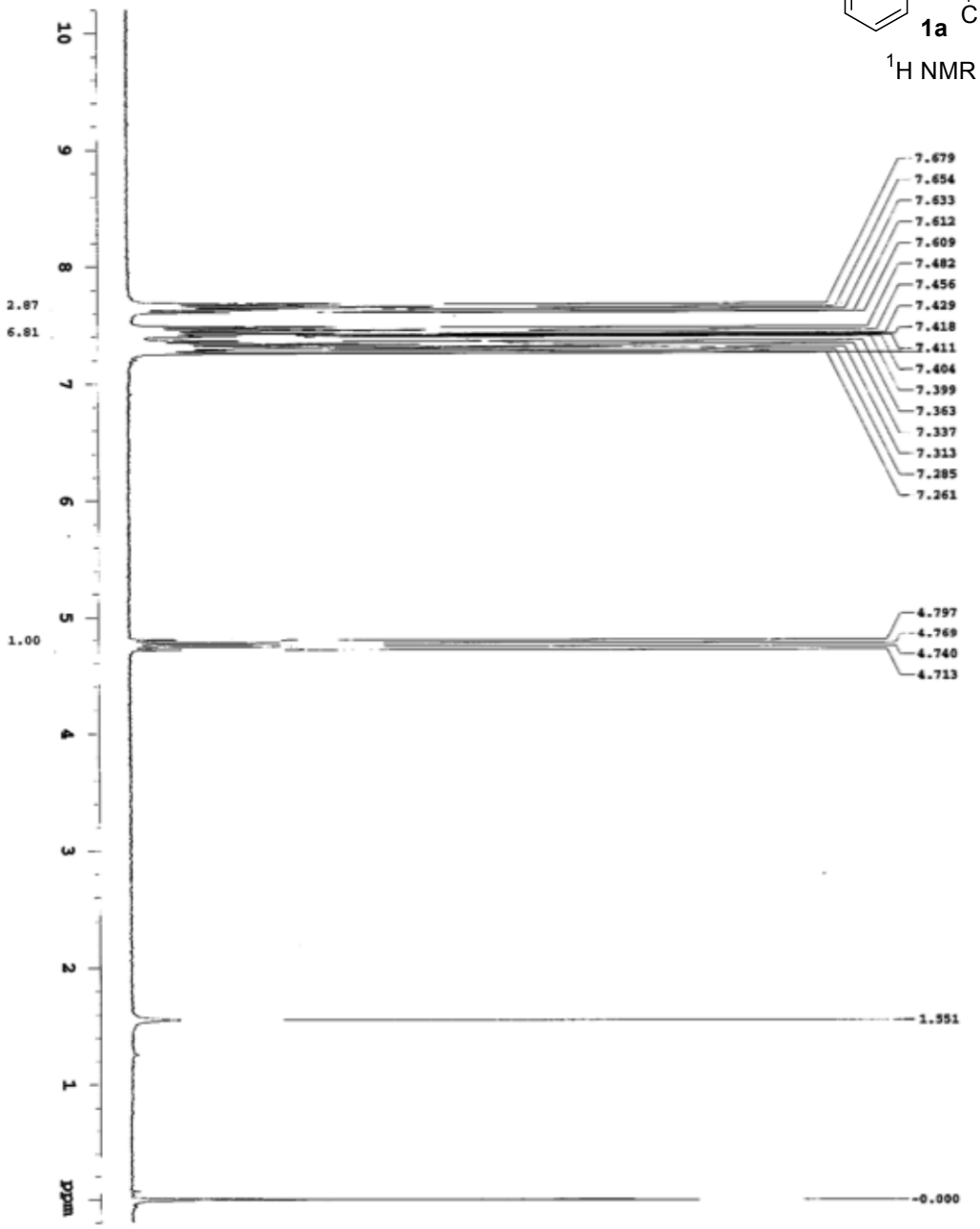
[2] Uneyama, K.; Momota, M. *Tetrahedron*, **1989**, *30*, 2265-2266.

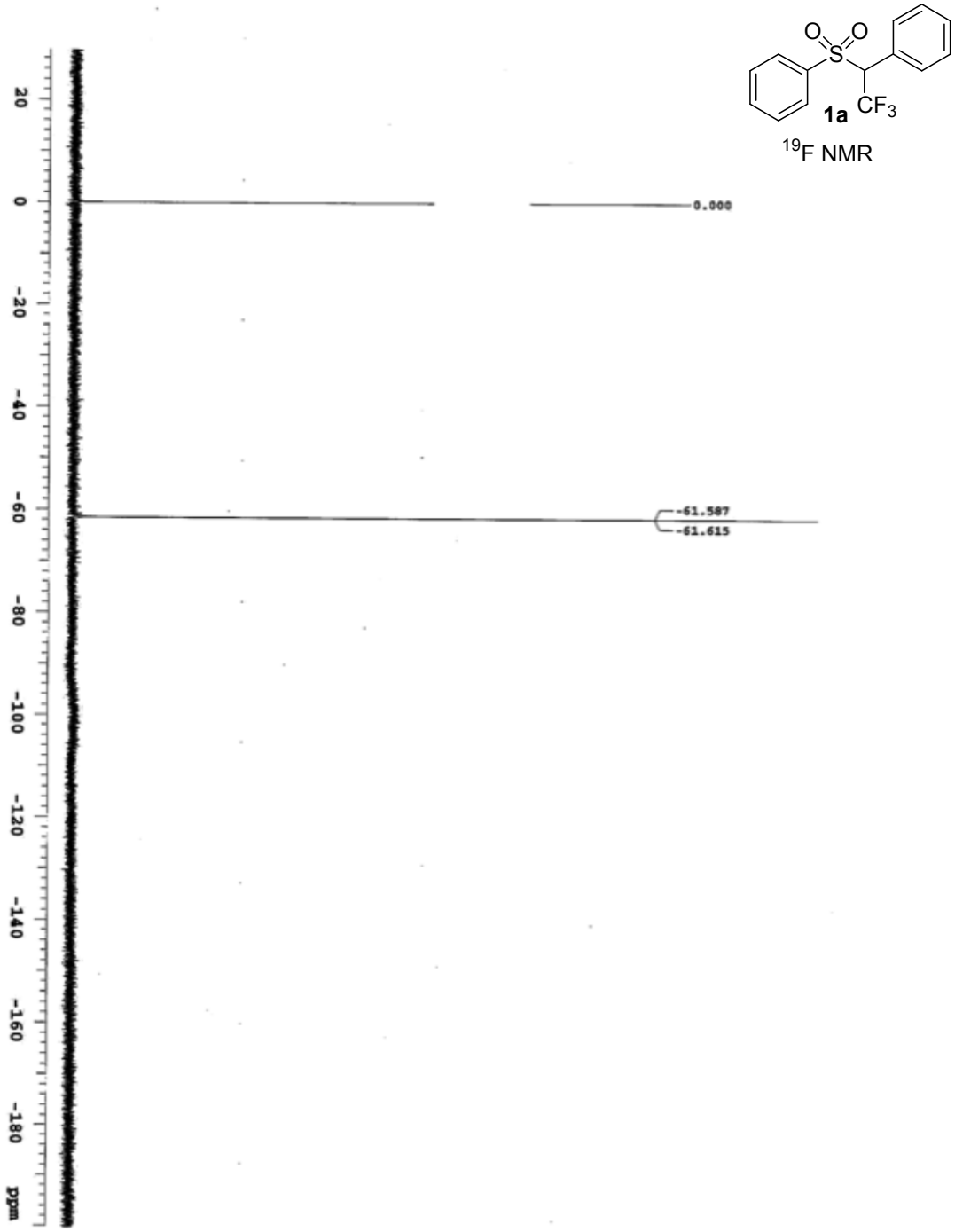
[3] Uneyama, K.; Momota, M.; Hayashida, K.; Itoh, T. *J. Org. Chem*, **1990**, *55*, 5364-5368.

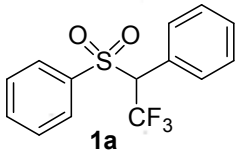

O
O
S
CF3

1a

^{1}H NMR

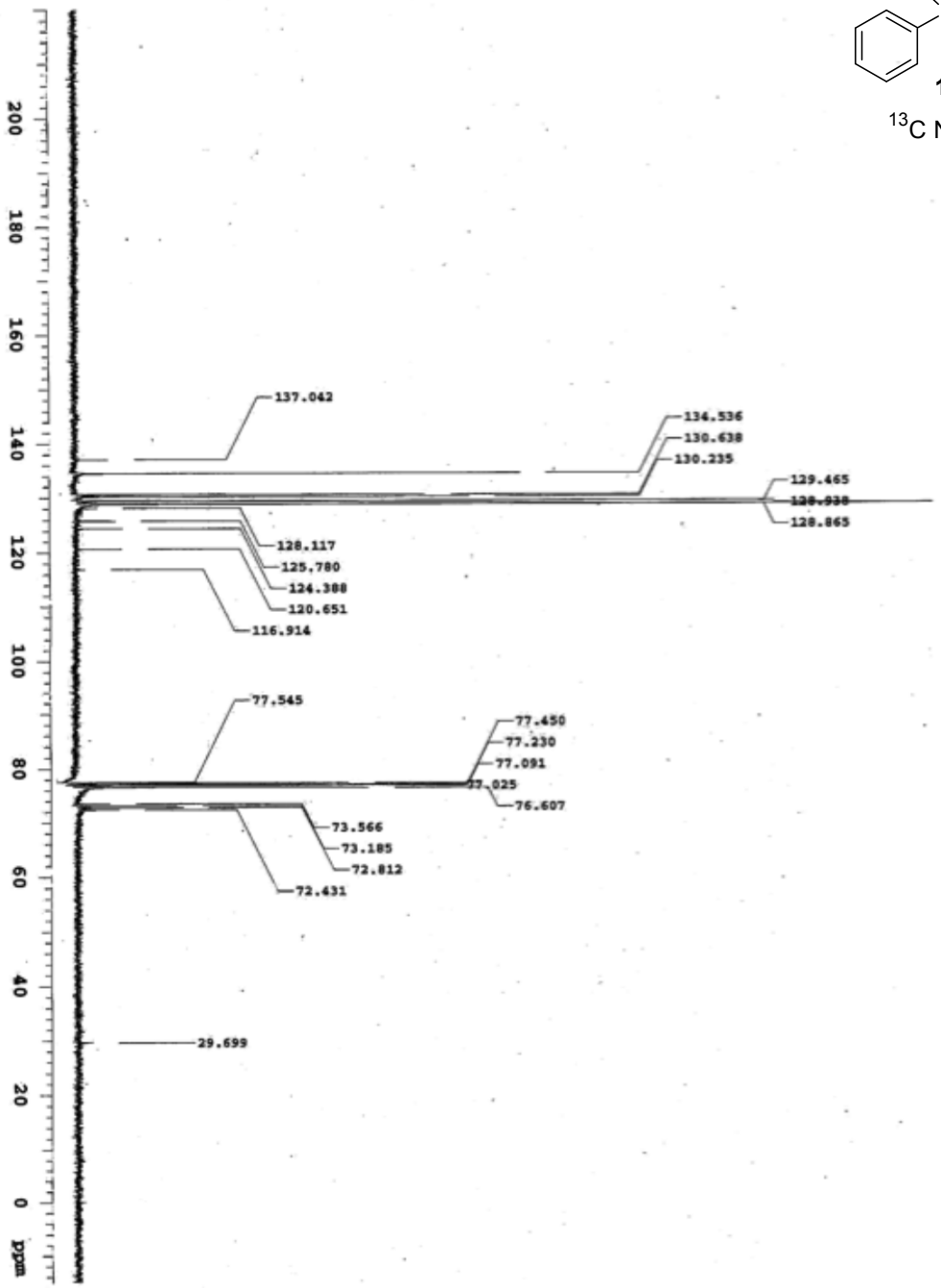

10
9
8
7
6
5
4
3
2
1
ppm
2.87
6.81
1.00
7.679
7.654
7.633
7.612
7.609
7.482
7.456
7.429
7.418
7.411
7.404
7.399
7.363
7.337
7.313
7.285
7.261
4.797
4.769
4.740
4.713
1.551
-0.000

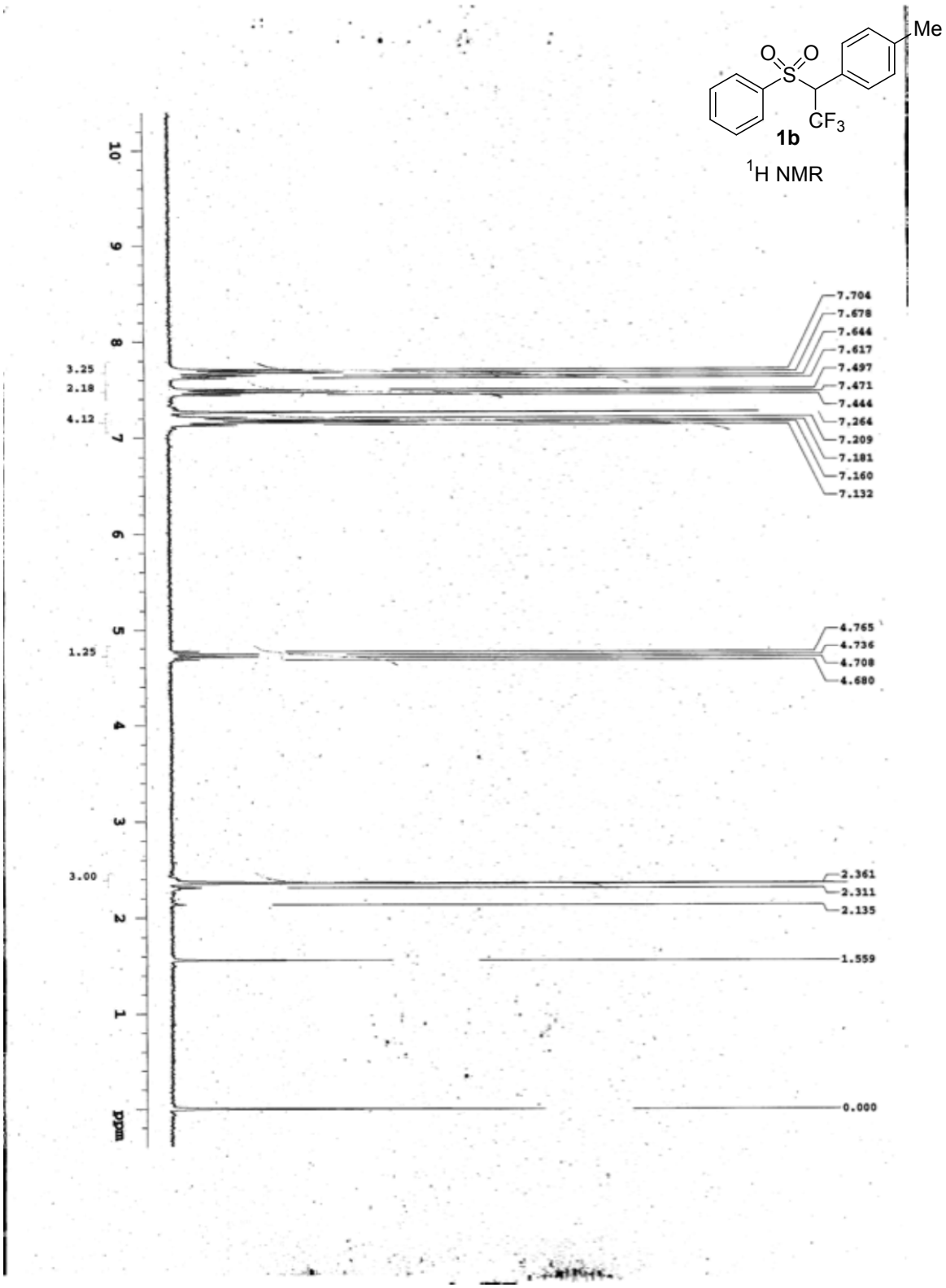

O
O
S
CF3
1a
19F NMR
0.000
-61.587
-61.615
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

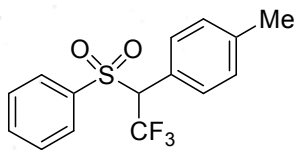

O
O
S
CF3

1a

^{13}C NMR

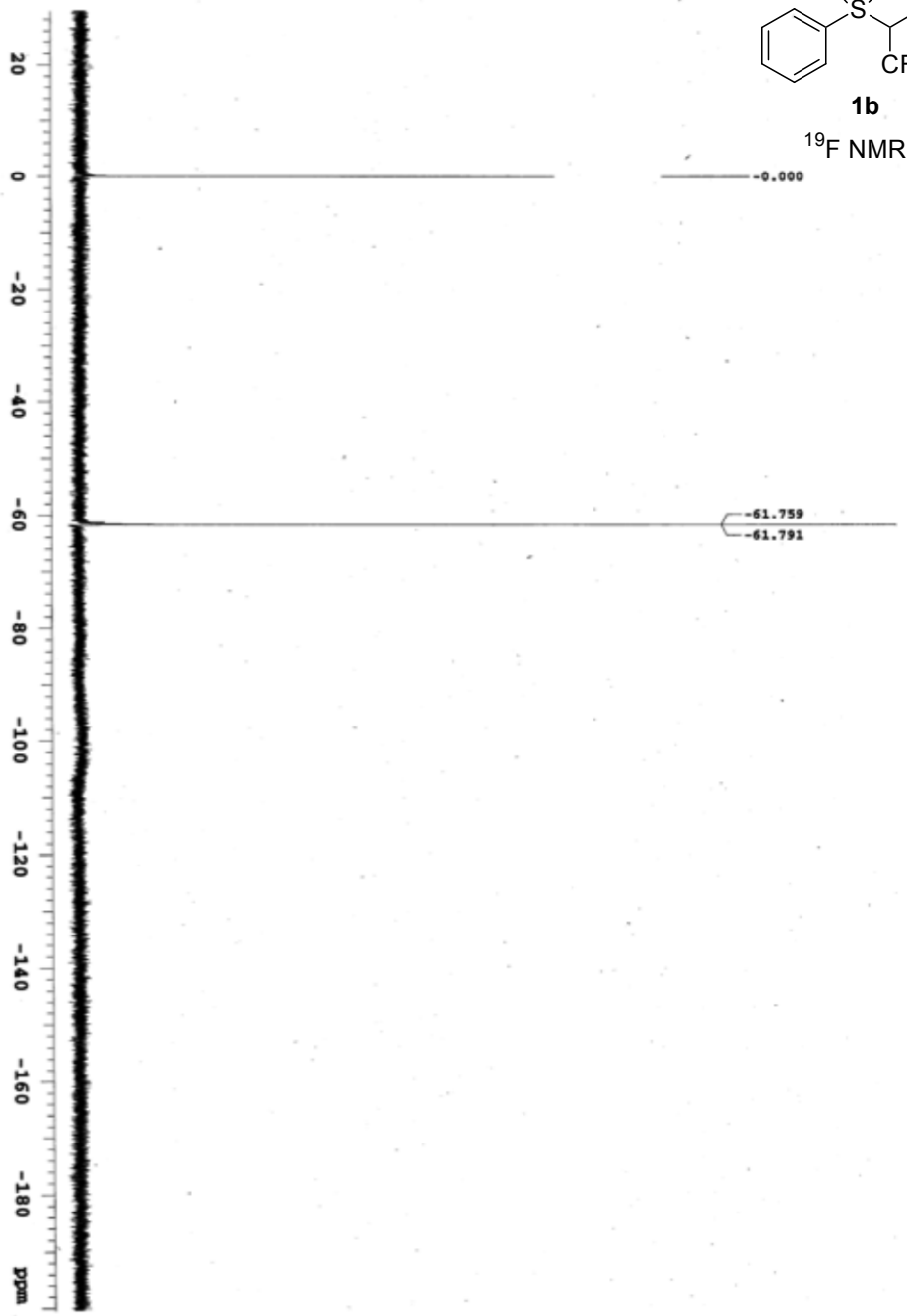

137.042
134.536
130.638
130.235
129.465
128.938
128.865
128.117
125.780
124.388
120.651
116.914
77.545
77.450
77.230
77.091
77.025
76.607
73.566
73.185
72.812
72.431
29.699
200
180
160
140
120
100
80
60
40
20
0
ppm

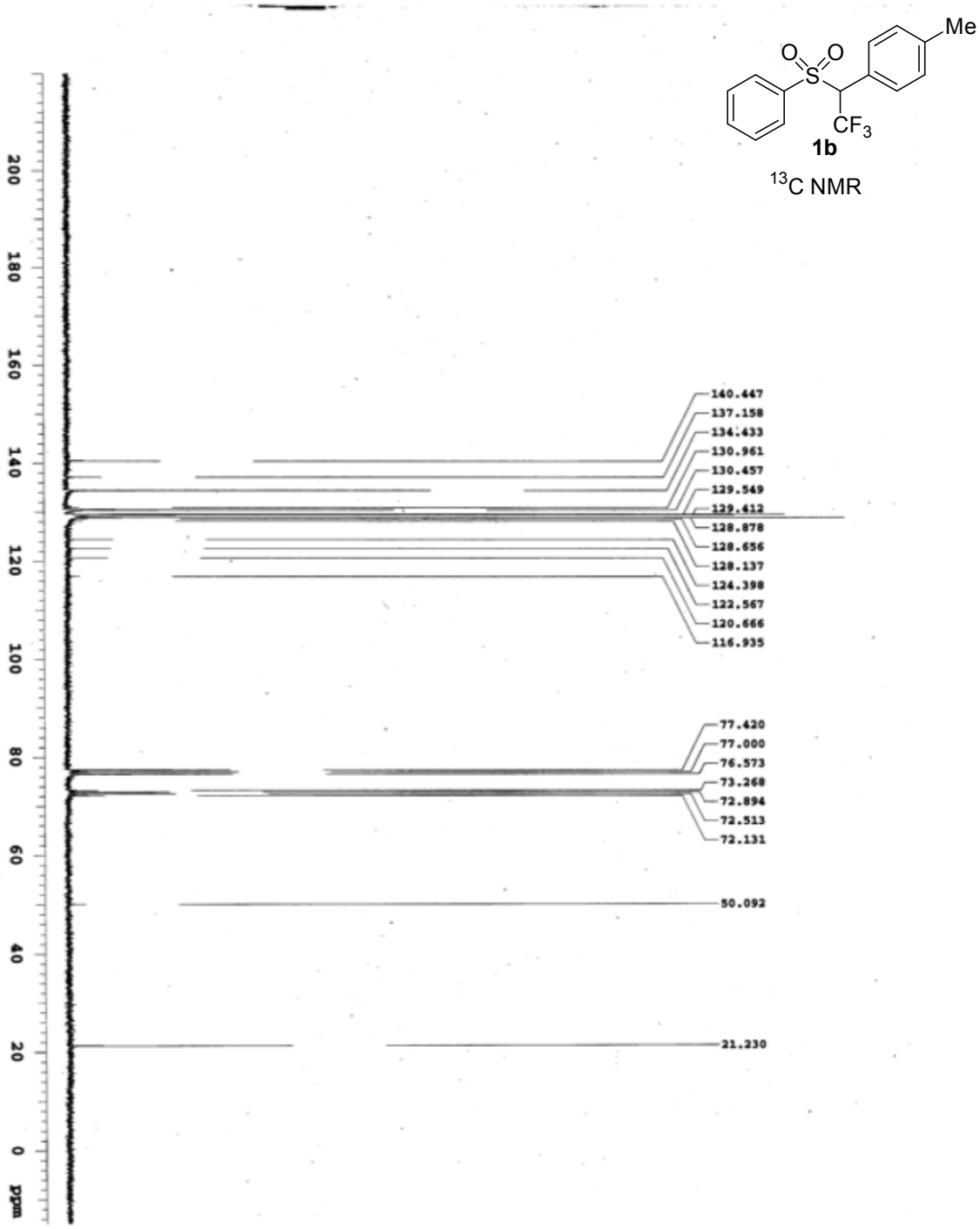

Me
O
O
S
CF3
1b
1H NMR
7.704
7.678
7.644
7.617
7.497
7.471
7.444
7.264
7.209
7.181
7.160
7.132
4.765
4.736
4.708
4.680
2.361
2.311
2.135
1.559
0.000
3.25
2.18
4.12
1.25
3.00
10
9
8
7
6
5
4
3
2
1
ppm

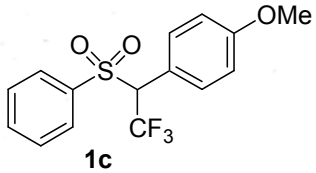

Me
O
O
S
CF3

1b

^{19}F NMR

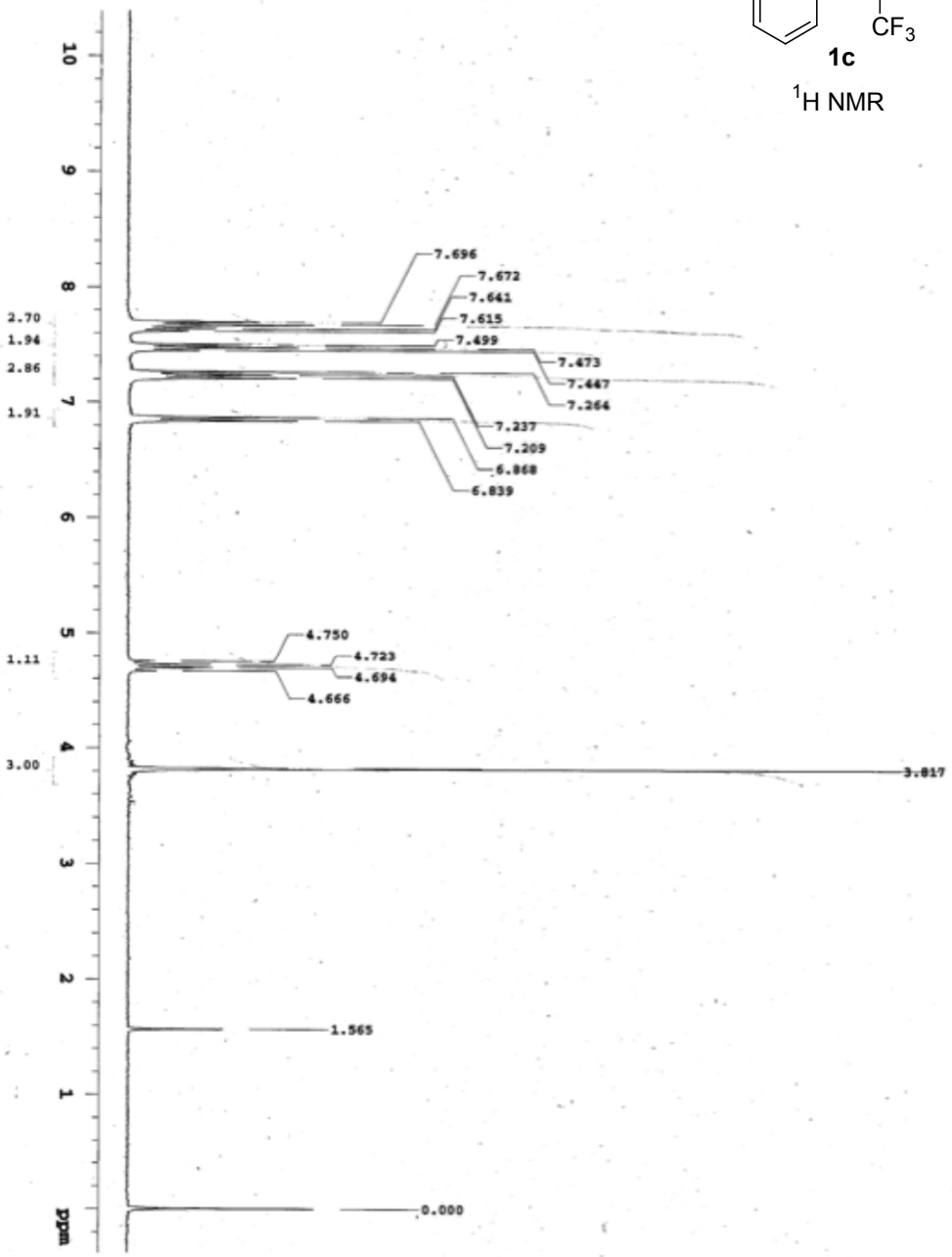

-0.000
-61.759
-61.791
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

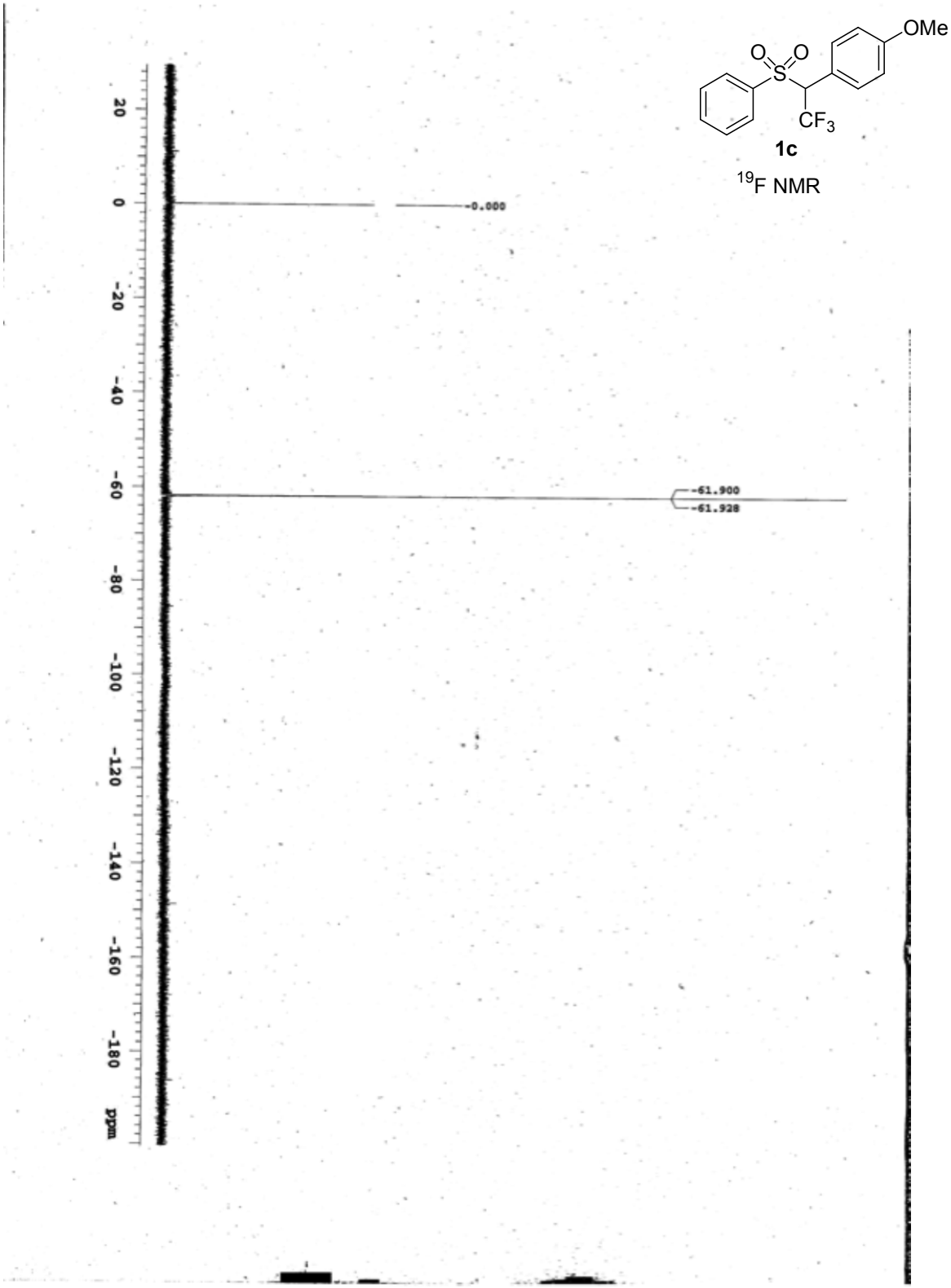

Me
O
O
S
CF3
1b
13C NMR
140.447
137.158
134.433
130.961
130.457
129.549
129.412
128.878
128.656
128.137
124.398
122.567
120.666
116.935
77.420
77.000
76.573
73.268
72.894
72.513
72.131
50.092
21.230
200
180
160
140
120
100
80
60
40
20
0
ppm

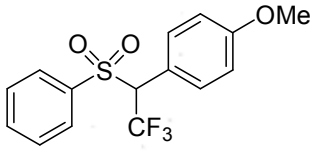

OMe
O
O
S
CF3

1c

^{1}H NMR

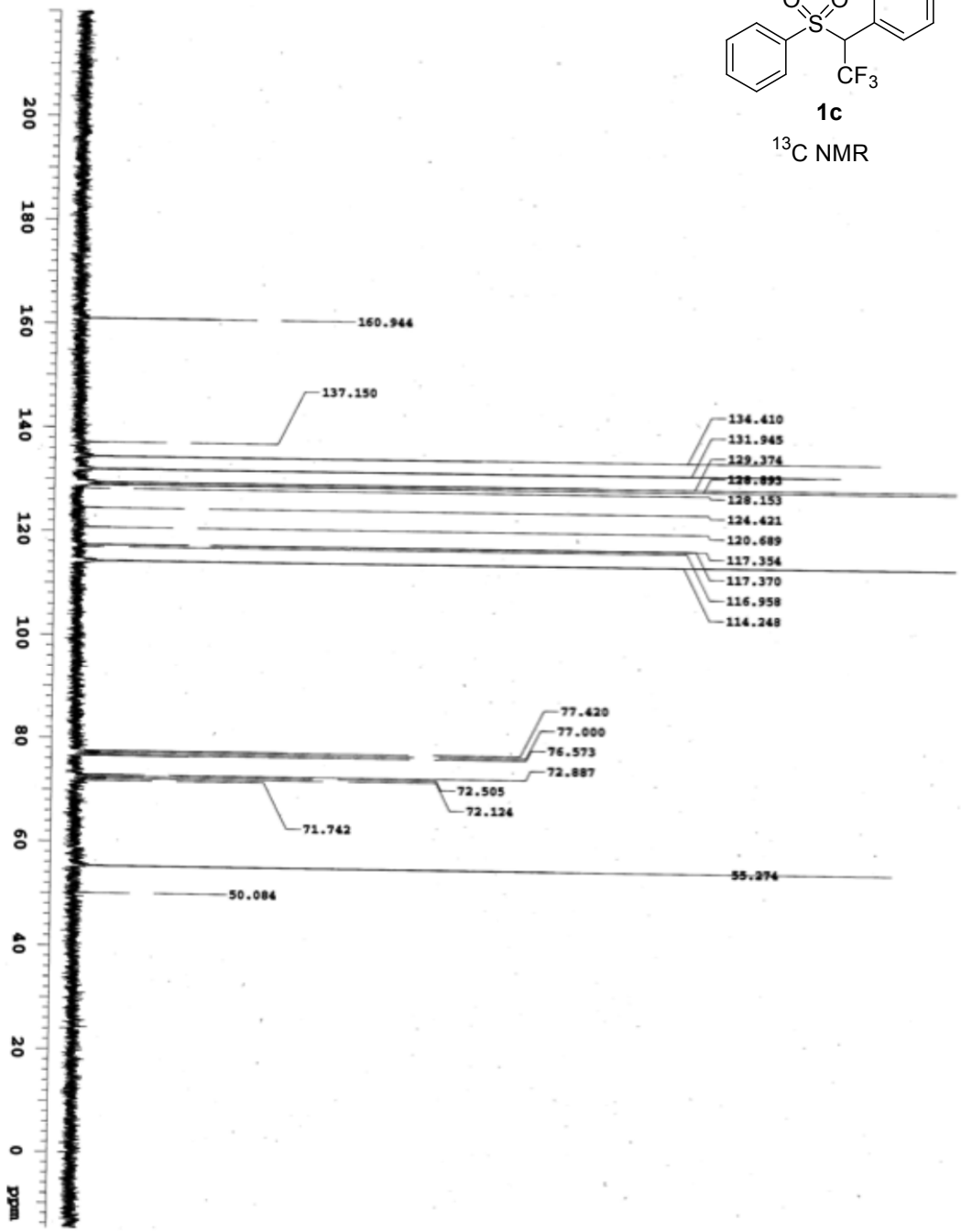

7.696
7.672
7.641
7.615
7.499
7.473
7.447
7.264
7.237
7.209
6.868
6.839
4.750
4.723
4.694
4.666
3.817
1.565
0.000
2.70
1.94
2.86
1.91
1.11
3.00
10
9
8
7
6
5
4
3
2
1
ppm

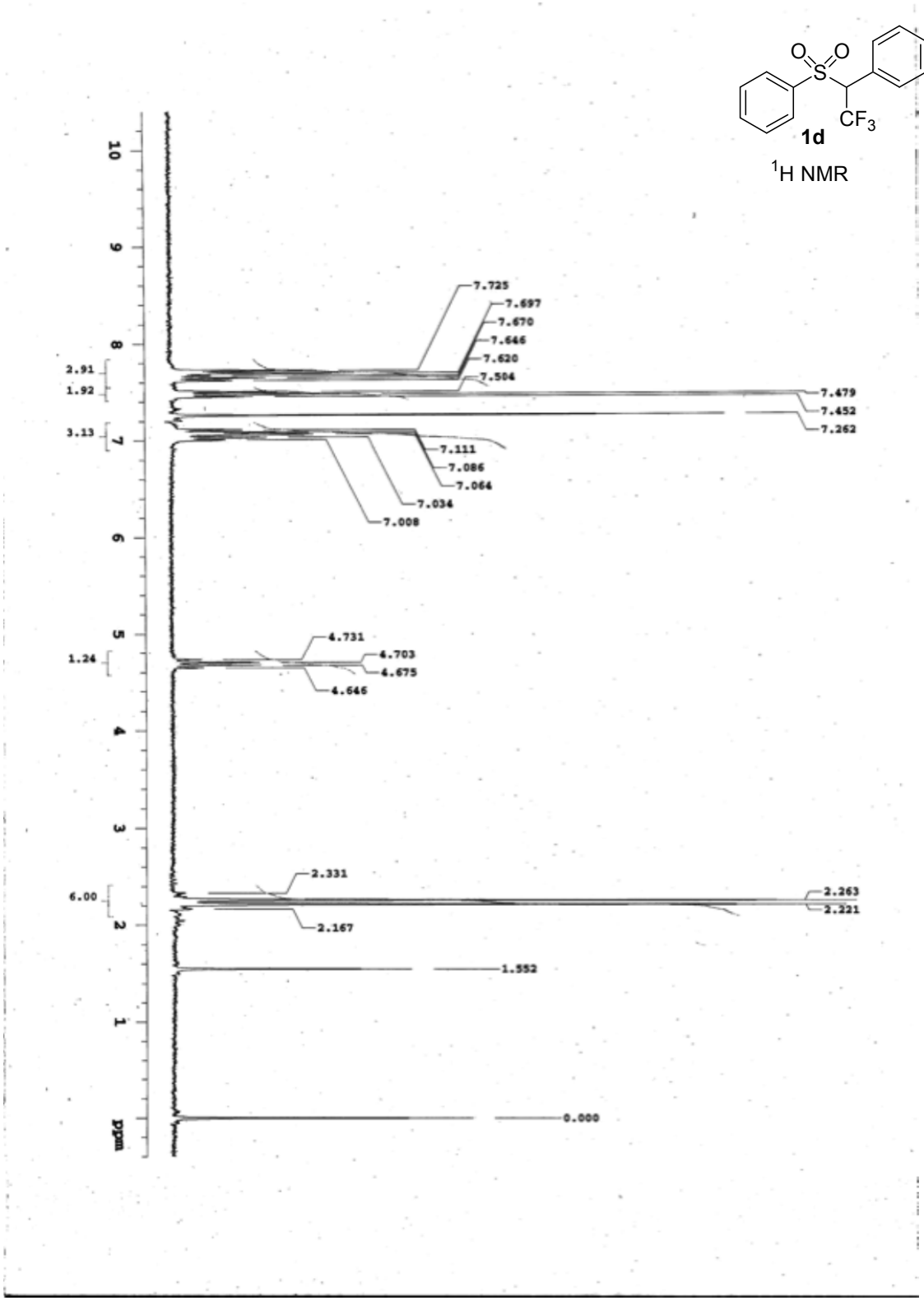

OMe
O
O
S
CF3
1c
19F NMR
-0.000
-61.900
-61.928
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

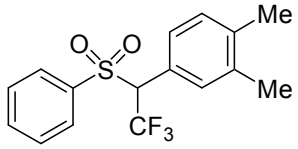

OMe
O
O
S
CF3

1c

^{13}C NMR

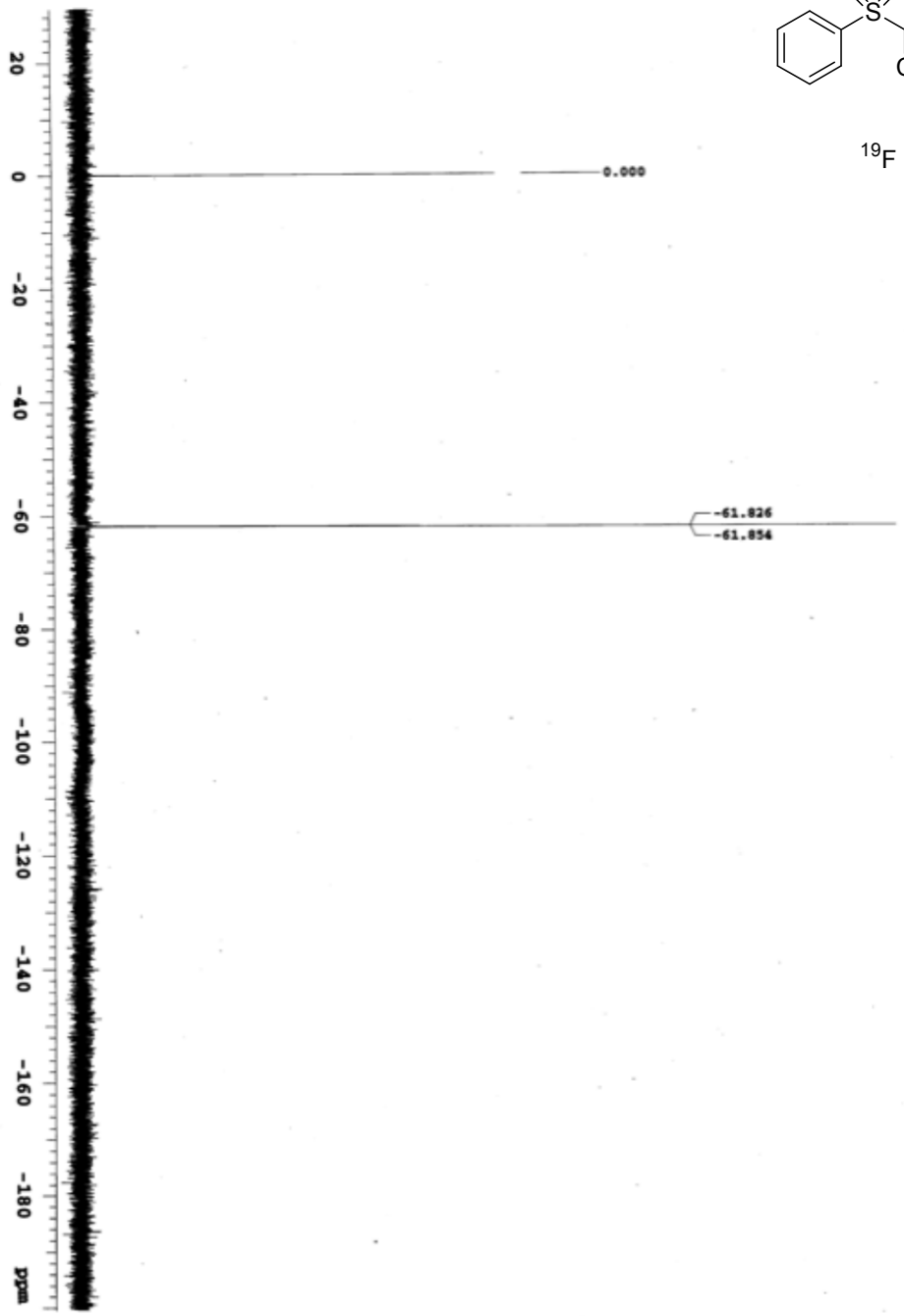

160.944
137.150
134.410
131.945
129.374
128.893
128.153
124.421
120.689
117.354
117.370
116.958
114.248
77.420
77.000
76.573
72.887
72.505
72.124
71.742
55.274
50.084
200
180
160
140
120
100
80
60
40
20
0
ppm

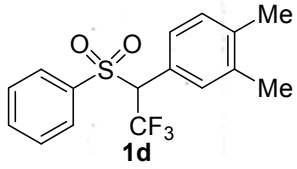

Me
Me
O
O
S
CF3
1d
1H NMR
7.725
7.697
7.670
7.646
7.620
7.504
7.479
7.452
7.262
7.111
7.086
7.064
7.034
7.008
4.731
4.703
4.675
4.646
2.331
2.263
2.221
2.167
1.552
0.000
2.91
1.92
3.13
1.24
6.00
10
9
8
7
6
5
4
3
2
1
ppm


Me
O
O
S
Me
CF3

1d

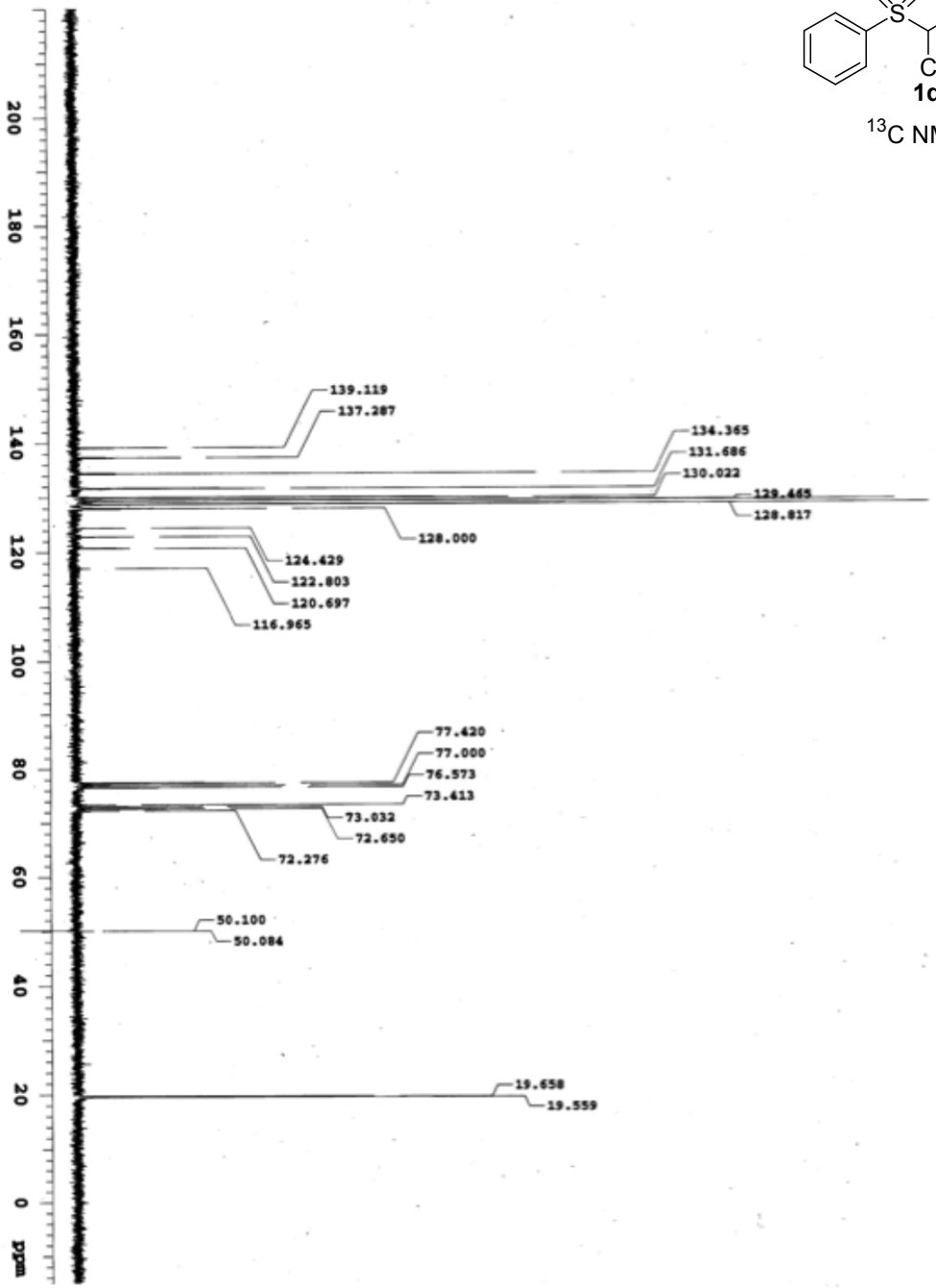
^{19}F NMR

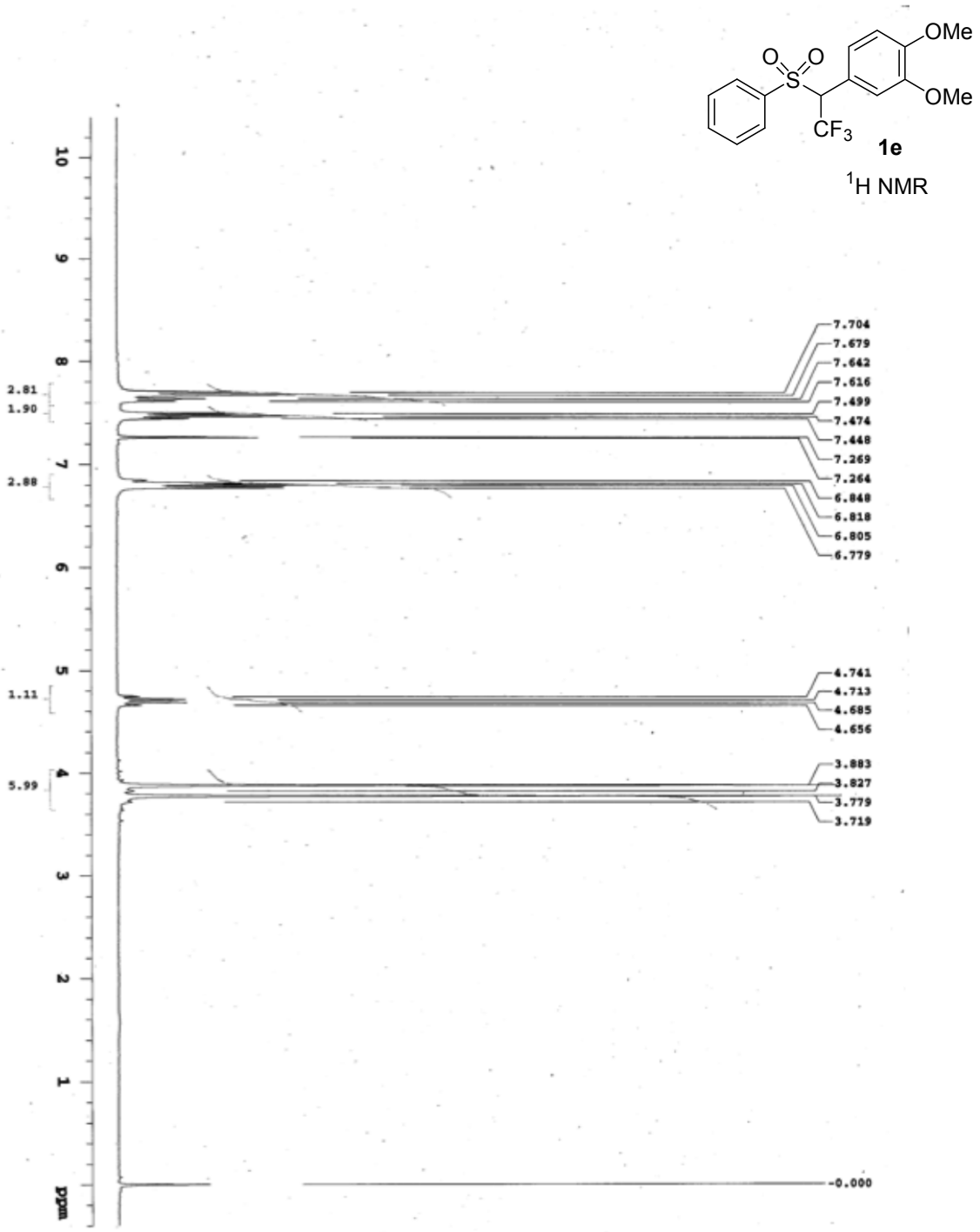

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.000
-61.826
-61.854

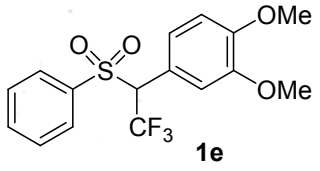

Me
Me
O
O
S
CF3

1d

^{13}C NMR

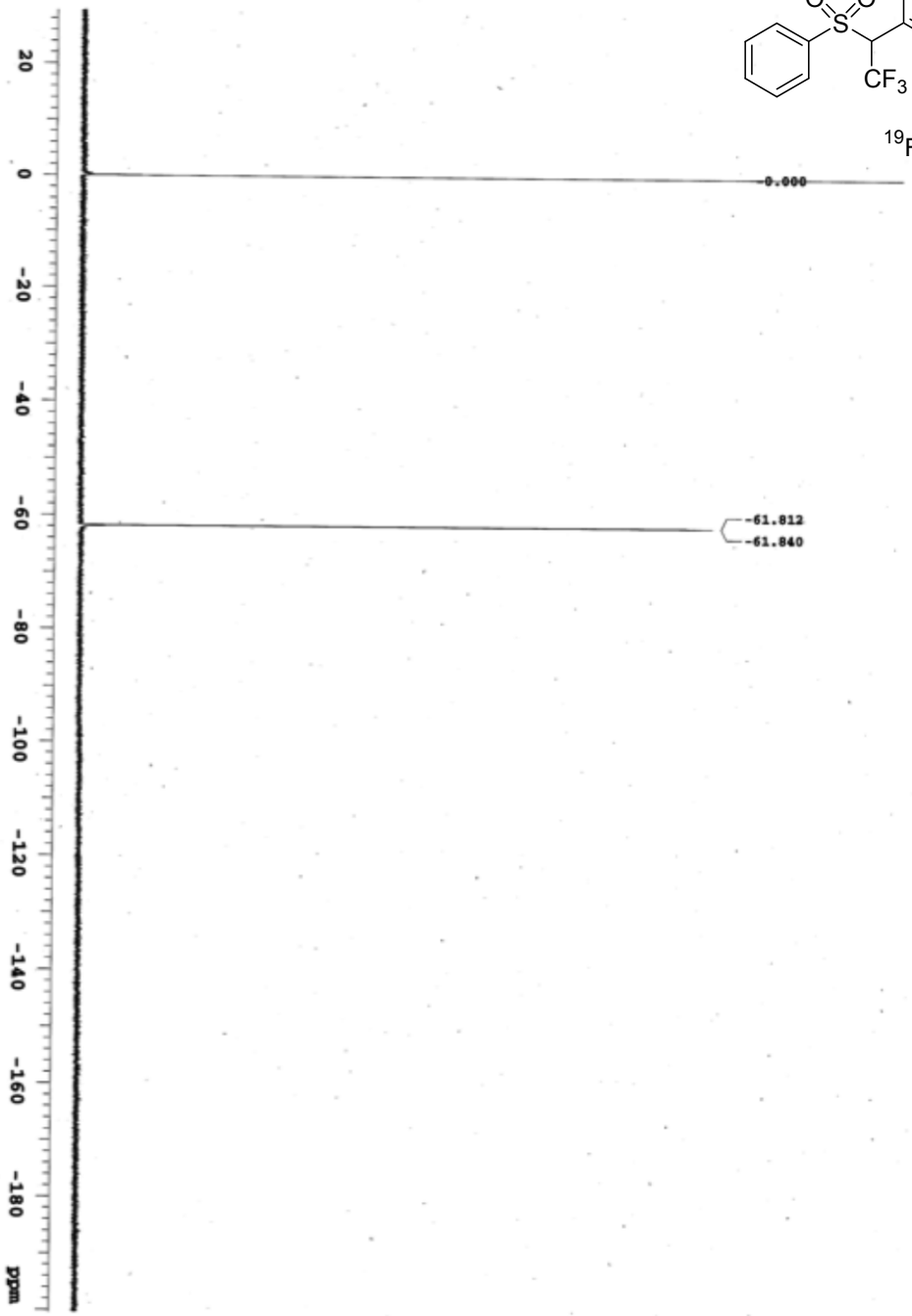

139.119
137.287
134.365
131.686
130.022
129.465
128.817
128.000
124.429
122.803
120.697
116.965
77.420
77.000
76.573
73.413
73.032
72.650
72.276
50.100
50.084
19.658
19.559
200
180
160
140
120
100
80
60
40
20
0
ppm

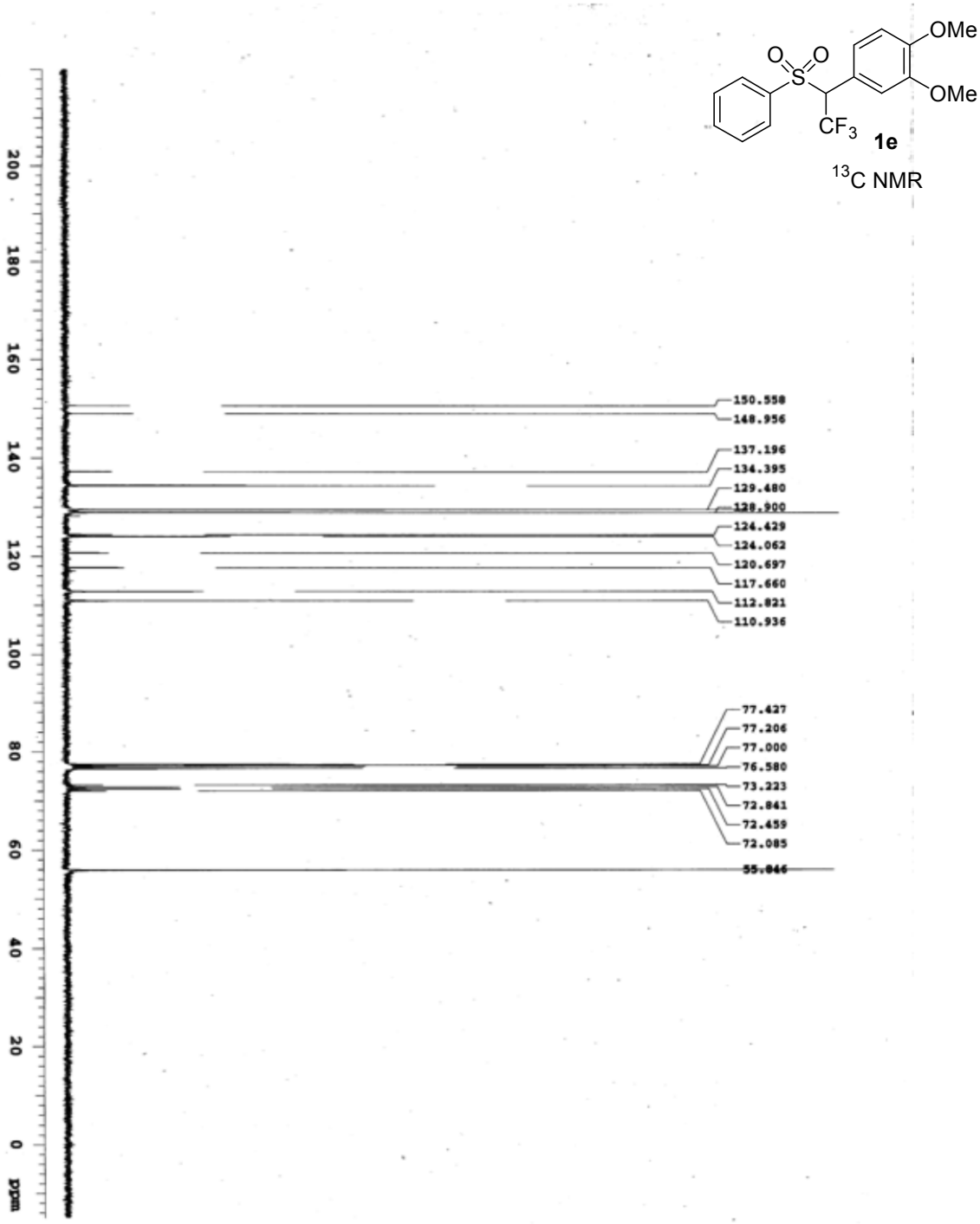

OMe
OMe
O
O
S
CF3
1e
1H NMR
7.704
7.679
7.642
7.616
7.499
7.474
7.448
7.269
7.264
6.848
6.818
6.805
6.779
4.741
4.713
4.685
4.656
3.883
3.827
3.779
3.719
-0.000
2.81
1.90
2.88
1.11
5.99
ppm

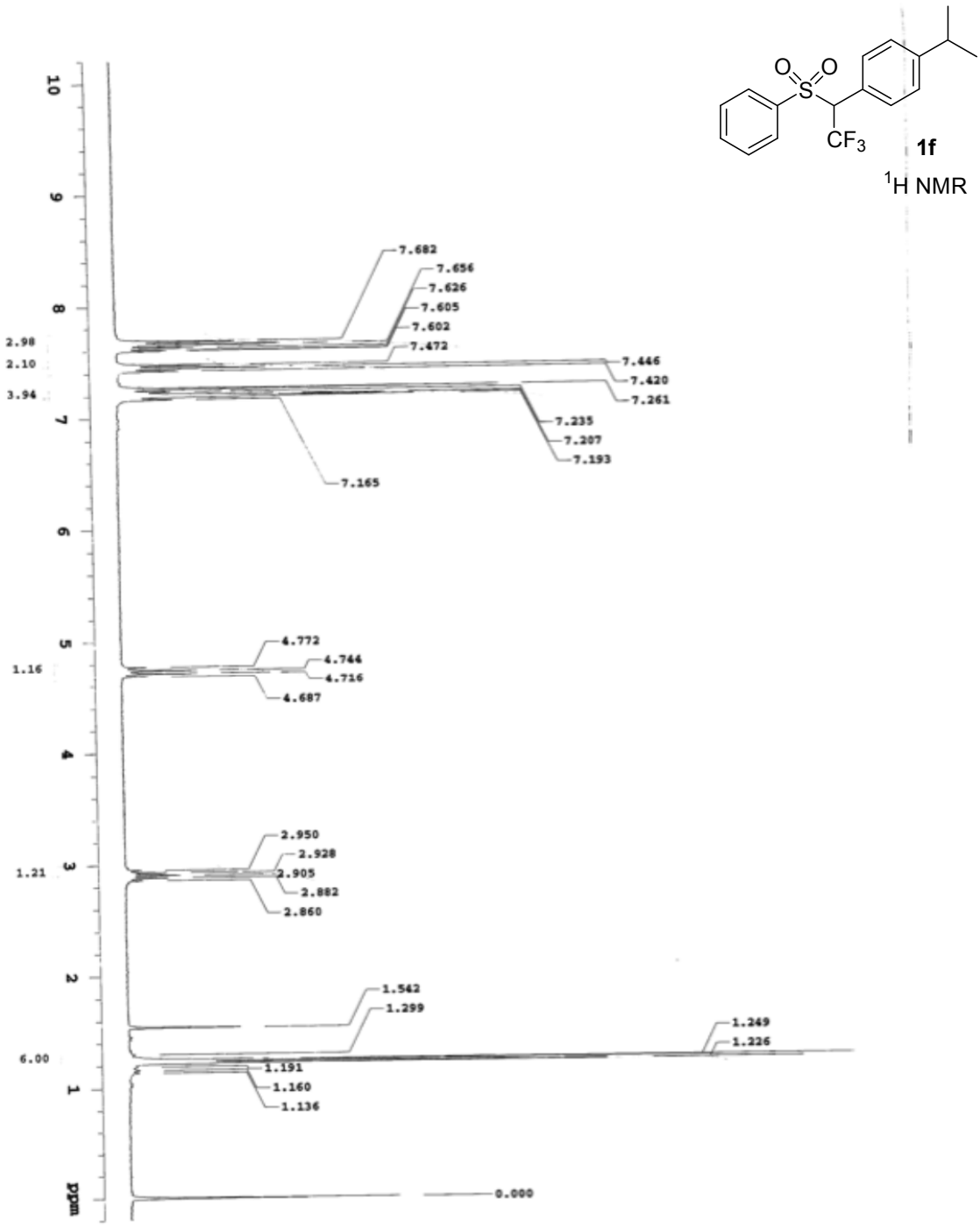

OMe
OMe
O
O
S
CF3

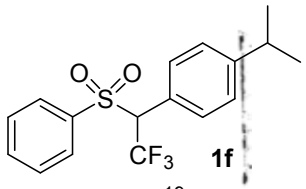
1e

^{19}F NMR


20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.000
-61.812
-61.840

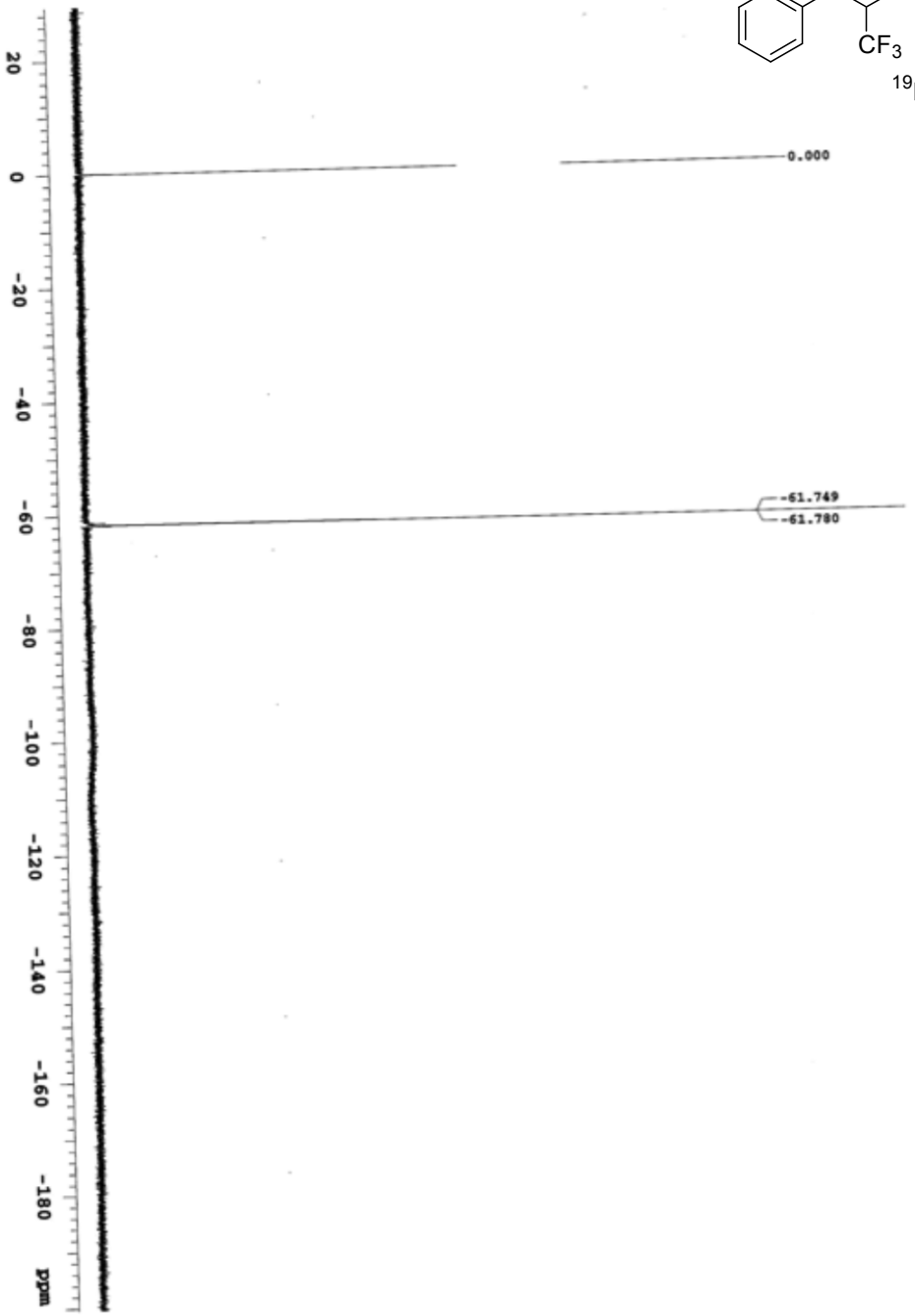

OMe
OMe
O
O
S
CF3
1e
13C NMR
150.558
148.956
137.196
134.395
129.480
128.900
124.429
124.062
120.697
117.660
112.821
110.936
77.427
77.206
77.000
76.580
73.223
72.841
72.459
72.085
55.846
200
180
160
140
120
100
80
60
40
20
0
ppm

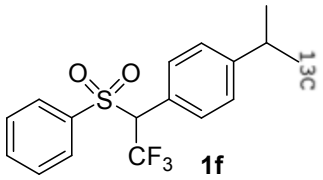

O
O
S
CF3
1f
1H NMR
7.682
7.656
7.626
7.605
7.602
7.472
7.446
7.420
7.261
7.235
7.207
7.193
7.165
4.772
4.744
4.716
4.687
2.950
2.928
2.905
2.882
2.860
1.542
1.299
1.249
1.226
1.191
1.160
1.136
0.000
2.98
2.10
3.94
1.16
1.21
6.00
ppm



1f

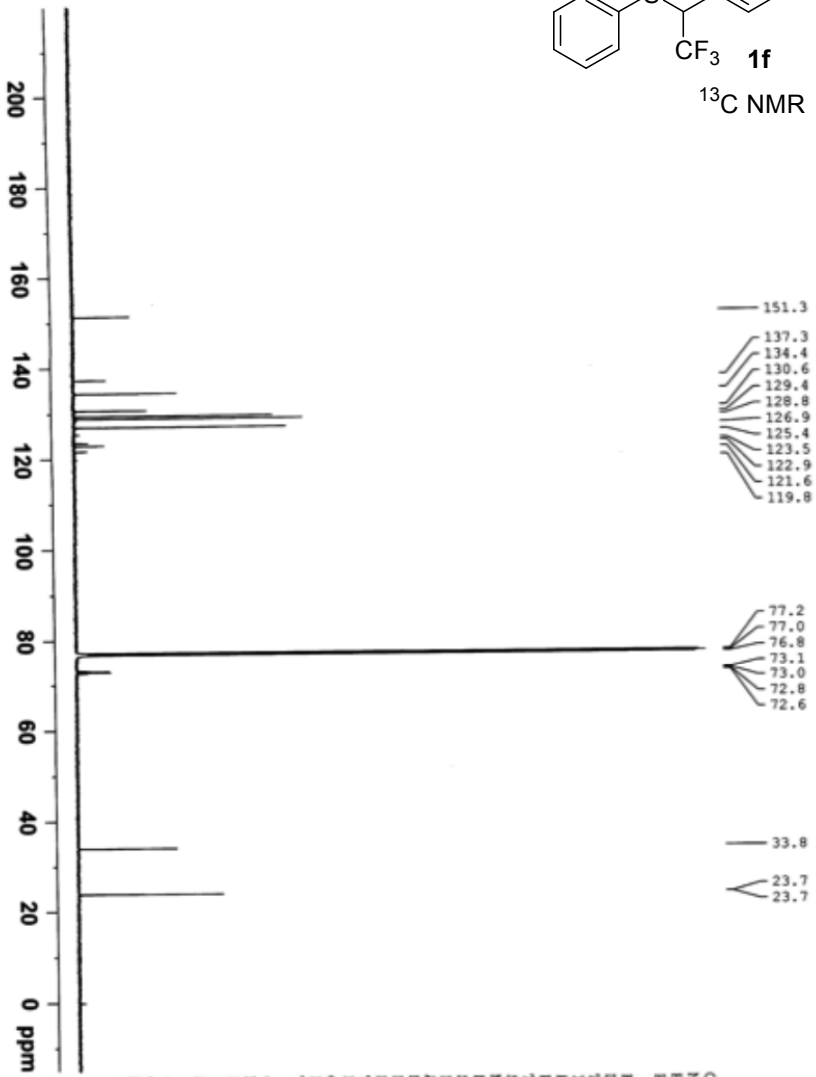
^{19}F NMR



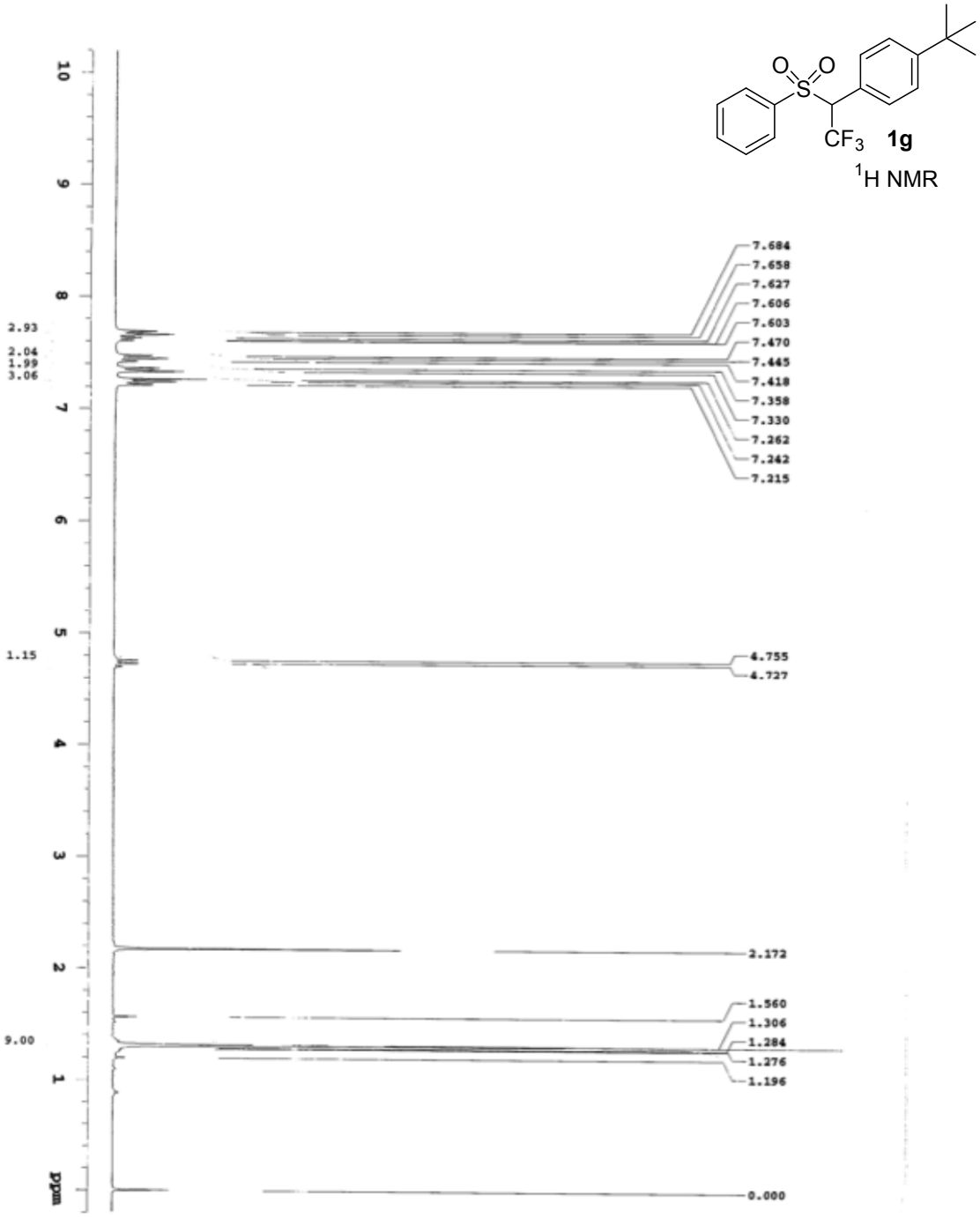


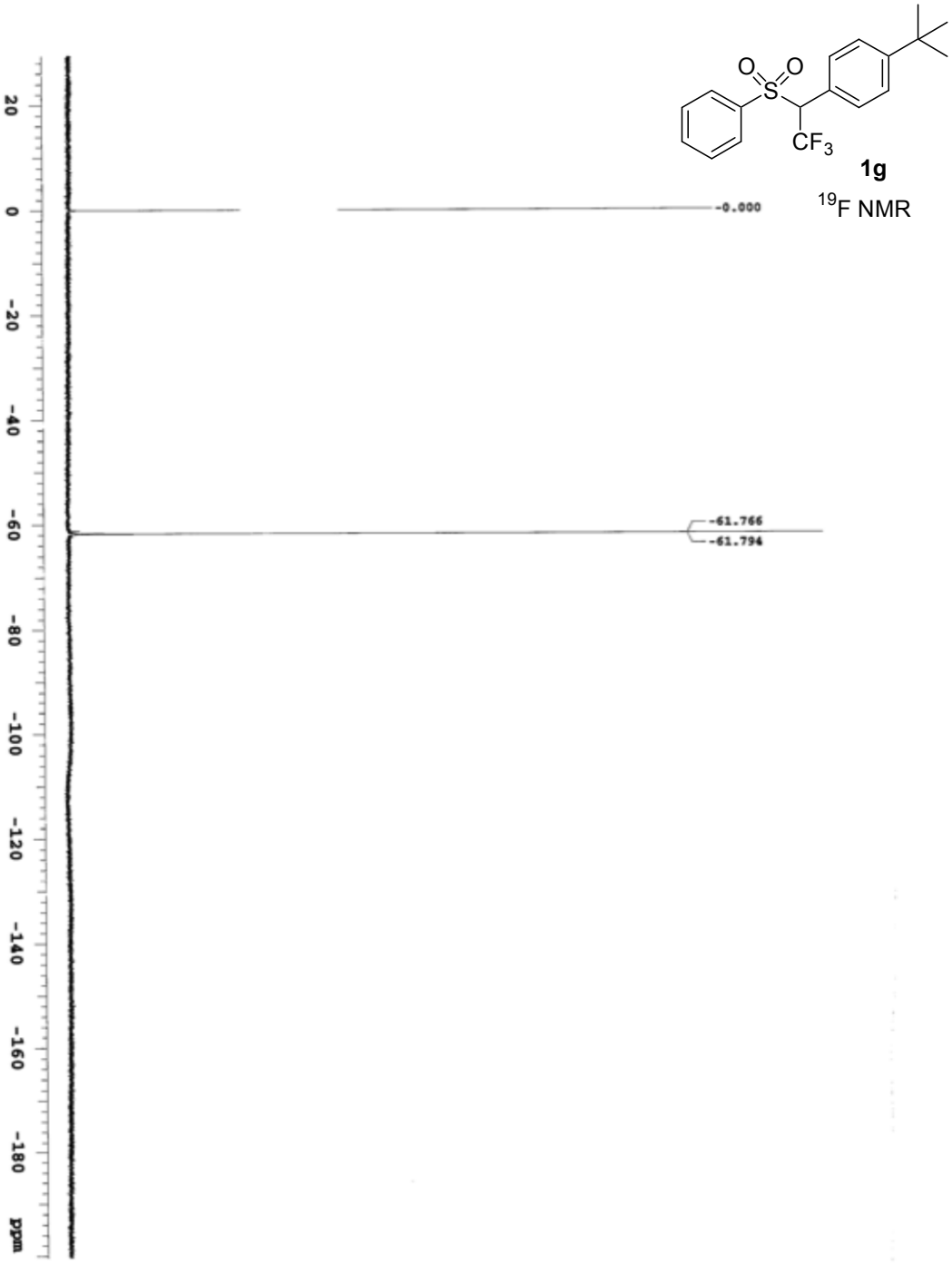
1f

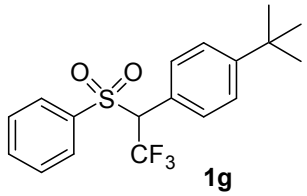
^{13}C NMR




```
Current Data Parameters
NAME                 zw-263
EXPNO                    10
PROCNO                   10

F2 - Acquisition Parameters
Date_             20120110
Time                 21.52
INSTRUM              dex600
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                   131072
SOLVENT              CDCl3
NS                     4000
DS                        4
SWH                45454.547 Hz
FIDRES             0.346791 Hz
AQ                 1.4418530 sec
RG                      8192
DW                    11.000 usec
DE                     6.00 usec
TE                    297.1 K
D1                0.60000002 sec
d11               0.03000000 sec
DELTA             0.50000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     8.20 usec
PL1                    4.50 dB
SFO1            150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 82.00 usec
PL2                   -4.00 dB
PL12                  15.00 dB
PL13                  15.00 dB
SFO2            600.1324005 MHz

F2 - Processing parameters
SI                     131072
SF              150.9028138 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

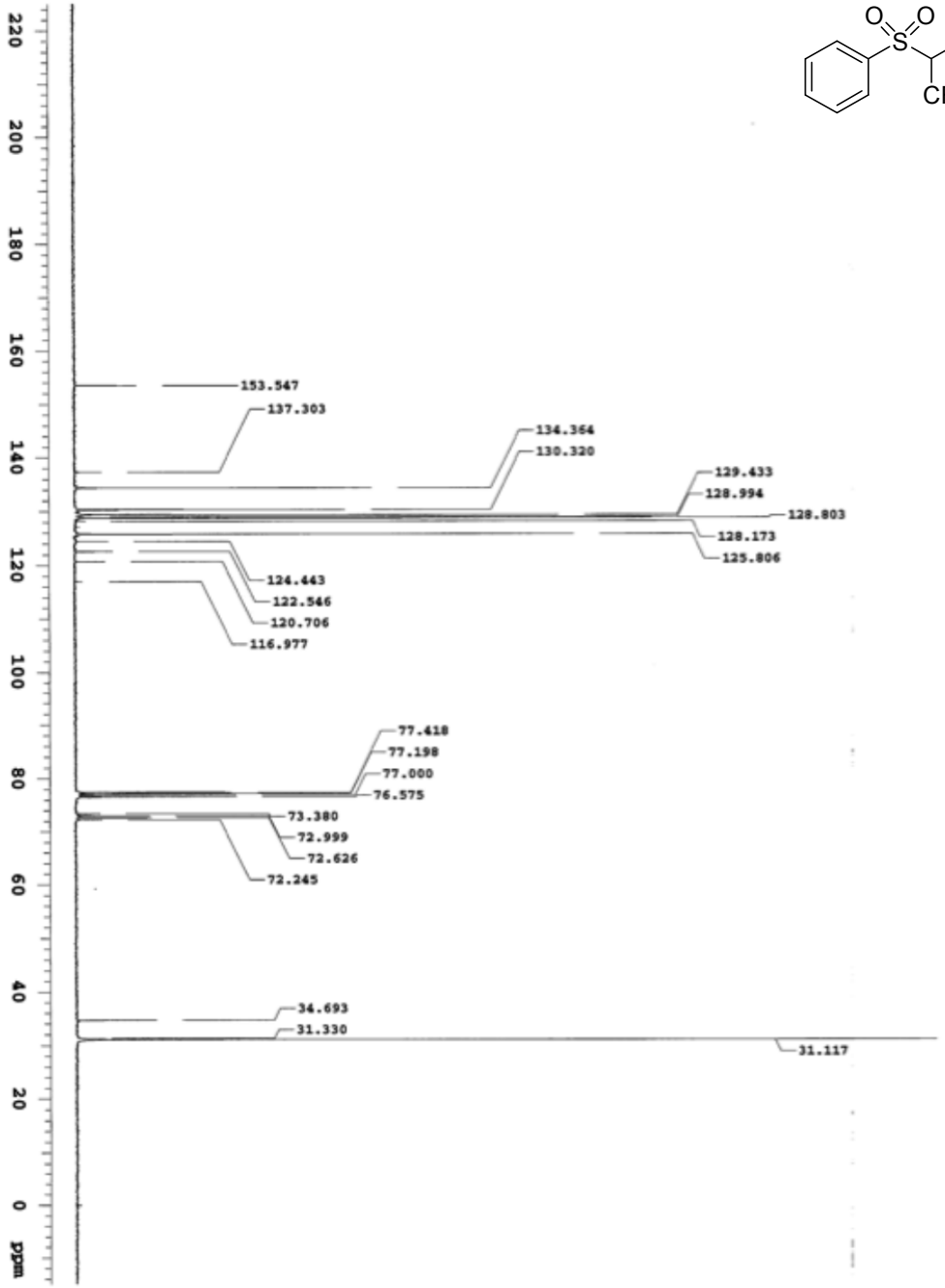

O
O
S
CF3
1g
1H NMR
7.684
7.658
7.627
7.606
7.603
7.470
7.445
7.418
7.358
7.330
7.262
7.242
7.215
4.755
4.727
2.172
1.560
1.306
1.284
1.276
1.196
0.000
2.93
2.04
1.99
3.06
1.15
9.00
10
9
8
7
6
5
4
3
2
1
ppm

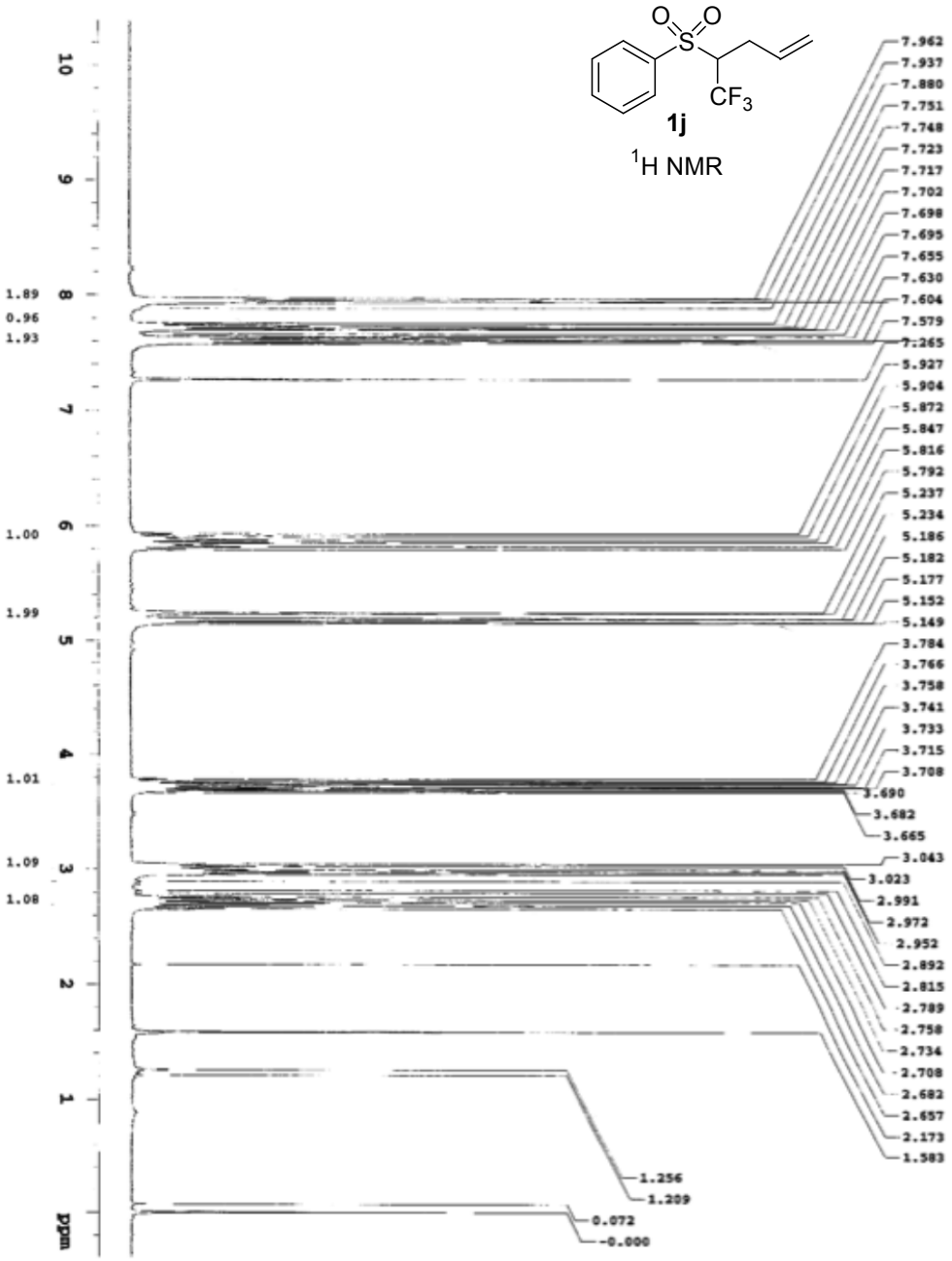

O
O
S
CF3
1g
19F NMR
-0.000
-61.766
-61.794
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

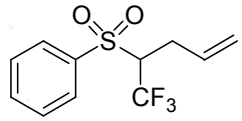

O
O
S
CF3

1g

^{13}C NMR

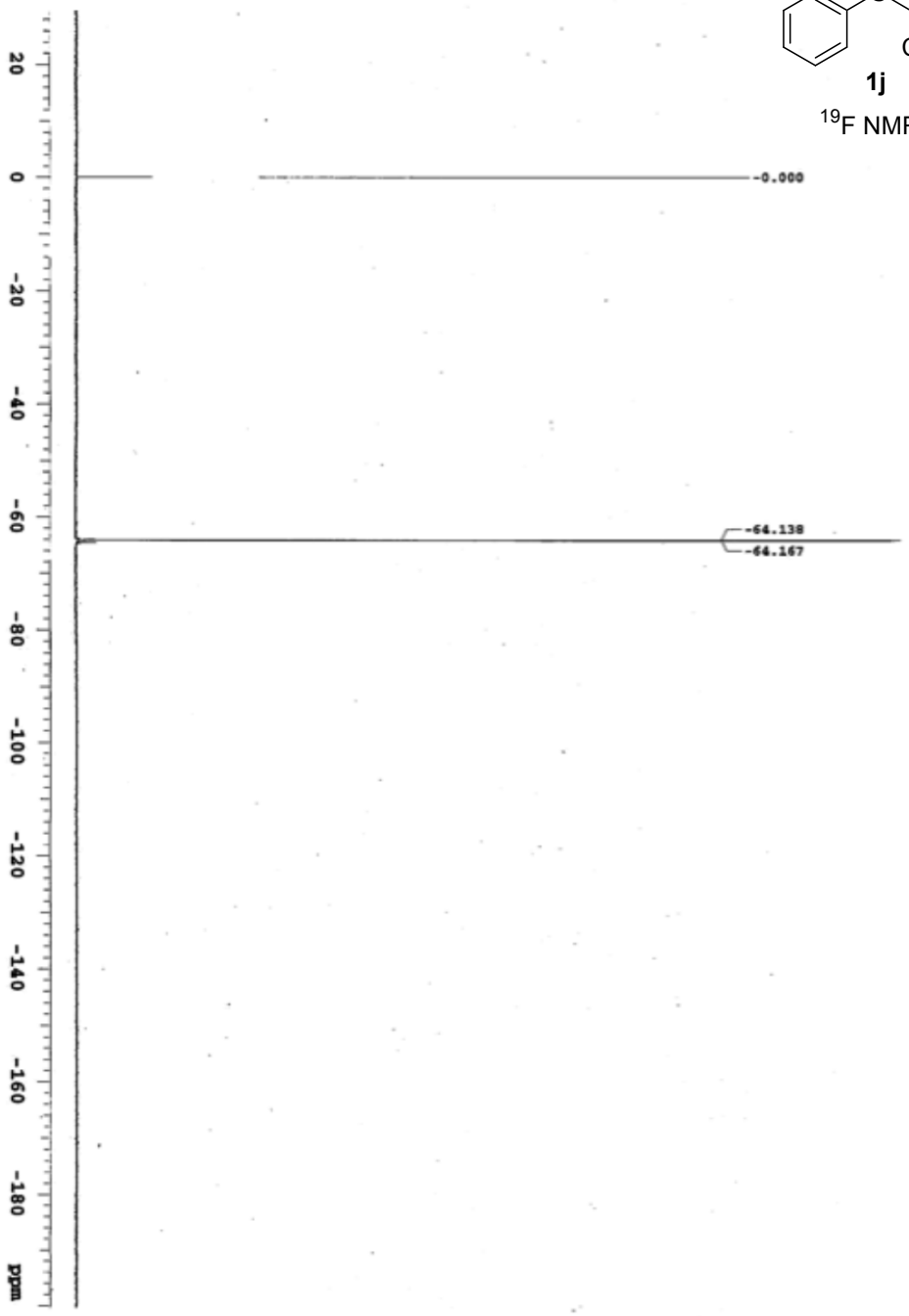

220
200
180
160
140
120
100
80
60
40
20
0
ppm
153.547
137.303
134.364
130.320
129.433
128.994
128.803
128.173
125.806
124.443
122.546
120.706
116.977
77.418
77.198
77.000
76.575
73.380
72.999
72.626
72.245
34.693
31.330
31.117

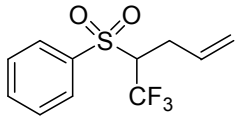

O
O
S
CF3
1j
1H NMR
7.962
7.937
7.880
7.751
7.748
7.723
7.717
7.702
7.698
7.695
7.655
7.630
7.604
7.579
7.265
5.927
5.904
5.872
5.847
5.816
5.792
5.237
5.234
5.186
5.182
5.177
5.152
5.149
3.784
3.766
3.758
3.741
3.733
3.715
3.708
3.690
3.682
3.665
3.043
3.023
2.991
2.972
2.952
2.892
2.815
2.789
2.758
2.734
2.708
2.682
2.657
2.173
1.583
1.256
1.209
0.072
-0.000
1.89
0.96
1.93
1.00
1.99
1.01
1.09
1.08
10
9
8
7
6
5
4
3
2
1
ppm



1j

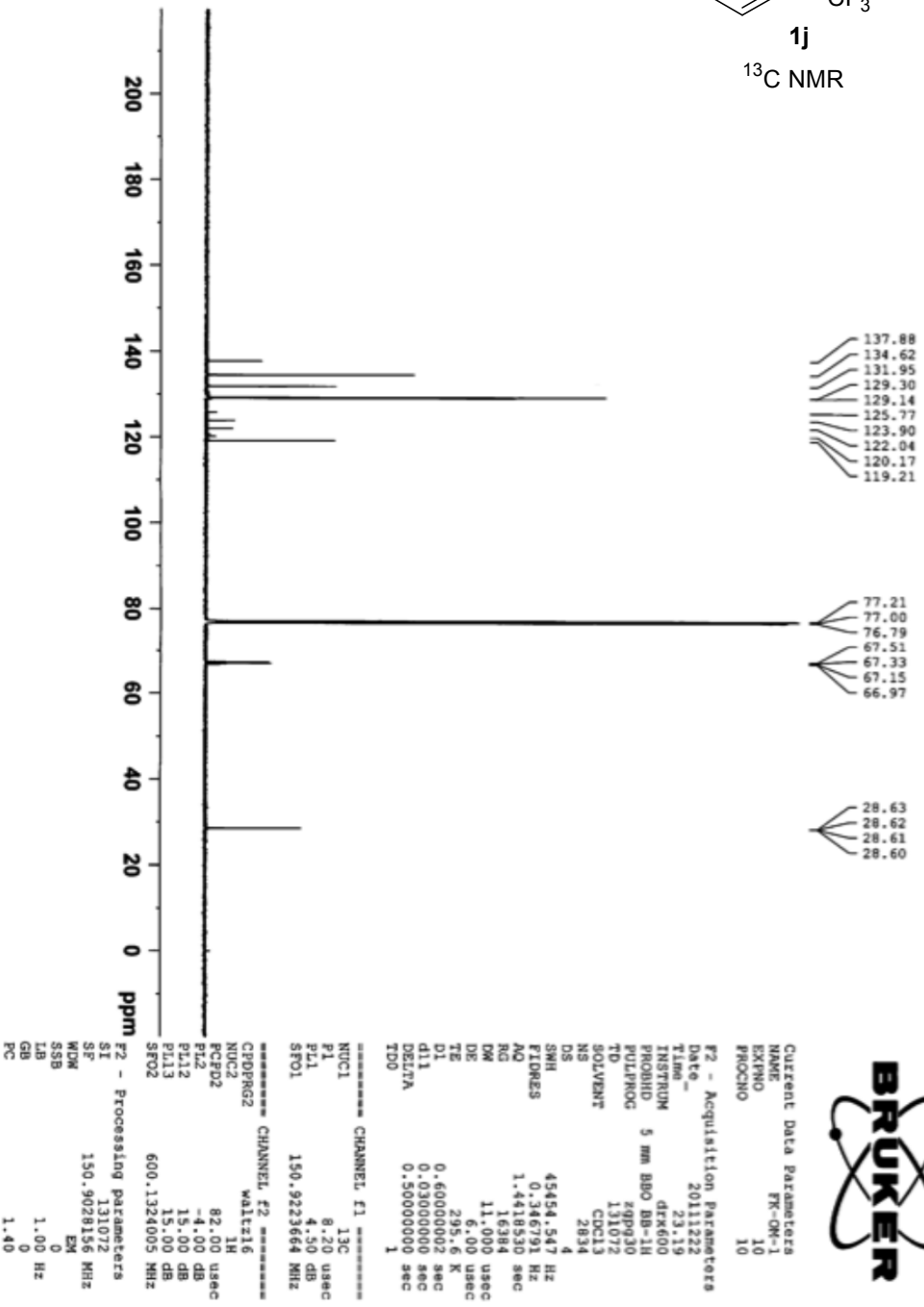
^{19}F NMR

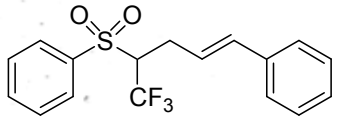



O
O
S
CF3

1j

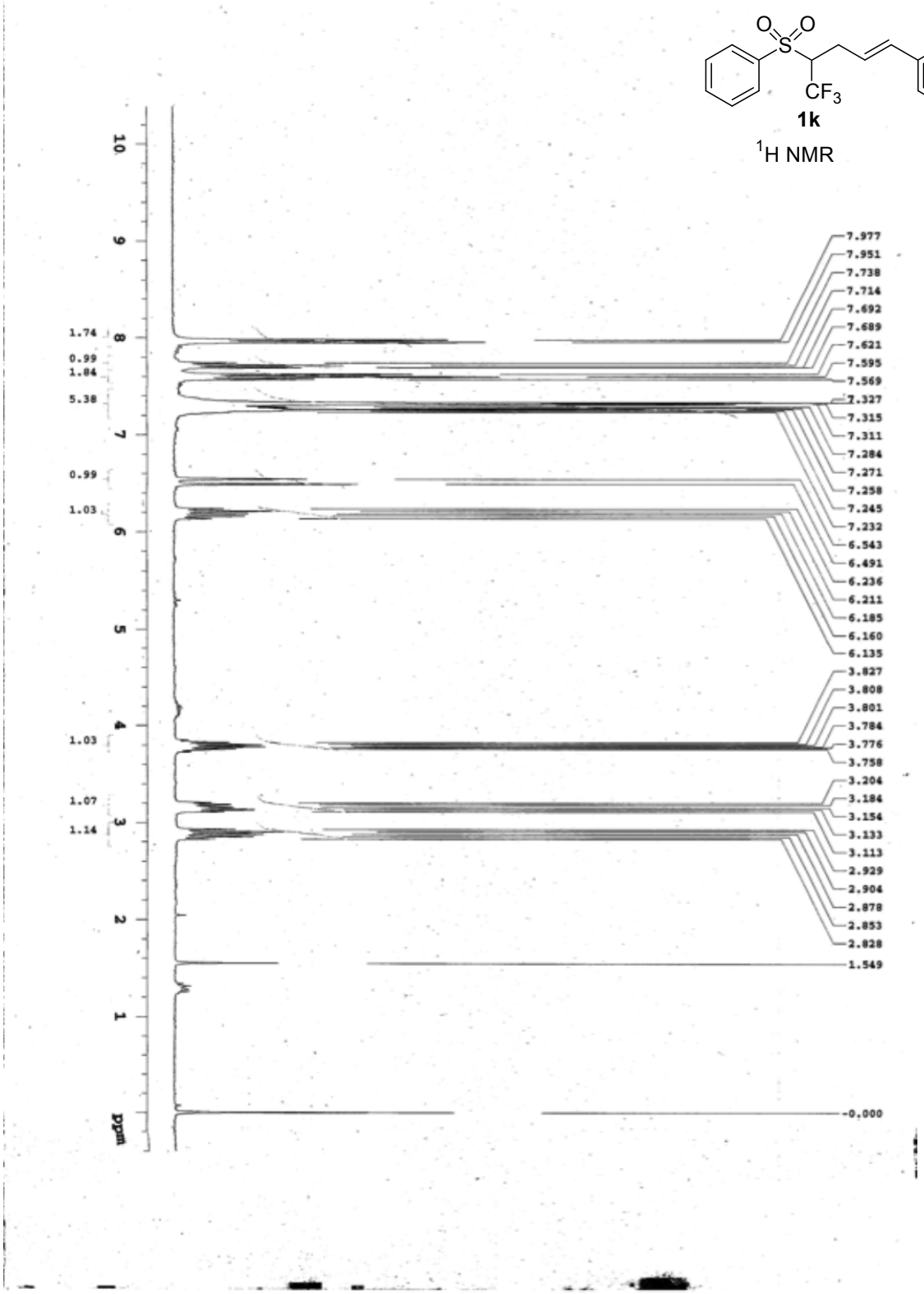
^{13}C NMR

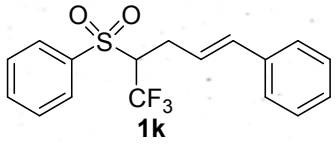

13C
137.88
134.62
131.95
129.30
129.14
125.77
123.90
122.04
120.17
119.21
77.21
77.00
76.79
67.51
67.33
67.15
66.97
28.63
28.62
28.61
28.60
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME FK-OM-1
EXPNO 10
PROCNO 10
F2 - Acquisition Parameters
Date_ 20111222
Time 23.19
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 2834
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 16384
DW 11.000 usec
DE 6.00 usec
TE 295.6 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028156 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
BRUKER


O
O
S
CF3

1k

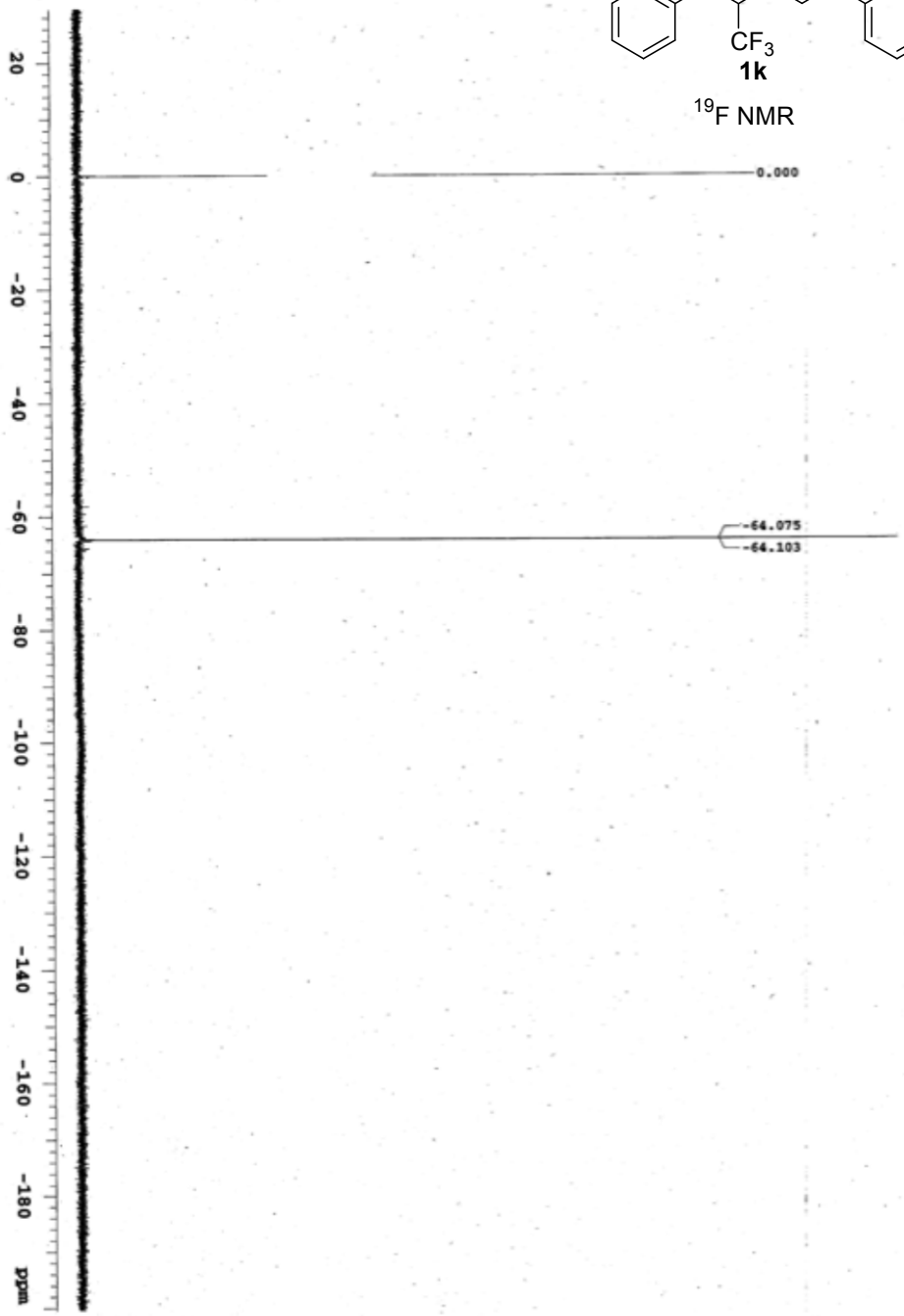
^{1}H NMR

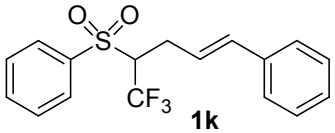

7.977
7.951
7.738
7.714
7.692
7.689
7.621
7.595
7.569
7.327
7.315
7.311
7.284
7.271
7.258
7.245
7.232
6.543
6.491
6.236
6.211
6.185
6.160
6.135
3.827
3.808
3.801
3.784
3.776
3.758
3.204
3.184
3.154
3.133
3.113
2.929
2.904
2.878
2.853
2.828
1.549
0.000
1.74
0.99
1.84
5.38
0.99
1.03
1.03
1.07
1.14
10
9
8
7
6
5
4
3
2
1
ppm



1k

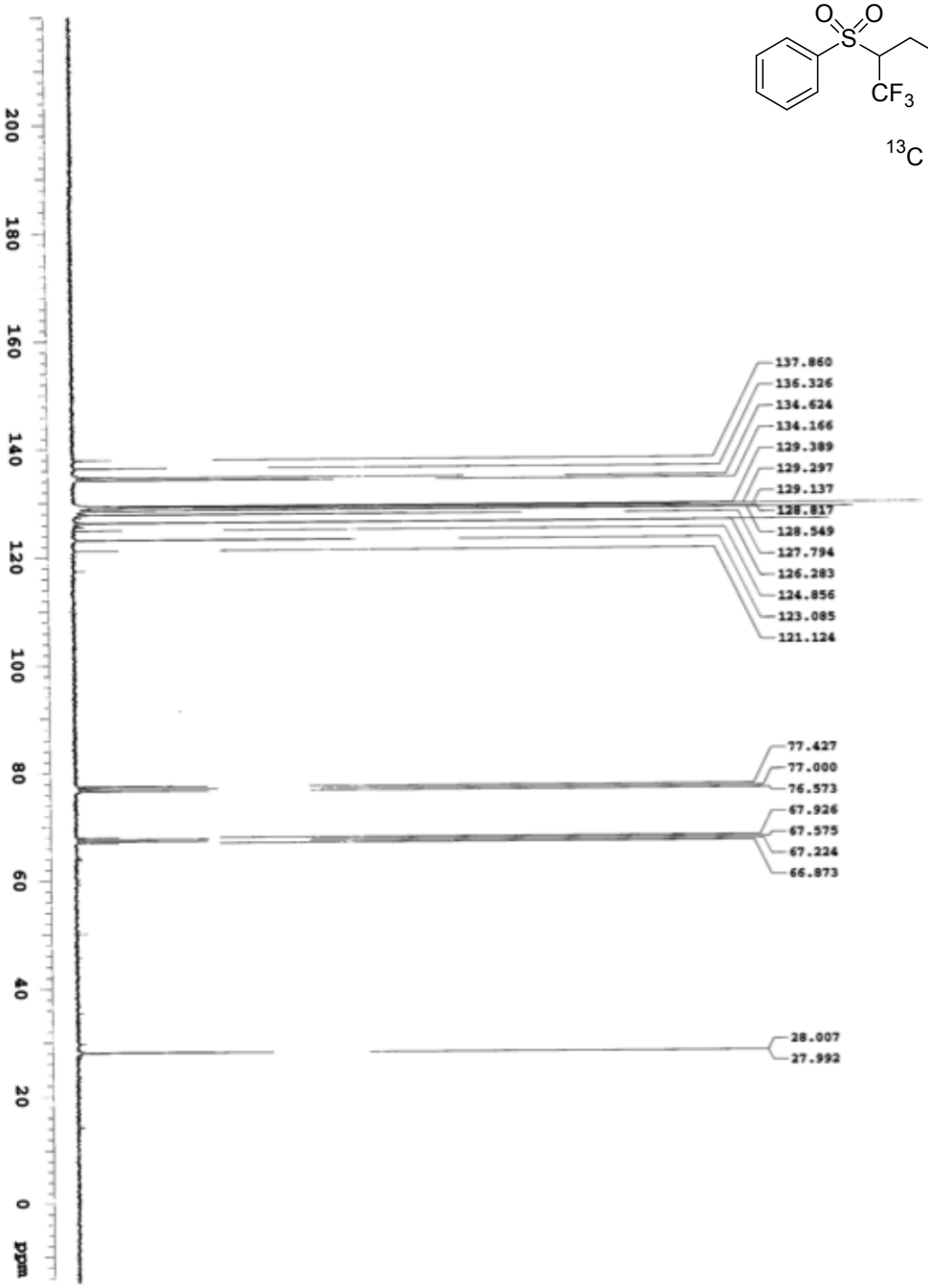
^{19}F NMR

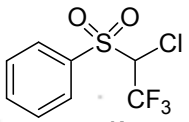



O
O
S
CF3

1k

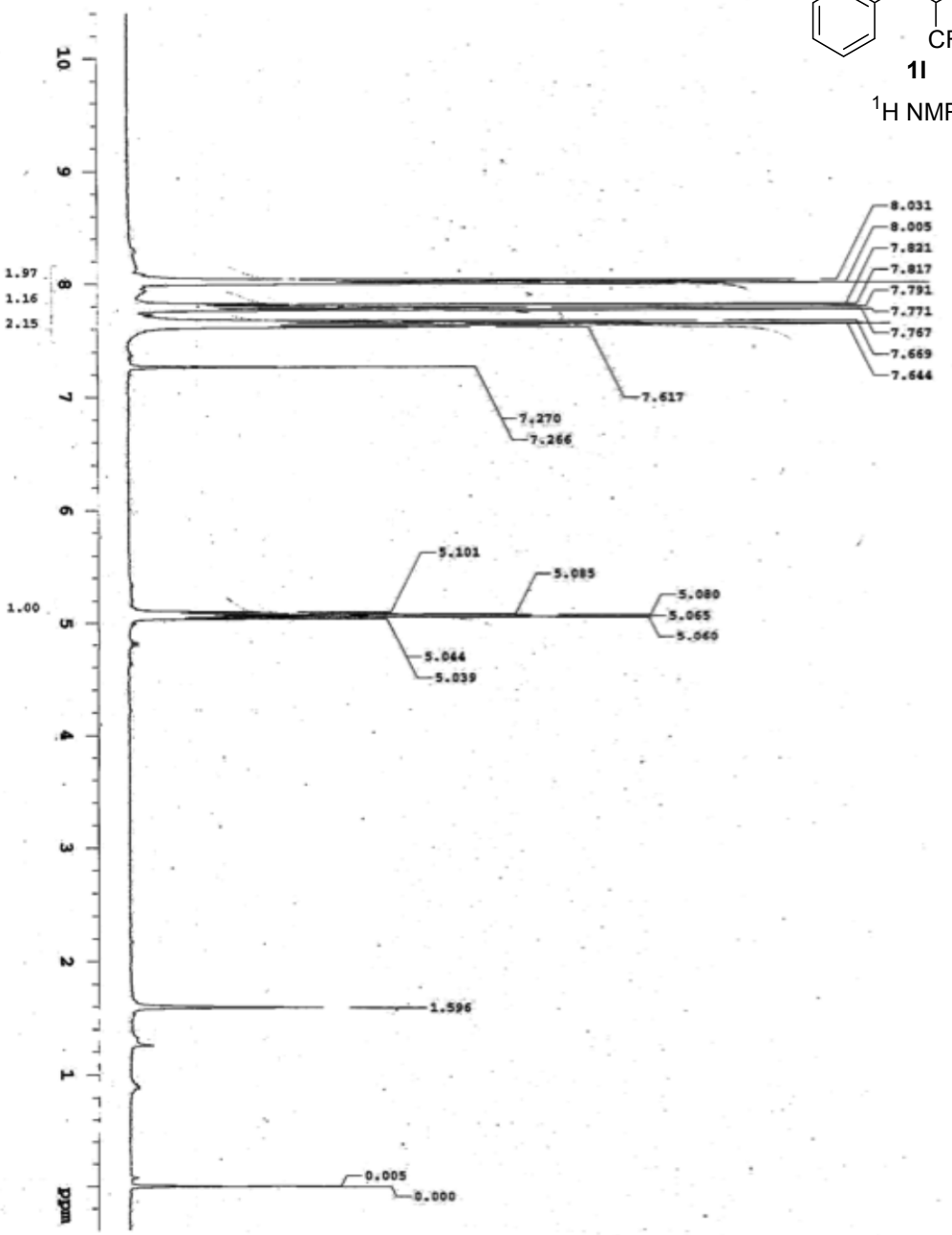
^{13}C NMR

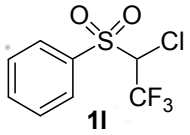

200
180
160
140
120
100
80
60
40
20
0
ppm
137.860
136.326
134.624
134.166
129.389
129.297
129.137
128.817
128.549
127.794
126.283
124.856
123.085
121.124
77.427
77.000
76.573
67.926
67.575
67.224
66.873
28.007
27.992


O
O
S
Cl
CF3

1l

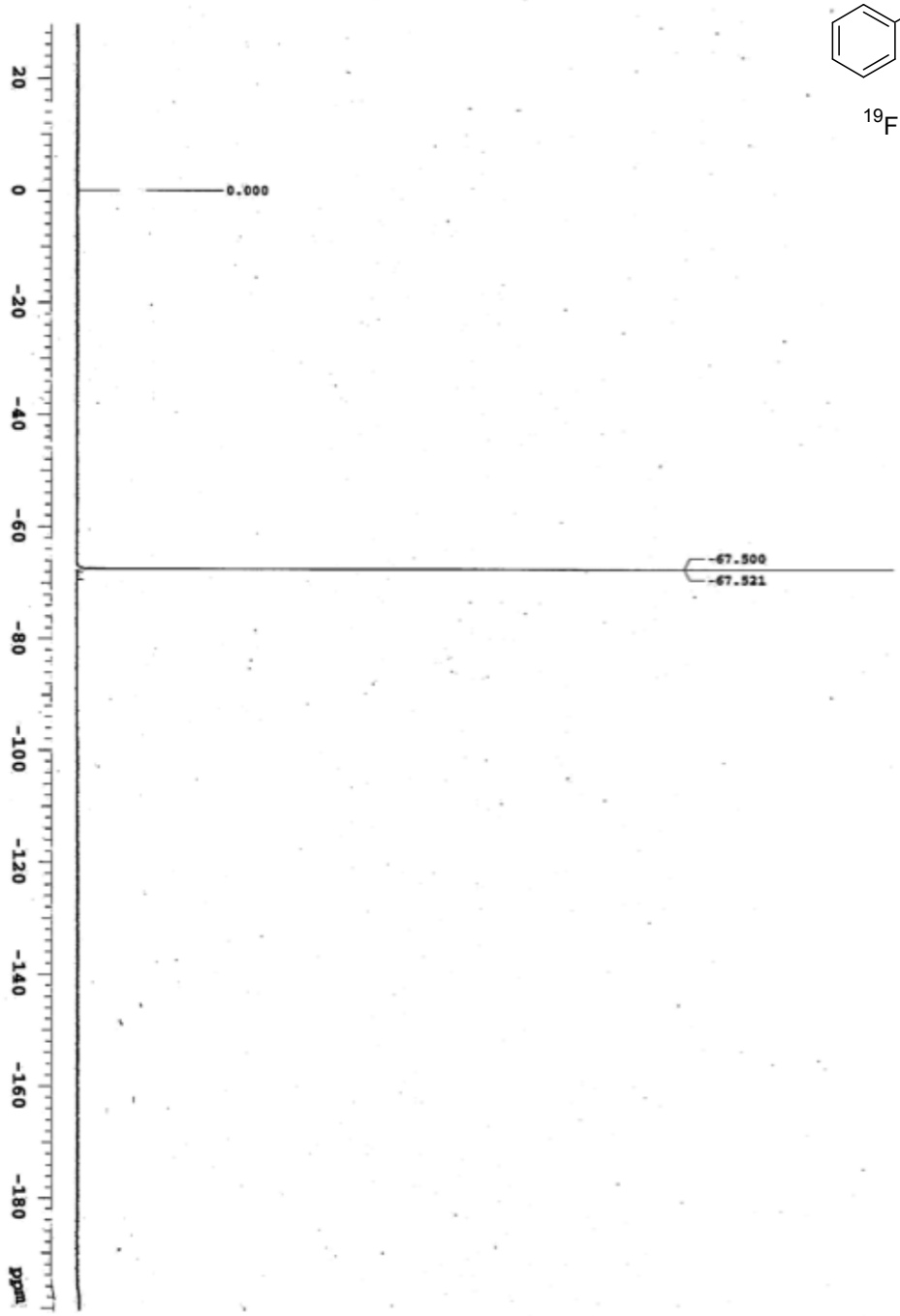
^{1}H NMR

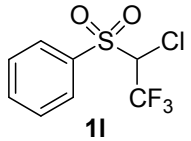

8.031
8.005
7.821
7.817
7.791
7.771
7.767
7.669
7.644
7.617
7.270
7.266
5.101
5.085
5.080
5.065
5.060
5.044
5.039
1.596
0.005
0.000
1.97
1.16
2.15
1.00
10
9
8
7
6
5
4
3
2
1
ppm


O
O
S
Cl
CF3

1l

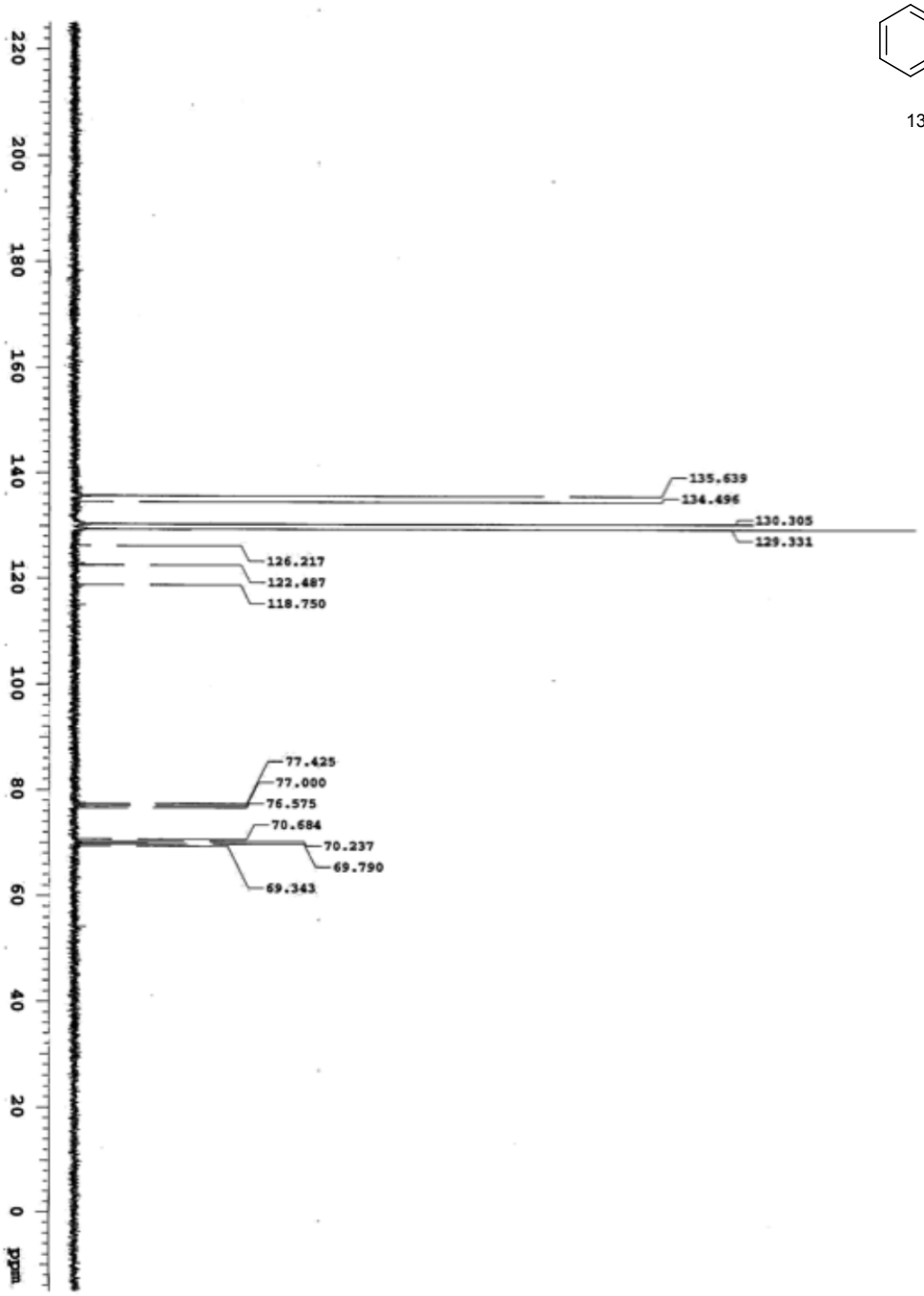
^{19}F NMR

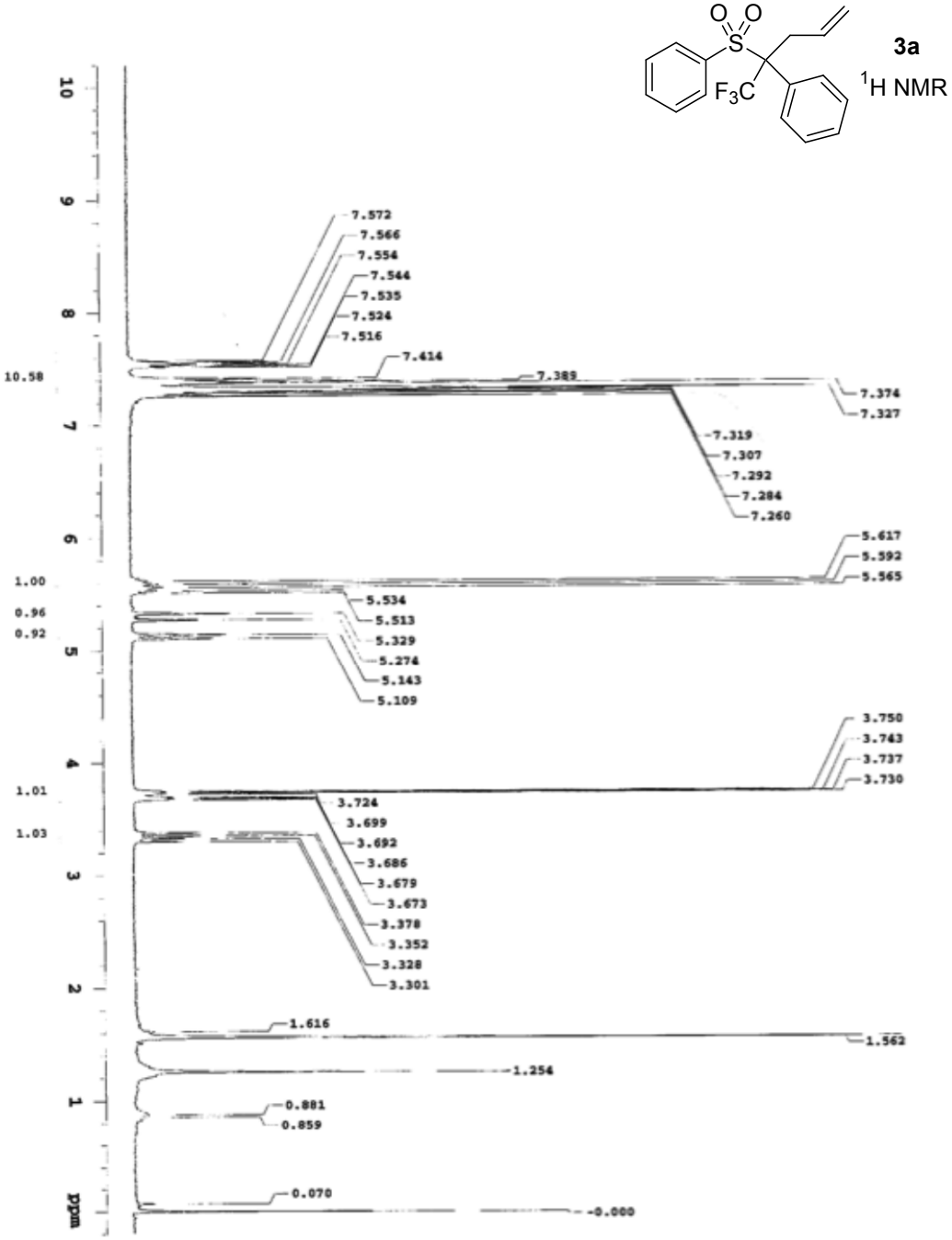

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.000
-67.500
-67.521

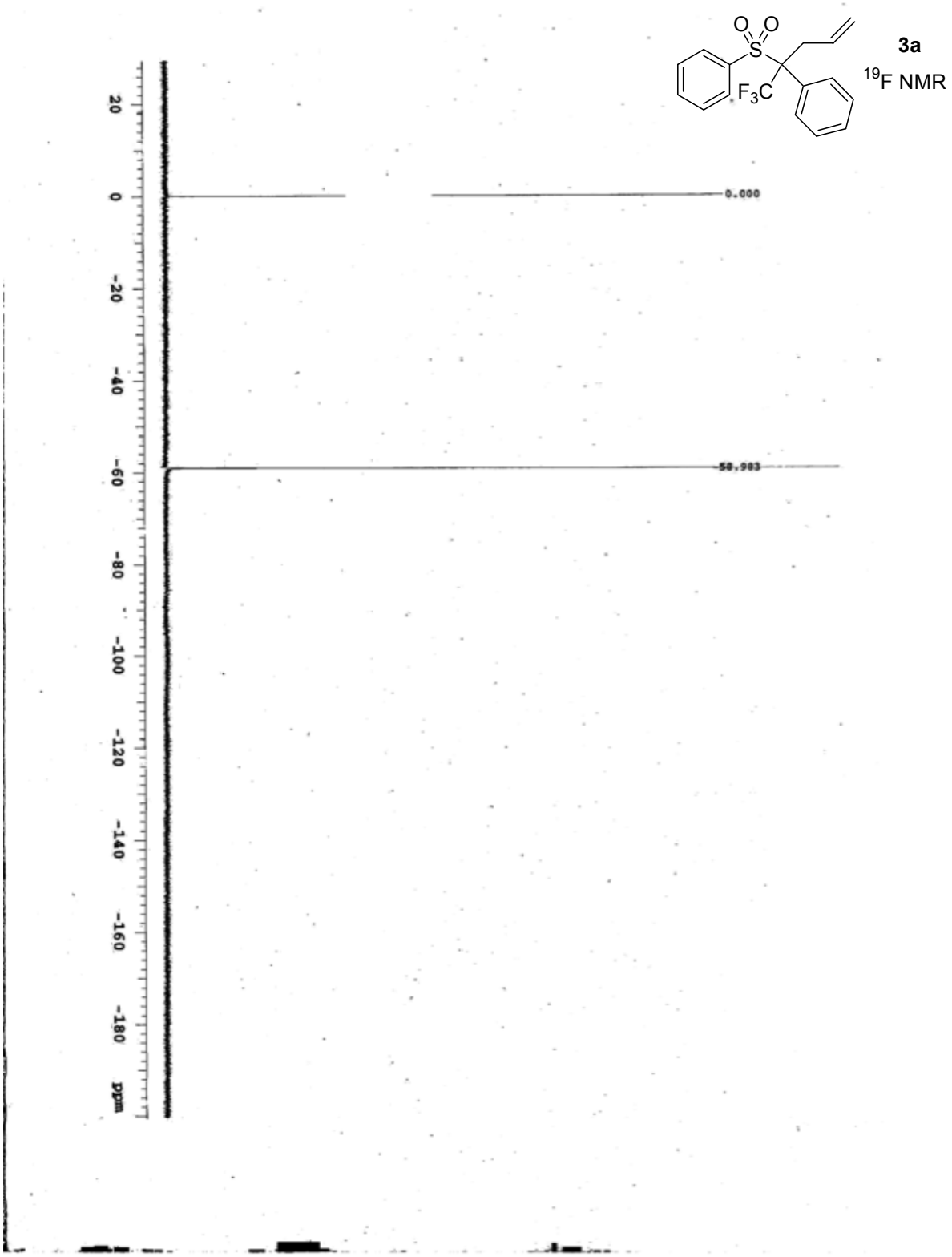

O
O
S
Cl
CF3

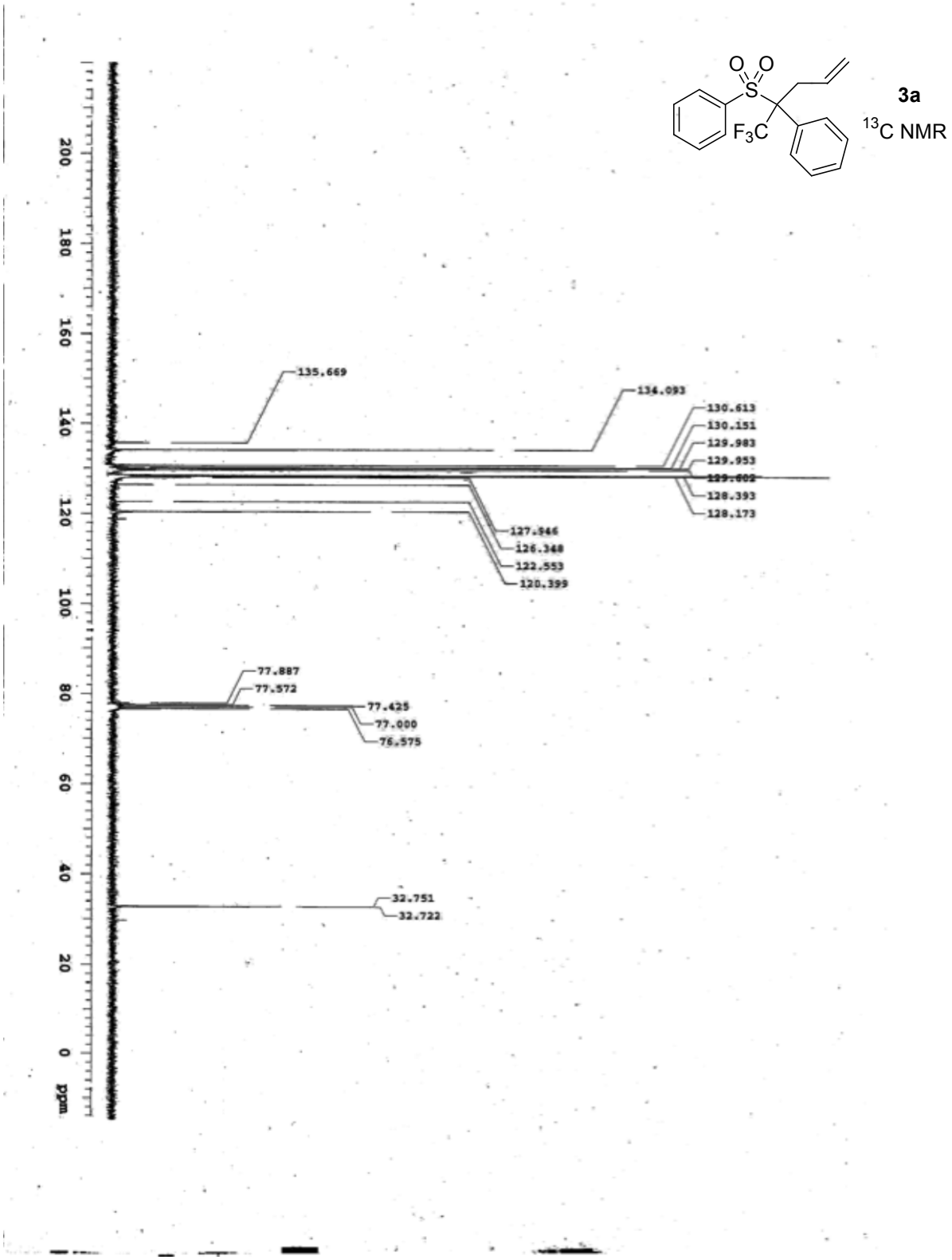
1l

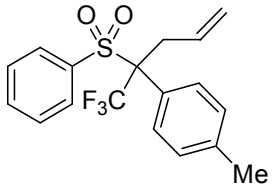
^{13}C NMR


220
200
180
160
140
120
100
80
60
40
20
0
ppm
135.639
134.496
130.305
129.331
126.217
122.487
118.750
77.425
77.000
76.575
70.684
70.237
69.790
69.343


3a
^{1}H NMR
7.572
7.566
7.554
7.544
7.535
7.524
7.516
7.414
7.389
7.374
7.327
7.319
7.307
7.292
7.284
7.260
5.617
5.592
5.565
5.534
5.513
5.329
5.274
5.143
5.109
3.750
3.743
3.737
3.730
3.724
3.699
3.692
3.686
3.679
3.673
3.378
3.352
3.328
3.301
1.616
1.562
1.254
0.881
0.859
0.070
-0.000
10.58
1.00
0.96
0.92
1.01
1.03
ppm

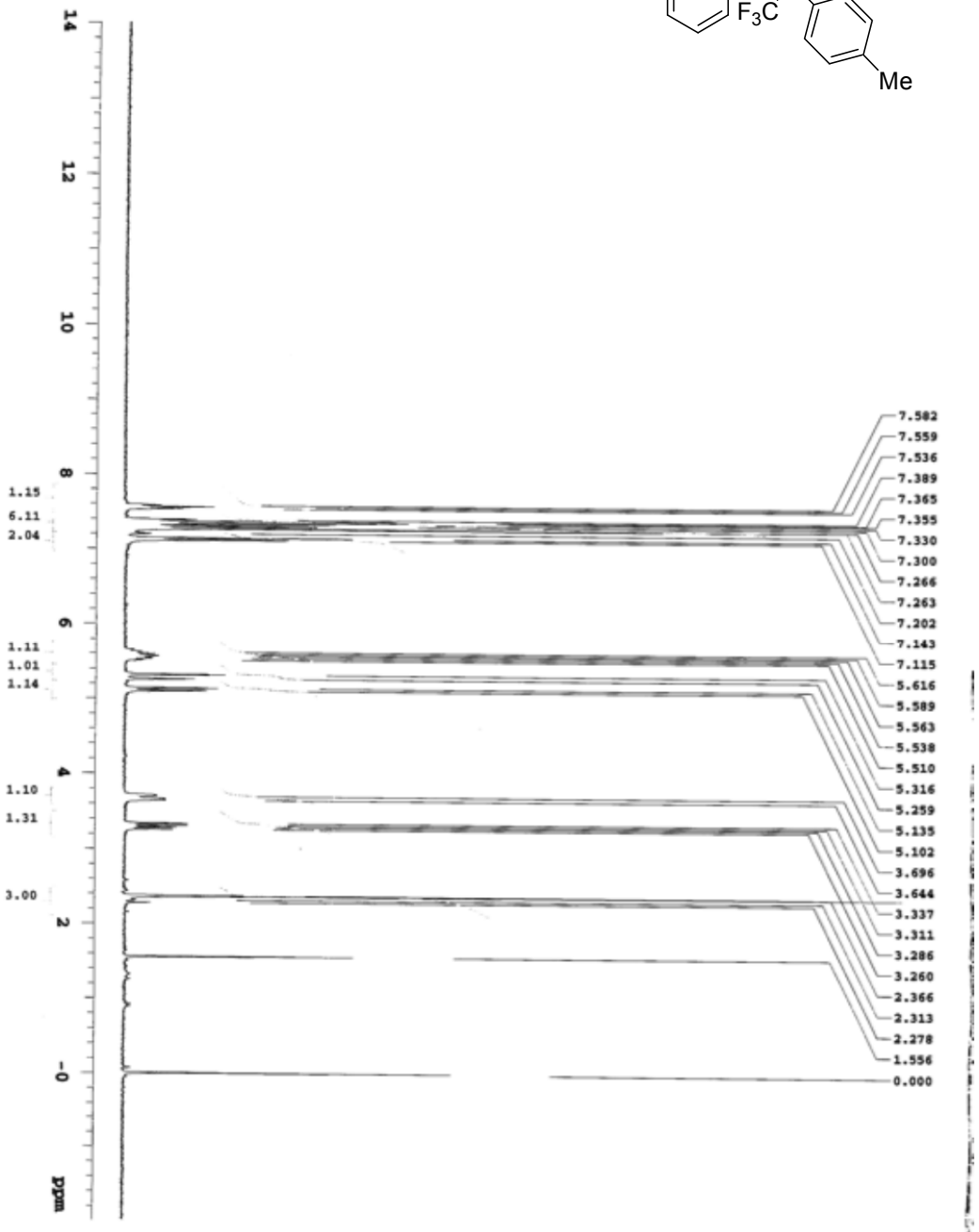

O O
S
F3C
3a
19F NMR
0.000
-58.903
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

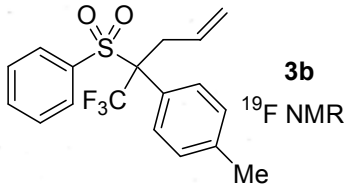

3a
13C NMR
135.669
134.093
130.613
130.151
129.983
129.953
129.602
128.393
128.173
127.946
126.348
122.553
120.399
77.887
77.572
77.425
77.000
76.575
32.751
32.722
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
F3C
Me

3b

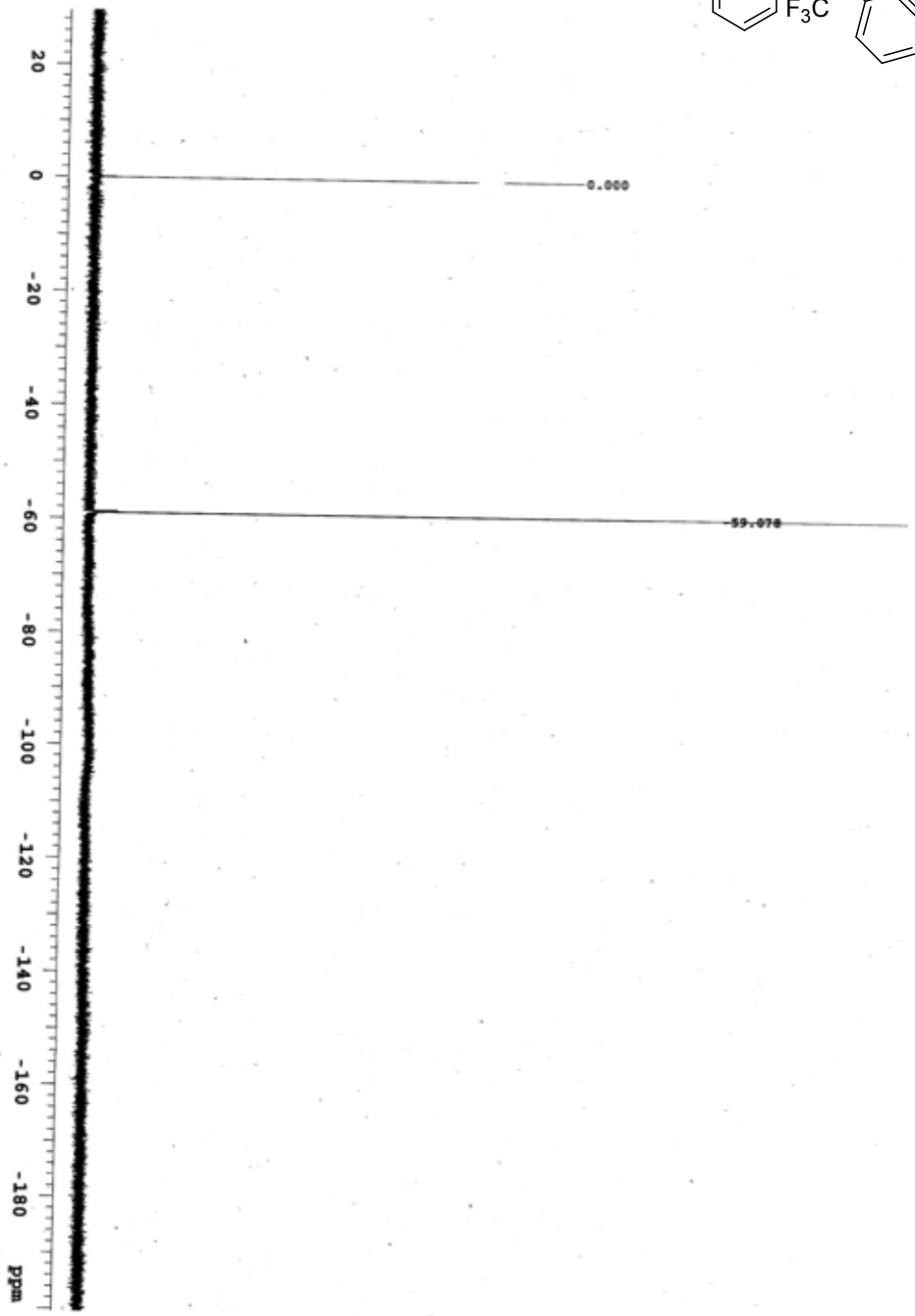
^{1}H NMR

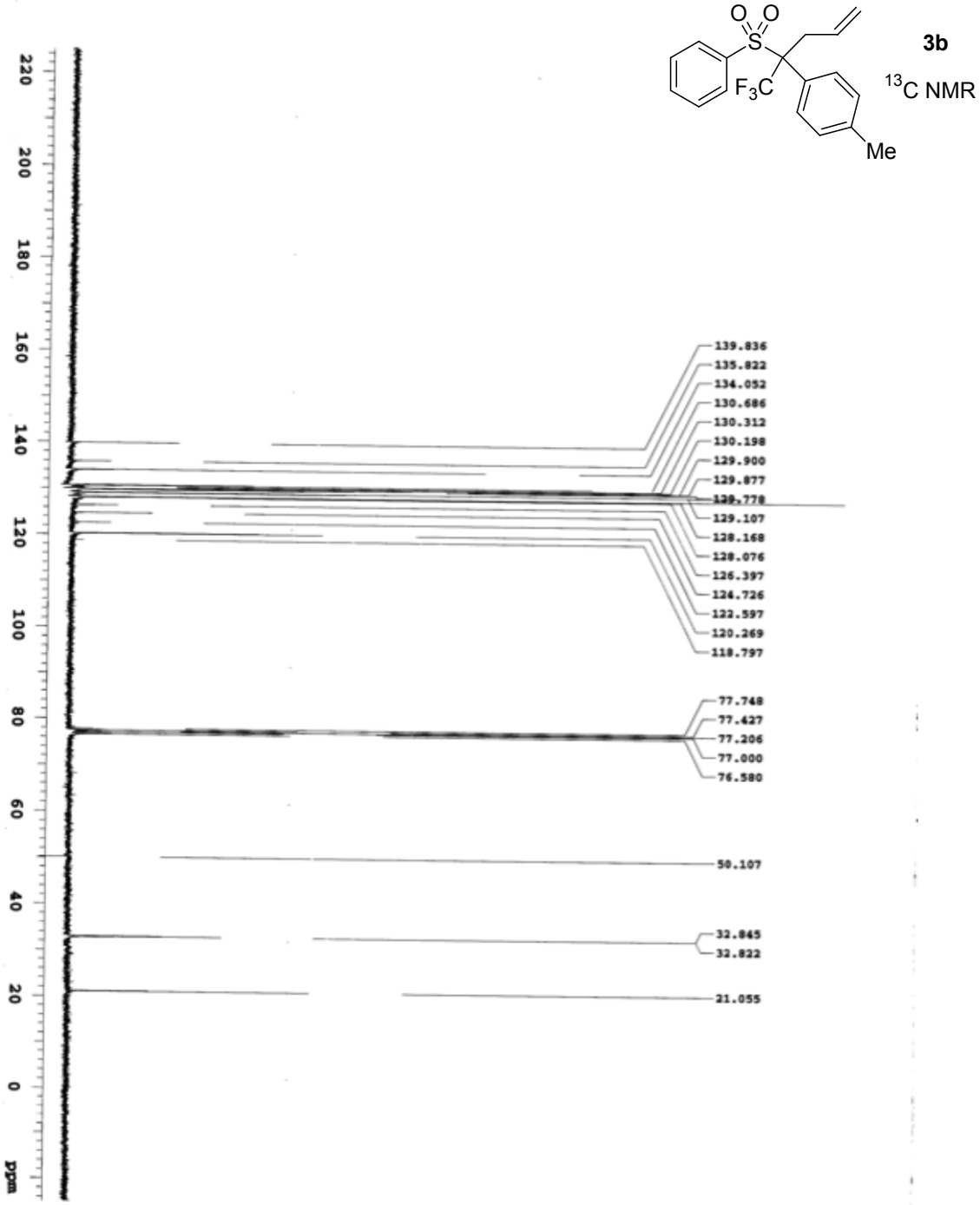

14
12
10
8
6
4
2
-0
ppm
1.15
6.11
2.04
1.11
1.01
1.14
1.10
1.31
3.00
7.582
7.559
7.536
7.389
7.365
7.355
7.330
7.300
7.266
7.263
7.202
7.143
7.115
5.616
5.589
5.563
5.538
5.510
5.316
5.259
5.135
5.102
3.696
3.644
3.337
3.311
3.286
3.260
2.366
2.313
2.278
1.556
0.000

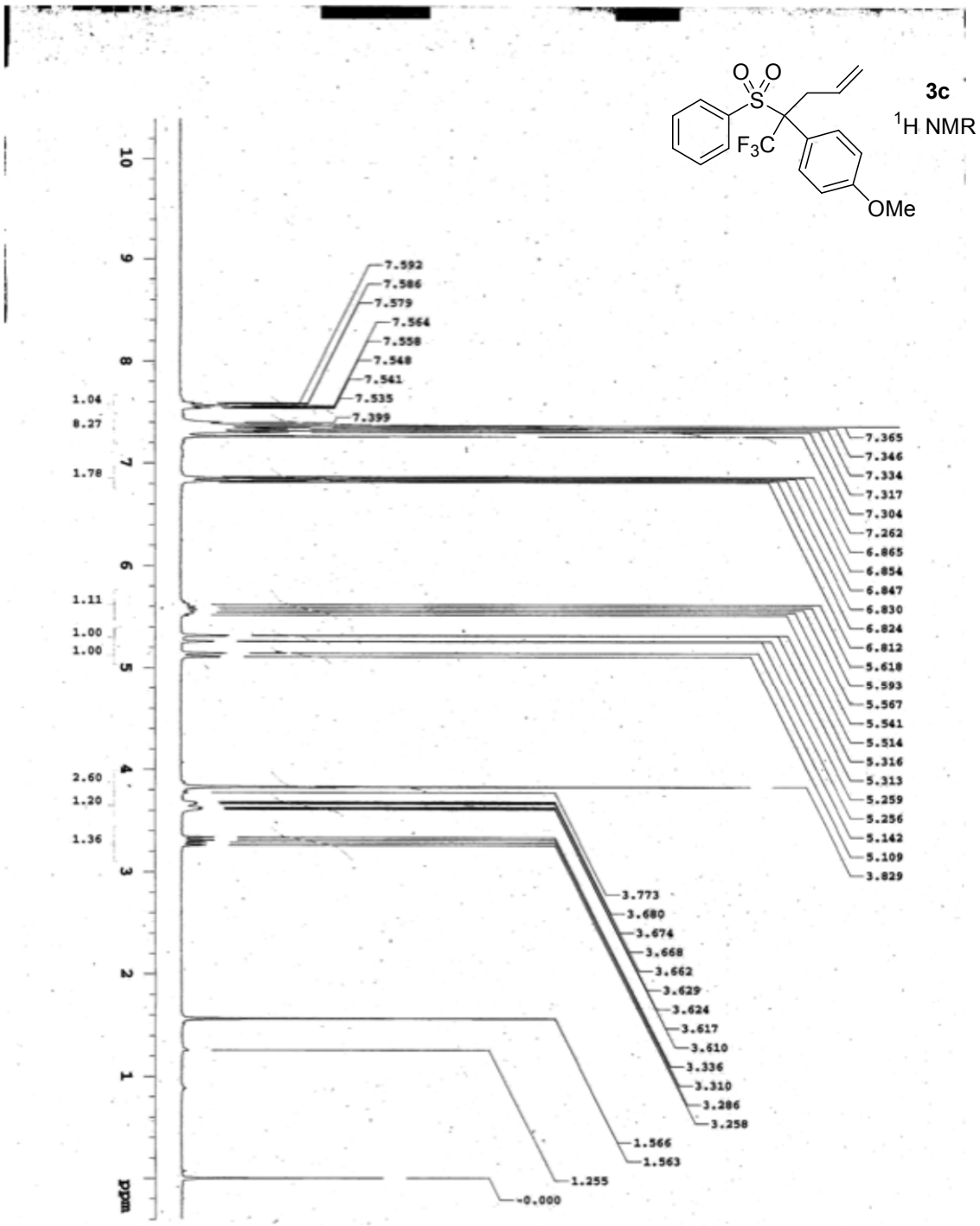


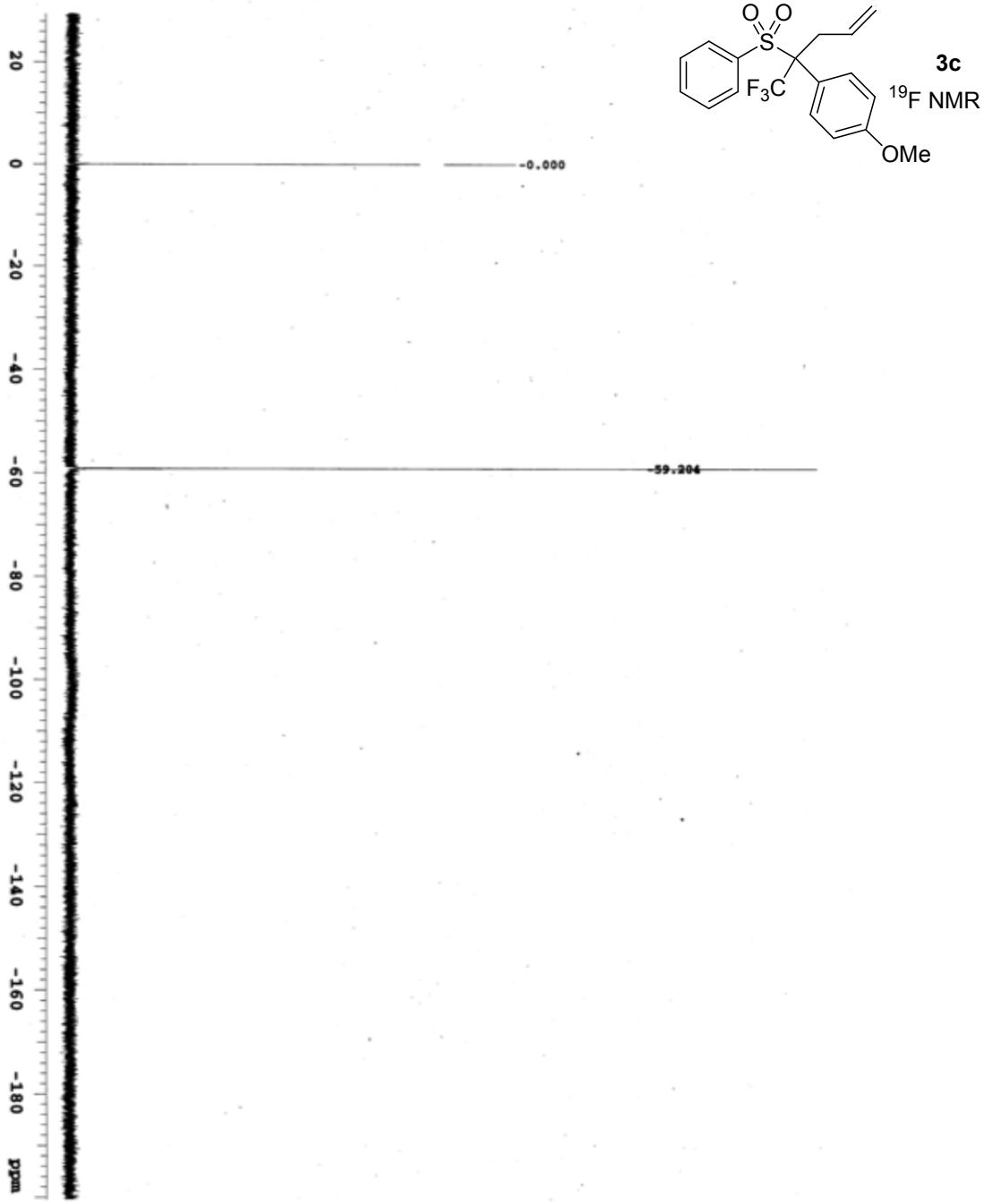
3b

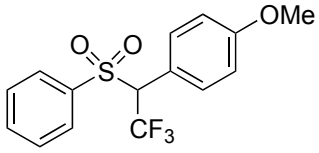
^{19}F NMR




3b
13C NMR
Me
F3C
139.836
135.822
134.052
130.686
130.312
130.198
129.900
129.877
129.778
129.107
128.168
128.076
126.397
124.726
122.597
120.269
118.797
77.748
77.427
77.206
77.000
76.580
50.107
32.845
32.822
21.055
ppm

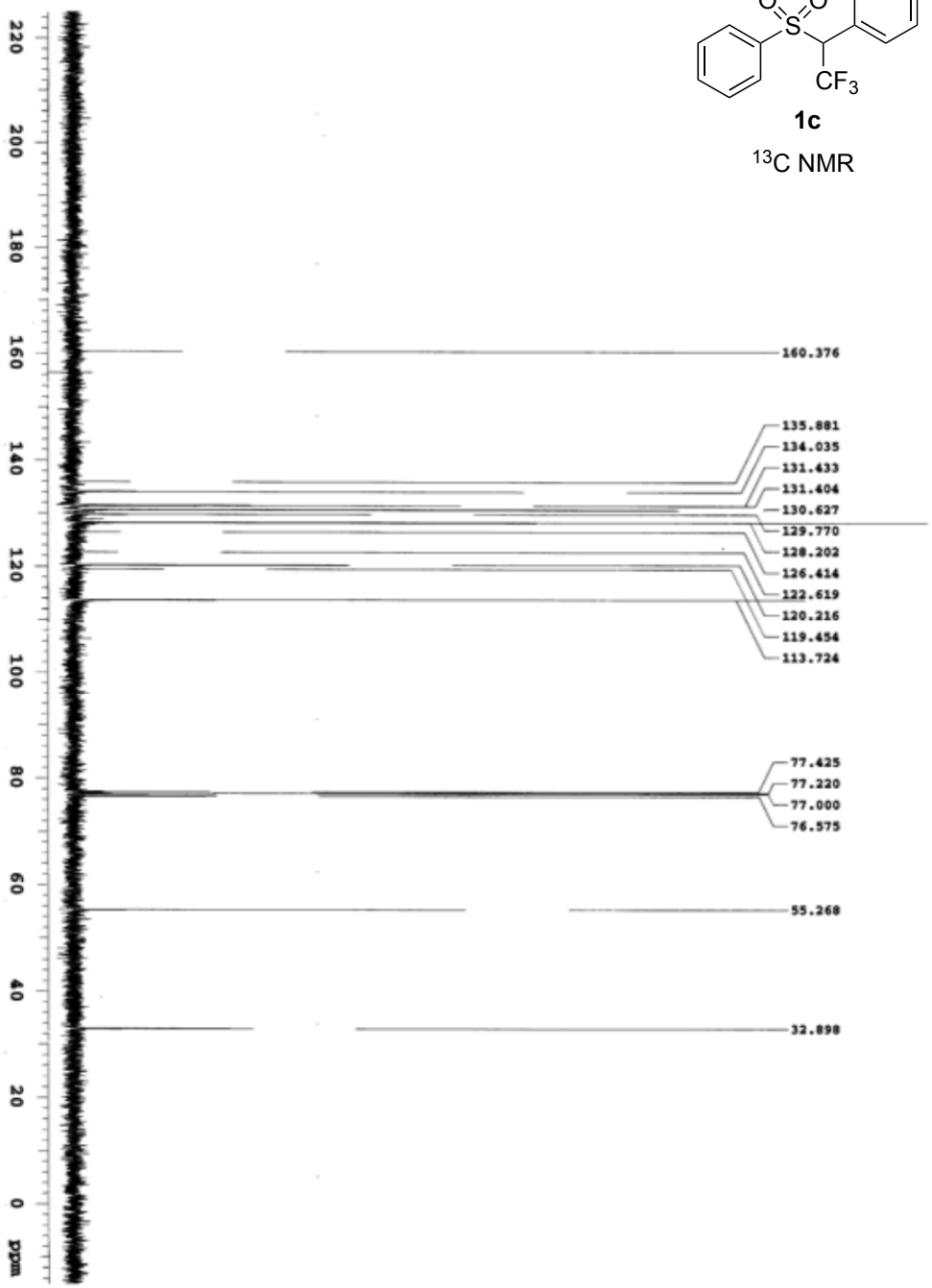

3c
1H NMR
OMe
F3C
7.592
7.586
7.579
7.564
7.558
7.548
7.541
7.535
7.399
7.365
7.346
7.334
7.317
7.304
7.262
6.865
6.854
6.847
6.830
6.824
6.812
5.618
5.593
5.567
5.541
5.514
5.316
5.313
5.259
5.256
5.142
5.109
3.829
3.773
3.680
3.674
3.668
3.662
3.629
3.624
3.617
3.610
3.336
3.310
3.286
3.258
1.566
1.563
1.255
-0.000
1.04
8.27
1.78
1.11
1.00
1.00
2.60
1.20
1.36
ppm

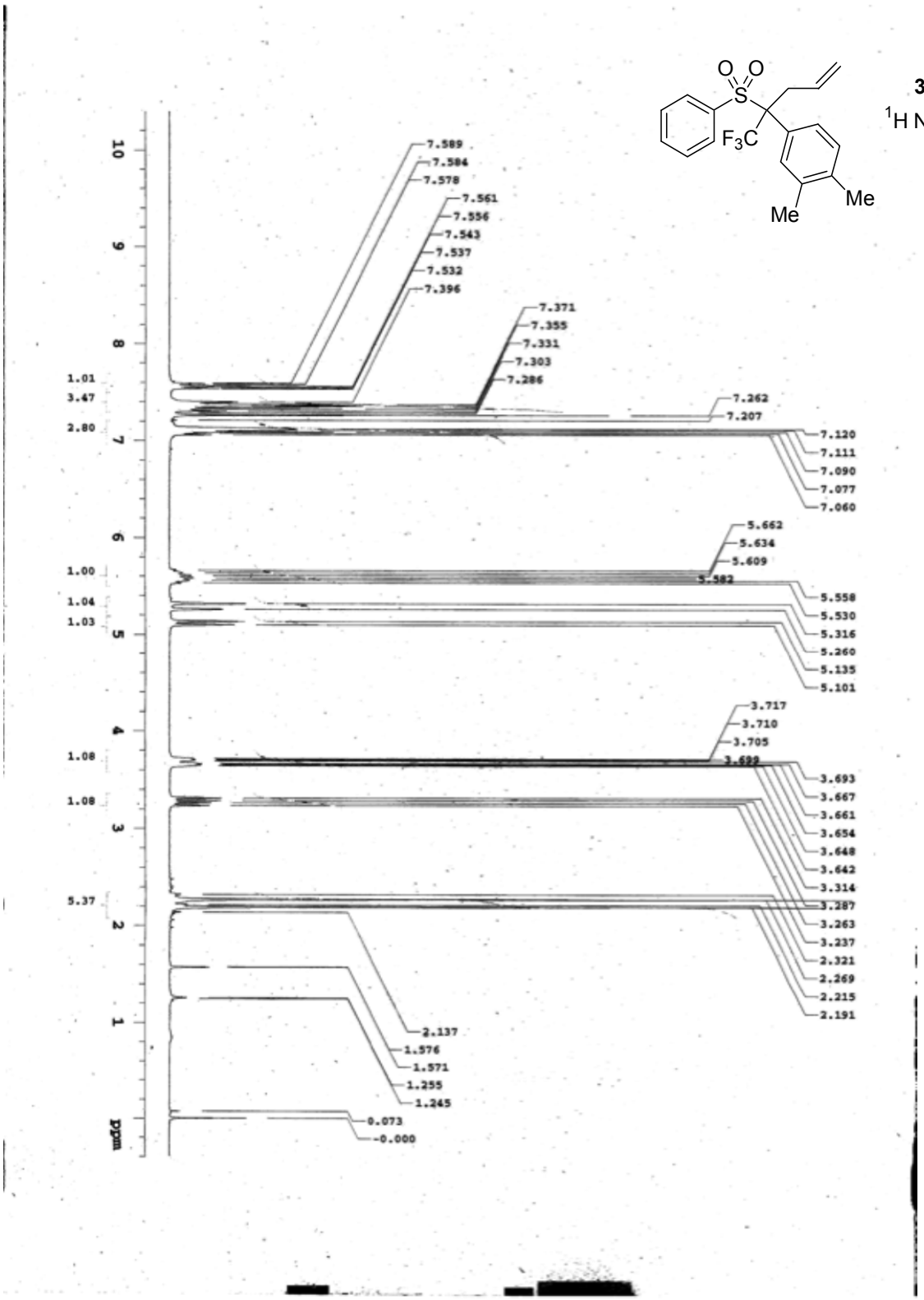

3c
^{19}F NMR
-0.000
-59.204
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

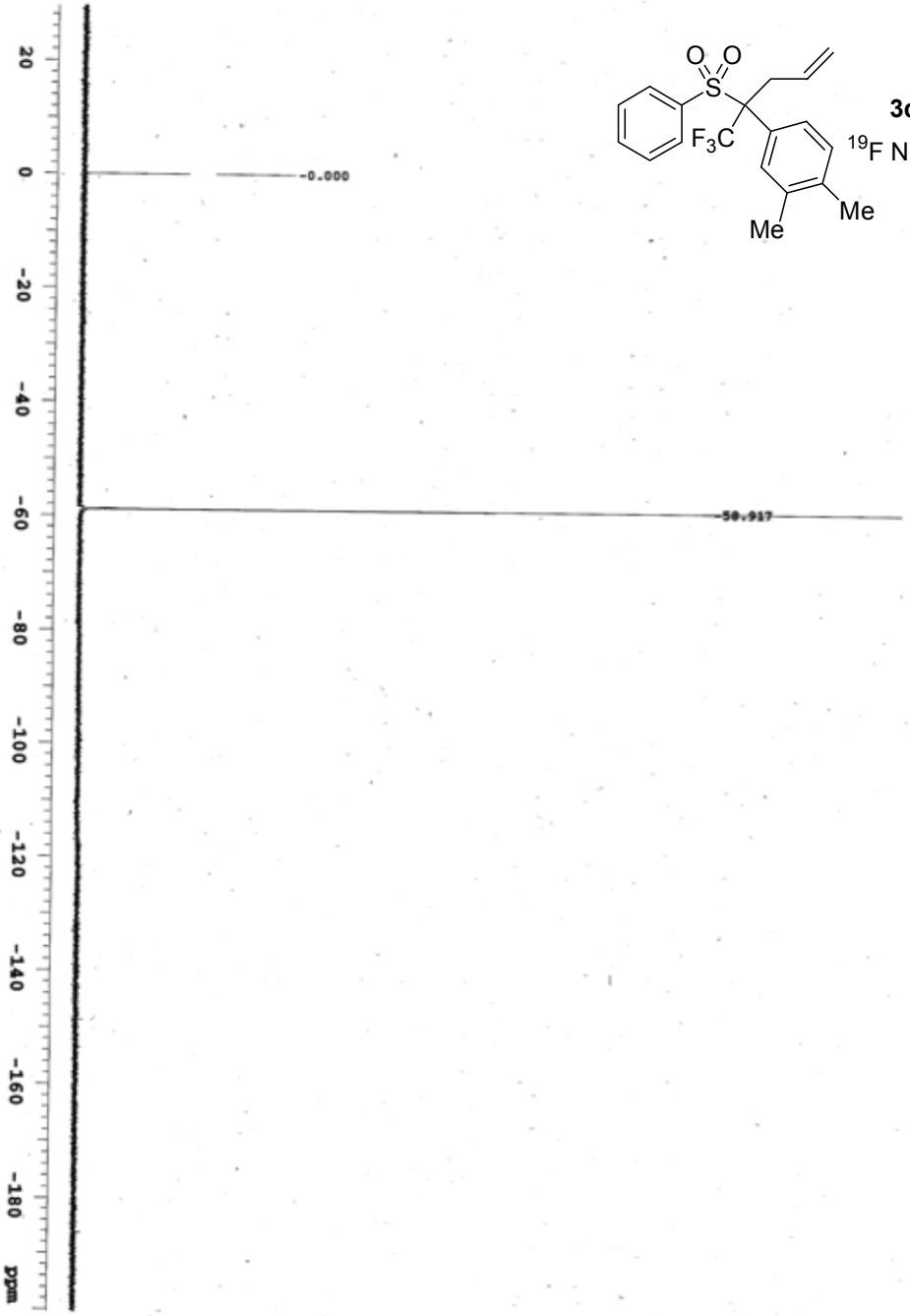

OMe
O
O
S
CF3

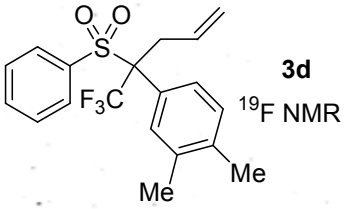
1c

^{13}C NMR


220
200
180
160
140
120
100
80
60
40
20
0
ppm
160.376
135.881
134.035
131.433
131.404
130.627
129.770
128.202
126.414
122.619
120.216
119.454
113.724
77.425
77.220
77.000
76.575
55.268
32.898

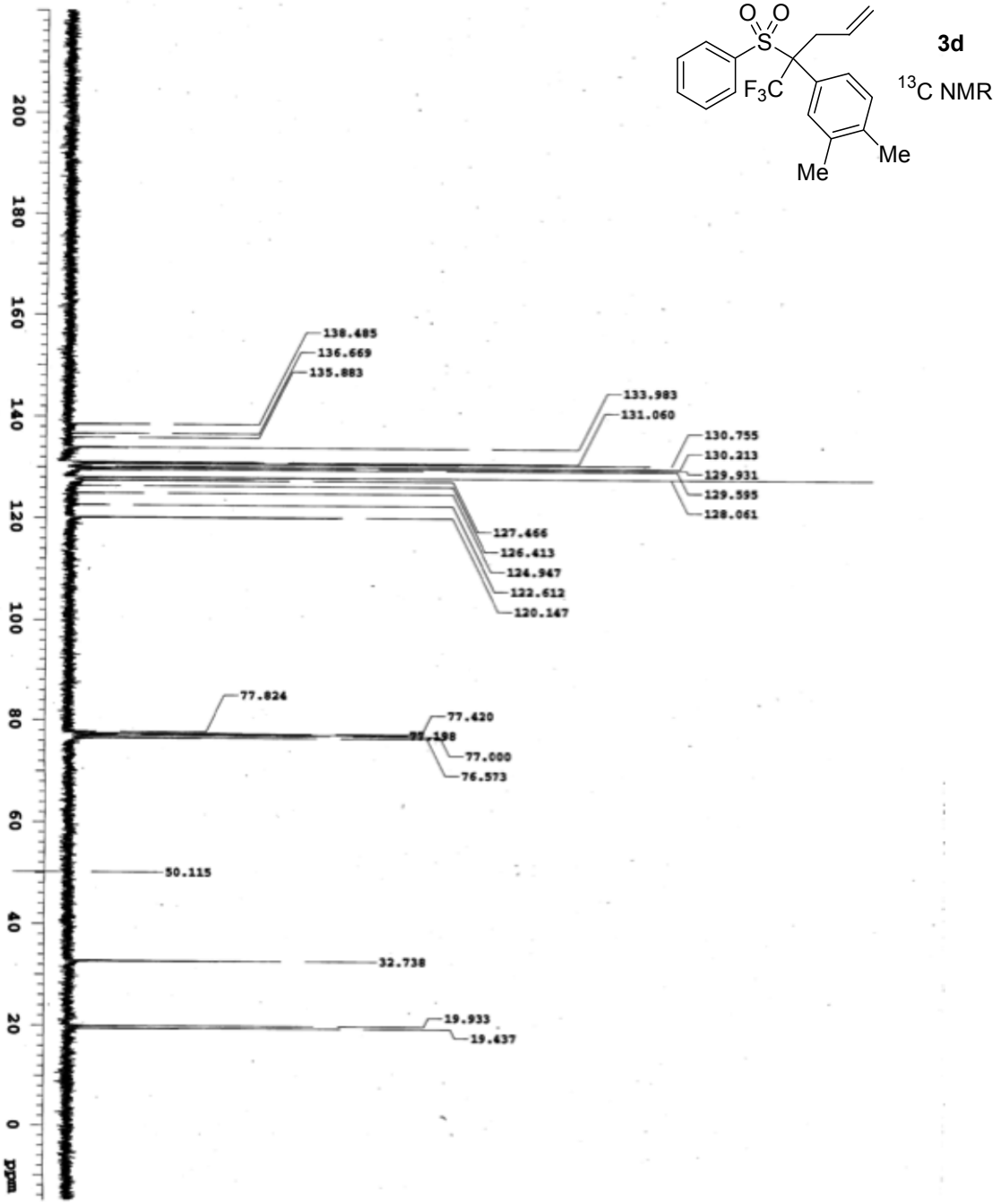

3d
^{1}H NMR
O
O
S
F_3C
Me
Me
7.589
7.584
7.578
7.561
7.556
7.543
7.537
7.532
7.396
7.371
7.355
7.331
7.303
7.286
7.262
7.207
7.120
7.111
7.090
7.077
7.060
5.662
5.634
5.609
5.582
5.558
5.530
5.316
5.260
5.135
5.101
3.717
3.710
3.705
3.699
3.693
3.667
3.661
3.654
3.648
3.642
3.314
3.287
3.263
3.237
2.321
2.269
2.215
2.191
2.137
1.576
1.571
1.255
1.245
0.073
-0.000
1.01
3.47
2.80
1.00
1.04
1.03
1.08
1.08
5.37
10
9
8
7
6
5
4
3
2
1
ppm

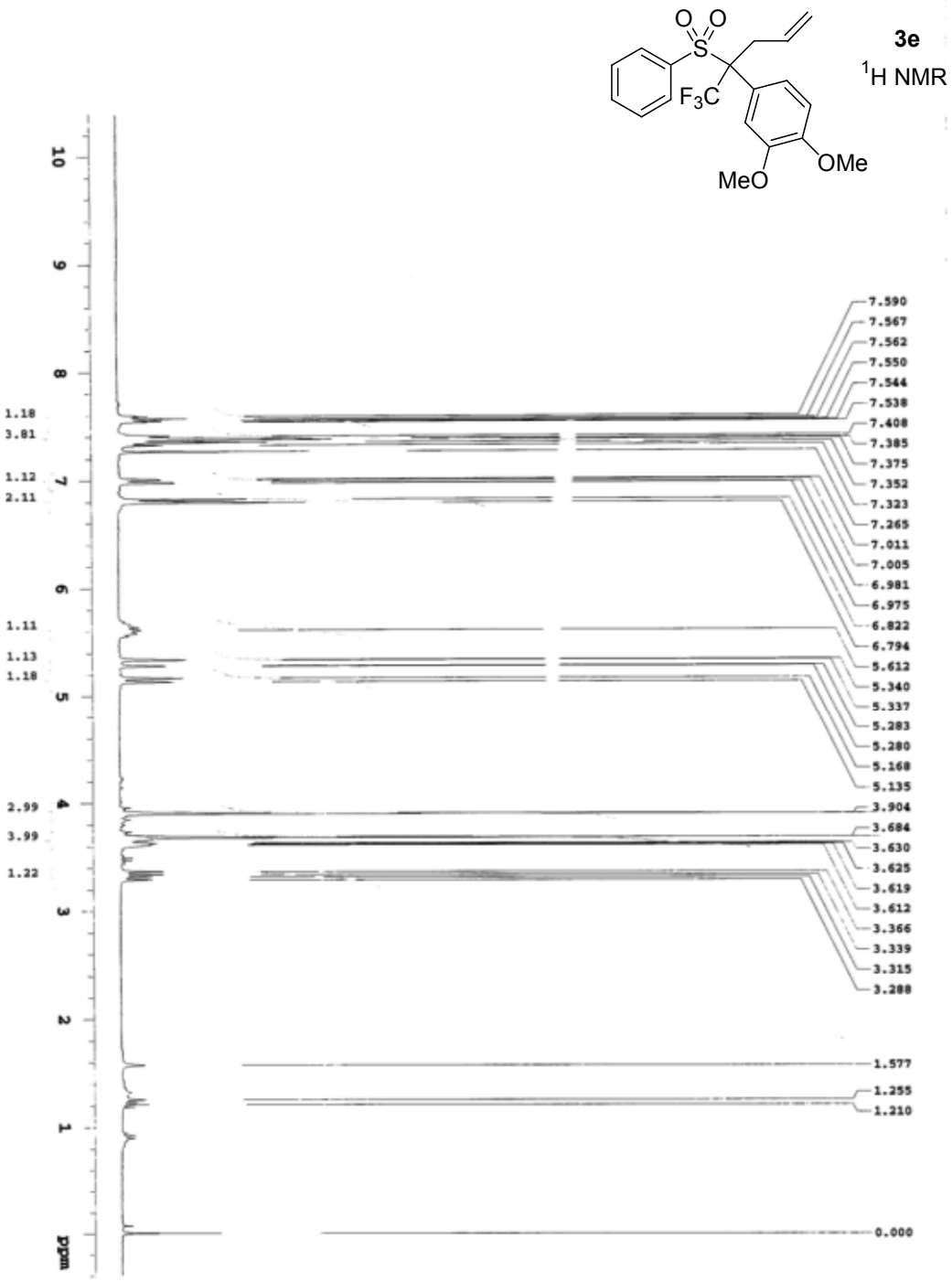


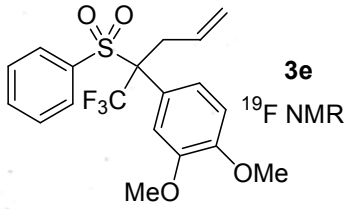


3d

^{19}F NMR

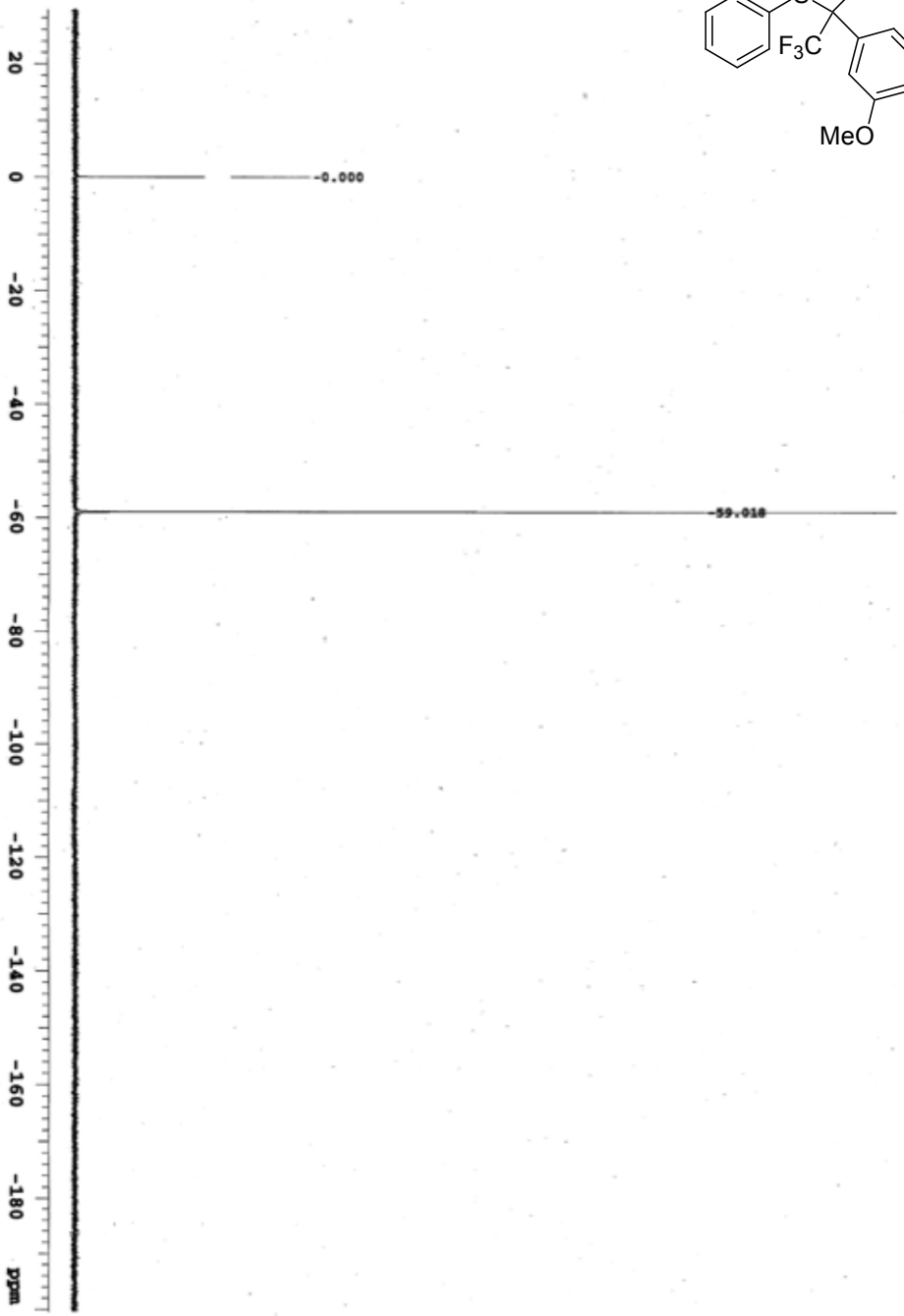

3d
^{13}C NMR
138.485
136.669
135.883
133.983
131.060
130.755
130.213
129.931
129.595
128.061
127.466
126.413
124.947
122.612
120.147
77.824
77.420
77.198
77.000
76.573
50.115
32.738
19.933
19.437
ppm

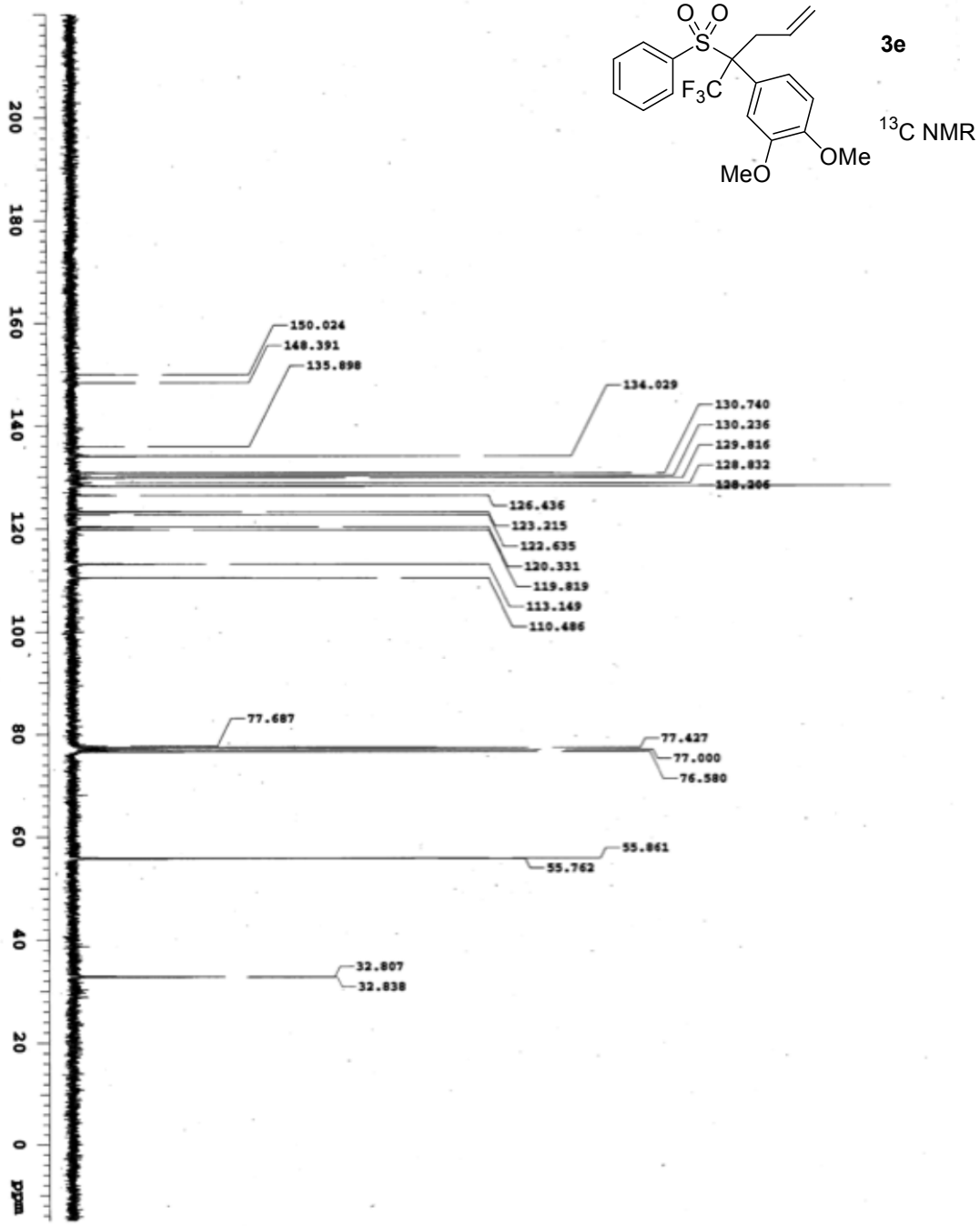

3e
1H NMR
O O
S
F3C
MeO
OMe
7.590
7.567
7.562
7.550
7.544
7.538
7.408
7.385
7.375
7.352
7.323
7.265
7.011
7.005
6.981
6.975
6.822
6.794
5.612
5.340
5.337
5.283
5.280
5.168
5.135
3.904
3.684
3.630
3.625
3.619
3.612
3.366
3.339
3.315
3.288
1.577
1.255
1.210
0.000
1.18
3.81
1.12
2.11
1.11
1.13
1.18
2.99
3.99
1.22
10
9
8
7
6
5
4
3
2
1
ppm

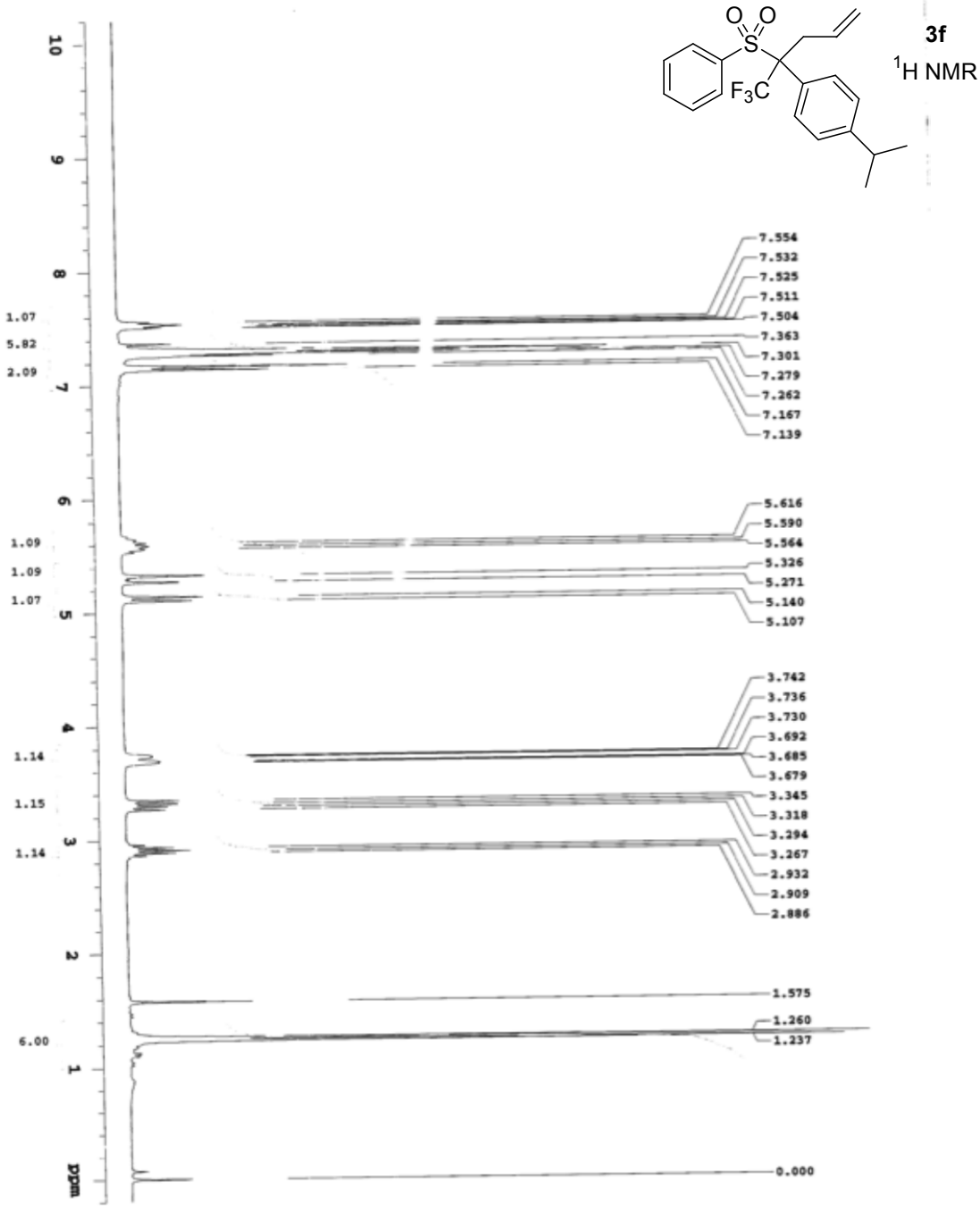

O
O
S
F3C
MeO
OMe

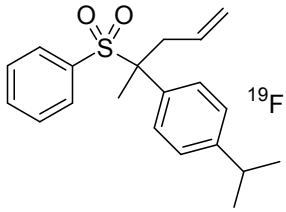
3e

^{19}F NMR


-0.000
-59.018
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

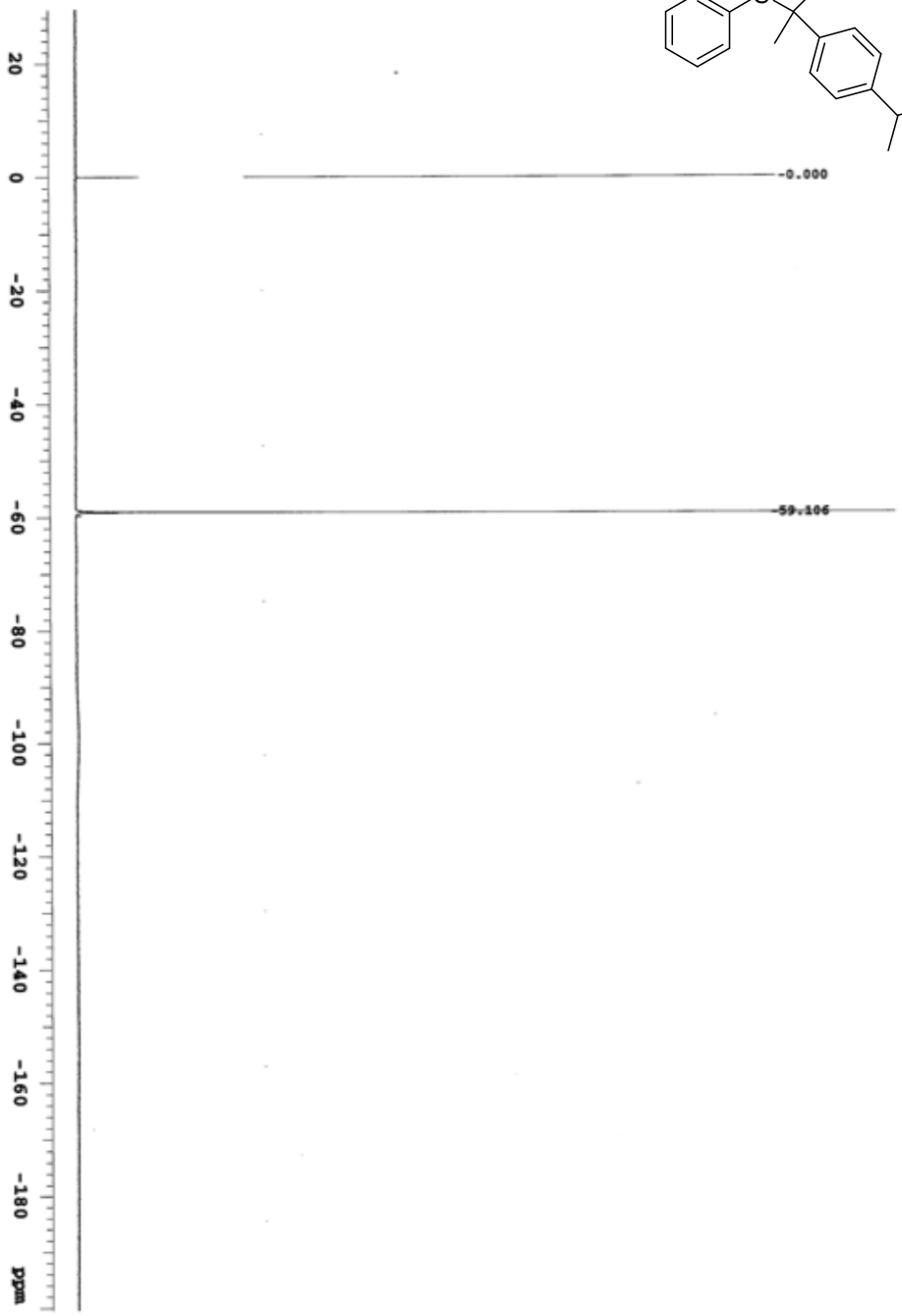

3e
^{13}C NMR
150.024
148.391
135.898
134.029
130.740
130.236
129.816
128.832
126.436
123.215
122.635
120.331
119.819
113.149
110.486
77.687
77.427
77.000
76.580
55.861
55.762
32.807
32.838
ppm

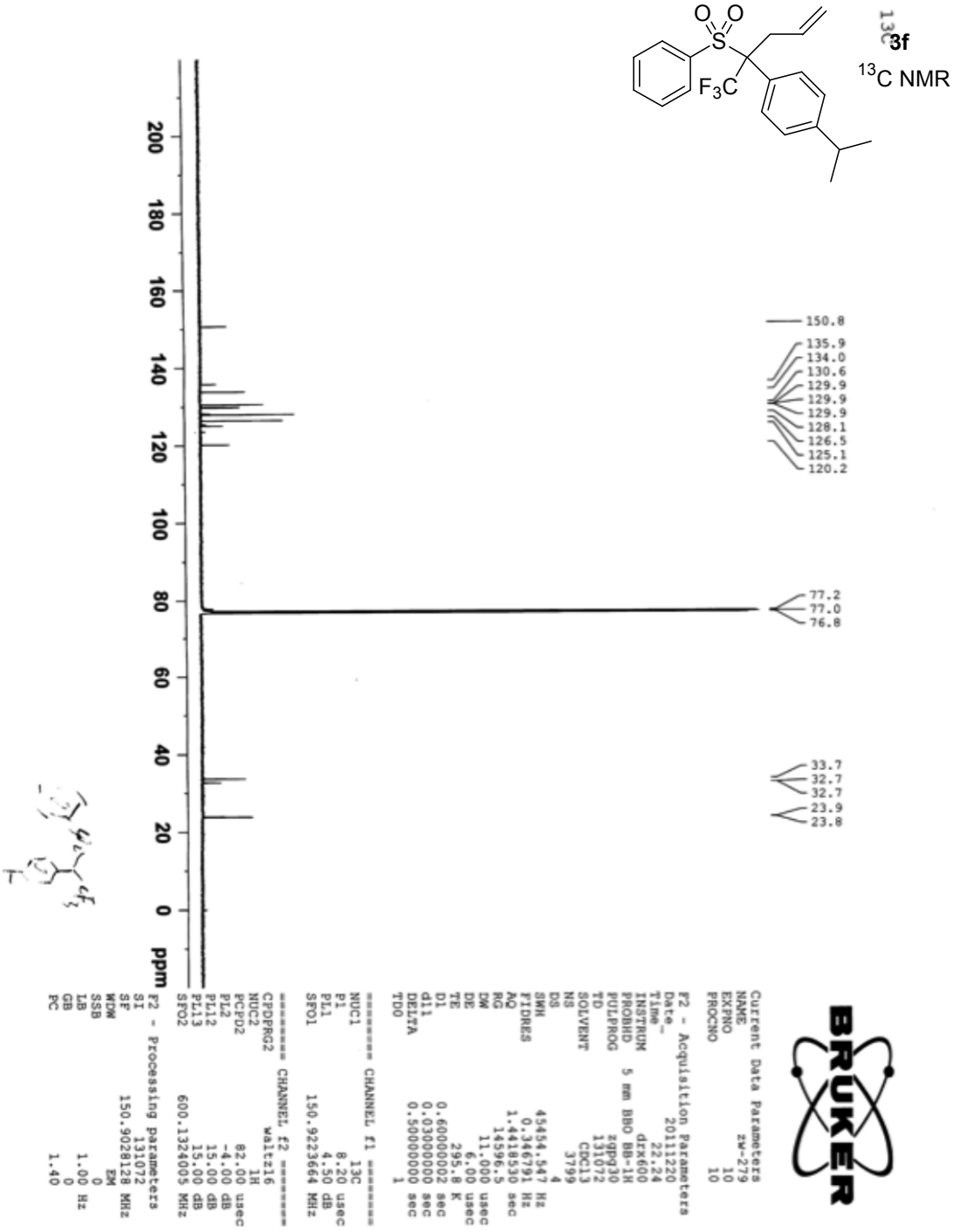

3f
1H NMR
O O
S
F3C
7.554
7.532
7.525
7.511
7.504
7.363
7.301
7.279
7.262
7.167
7.139
5.616
5.590
5.564
5.326
5.271
5.140
5.107
3.742
3.736
3.730
3.692
3.685
3.679
3.345
3.318
3.294
3.267
2.932
2.909
2.886
1.575
1.260
1.237
0.000
1.07
5.82
2.09
1.09
1.09
1.07
1.14
1.15
1.14
6.00
ppm

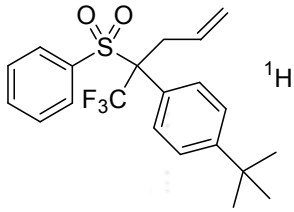


3f

^{19}F NMR

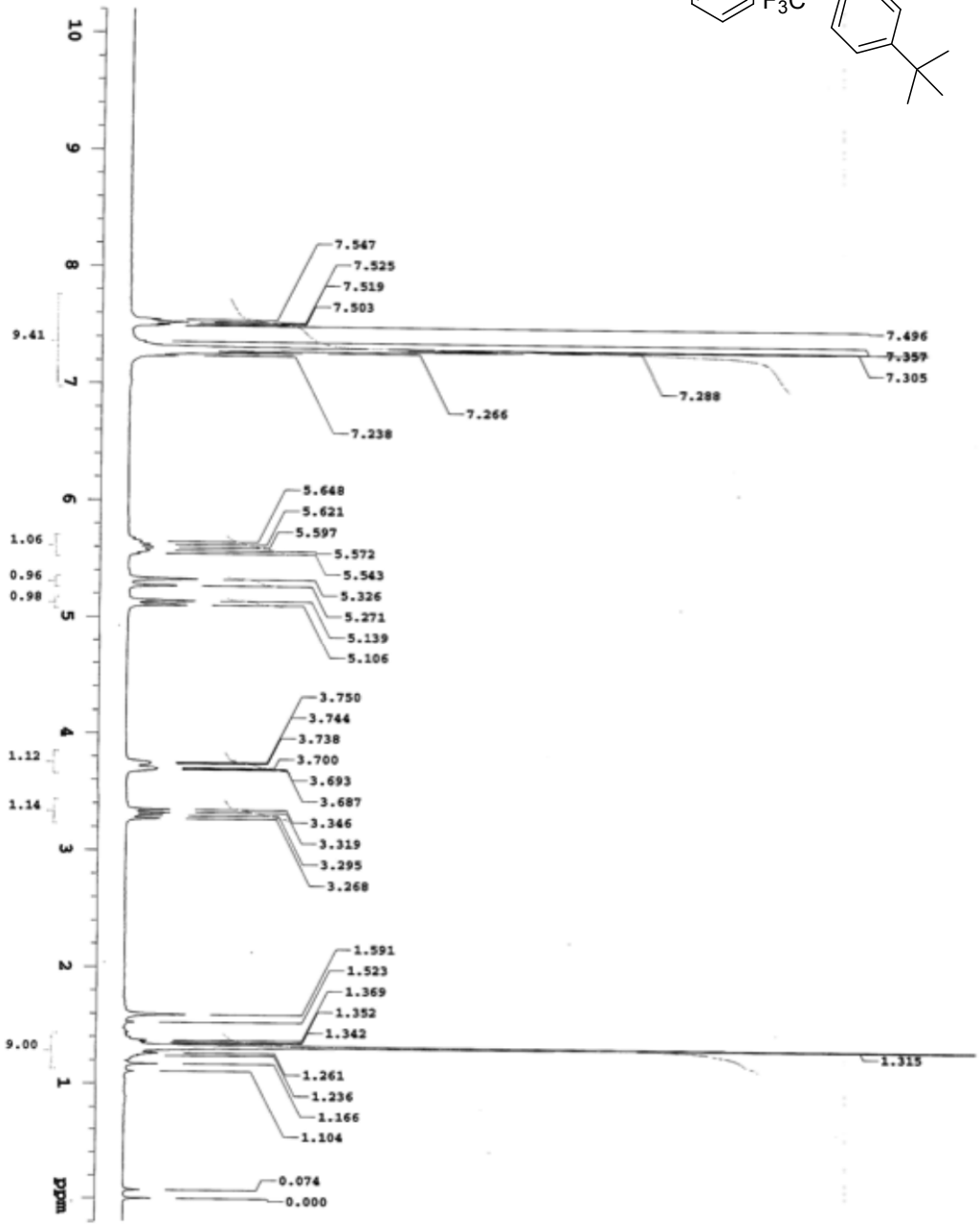


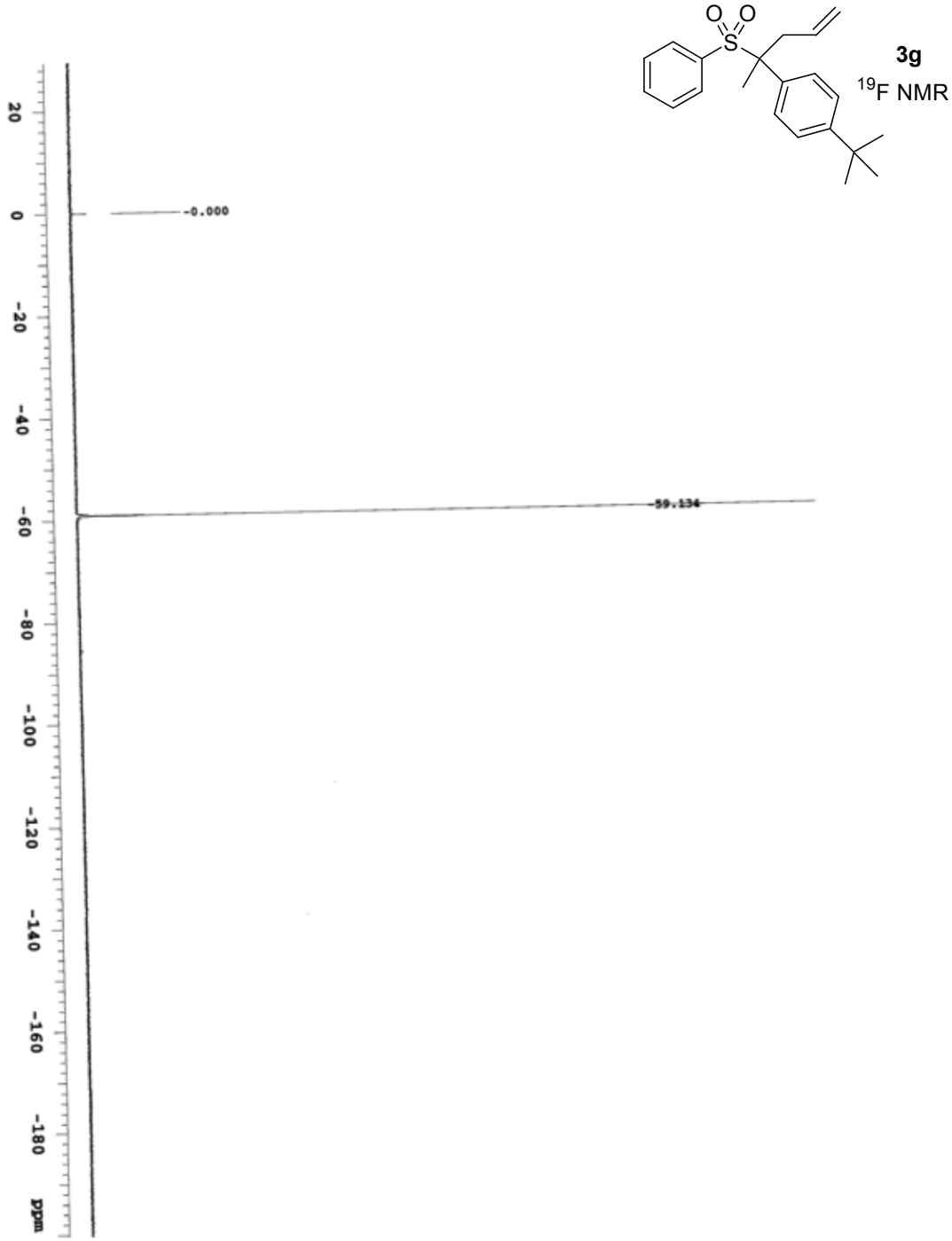

13C 3f
13C NMR
150.8
135.9
134.0
130.6
129.9
129.9
129.9
128.1
126.5
125.1
120.2
77.2
77.0
76.8
33.7
32.7
32.7
23.9
23.8
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME
EXPNO 10
PROCNO 10
F2 - Acquisition Parameters
Date_ 20111220
Time 22.24
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 3799
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 14596.5
DW 11.000 usec
DE 6.00 usec
TE 295.8 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028128 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

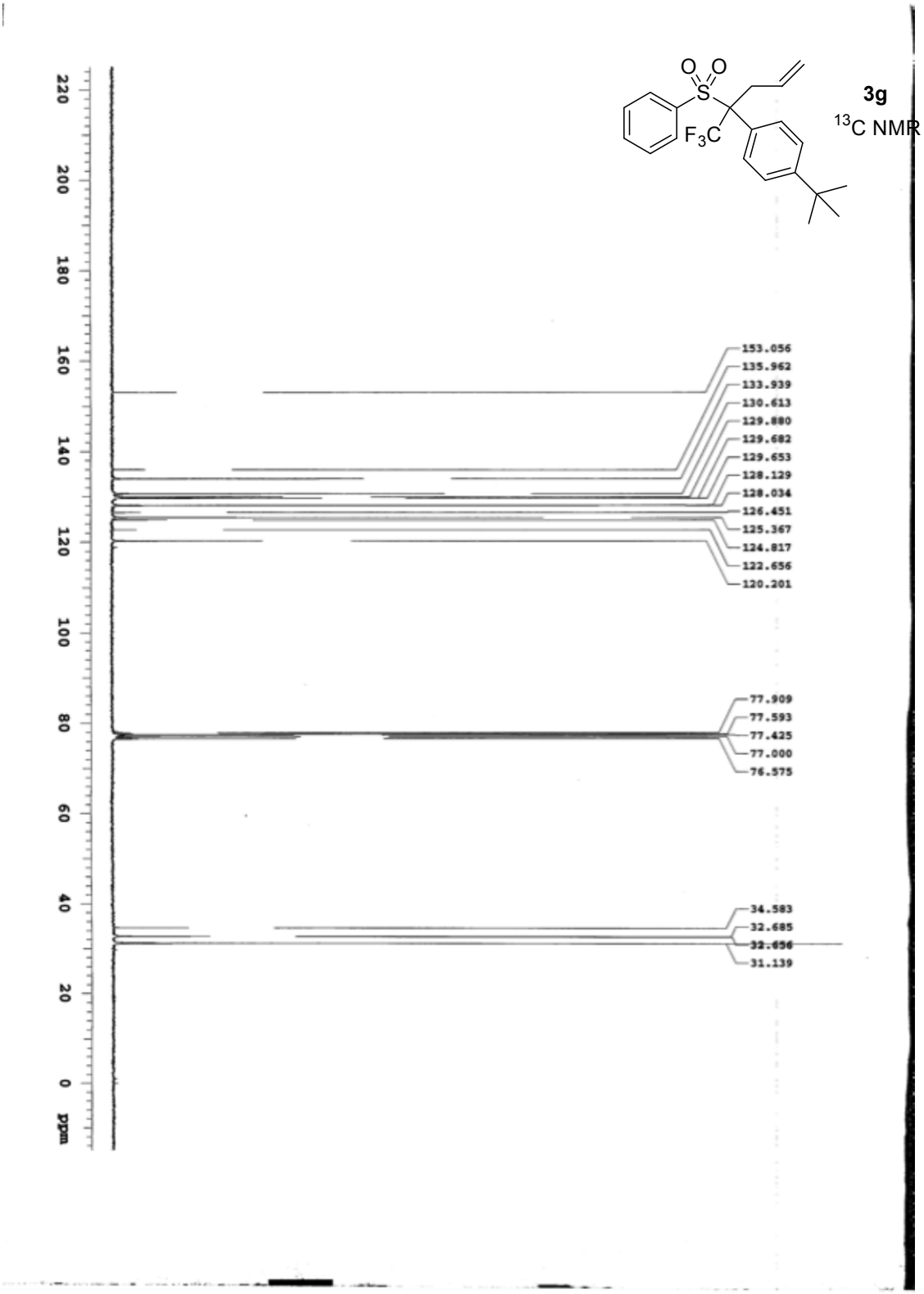

O
O
S
F3C

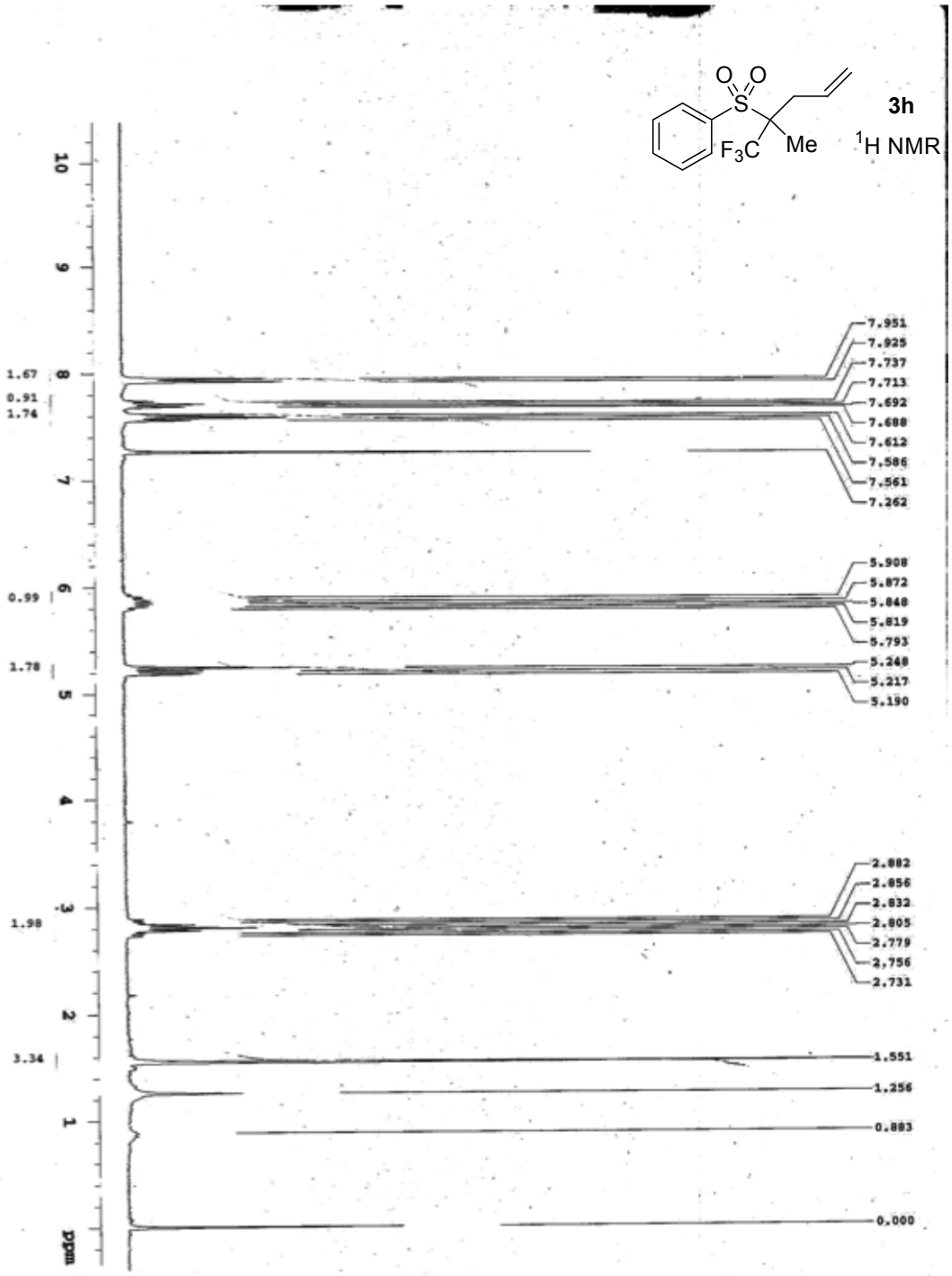
3g

^{1}H NMR


7.547
7.525
7.519
7.503
7.496
7.359
7.305
7.288
7.266
7.238
5.648
5.621
5.597
5.572
5.543
5.326
5.271
5.139
5.106
3.750
3.744
3.738
3.700
3.693
3.687
3.346
3.319
3.295
3.268
1.591
1.523
1.369
1.352
1.342
1.315
1.261
1.236
1.166
1.104
0.074
0.000
9.41
1.06
0.96
0.98
1.12
1.14
9.00
ppm

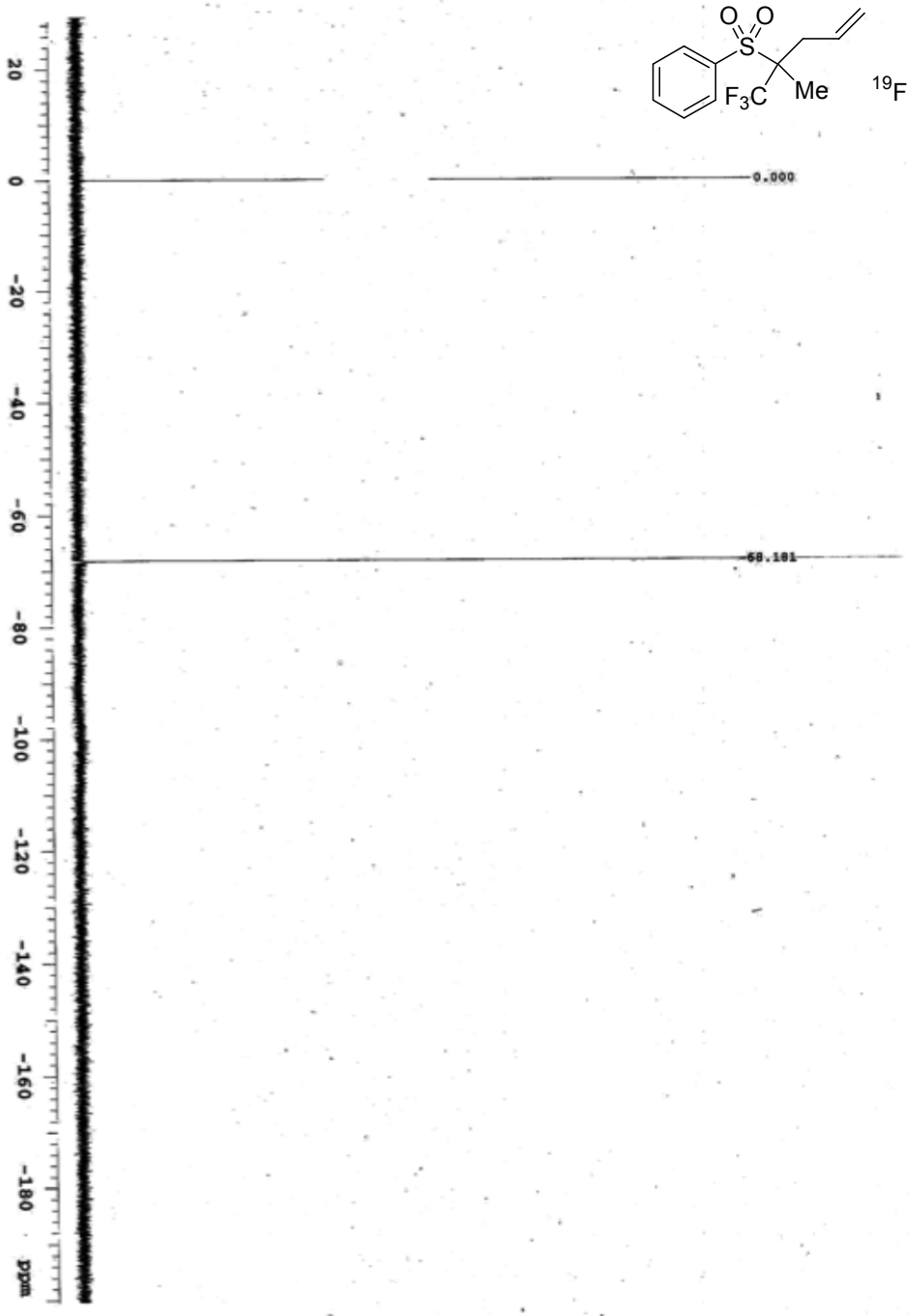

3g
^{19}F NMR
-0.000
-59.134
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

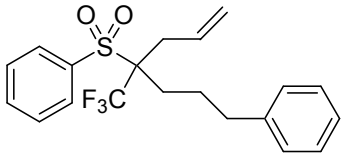

3g
13C NMR
O
O
S
F3C
220
200
180
160
140
120
100
80
60
40
20
0
ppm
153.056
135.962
133.939
130.613
129.880
129.682
129.653
128.129
128.034
126.451
125.367
124.817
122.656
120.201
77.909
77.593
77.425
77.000
76.575
34.583
32.685
32.656
31.139


3h
^{1}H NMR
Me
F_3C
7.951
7.925
7.737
7.713
7.692
7.688
7.612
7.586
7.561
7.262
5.908
5.872
5.848
5.819
5.793
5.248
5.217
5.190
2.882
2.856
2.832
2.805
2.779
2.756
2.731
1.551
1.256
0.883
0.000
1.67
0.91
1.74
0.99
1.78
1.98
3.34
ppm

3h

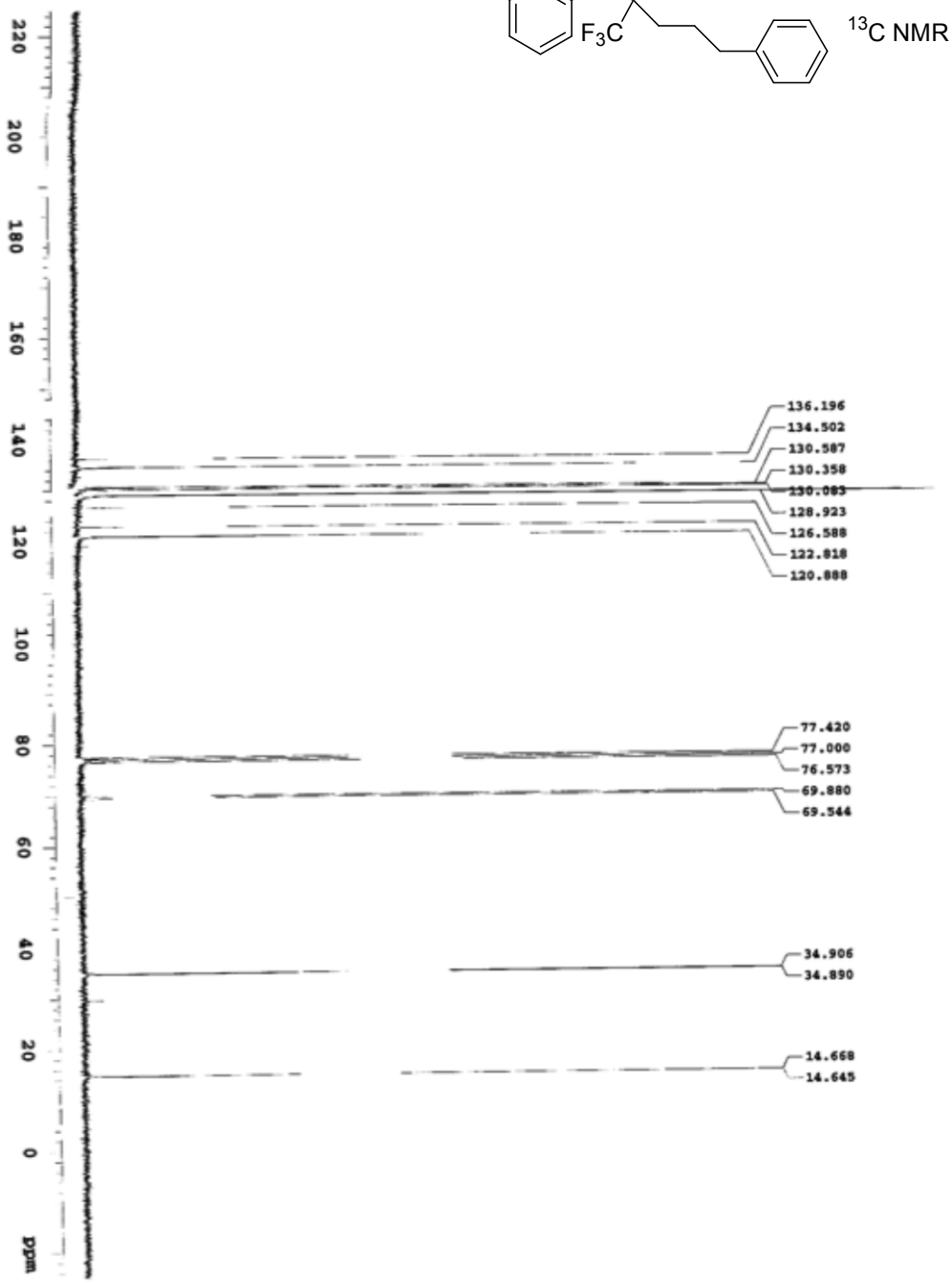
^{19}F NMR

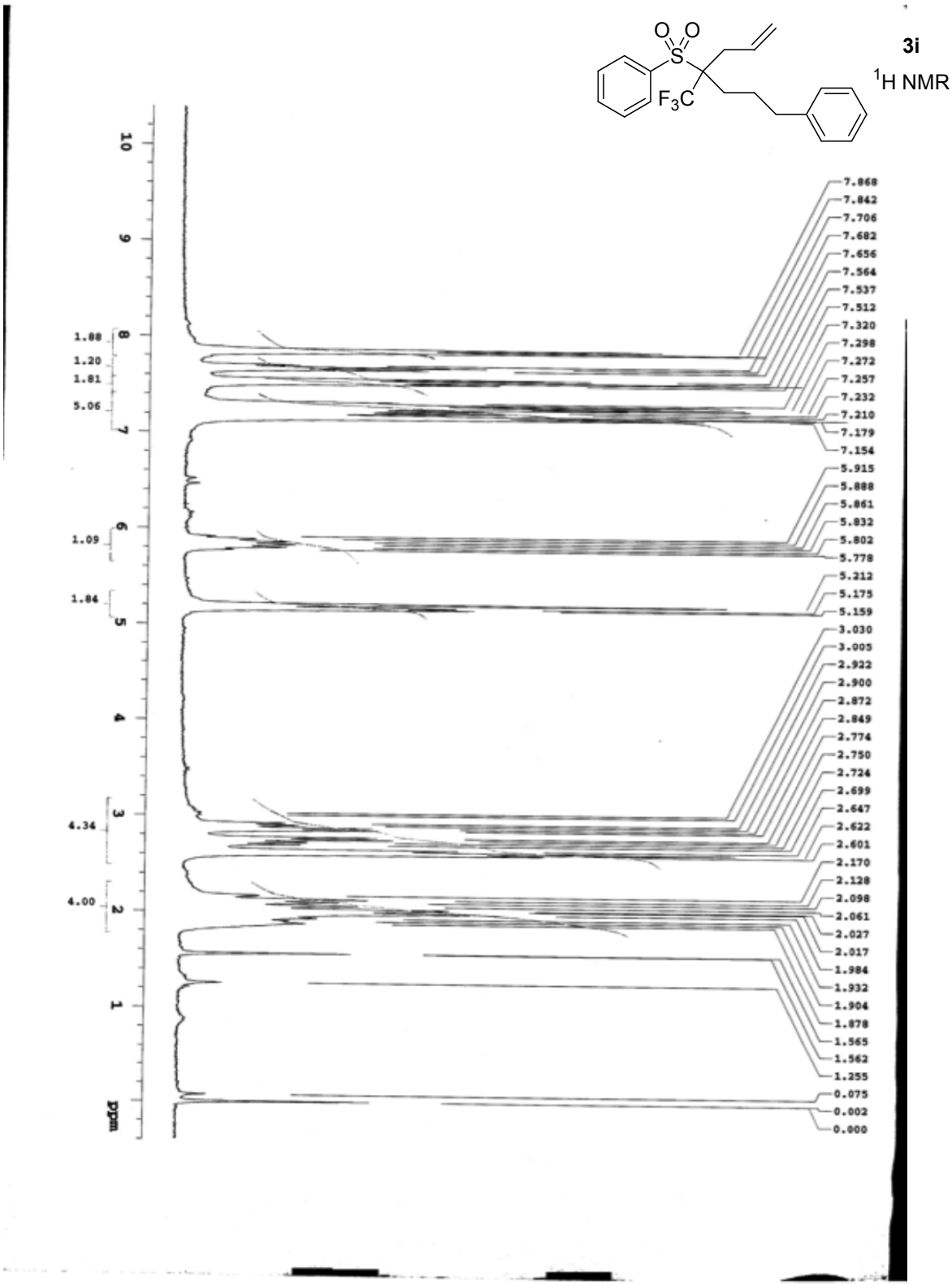


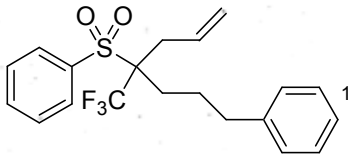

O
O
S
F3C

3i

^{13}C NMR

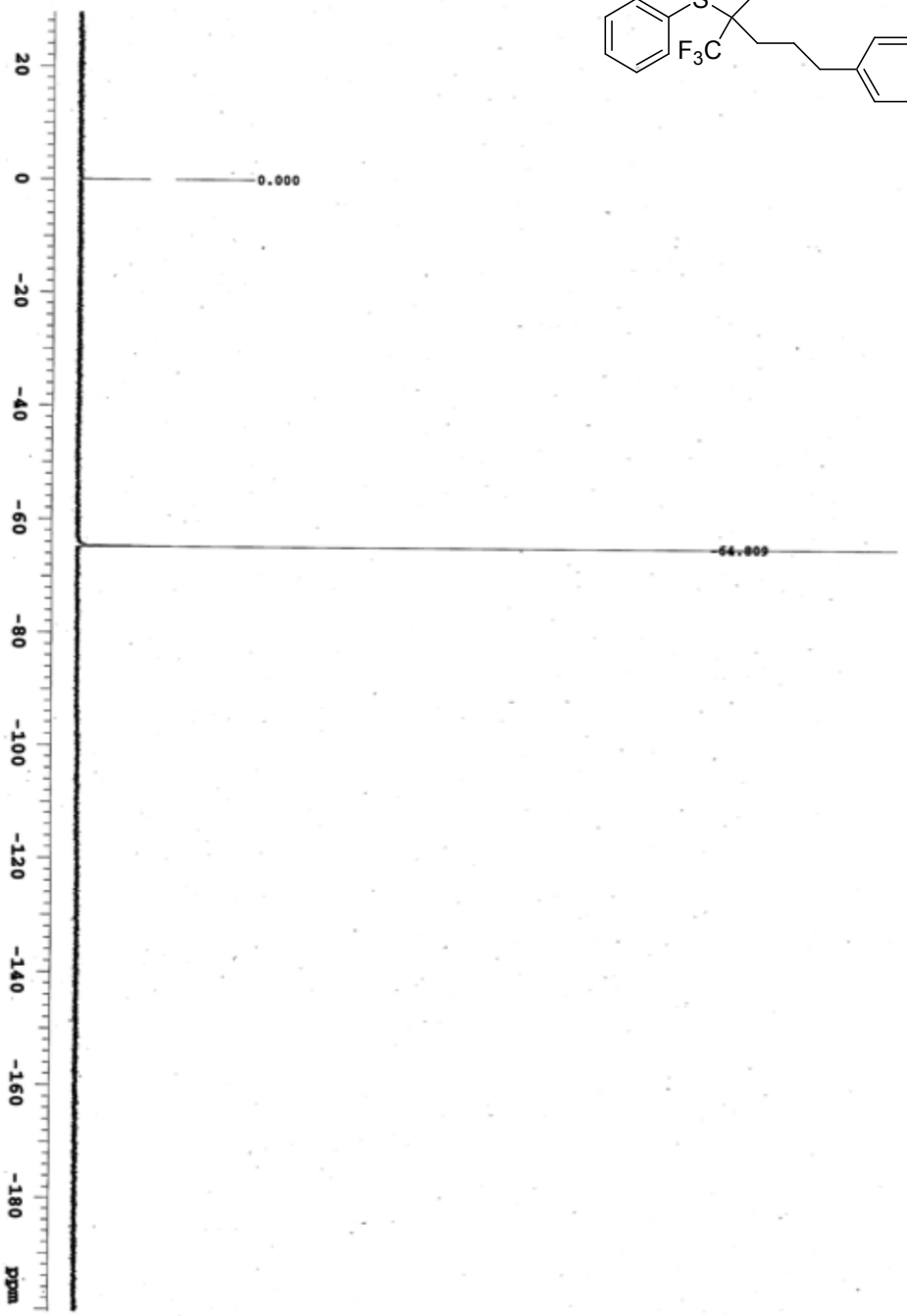

220
200
180
160
140
120
100
80
60
40
20
0
ppm
136.196
134.502
130.587
130.358
130.083
128.923
126.588
122.818
120.888
77.420
77.000
76.573
69.880
69.544
34.906
34.890
14.668
14.645

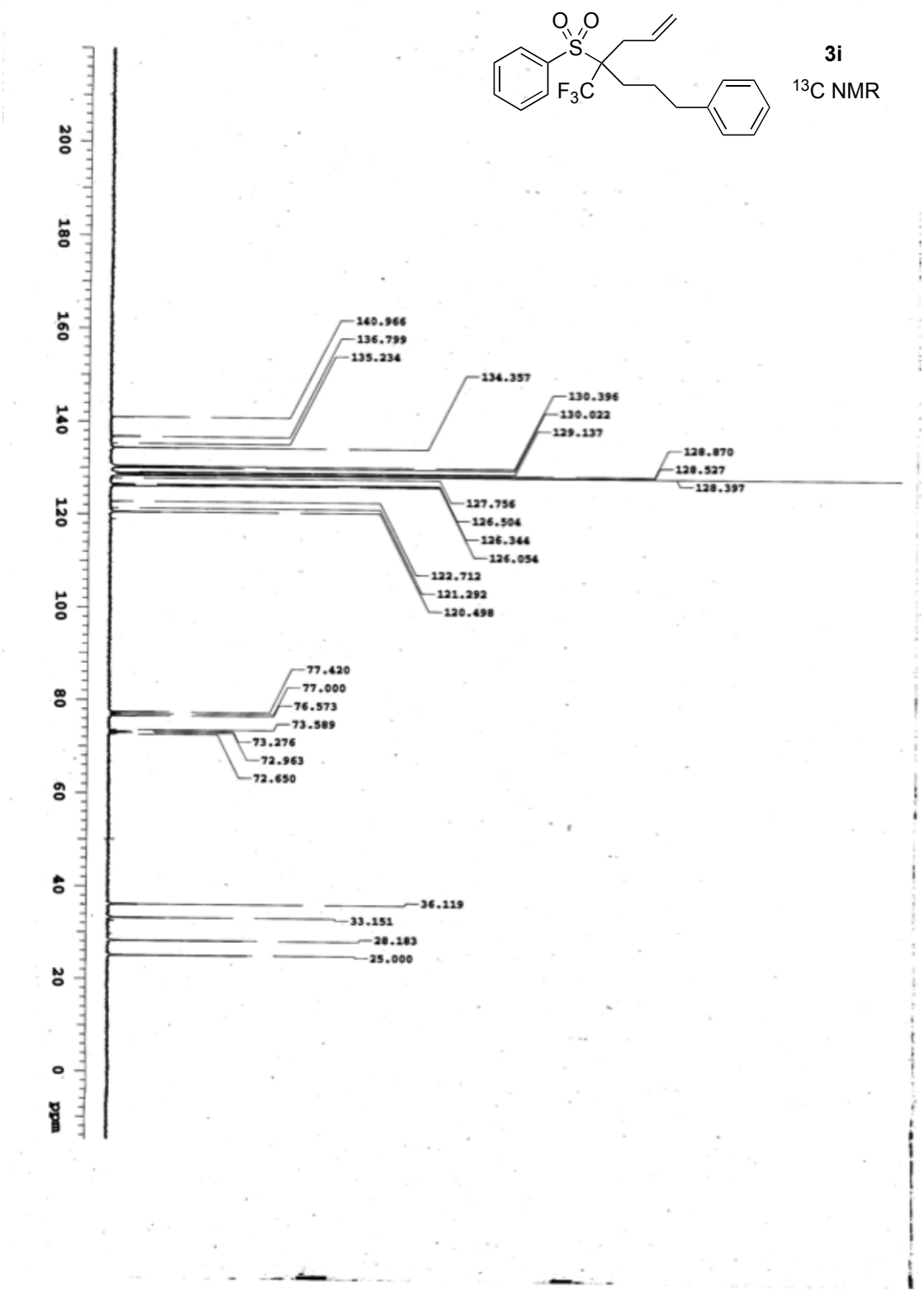

3i
1H NMR
F3C
O
O
S
ppm
10
9
8
7
6
5
4
3
2
1
1.88
1.20
1.81
5.06
1.09
1.84
4.34
4.00
7.868
7.842
7.706
7.682
7.656
7.564
7.537
7.512
7.320
7.298
7.272
7.257
7.232
7.210
7.179
7.154
5.915
5.888
5.861
5.832
5.802
5.778
5.212
5.175
5.159
3.030
3.005
2.922
2.900
2.872
2.849
2.774
2.750
2.724
2.699
2.647
2.622
2.601
2.170
2.128
2.098
2.061
2.027
2.017
1.984
1.932
1.904
1.878
1.565
1.562
1.255
0.075
0.002
0.000

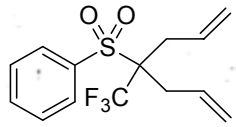


3i

^{19}F NMR

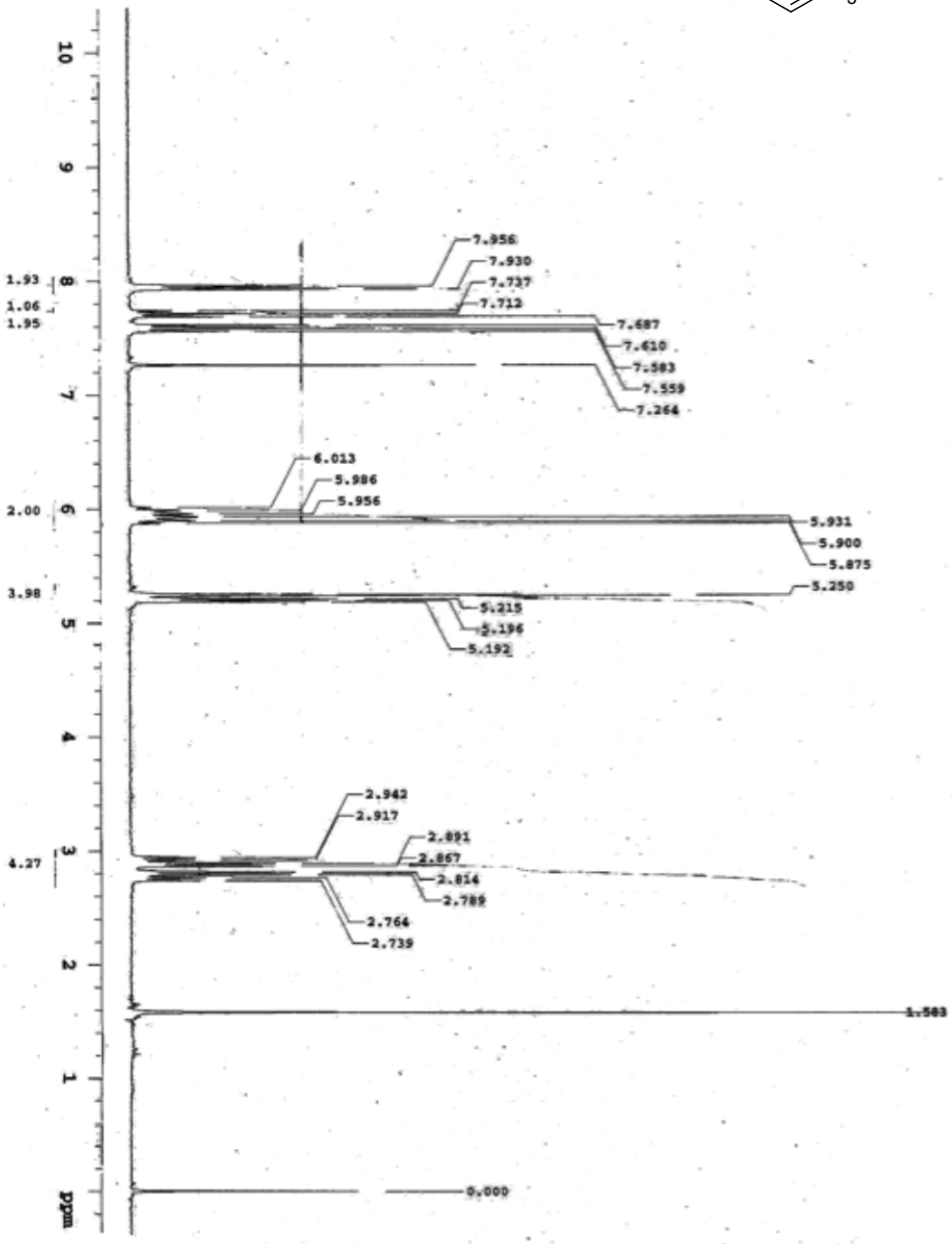



3i
13C NMR
140.966
136.799
135.234
134.357
130.396
130.022
129.137
128.870
128.527
128.397
127.756
126.504
126.344
126.054
122.712
121.292
120.498
77.420
77.000
76.573
73.589
73.276
72.963
72.650
36.119
33.151
28.183
25.000
ppm


O
O
S
F3C

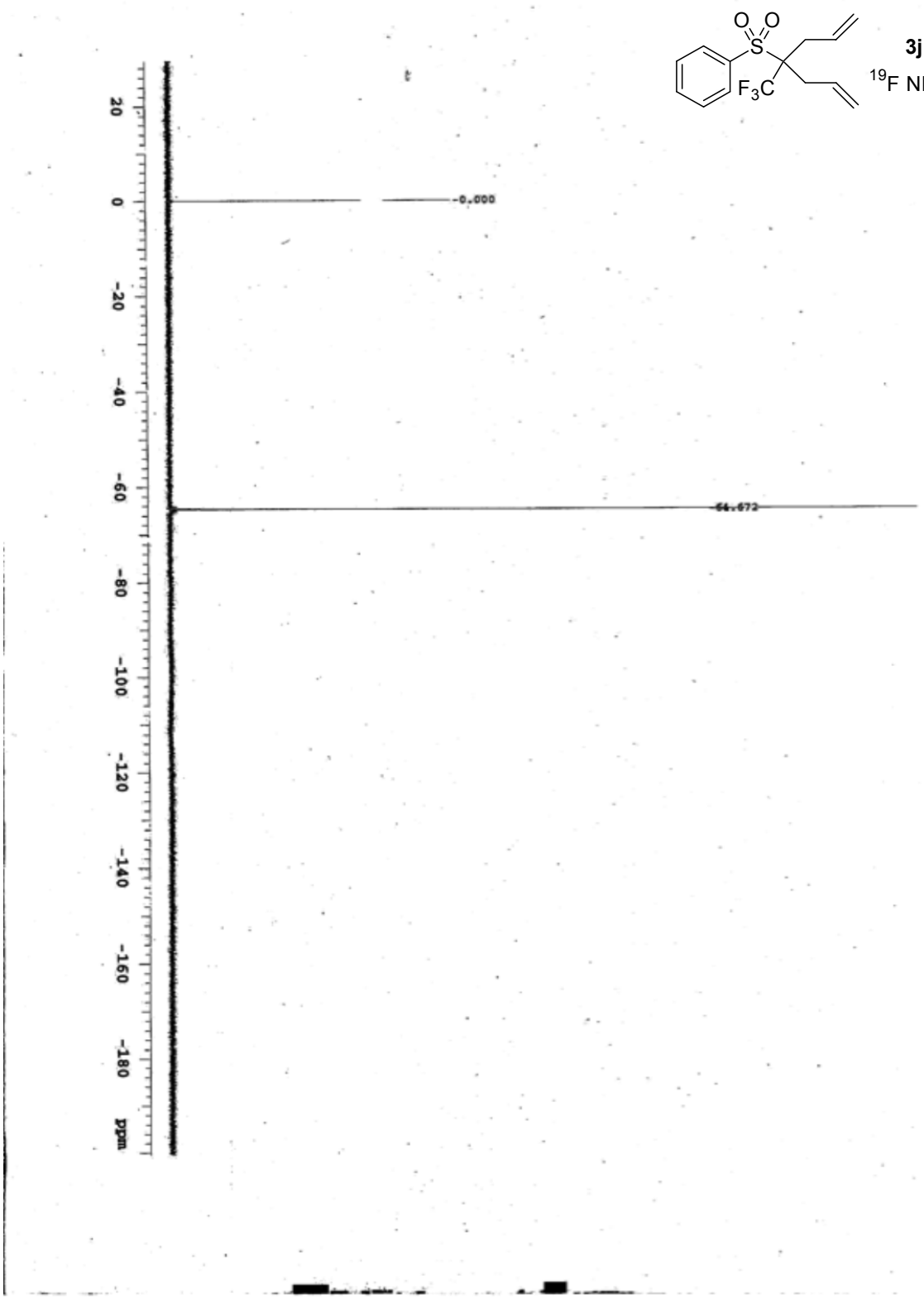
3j

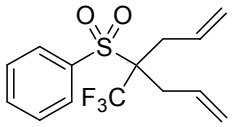
^{1}H NMR


10
9
8
7
6
5
4
3
2
1
ppm
1.93
1.06
1.95
2.00
3.98
4.27
7.956
7.930
7.737
7.712
7.687
7.610
7.583
7.559
7.264
6.013
5.986
5.956
5.931
5.900
5.875
5.250
5.215
5.196
5.192
2.942
2.917
2.891
2.867
2.814
2.789
2.764
2.739
1.583
0.000

3j

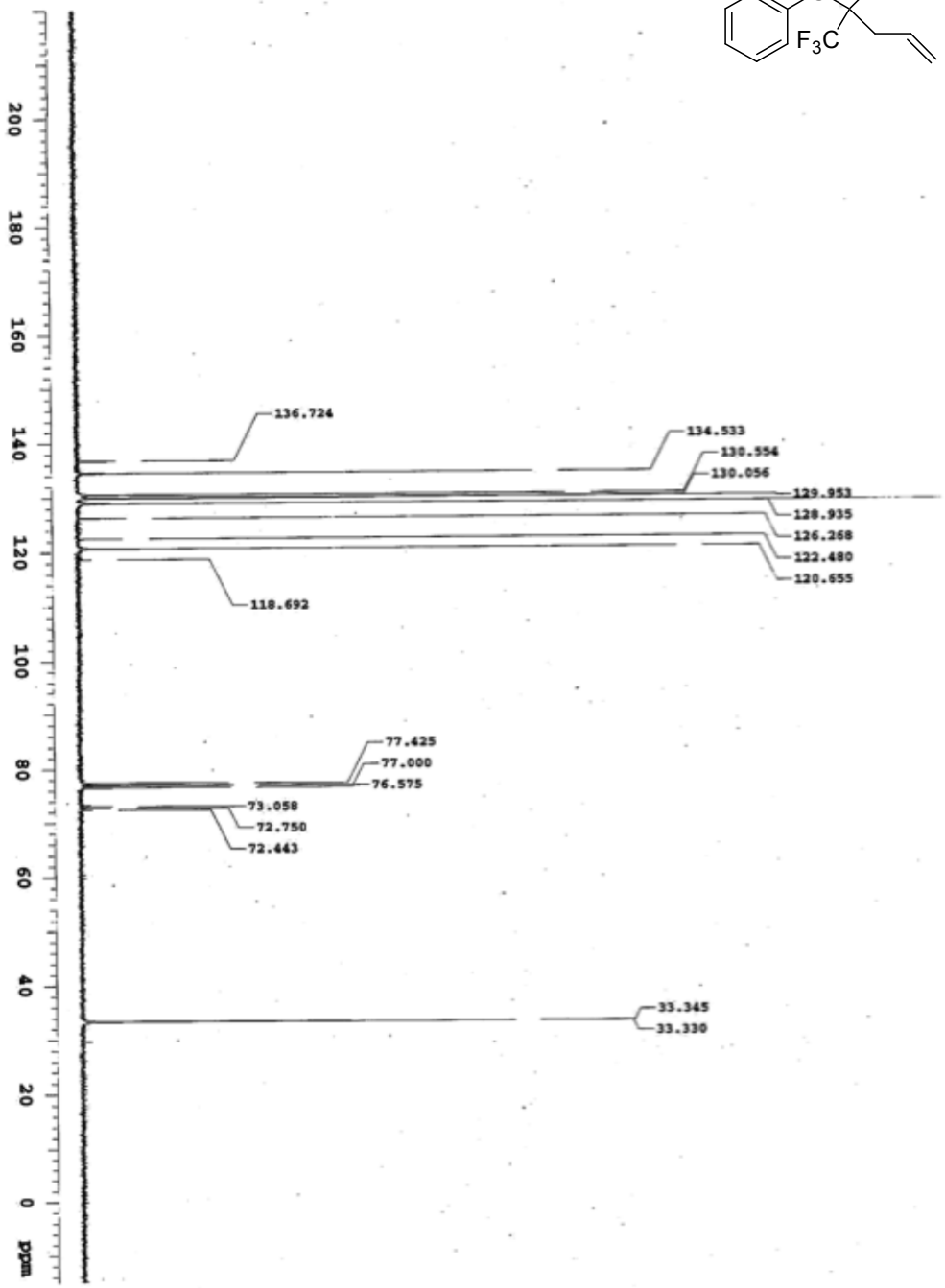
^{19}F NMR

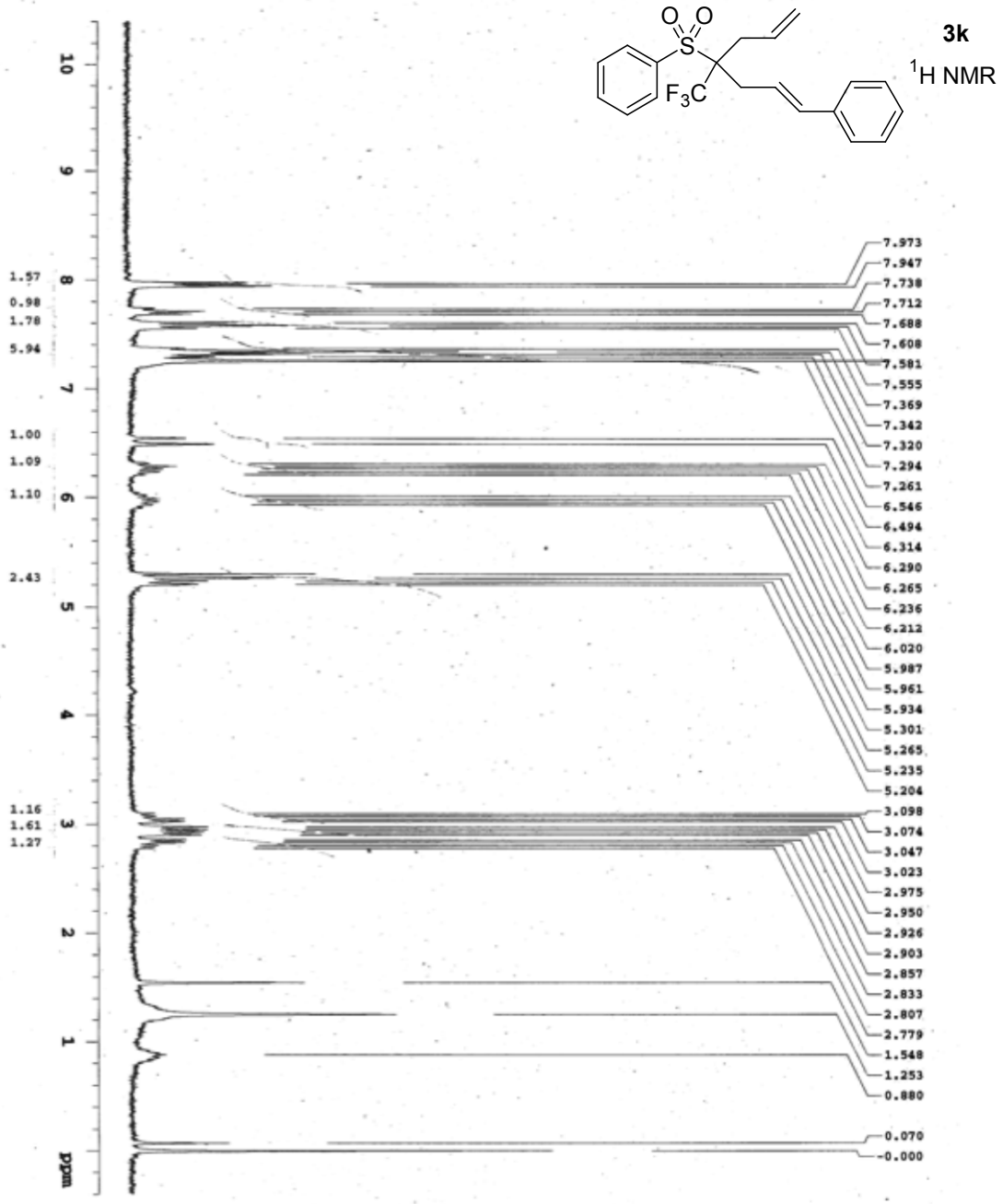


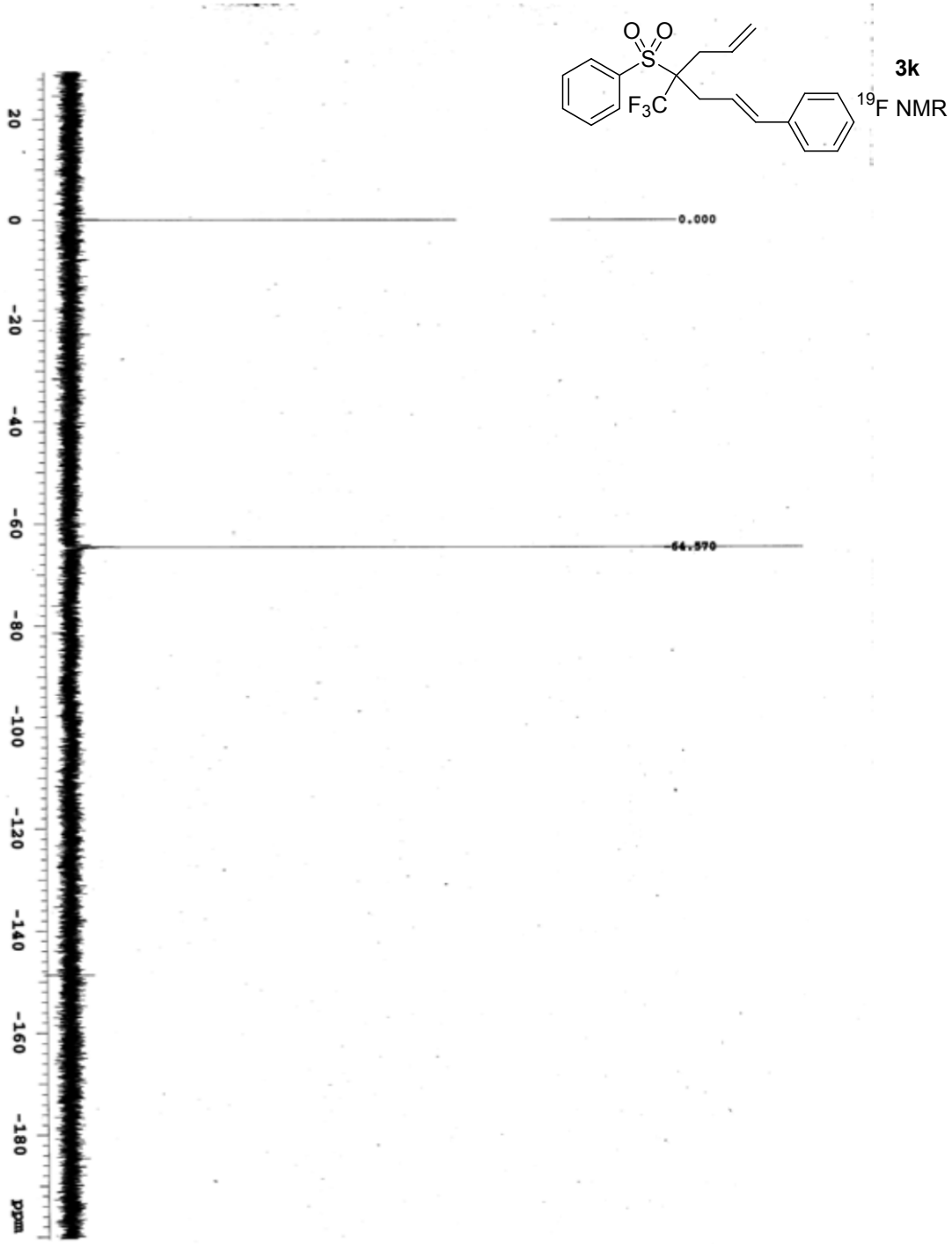

O
O
S
F3C

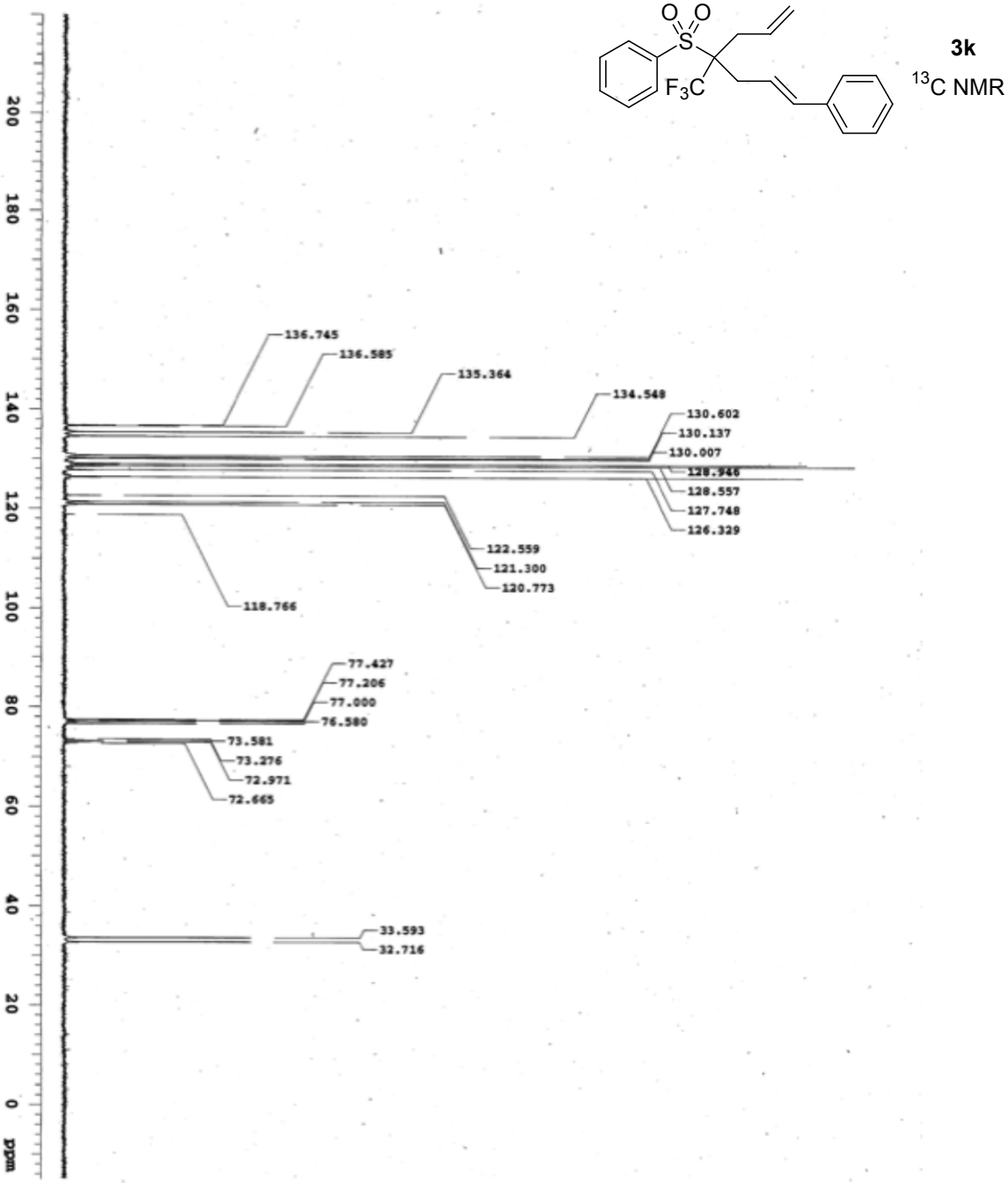
3j

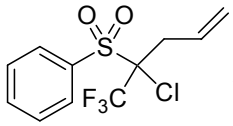
^{13}C NMR


136.724
134.533
130.554
130.056
129.953
128.935
126.268
122.480
120.655
118.692
77.425
77.000
76.575
73.058
72.750
72.443
33.345
33.330
200
180
160
140
120
100
80
60
40
20
0
ppm


3k
^{1}H NMR
O O
S
F_3C
7.973
7.947
7.738
7.712
7.688
7.608
7.581
7.555
7.369
7.342
7.320
7.294
7.261
6.546
6.494
6.314
6.290
6.265
6.236
6.212
6.020
5.987
5.961
5.934
5.301
5.265
5.235
5.204
3.098
3.074
3.047
3.023
2.975
2.950
2.926
2.903
2.857
2.833
2.807
2.779
1.548
1.253
0.880
0.070
-0.000
1.57
0.98
1.78
5.94
1.00
1.09
1.10
2.43
1.16
1.61
1.27
10
9
8
7
6
5
4
3
2
1
ppm

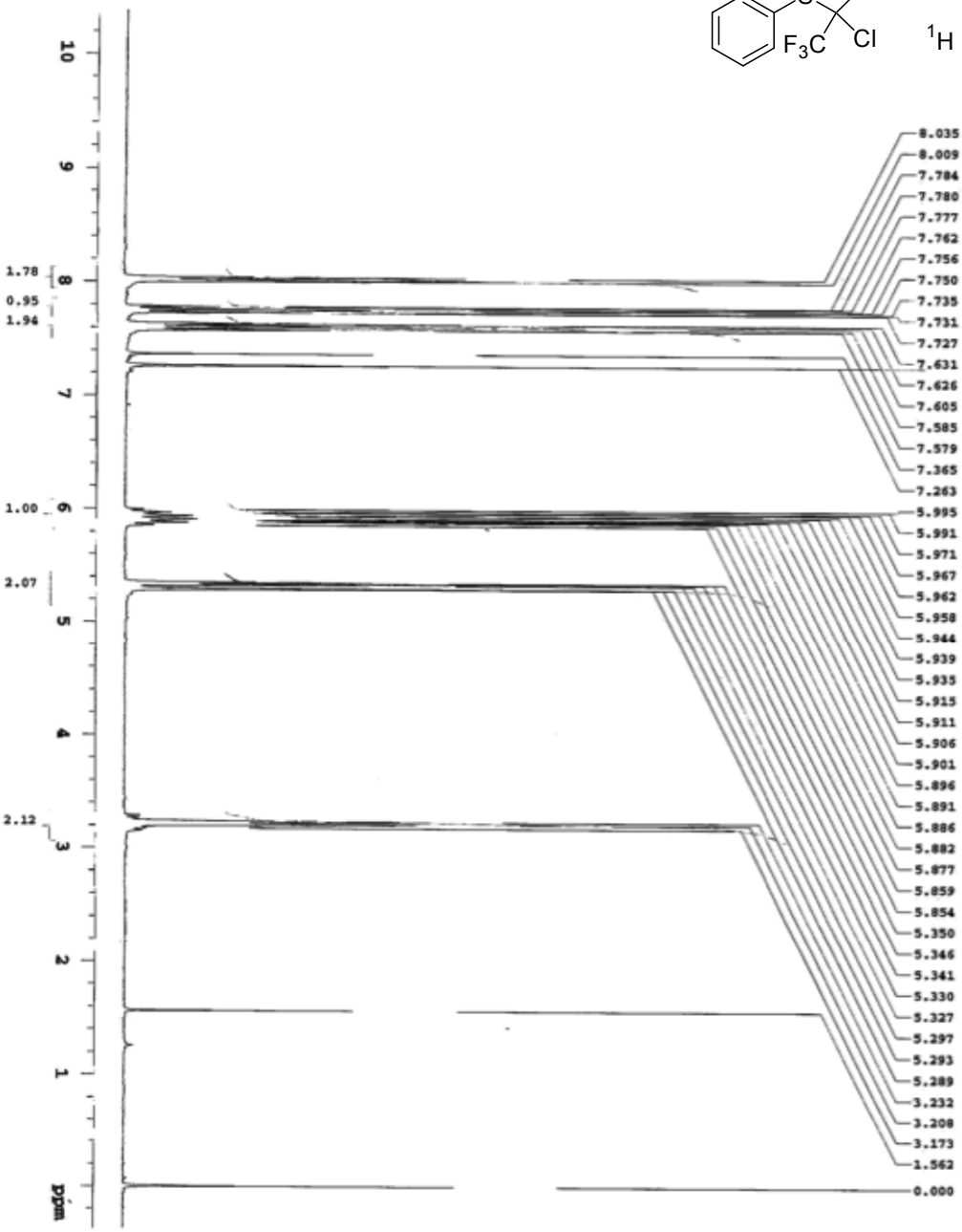

3k
^{19}F NMR
0.000
-64.570
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

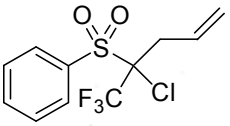

3k
13C NMR
136.745
136.585
135.364
134.548
130.602
130.137
130.007
128.946
128.557
127.748
126.329
122.559
121.300
120.773
118.766
77.427
77.206
77.000
76.580
73.581
73.276
72.971
72.665
33.593
32.716
ppm


O
O
S
F3C
Cl

3l

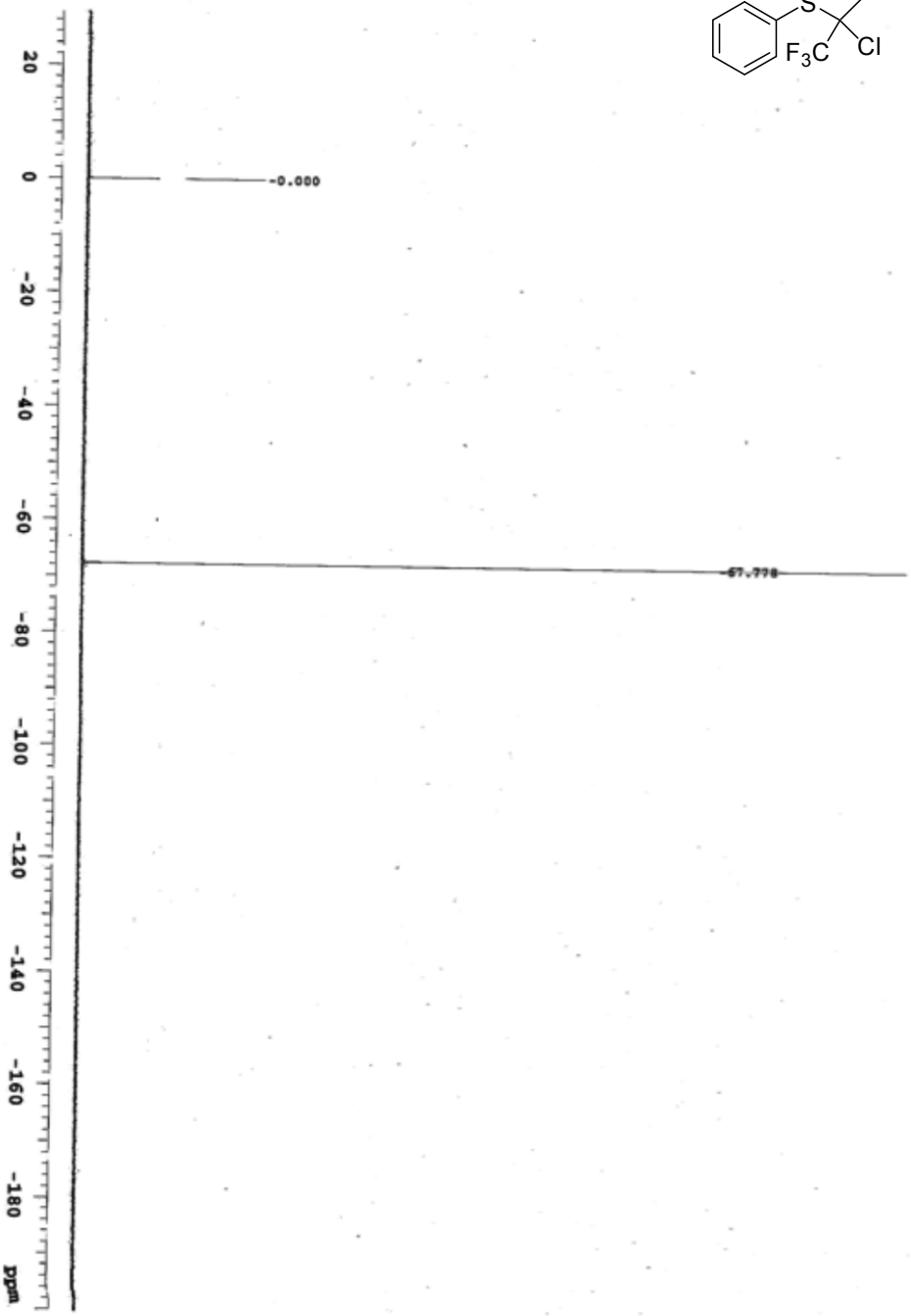
^{1}H NMR

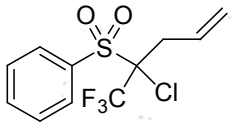

10
9
8
7
6
5
4
3
2
1
ppm
1.78
0.95
1.94
1.00
2.07
2.12
8.035
8.009
7.784
7.780
7.777
7.762
7.756
7.750
7.735
7.731
7.727
7.631
7.626
7.605
7.585
7.579
7.365
7.263
5.995
5.991
5.971
5.967
5.962
5.958
5.944
5.939
5.935
5.915
5.911
5.906
5.901
5.896
5.891
5.886
5.882
5.877
5.859
5.854
5.350
5.346
5.341
5.330
5.327
5.297
5.293
5.289
3.232
3.208
3.173
1.562
0.000



3l

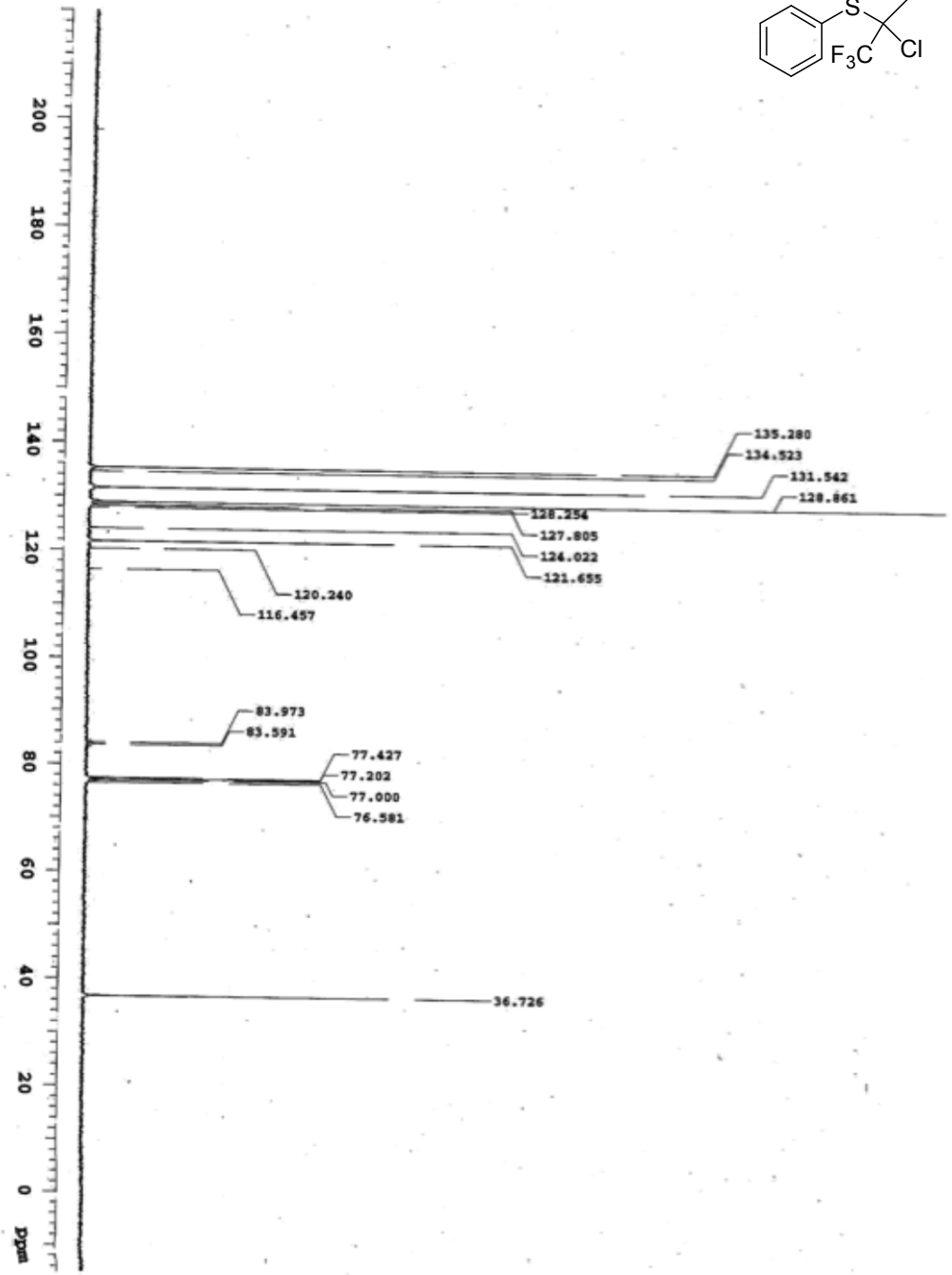
^{19}F NMR

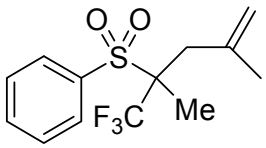




3l

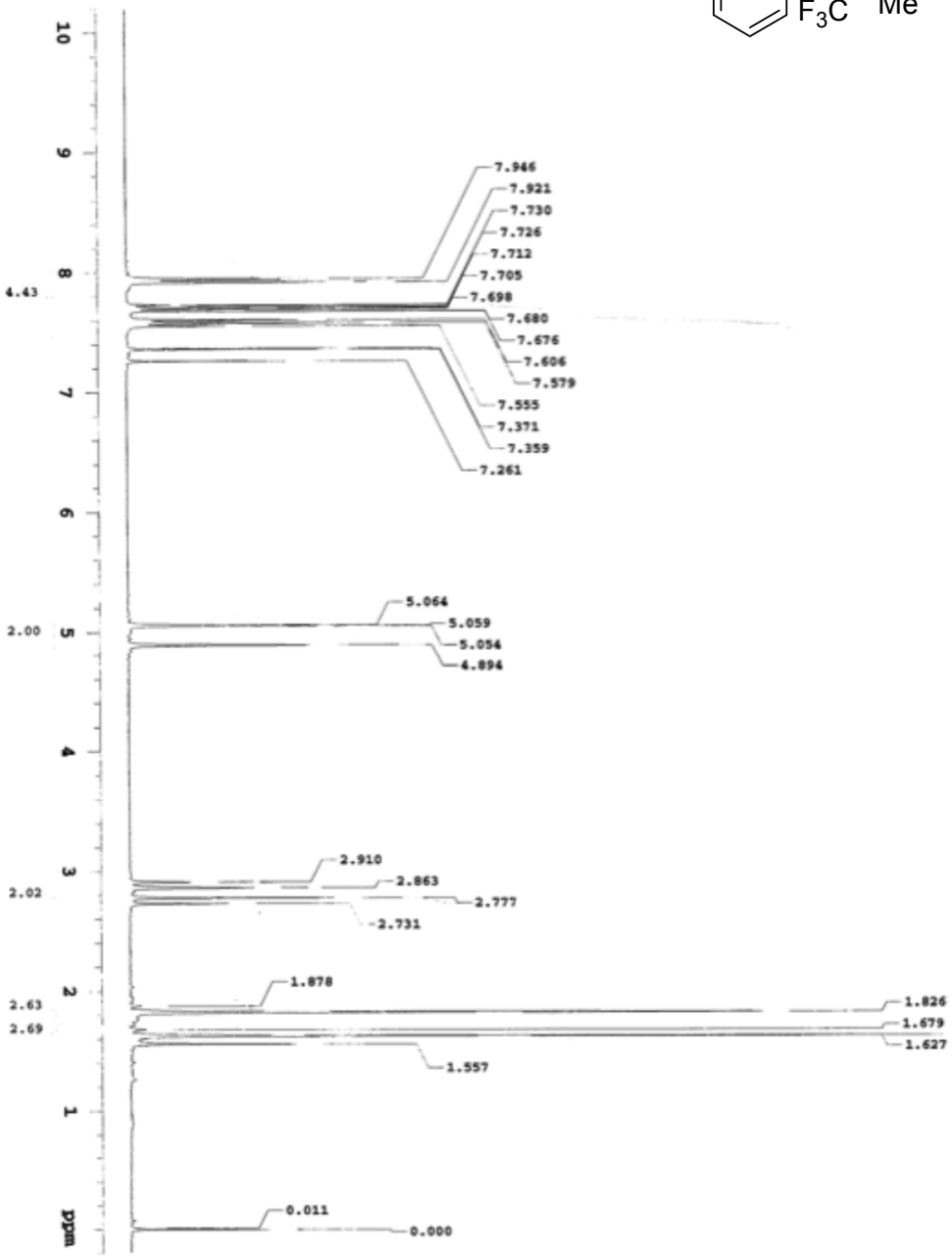
^{13}C NMR

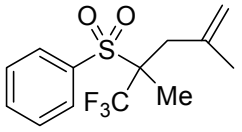

135.280
134.523
131.542
128.861
128.254
127.805
124.022
121.655
120.240
116.457
83.973
83.591
77.427
77.202
77.000
76.581
36.726
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
F3C
Me

3m

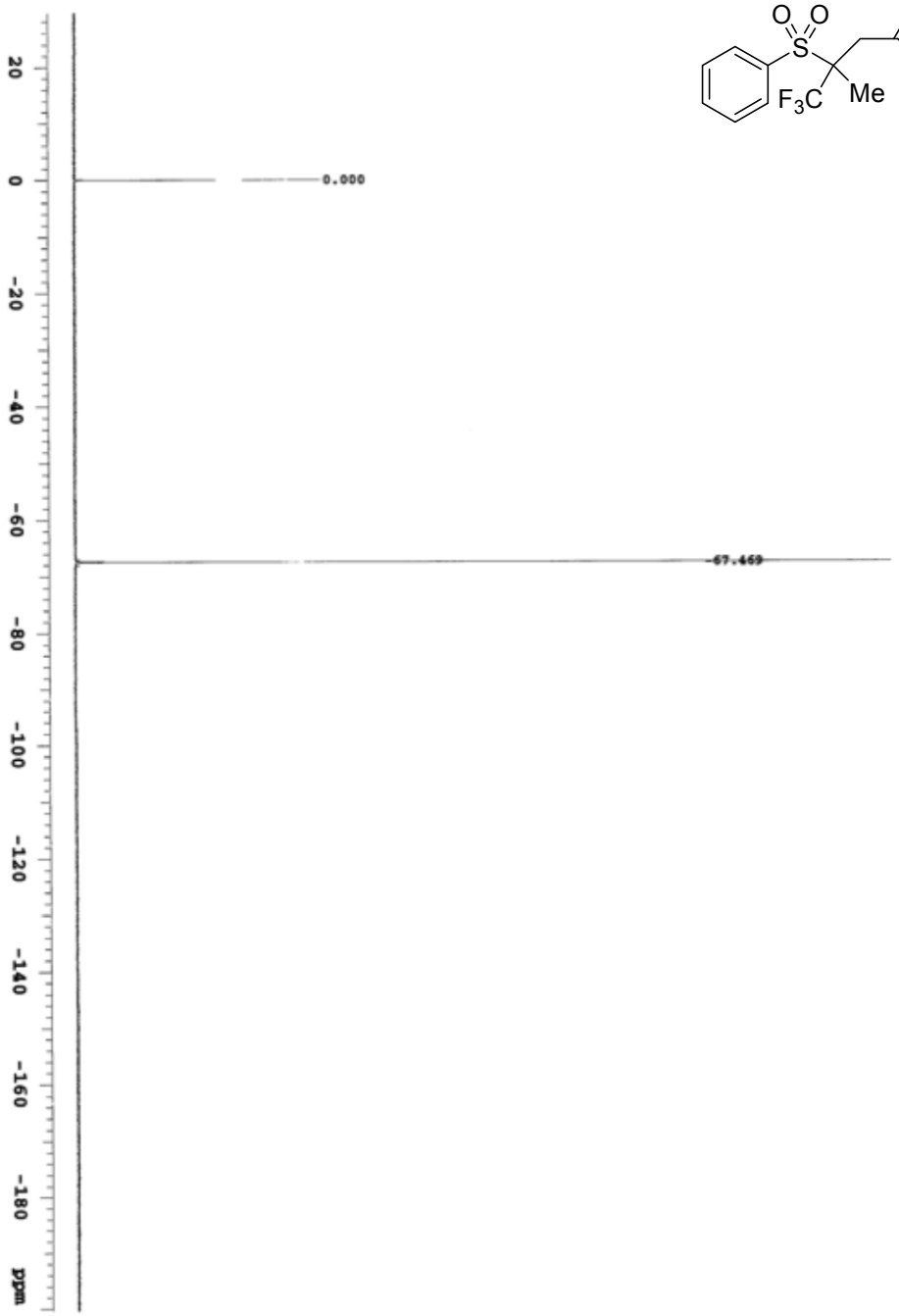
^{1}H NMR

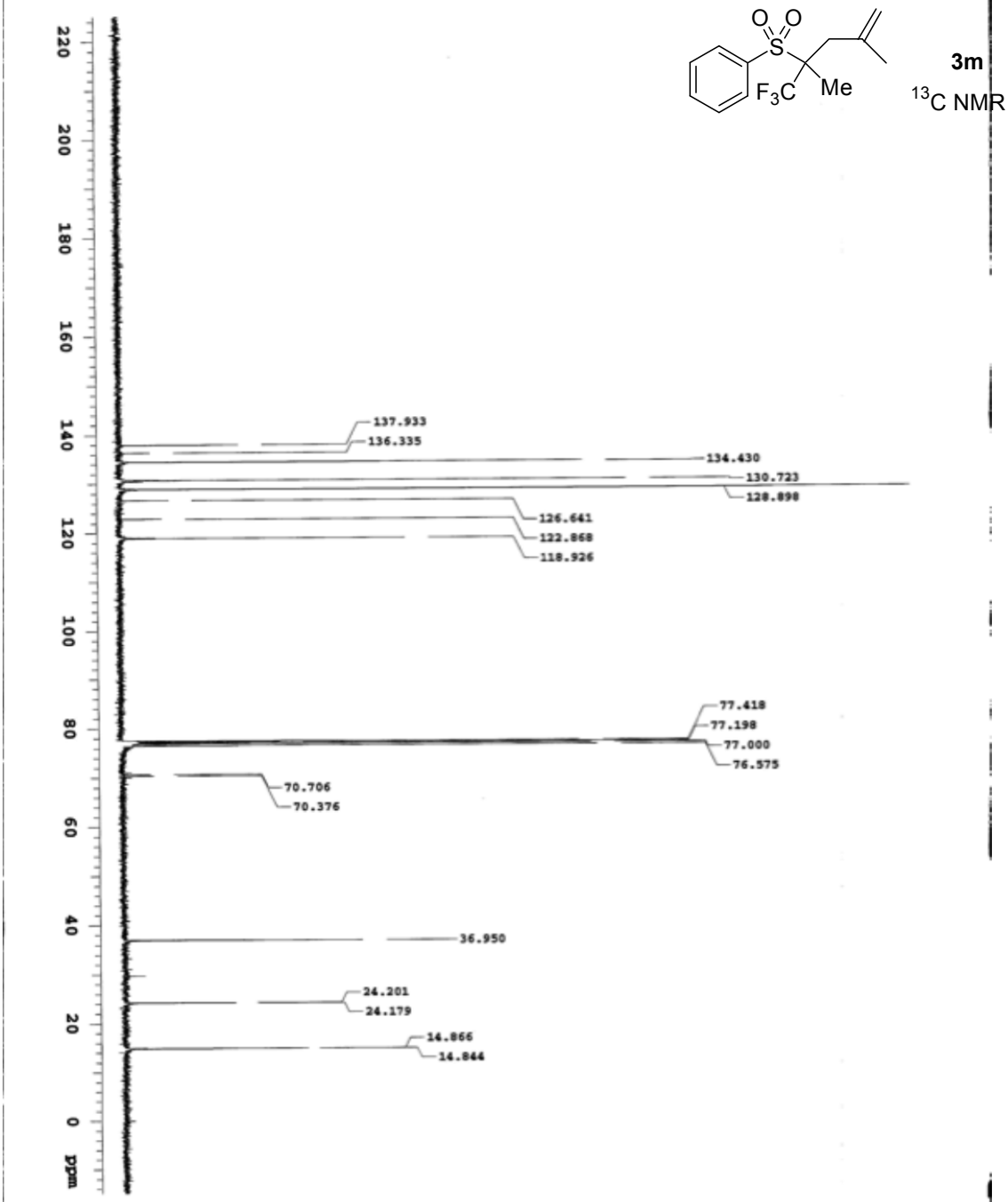

10
9
8
7
6
5
4
3
2
1
ppm
4.43
2.00
2.02
2.63
2.69
7.946
7.921
7.730
7.726
7.712
7.705
7.698
7.680
7.676
7.606
7.579
7.555
7.371
7.359
7.261
5.064
5.059
5.054
4.894
2.910
2.863
2.777
2.731
1.878
1.826
1.679
1.627
1.557
0.011
0.000

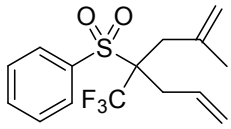


3m

^{19}F NMR

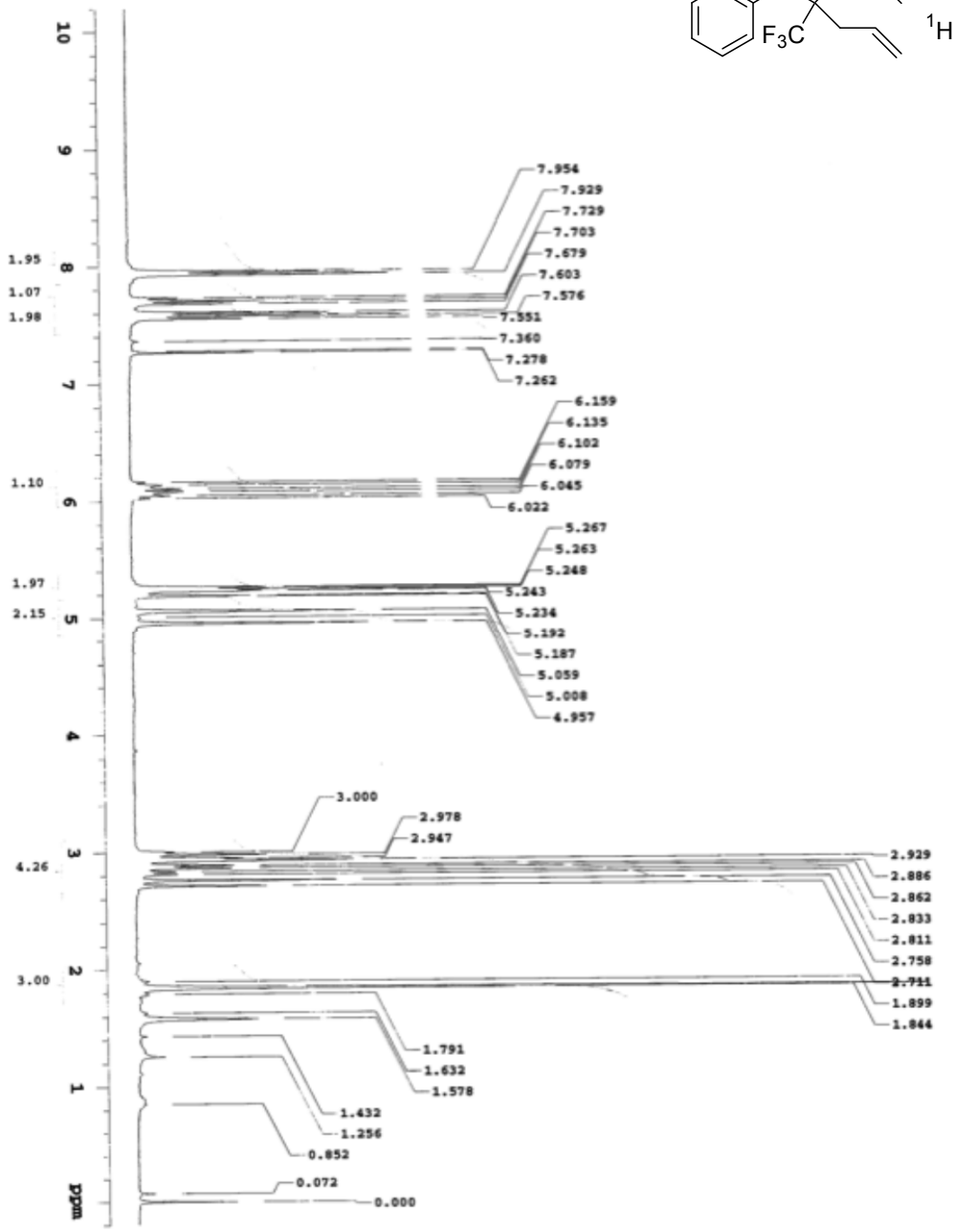


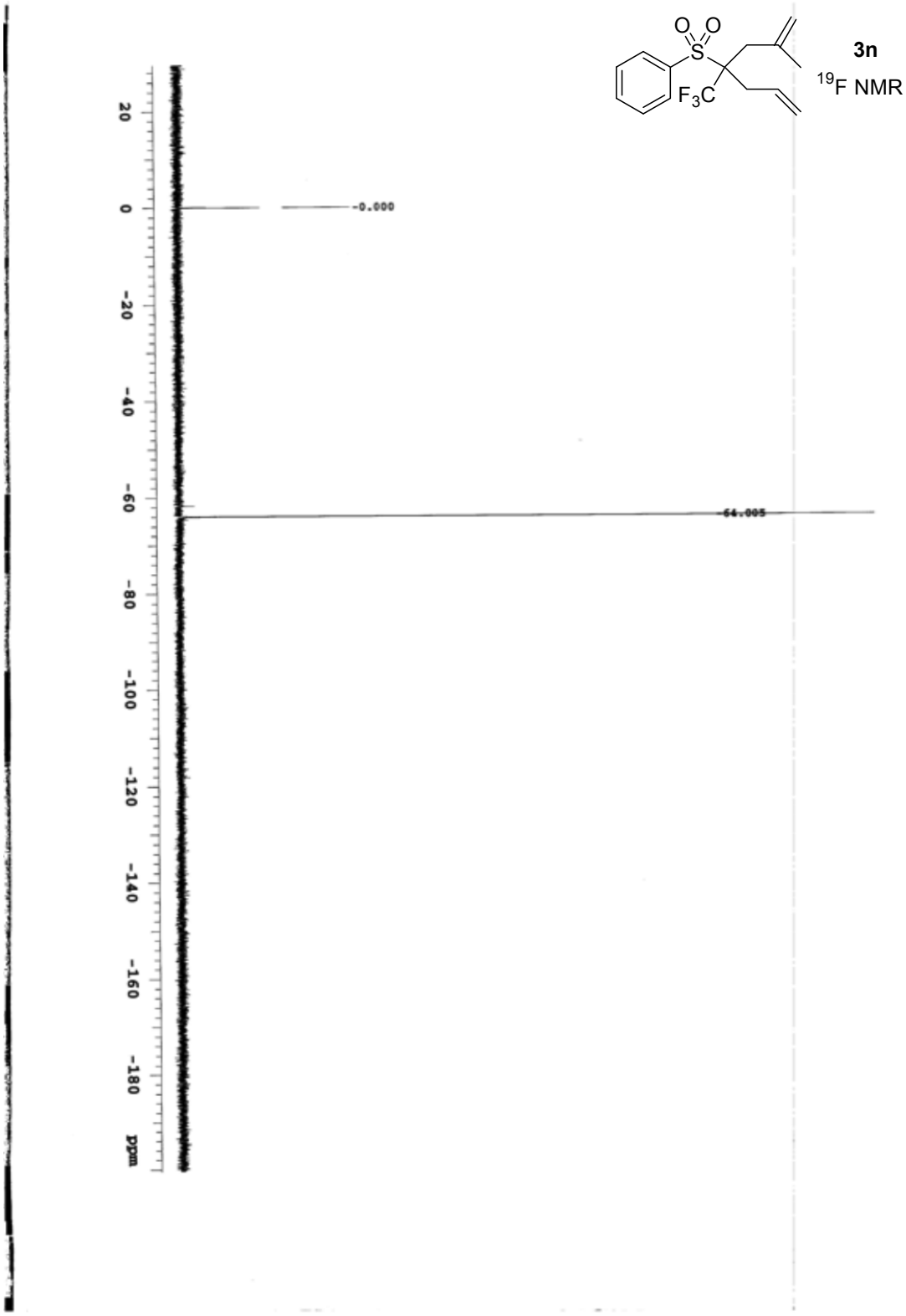

O O
S
F3C
Me
3m
13C NMR
137.933
136.335
134.430
130.723
128.898
126.641
122.868
118.926
77.418
77.198
77.000
76.575
70.706
70.376
36.950
24.201
24.179
14.866
14.844
220
200
180
160
140
120
100
80
60
40
20
0
ppm



3n

^{1}H NMR

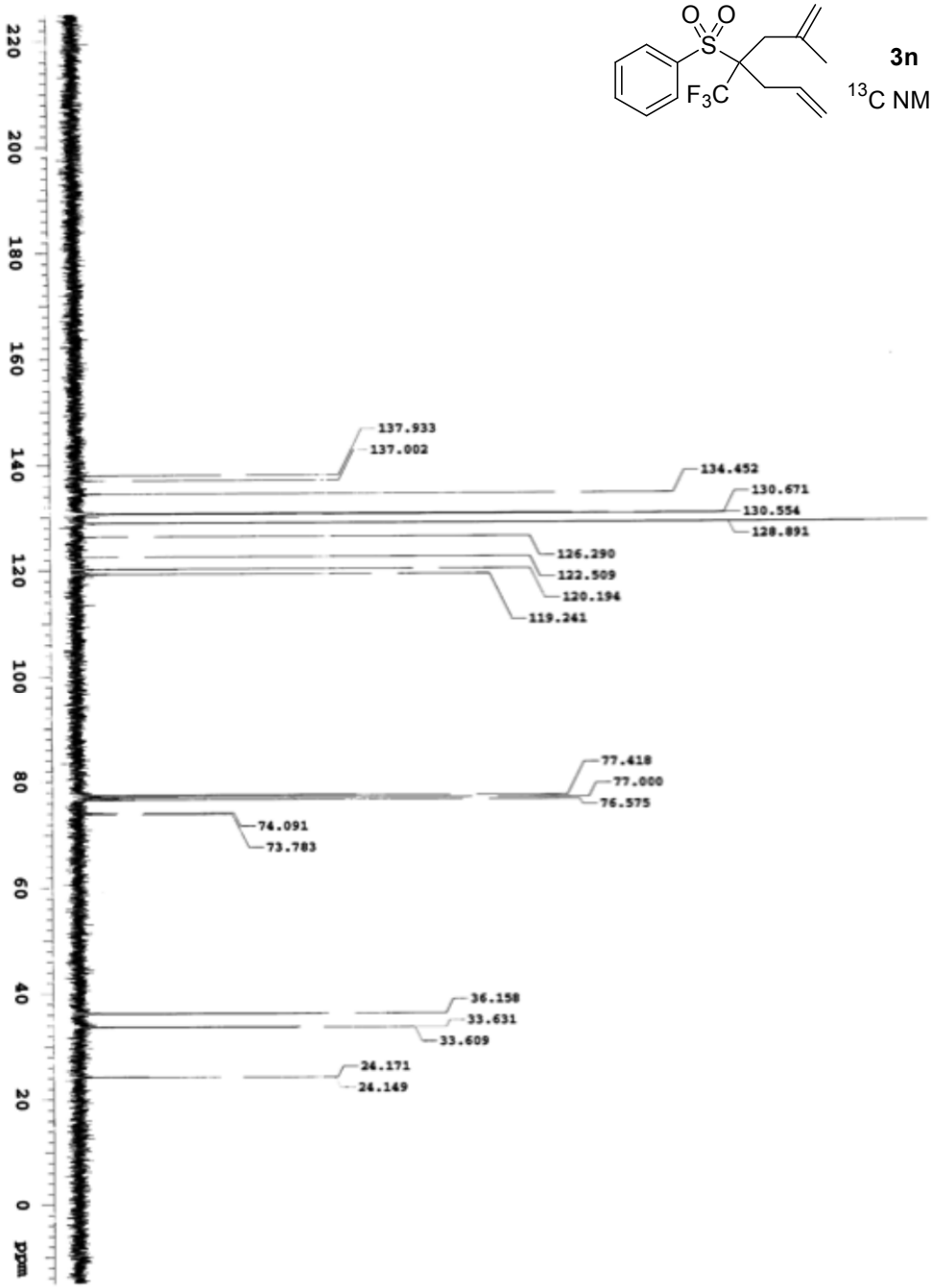

7.954
7.929
7.729
7.703
7.679
7.603
7.576
7.551
7.360
7.278
7.262
6.159
6.135
6.102
6.079
6.045
6.022
5.267
5.263
5.248
5.243
5.234
5.192
5.187
5.059
5.008
4.957
3.000
2.978
2.947
2.929
2.886
2.862
2.833
2.811
2.758
2.711
1.899
1.844
1.791
1.632
1.578
1.432
1.256
0.852
0.072
0.000
1.95
1.07
1.98
1.10
1.97
2.15
4.26
3.00
ppm

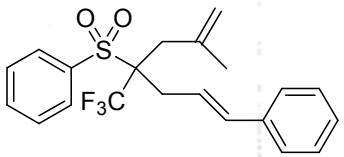

3n
19F NMR
-0.000
-64.005
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

O
O
S
F3C

3n

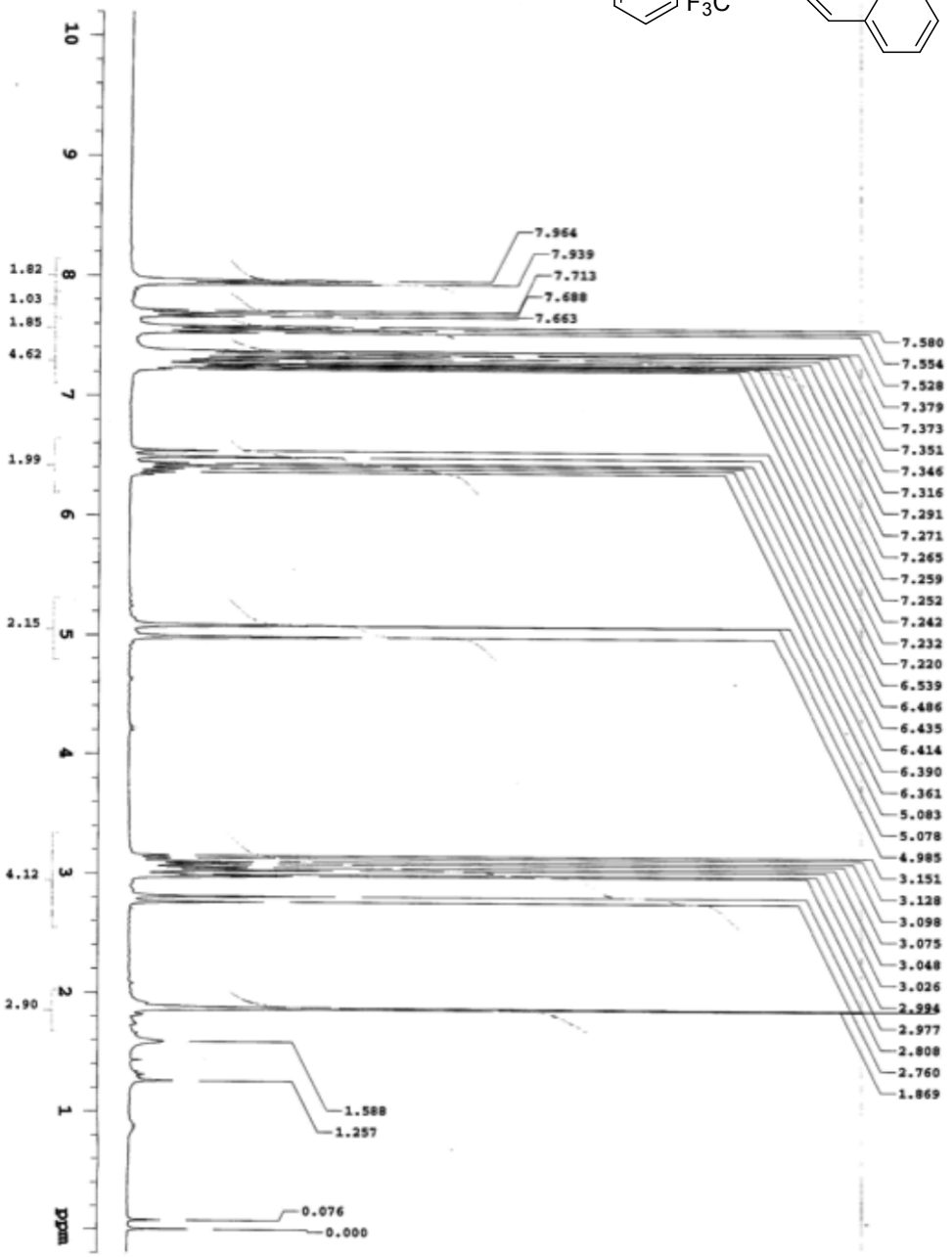
^{13}C NMR

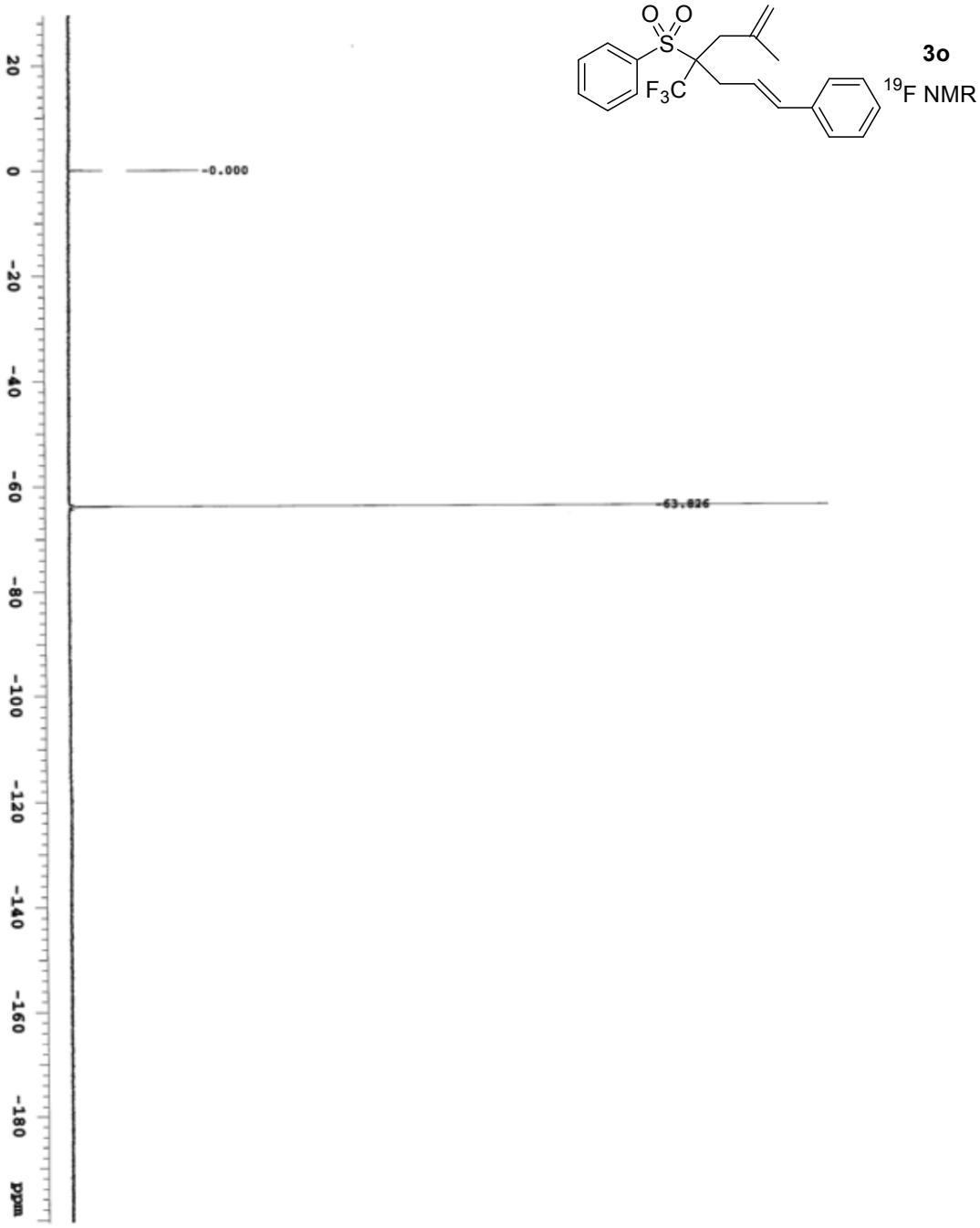

220
200
180
160
140
120
100
80
60
40
20
0
ppm
137.933
137.002
134.452
130.671
130.554
128.891
126.290
122.509
120.194
119.241
77.418
77.000
76.575
74.091
73.783
36.158
33.631
33.609
24.171
24.149

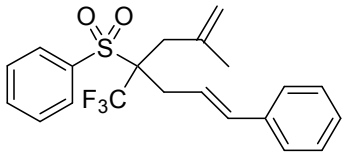

O
O
S
F3C

3o

^{1}H NMR

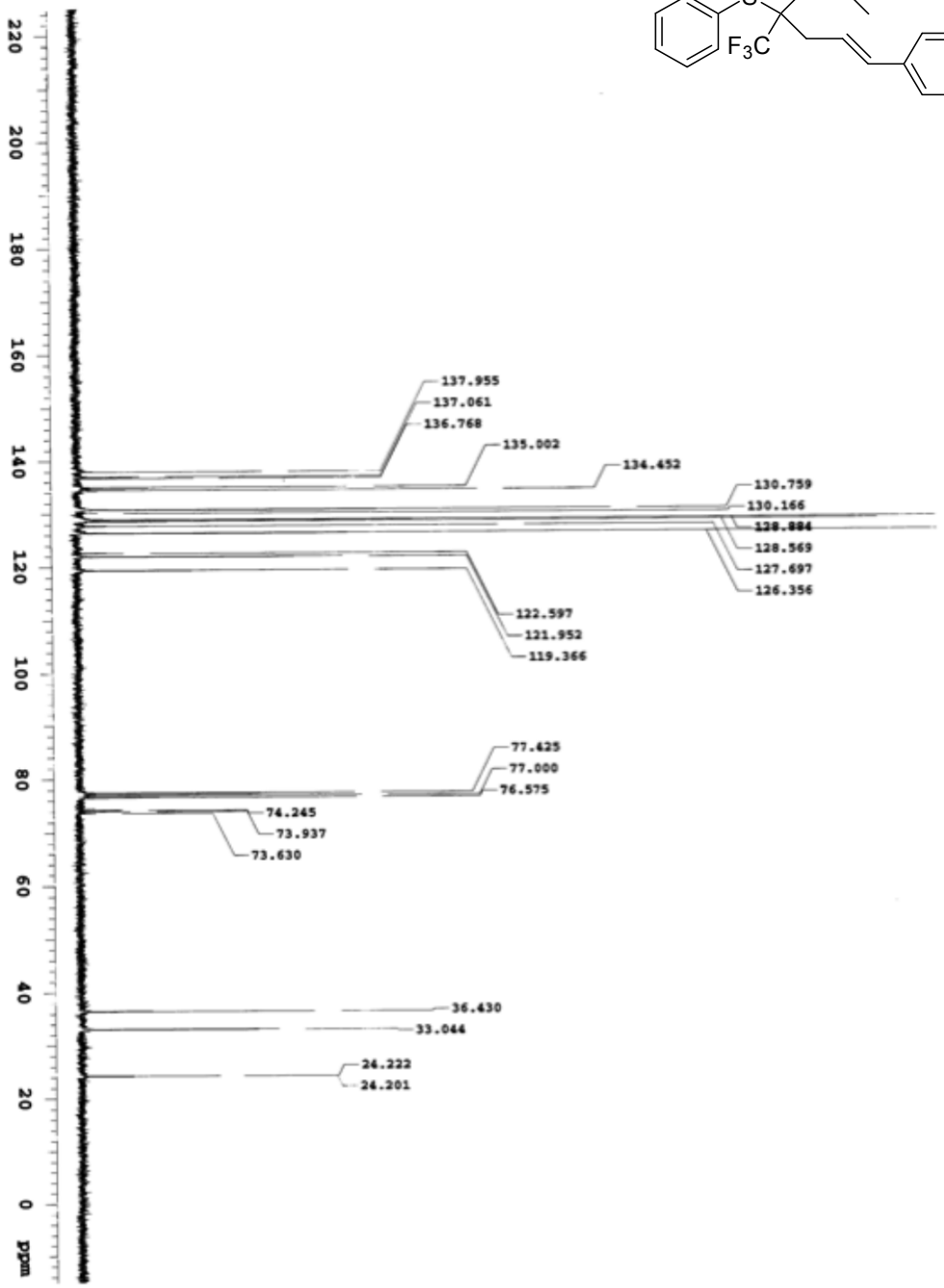

10
9
8
7
6
5
4
3
2
1
ppm
1.82
1.03
1.85
4.62
1.99
2.15
4.12
2.90
7.964
7.939
7.713
7.688
7.663
7.580
7.554
7.528
7.379
7.373
7.351
7.346
7.316
7.291
7.271
7.265
7.259
7.252
7.242
7.232
7.220
6.539
6.486
6.435
6.414
6.390
6.361
5.083
5.078
4.985
3.151
3.128
3.098
3.075
3.048
3.026
2.994
2.977
2.808
2.760
1.869
1.588
1.257
0.076
0.000

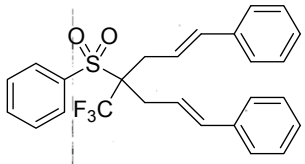

O O
S
F3C
3o
19F NMR
-0.000
-63.826
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


O
O
S
F3C

3o

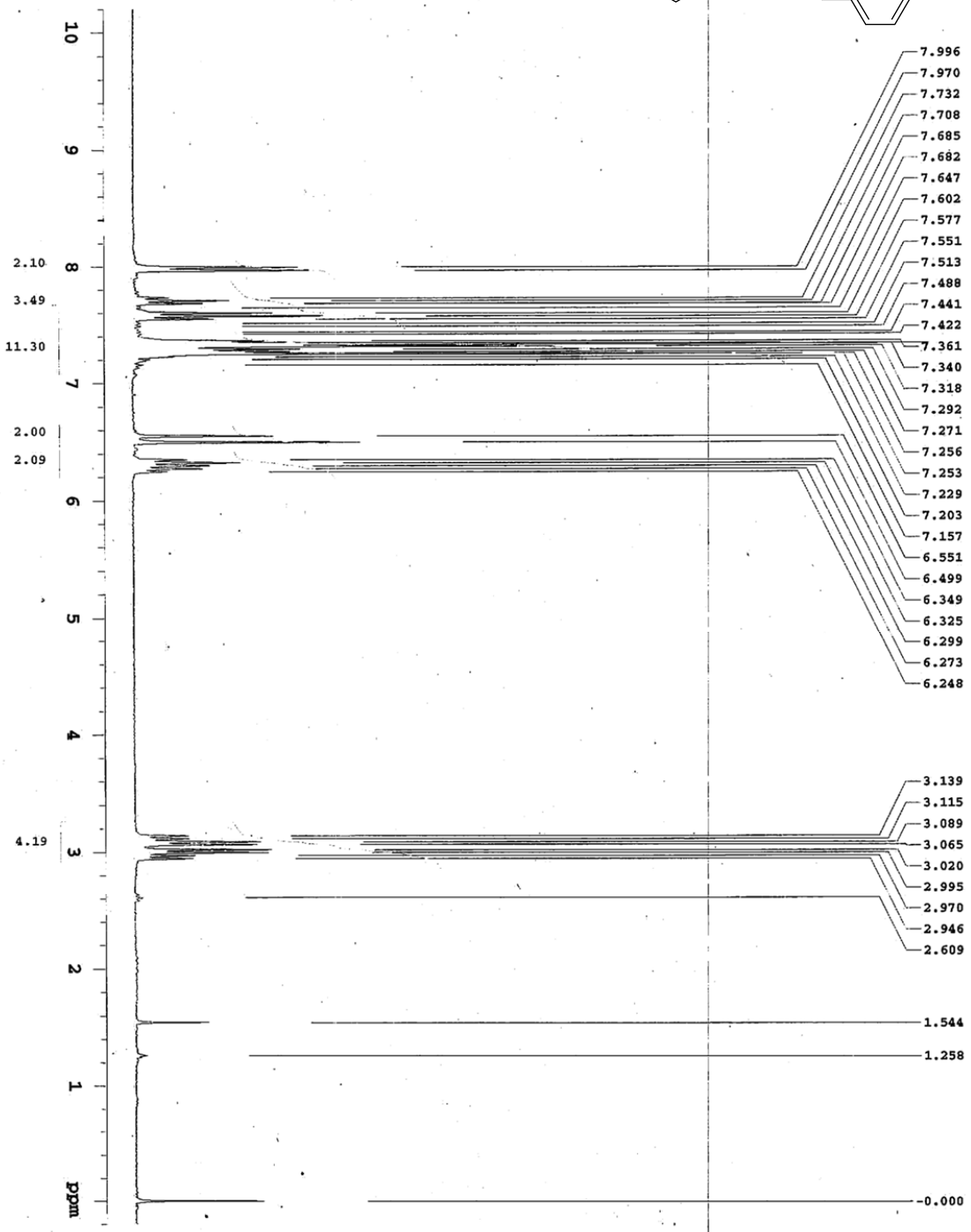
^{13}C NMR

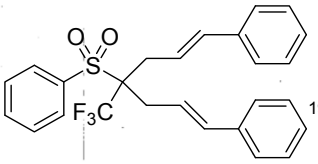

220
200
180
160
140
120
100
80
60
40
20
0
ppm
137.955
137.061
136.768
135.002
134.452
130.759
130.166
128.884
128.569
127.697
126.356
122.597
121.952
119.366
77.425
77.000
76.575
74.245
73.937
73.630
36.430
33.044
24.222
24.201


O
O
S
F3C

3p

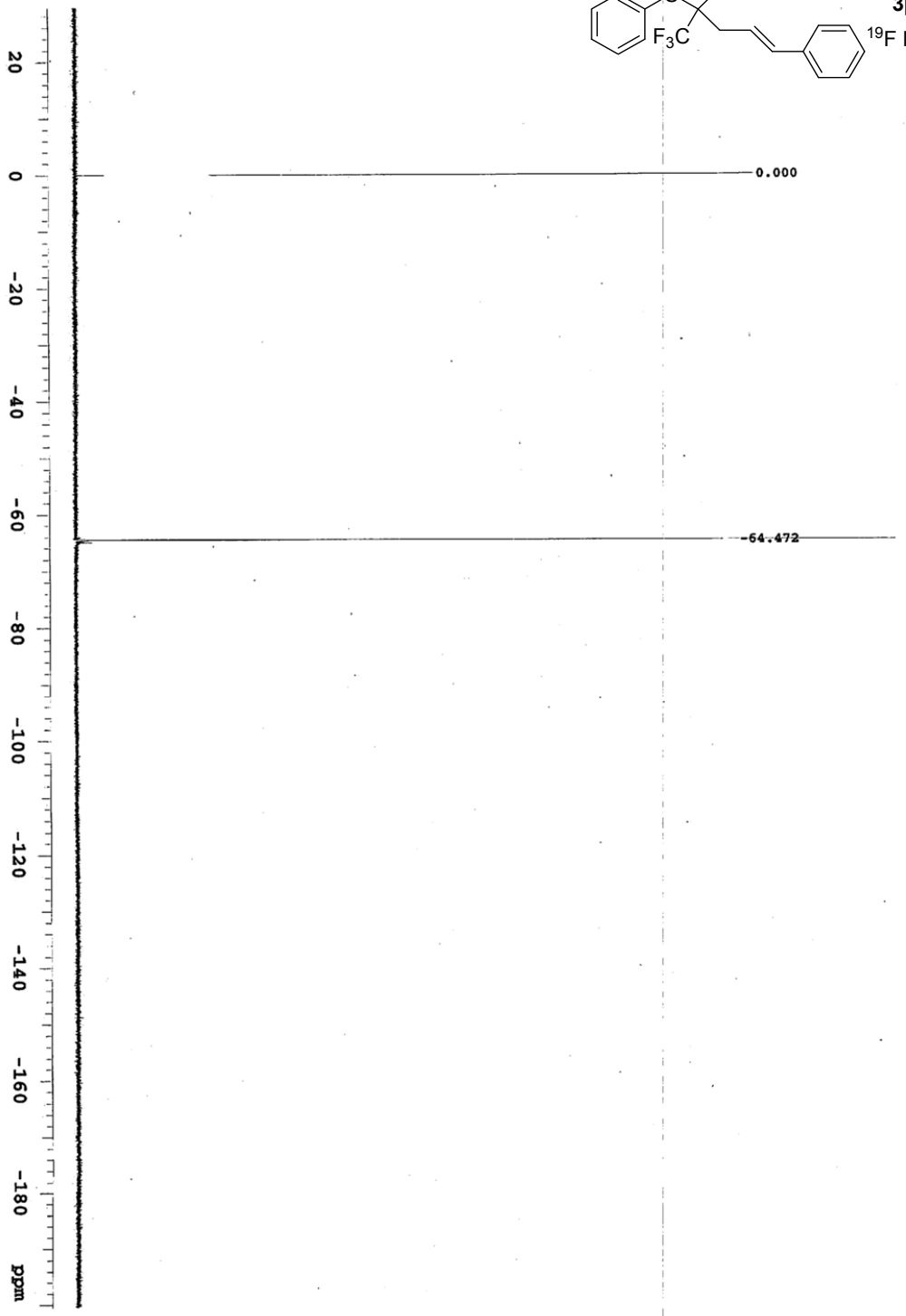
^{1}H NMR

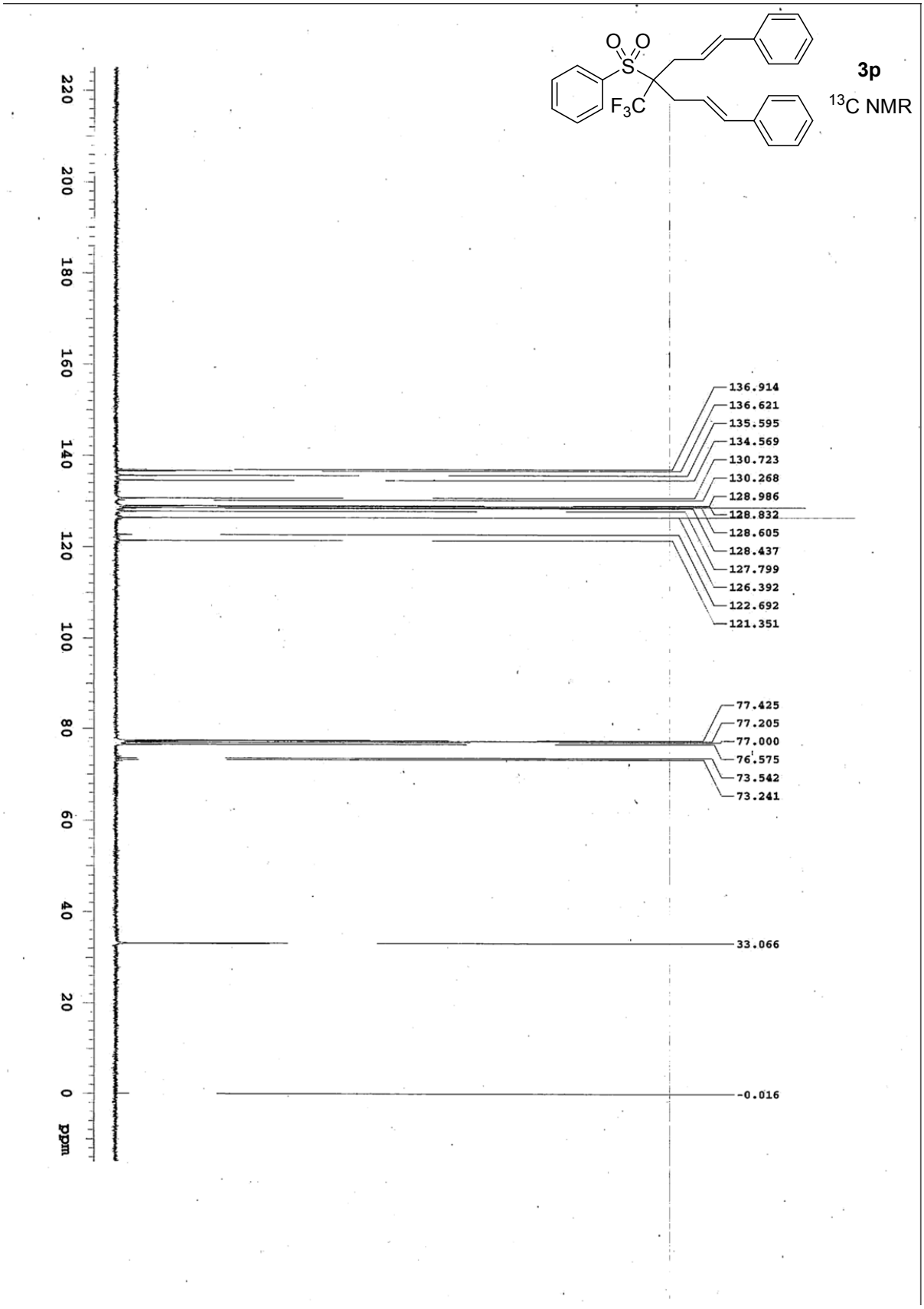

10
9
8
7
6
5
4
3
2
1
ppm
2.10
3.49
11.30
2.00
2.09
4.19
7.996
7.970
7.732
7.708
7.685
7.682
7.647
7.602
7.577
7.551
7.513
7.488
7.441
7.422
7.361
7.340
7.318
7.292
7.271
7.256
7.253
7.229
7.203
7.157
6.551
6.499
6.349
6.325
6.299
6.273
6.248
3.139
3.115
3.089
3.065
3.020
2.995
2.970
2.946
2.609
1.544
1.258
-0.000

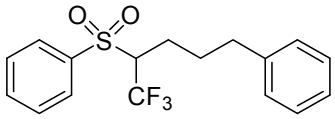


3p

^{19}F NMR

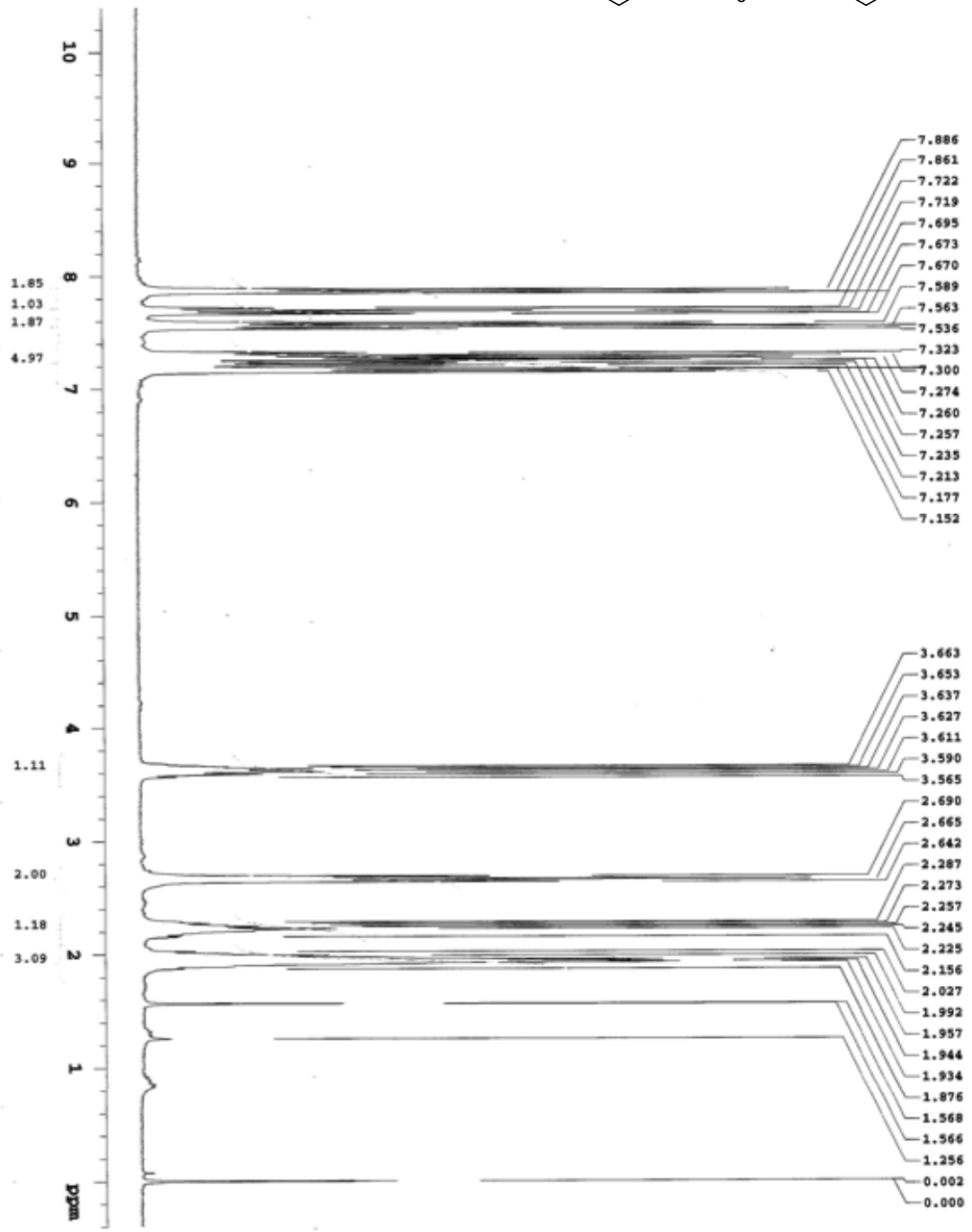


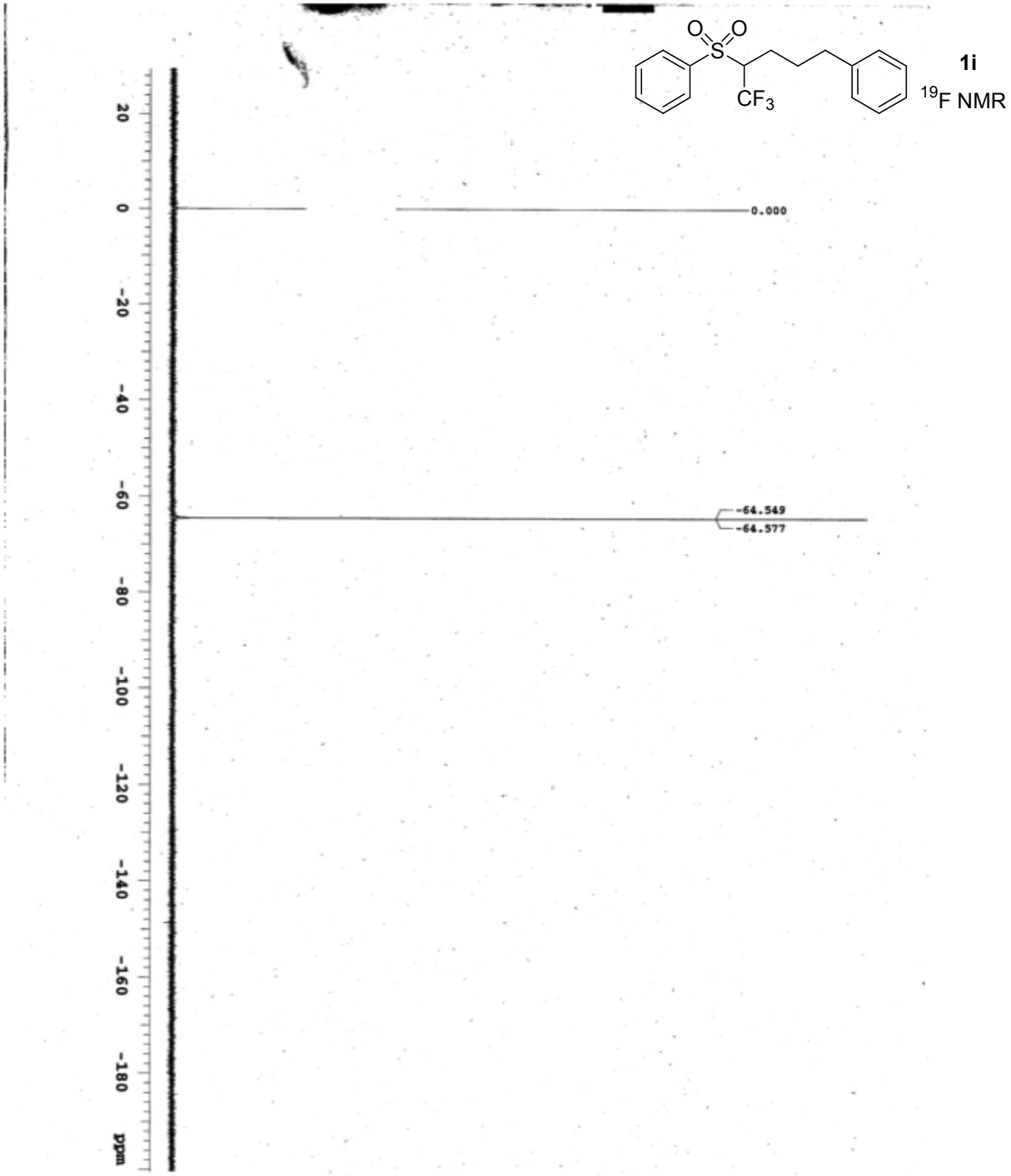

3p
13C NMR
136.914
136.621
135.595
134.569
130.723
130.268
128.986
128.832
128.605
128.437
127.799
126.392
122.692
121.351
77.425
77.205
77.000
76.575
73.542
73.241
33.066
-0.016
ppm

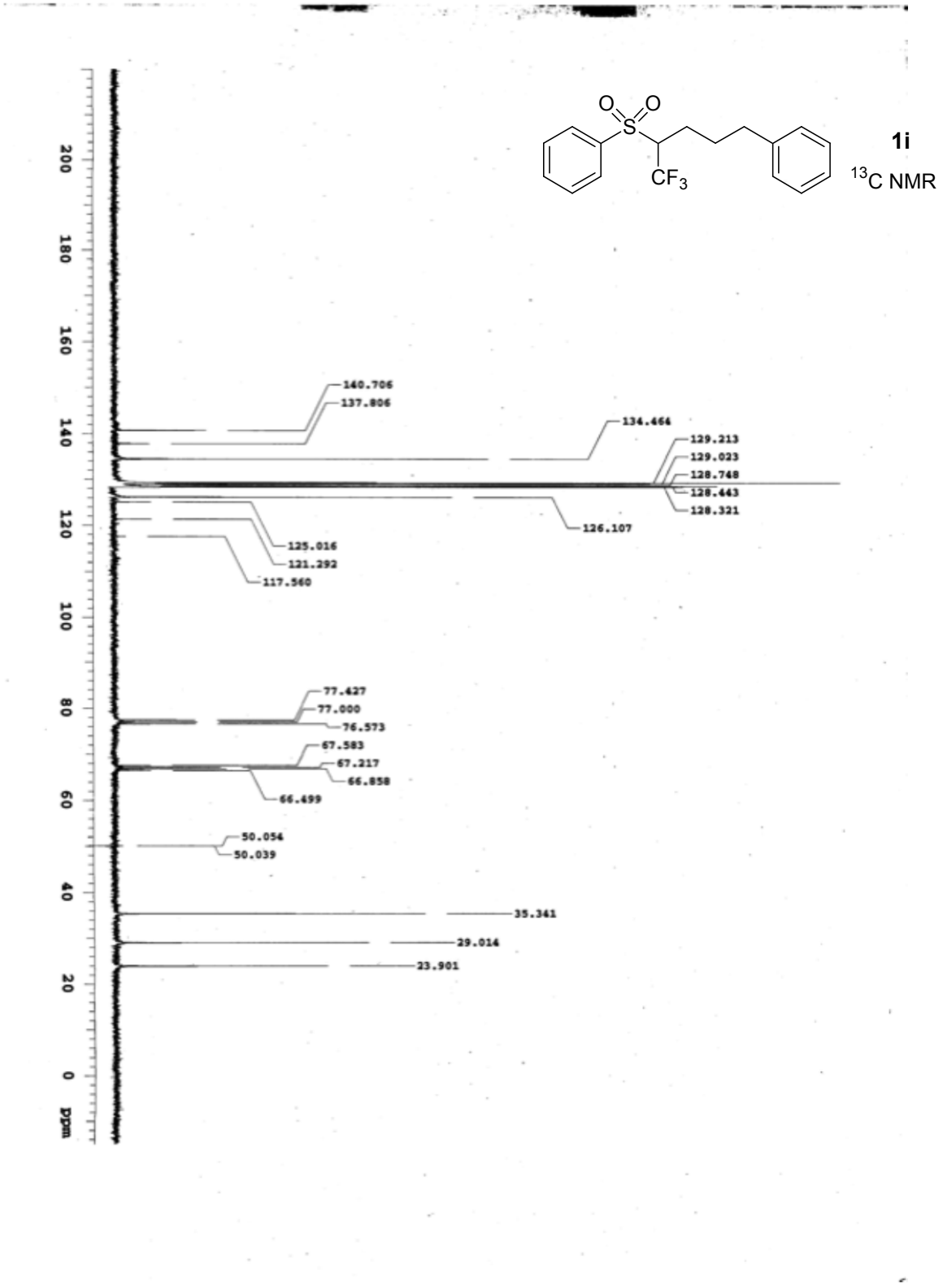

O
O
S
CF3

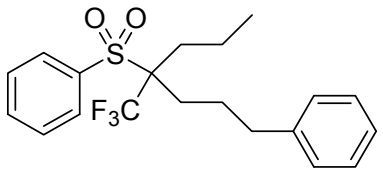
1i

^{1}H NMR


10
9
8
7
6
5
4
3
2
1
ppm
1.85
1.03
1.87
4.97
1.11
2.00
1.18
3.09
7.886
7.861
7.722
7.719
7.695
7.673
7.670
7.589
7.563
7.536
7.323
7.300
7.274
7.260
7.257
7.235
7.213
7.177
7.152
3.663
3.653
3.637
3.627
3.611
3.590
3.565
2.690
2.665
2.642
2.287
2.273
2.257
2.245
2.225
2.156
2.027
1.992
1.957
1.944
1.934
1.876
1.568
1.566
1.256
0.002
0.000

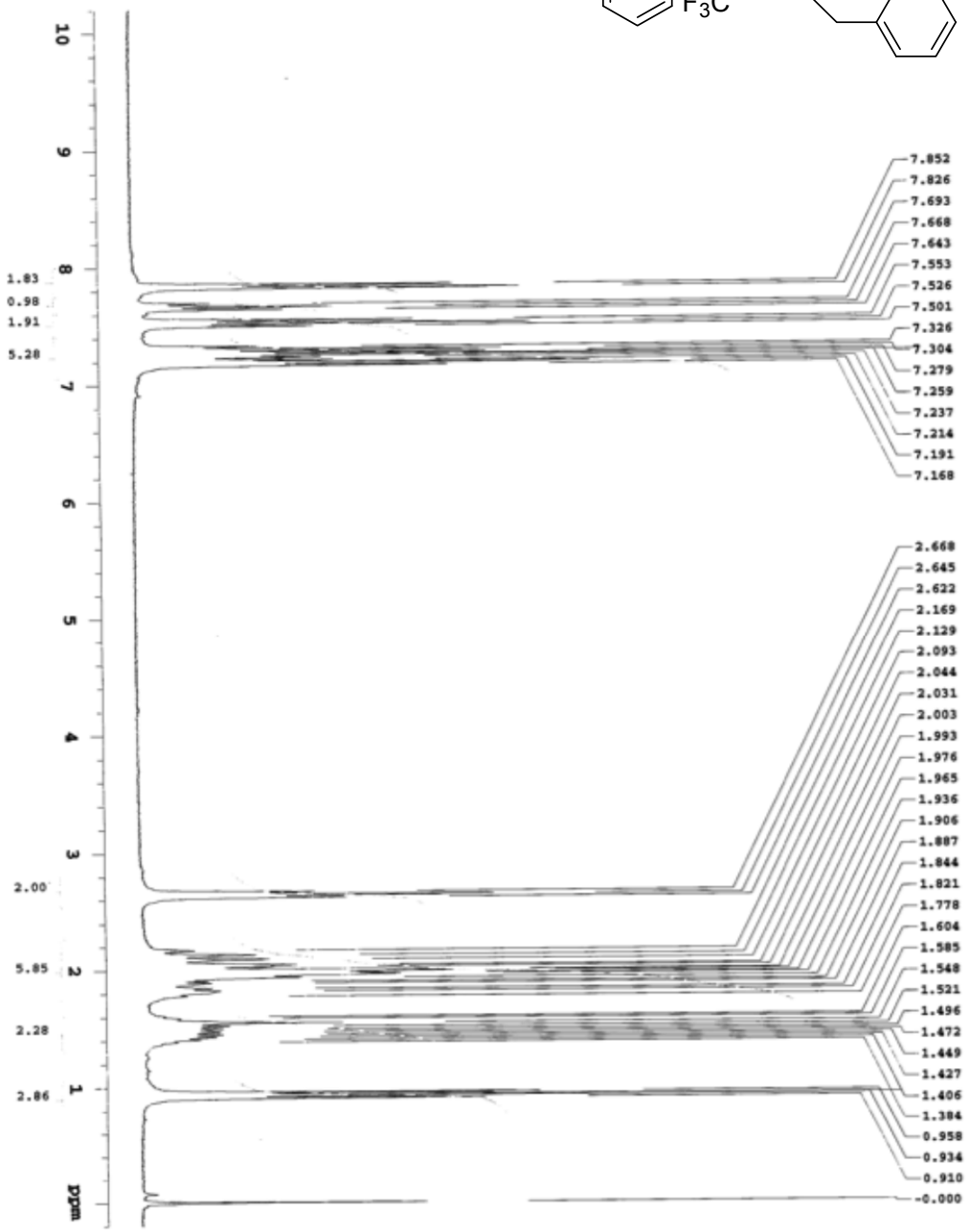

O
O
S
CF3
1i
19F NMR
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.000
-64.549
-64.577

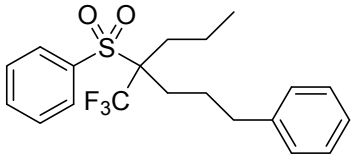

1i
13C NMR
CF3
140.706
137.806
134.464
129.213
129.023
128.748
128.443
128.321
126.107
125.016
121.292
117.560
77.427
77.000
76.573
67.583
67.217
66.858
66.499
50.054
50.039
35.341
29.014
23.901
ppm


O
O
S
F3C

5a

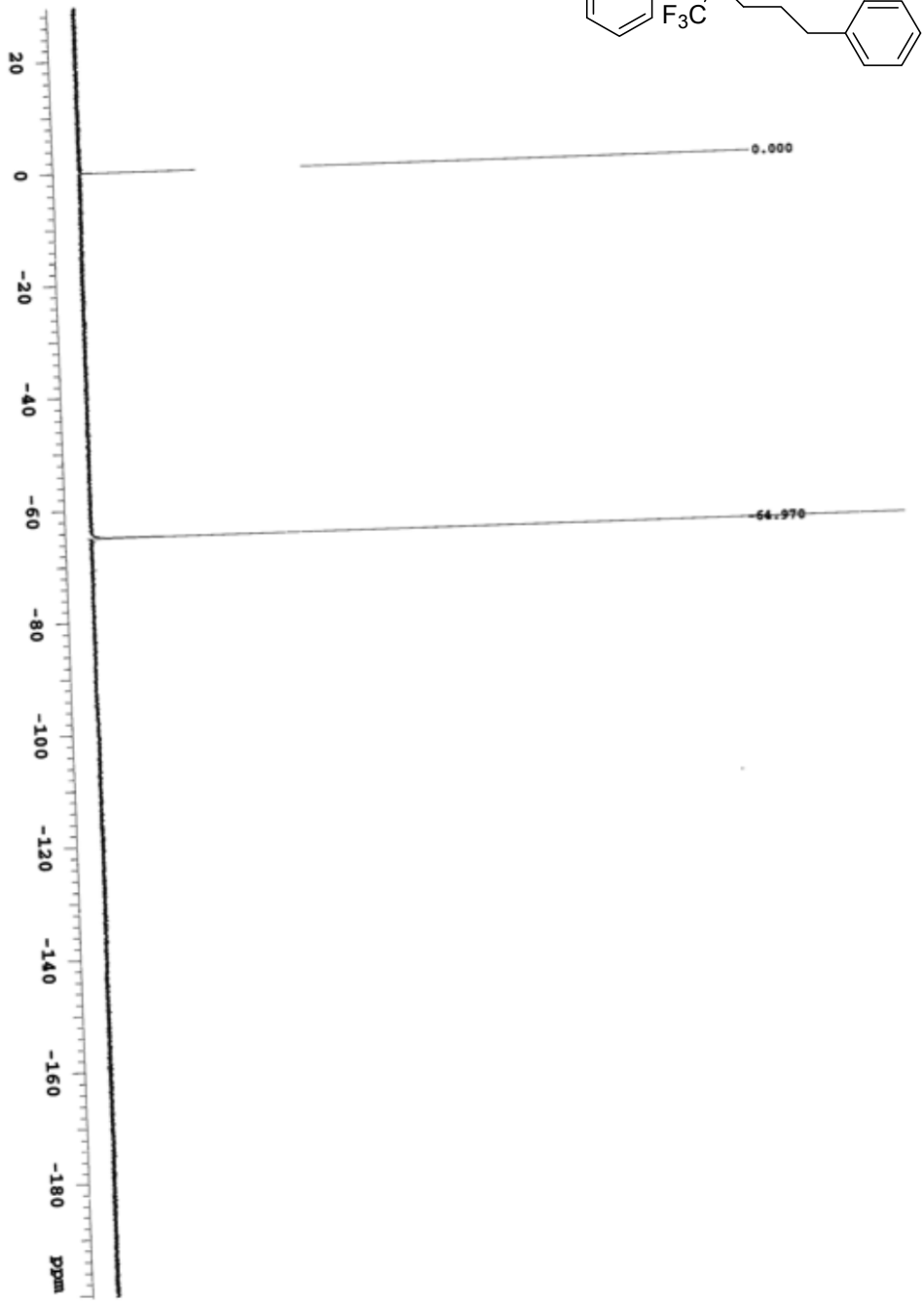
^{1}H NMR

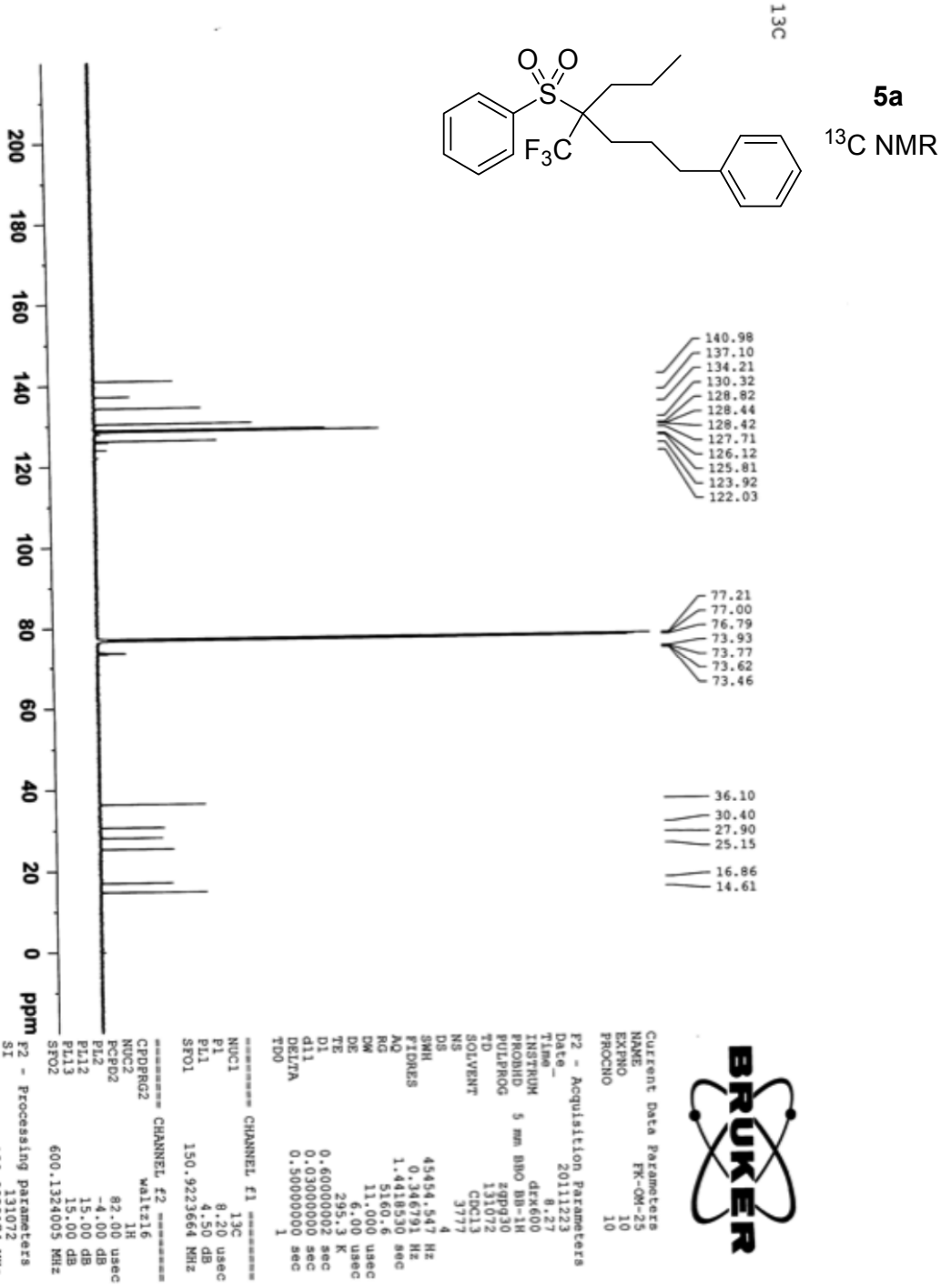

10
9
8
7
6
5
4
3
2
1
ppm
1.83
0.98
1.91
5.28
2.00
5.85
2.28
2.86
7.852
7.826
7.693
7.668
7.643
7.553
7.526
7.501
7.326
7.304
7.279
7.259
7.237
7.214
7.191
7.168
2.668
2.645
2.622
2.169
2.129
2.093
2.044
2.031
2.003
1.993
1.976
1.965
1.936
1.906
1.887
1.844
1.821
1.778
1.604
1.585
1.548
1.521
1.496
1.472
1.449
1.427
1.406
1.384
0.958
0.934
0.910
-0.000



5a

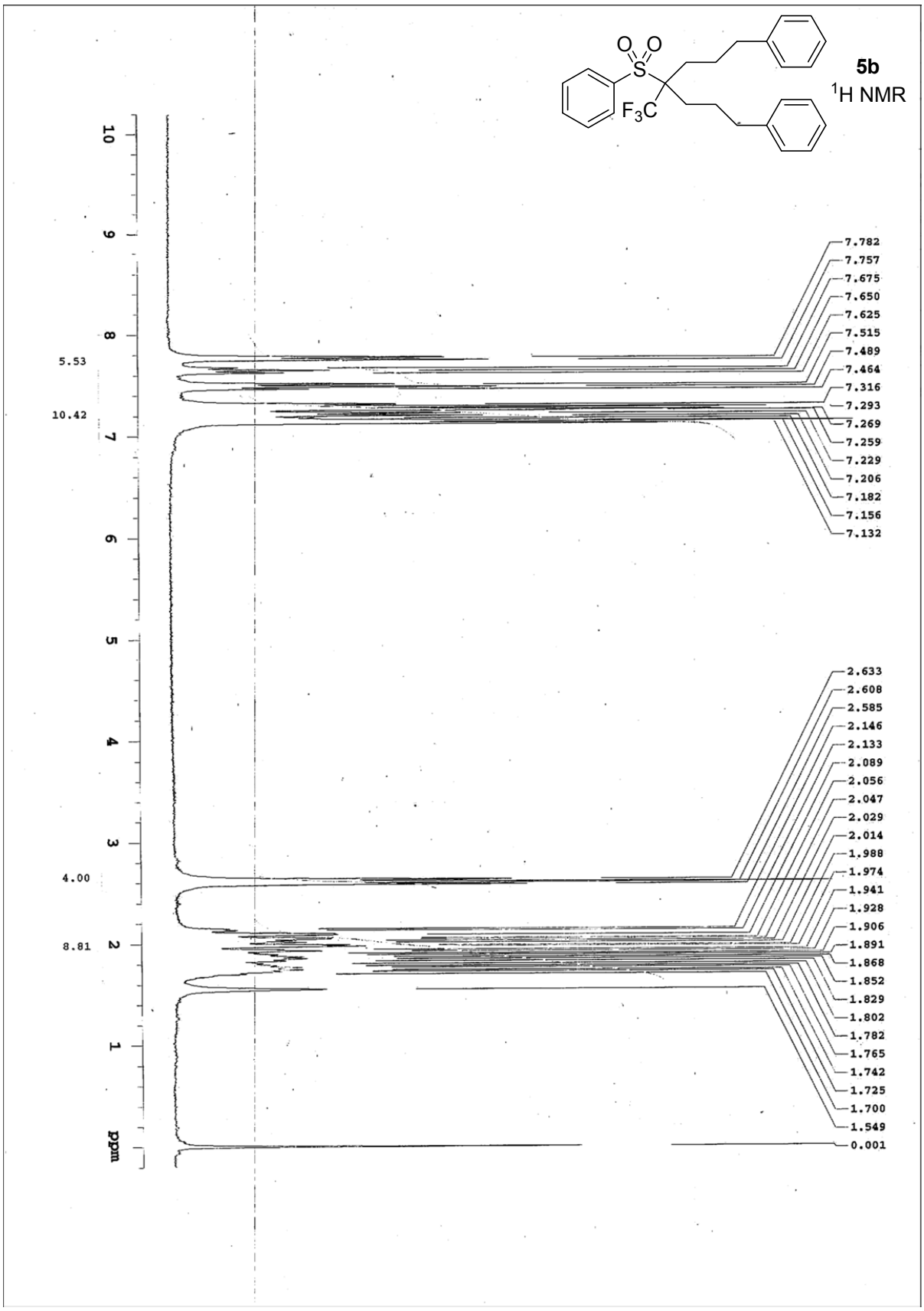
^{19}F NMR

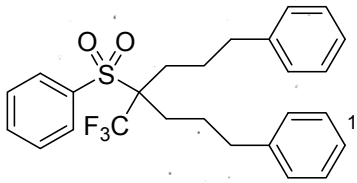



13C
O
O
S
F3C
140.98
137.10
134.21
130.32
128.82
128.44
128.42
127.71
126.12
125.81
123.92
122.03
77.21
77.00
76.79
73.93
73.77
73.62
73.46
36.10
30.40
27.90
25.15
16.86
14.61
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME FK-OM-25
EXPNO 10
PROCNO 10
F2 - Acquisition Parameters
Date_ 20111223
Time 8.27
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 3777
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 5160.6
DW 11.000 usec
DE 6.00 usec
TE 295.3 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13c
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028174 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

5a

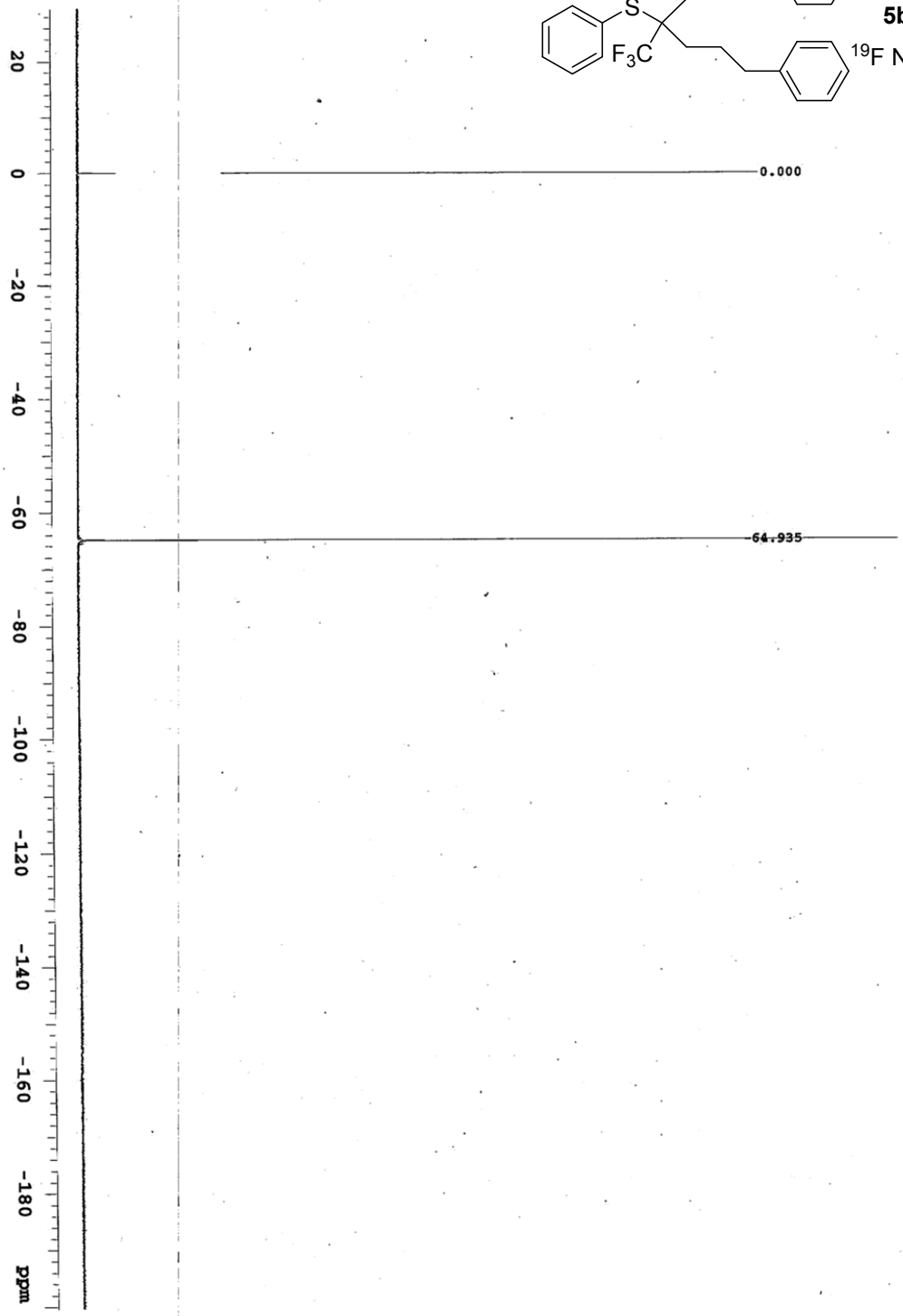
^{13}C NMR

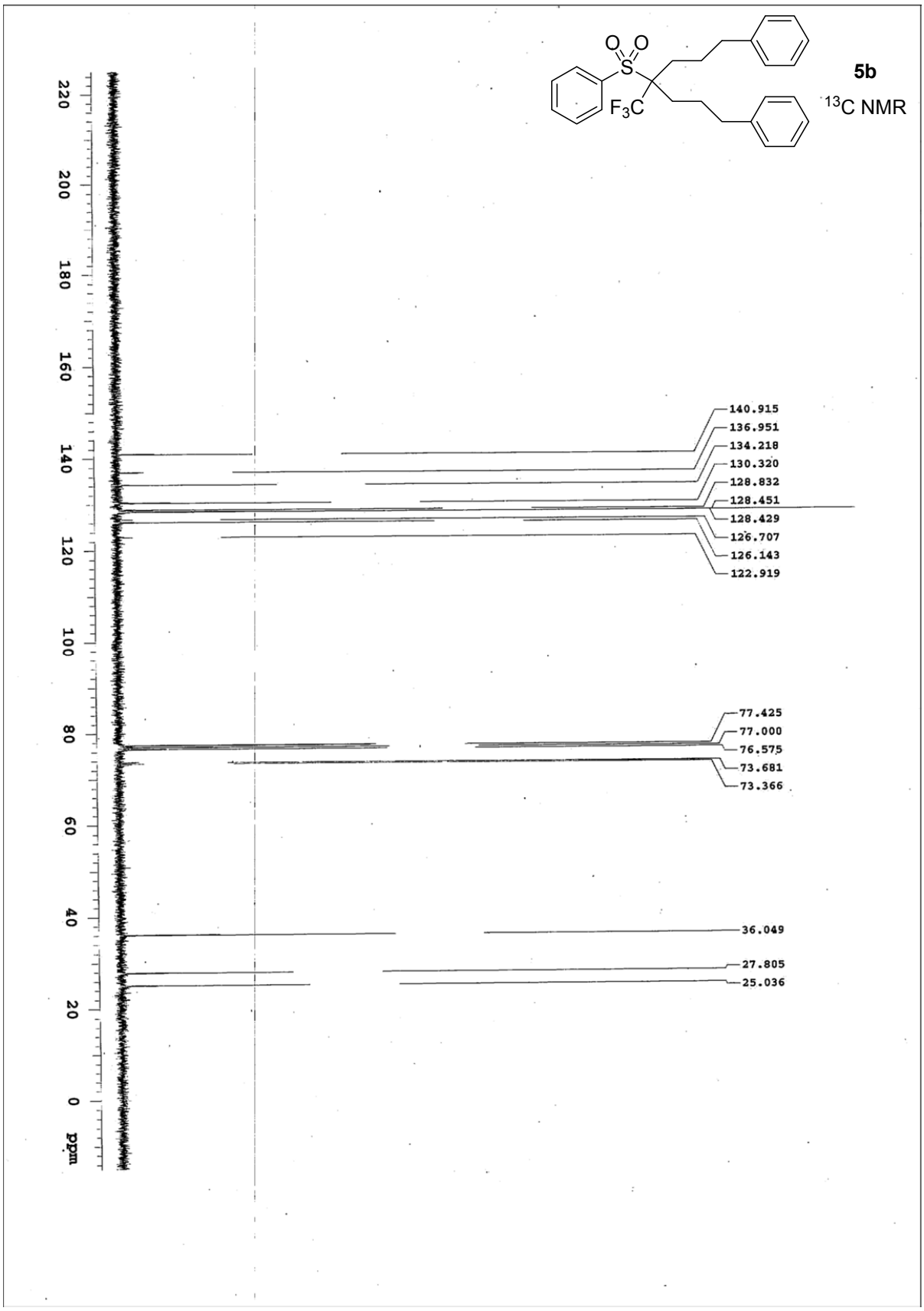

5b
^{1}H NMR
O
O
S
F_3C
10
9
8
7
6
5
4
3
2
1
ppm
5.53
10.42
4.00
8.81
7.782
7.757
7.675
7.650
7.625
7.515
7.489
7.464
7.316
7.293
7.269
7.259
7.229
7.206
7.182
7.156
7.132
2.633
2.608
2.585
2.146
2.133
2.089
2.056
2.047
2.029
2.014
1.988
1.974
1.941
1.928
1.906
1.891
1.868
1.852
1.829
1.802
1.782
1.765
1.742
1.725
1.700
1.549
0.001

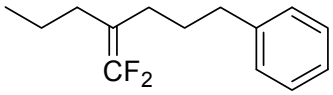


5b

^{19}F NMR

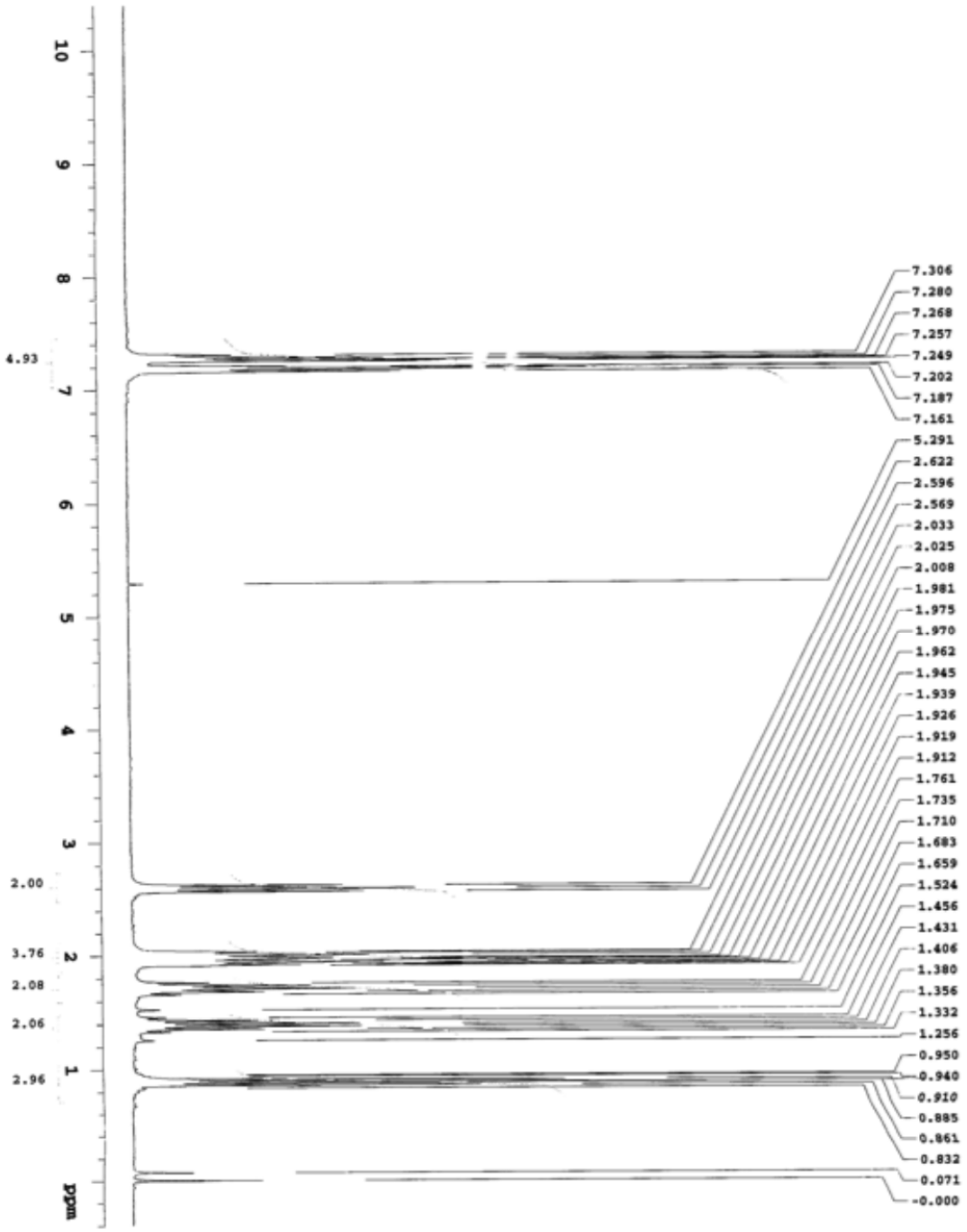


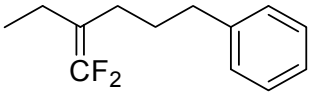

O O
S
F3C
5b
13C NMR
140.915
136.951
134.218
130.320
128.832
128.451
128.429
126.707
126.143
122.919
77.425
77.000
76.575
73.681
73.366
36.049
27.805
25.036
220
200
180
160
140
120
100
80
60
40
20
0
ppm


CF2

S1a

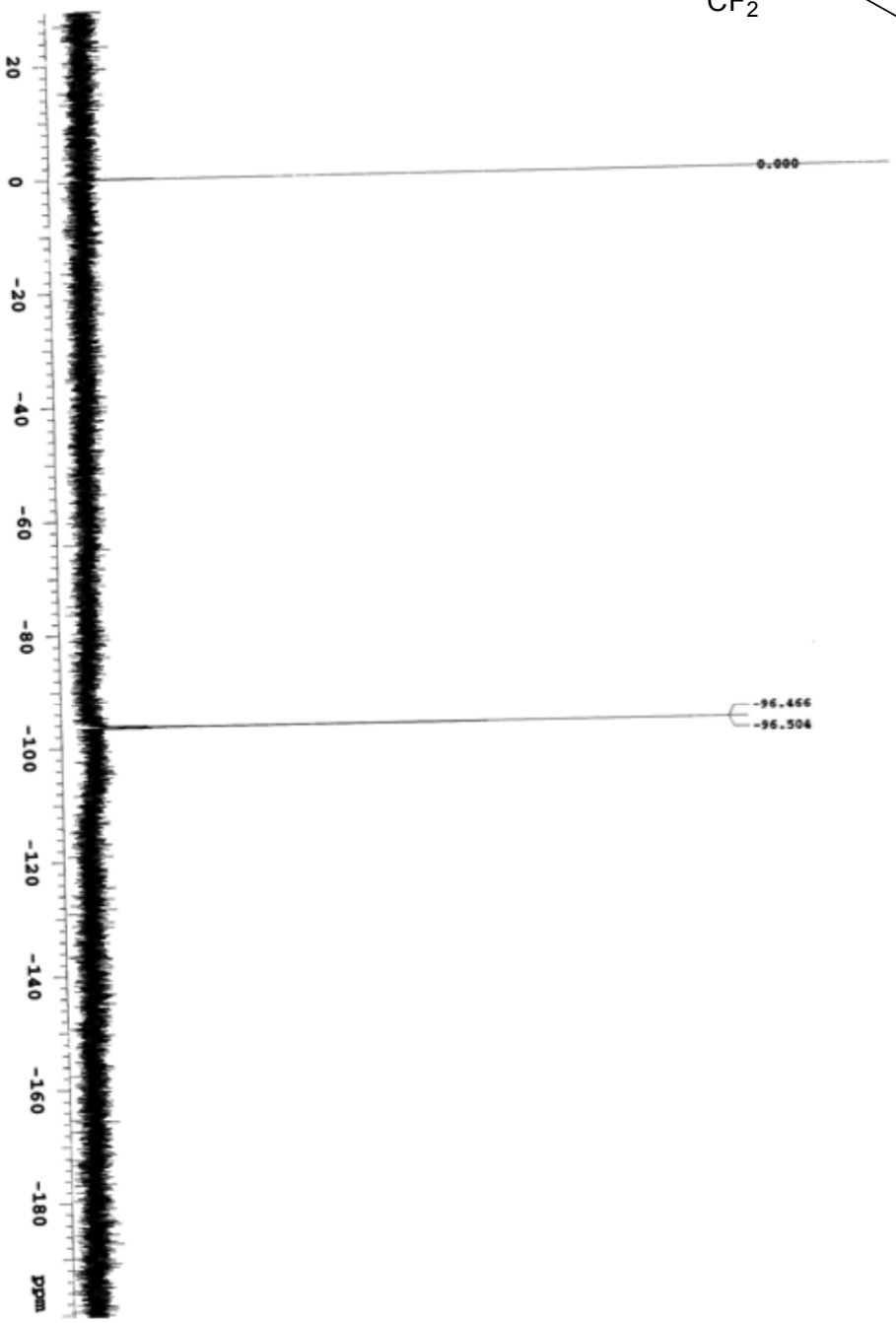
^{1}H NMR

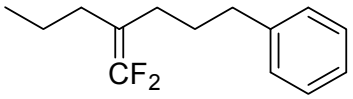

10
9
8
7
6
5
4
3
2
1
ppm
4.93
2.00
3.76
2.08
2.06
2.96
7.306
7.280
7.268
7.257
7.249
7.202
7.187
7.161
5.291
2.622
2.596
2.569
2.033
2.025
2.008
1.981
1.975
1.970
1.962
1.945
1.939
1.926
1.919
1.912
1.761
1.735
1.710
1.683
1.659
1.524
1.456
1.431
1.406
1.380
1.356
1.332
1.256
0.950
0.940
0.910
0.885
0.861
0.832
0.071
-0.000



S1a

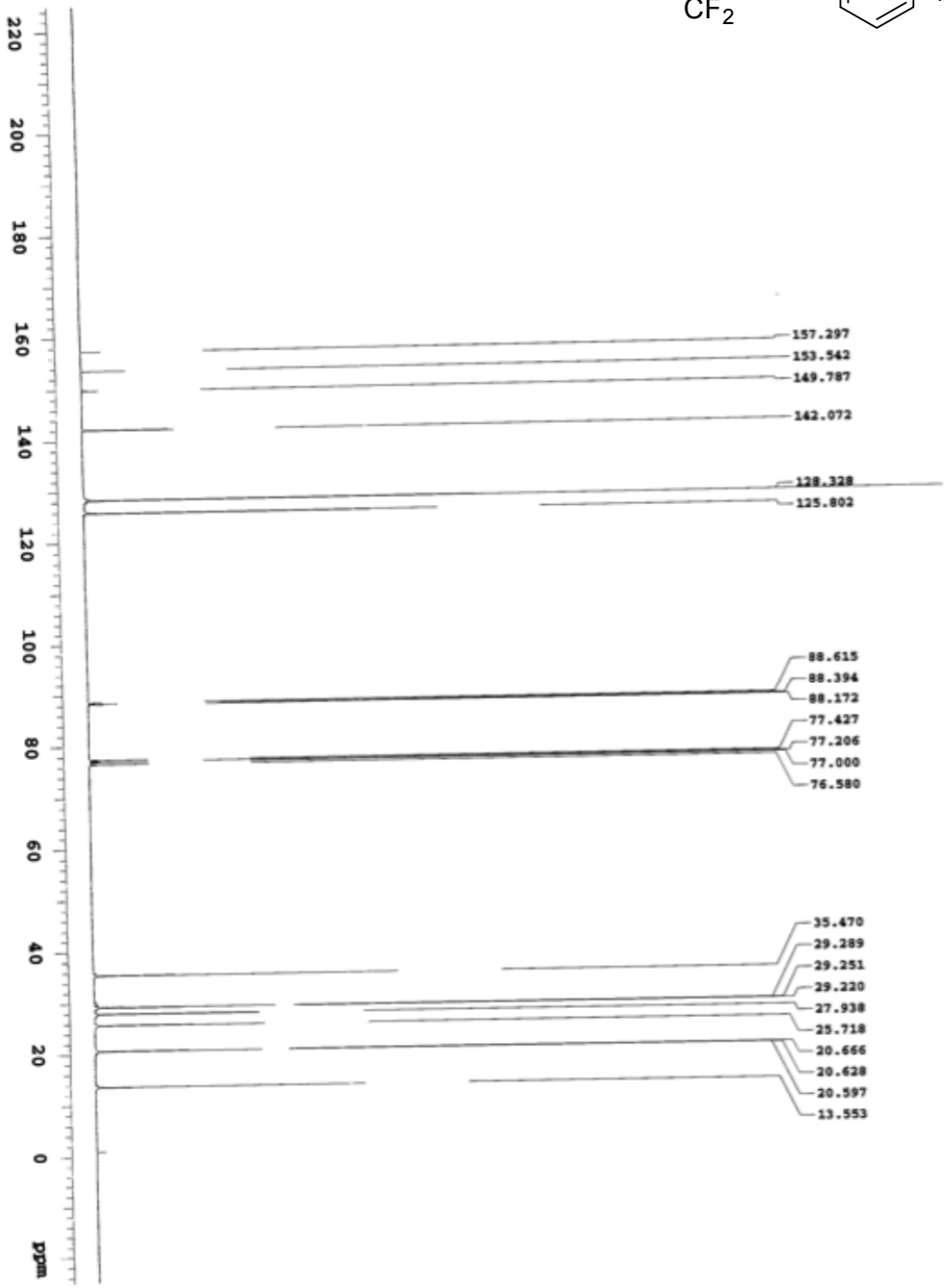
^{19}F NMR

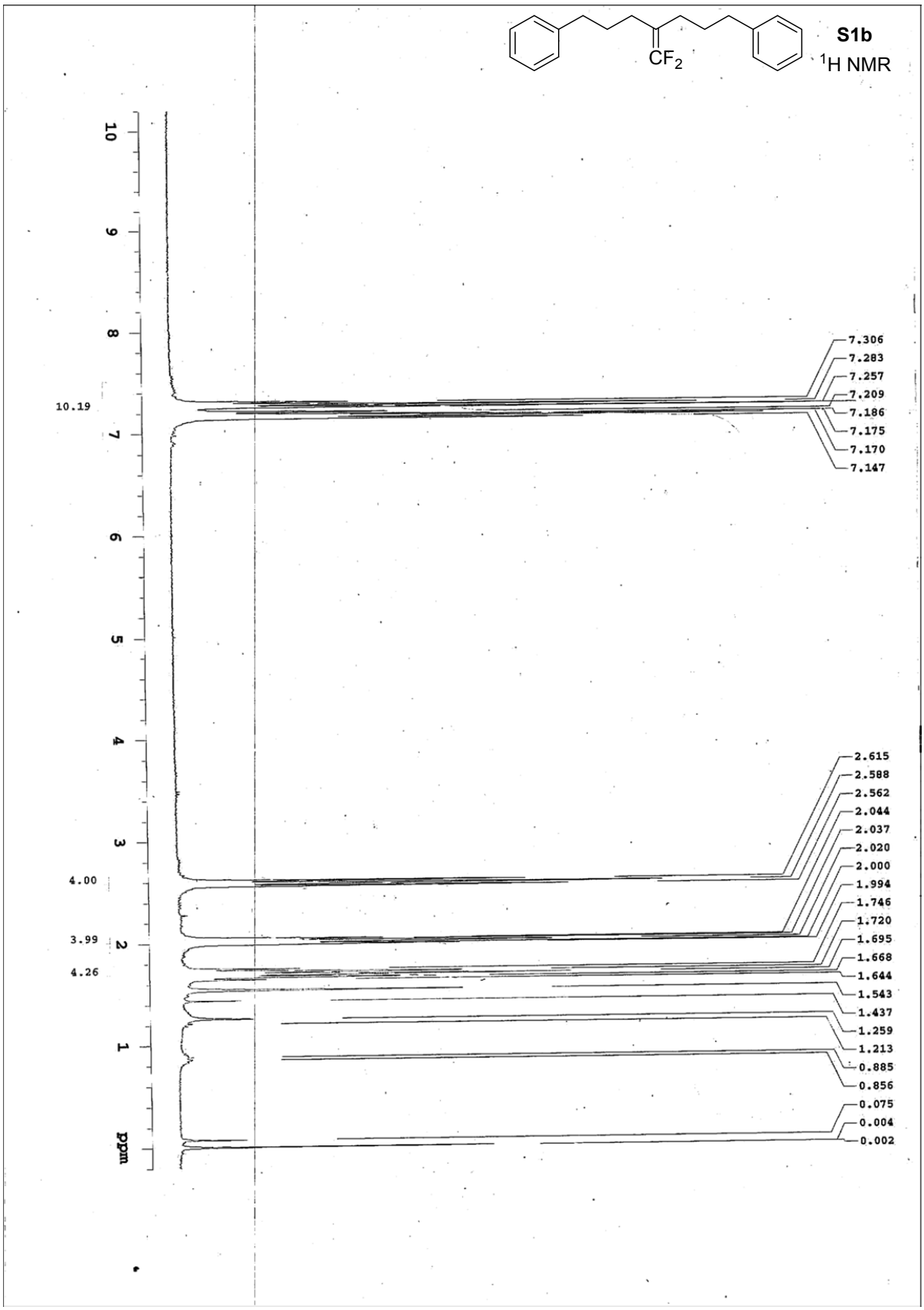


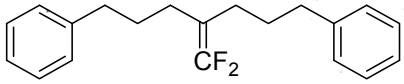

CF2

S1a

^{13}C NMR

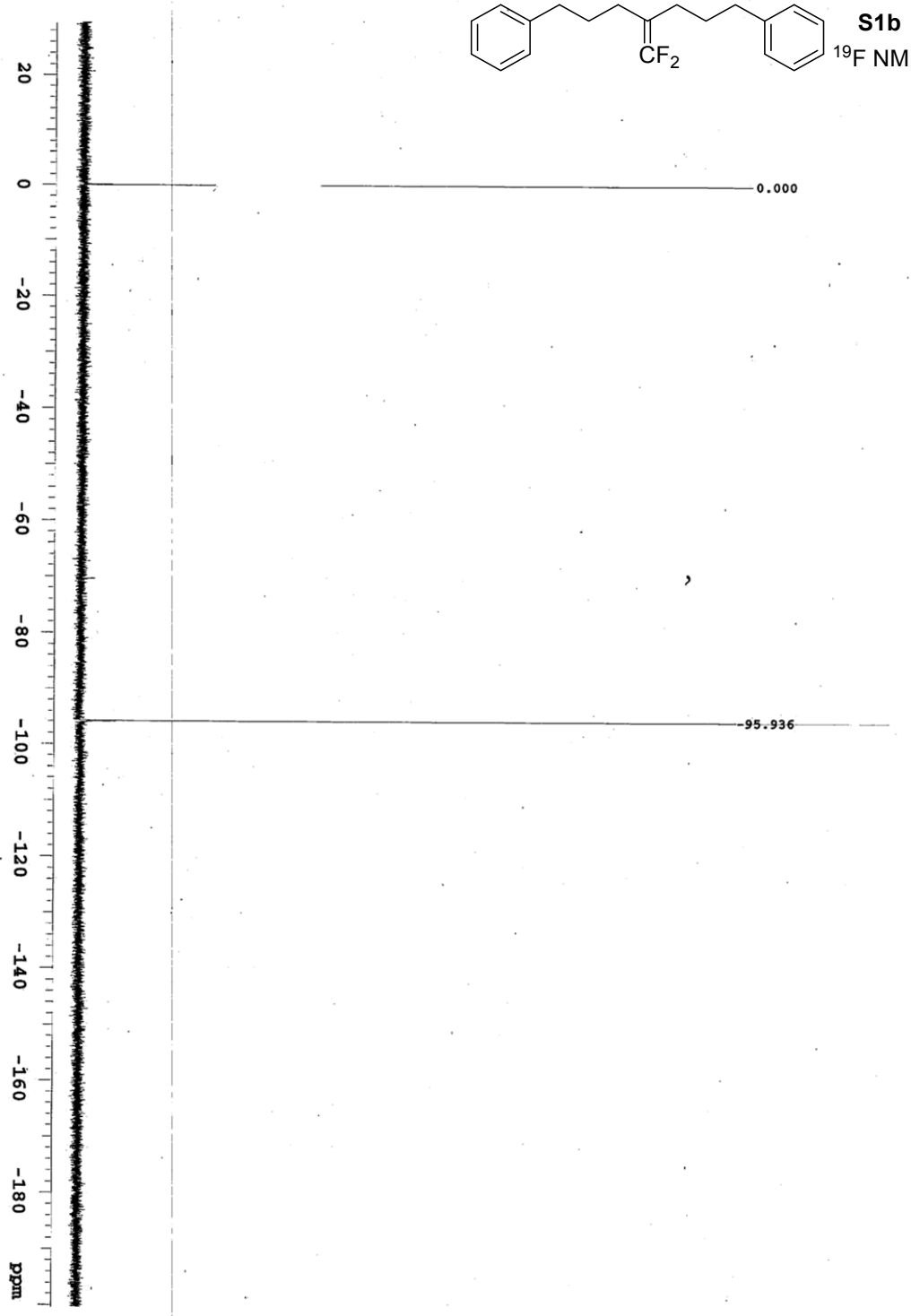

157.297
153.542
149.787
142.072
128.328
125.802
88.615
88.394
88.172
77.427
77.206
77.000
76.580
35.470
29.289
29.251
29.220
27.938
25.718
20.666
20.628
20.597
13.553
220
200
180
160
140
120
100
80
60
40
20
0
ppm

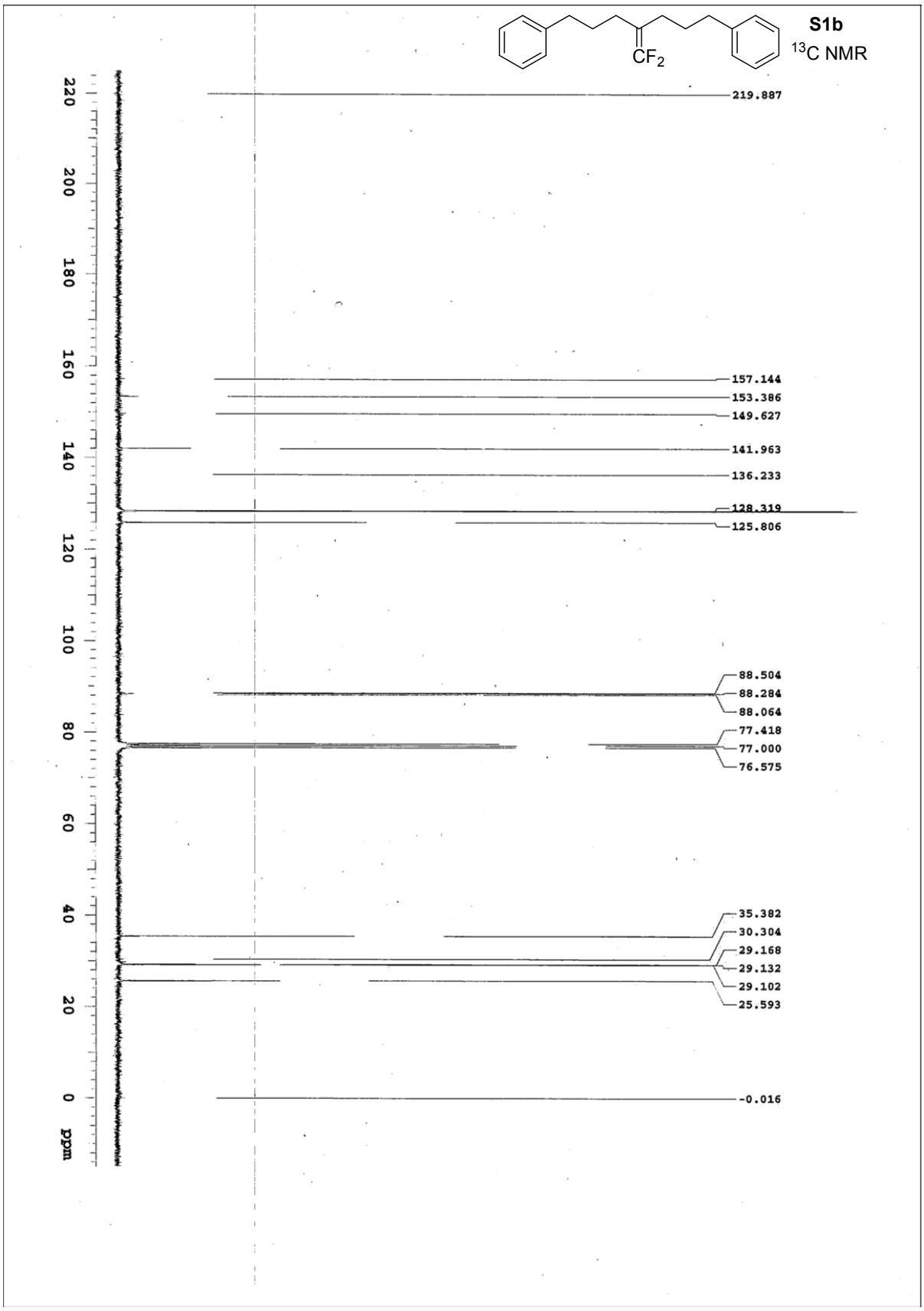

S1b
^{1}H NMR
CF$_2$
10.19
4.00
3.99
4.26
7.306
7.283
7.257
7.209
7.186
7.175
7.170
7.147
2.615
2.588
2.562
2.044
2.037
2.020
2.000
1.994
1.746
1.720
1.695
1.668
1.644
1.543
1.437
1.259
1.213
0.885
0.856
0.075
0.004
0.002
ppm

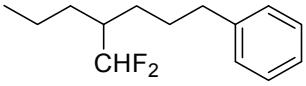


S1b

^{19}F NMR

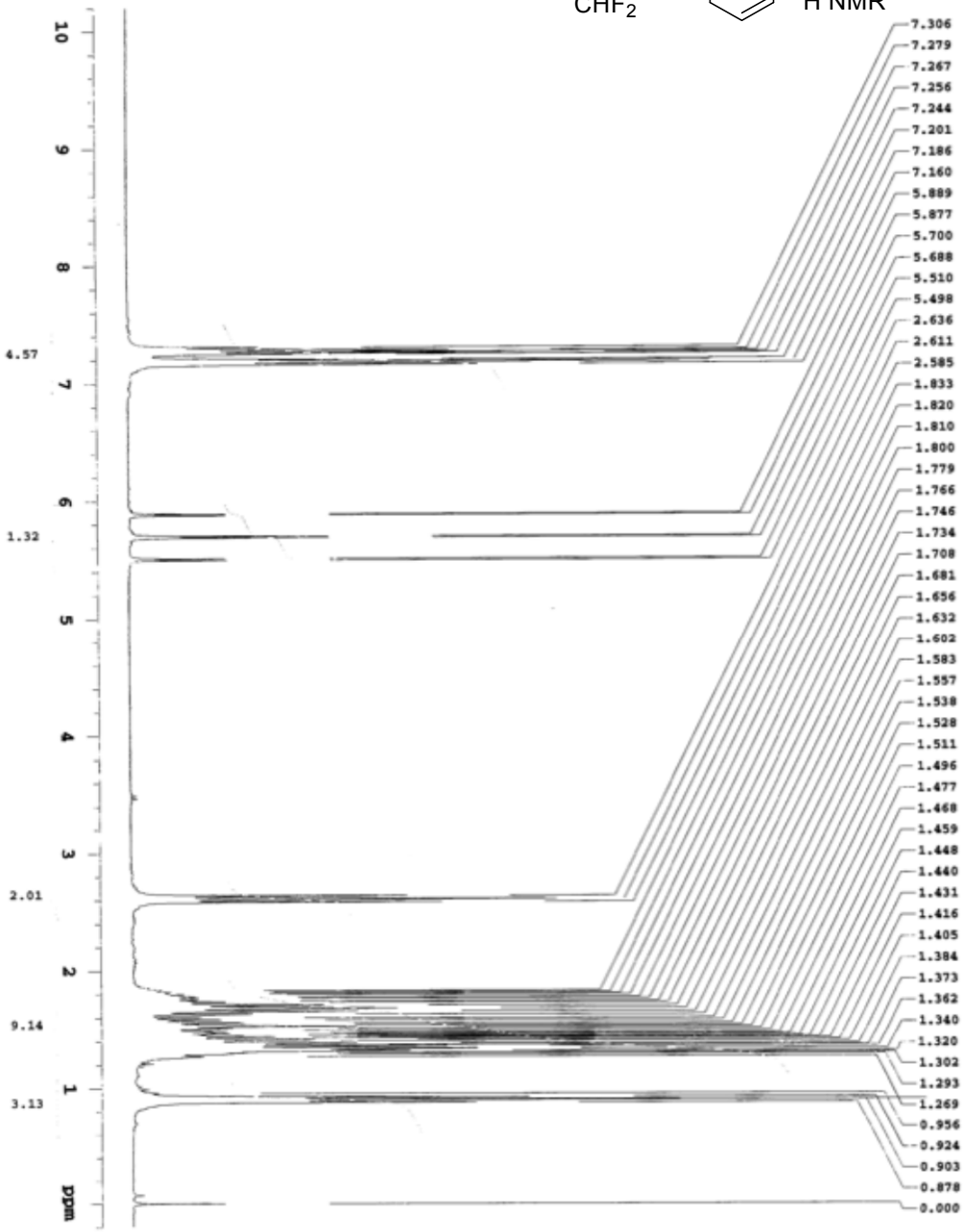


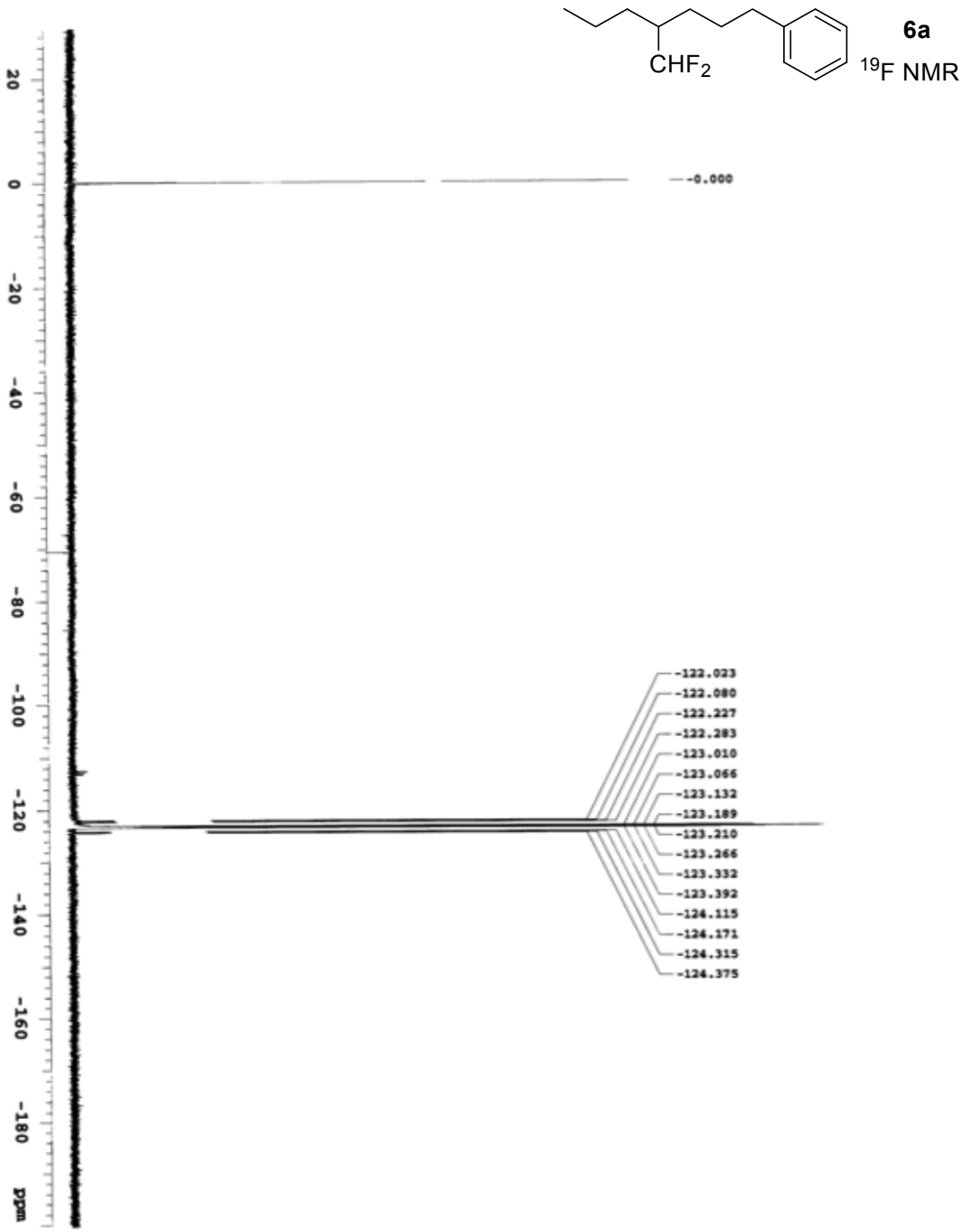

S1b
13C NMR
CF2
219.887
157.144
153.386
149.627
141.963
136.233
128.319
125.806
88.504
88.284
88.064
77.418
77.000
76.575
35.382
30.304
29.168
29.132
29.102
25.593
-0.016
220
200
180
160
140
120
100
80
60
40
20
0
ppm

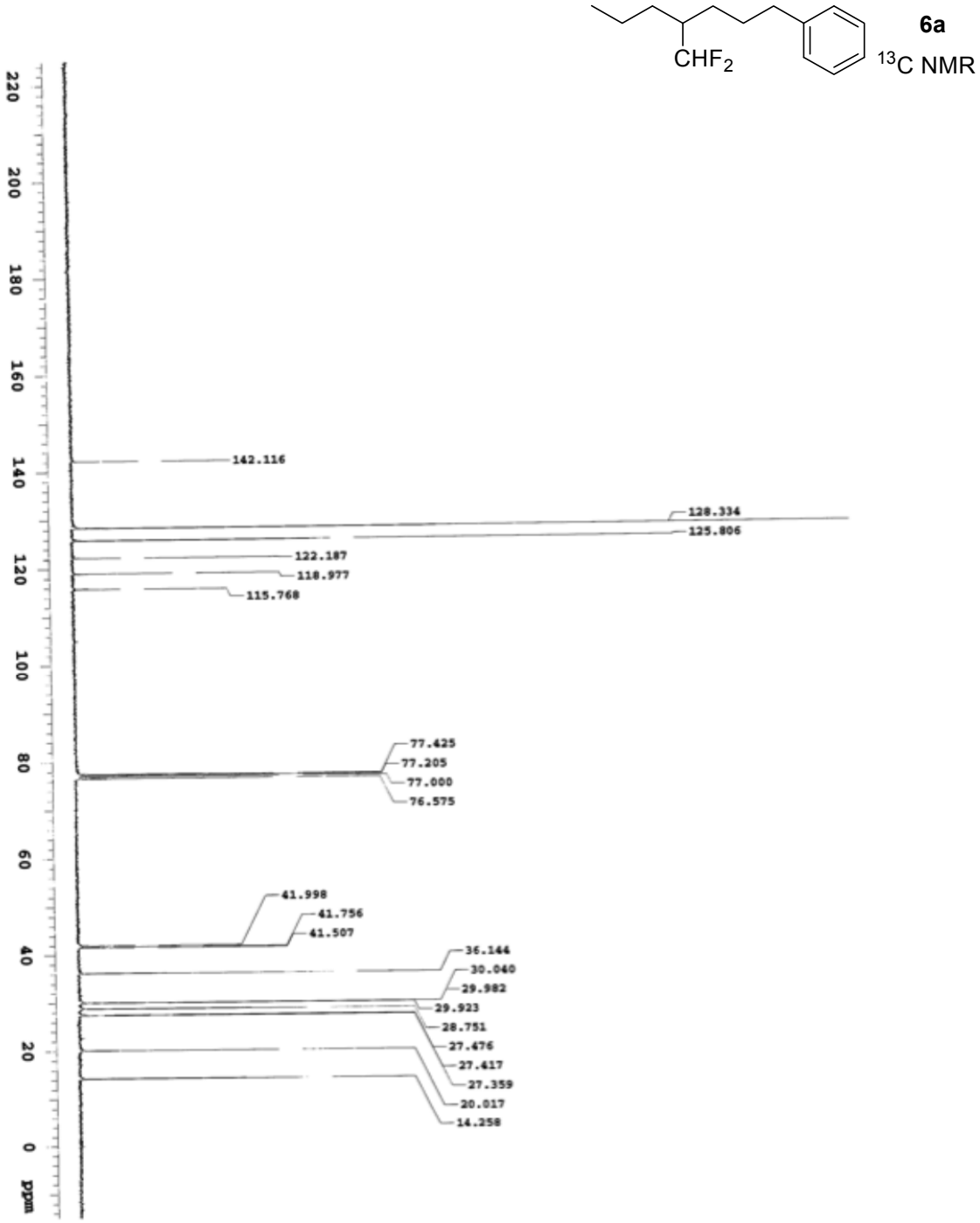

CHF2

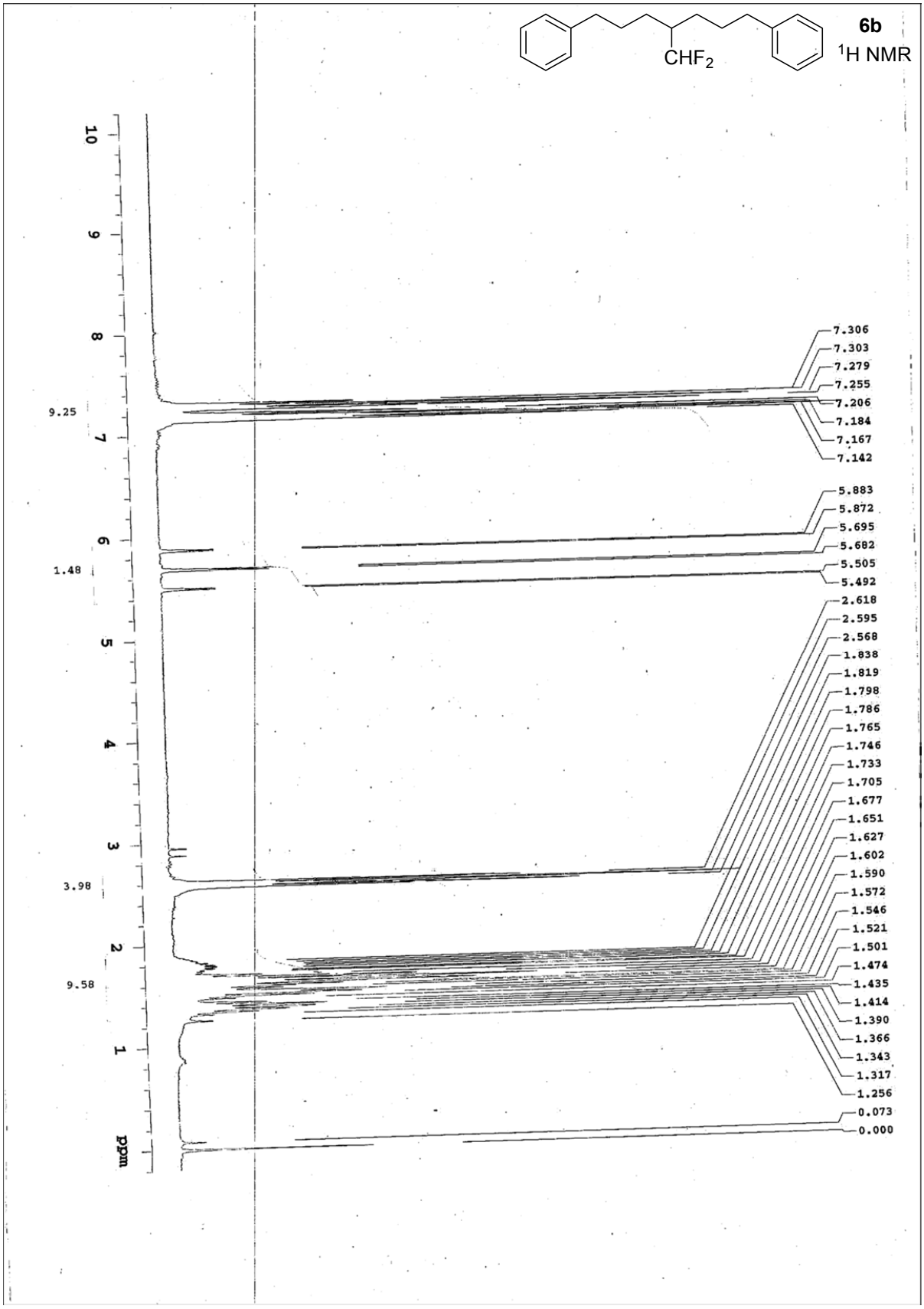
6a

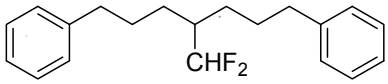
^{1}H NMR


10
9
8
7
6
5
4
3
2
1
ppm
4.57
1.32
2.01
9.14
3.13
7.306
7.279
7.267
7.256
7.244
7.201
7.186
7.160
5.889
5.877
5.700
5.688
5.510
5.498
2.636
2.611
2.585
1.833
1.820
1.810
1.800
1.779
1.766
1.746
1.734
1.708
1.681
1.656
1.632
1.602
1.583
1.557
1.538
1.528
1.511
1.496
1.477
1.468
1.459
1.448
1.440
1.431
1.416
1.405
1.384
1.373
1.362
1.340
1.320
1.302
1.293
1.269
0.956
0.924
0.903
0.878
0.000


CHF2
6a
19F NMR
-0.000
-122.023
-122.080
-122.227
-122.283
-123.010
-123.066
-123.132
-123.189
-123.210
-123.266
-123.332
-123.392
-124.115
-124.171
-124.315
-124.375
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

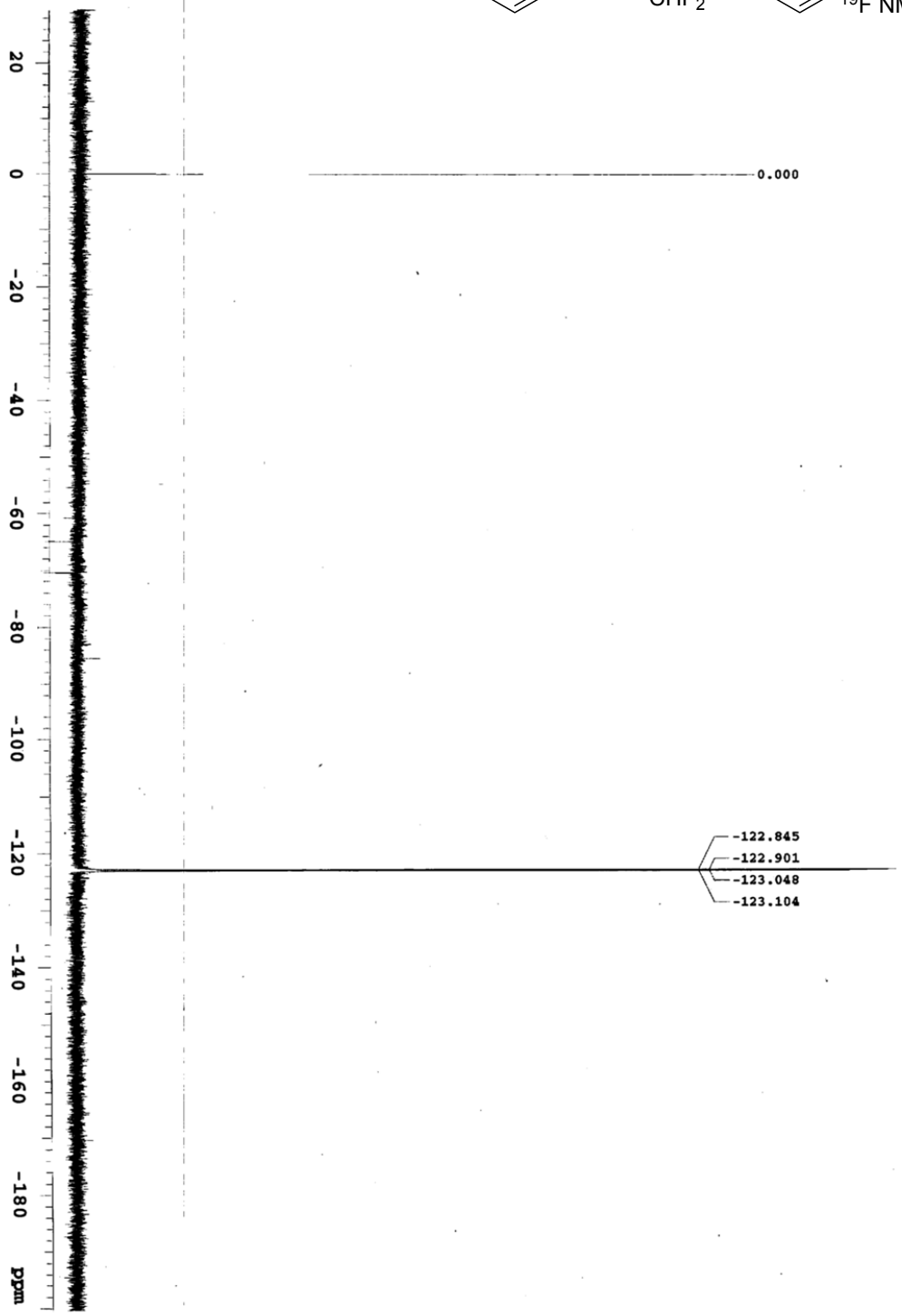

CHF2
6a
13C NMR
142.116
128.334
125.806
122.187
118.977
115.768
77.425
77.205
77.000
76.575
41.998
41.756
41.507
36.144
30.040
29.982
29.923
28.751
27.476
27.417
27.359
20.017
14.258
ppm

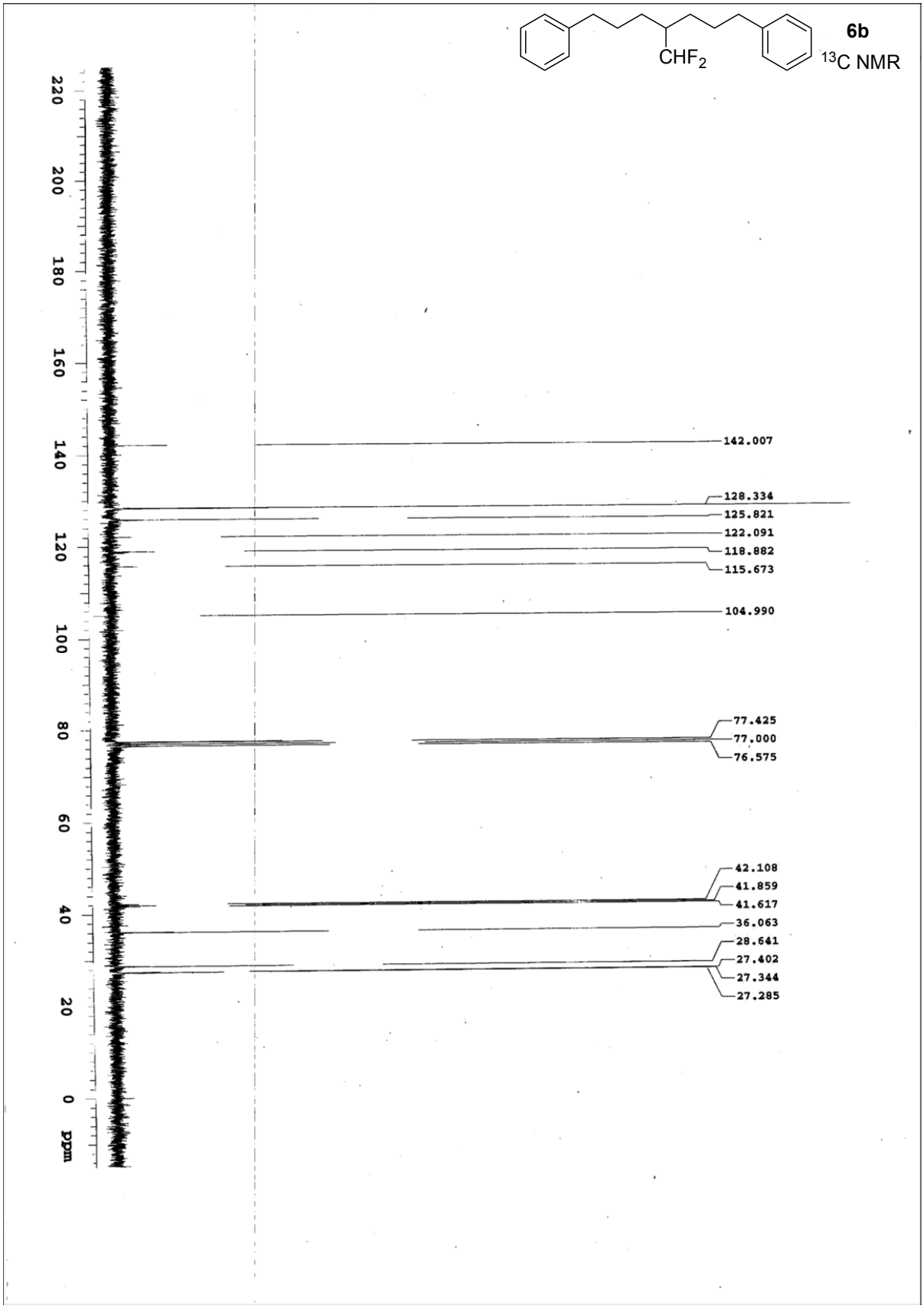

6b
^{1}H NMR
CHF$_2$
7.306
7.303
7.279
7.255
7.206
7.184
7.167
7.142
5.883
5.872
5.695
5.682
5.505
5.492
2.618
2.595
2.568
1.838
1.819
1.798
1.786
1.765
1.746
1.733
1.705
1.677
1.651
1.627
1.602
1.590
1.572
1.546
1.521
1.501
1.474
1.435
1.414
1.390
1.366
1.343
1.317
1.256
0.073
0.000
9.25
1.48
3.98
9.58
10
9
8
7
6
5
4
3
2
1
ppm

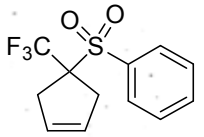

CHF2

6b

^{19}F NMR

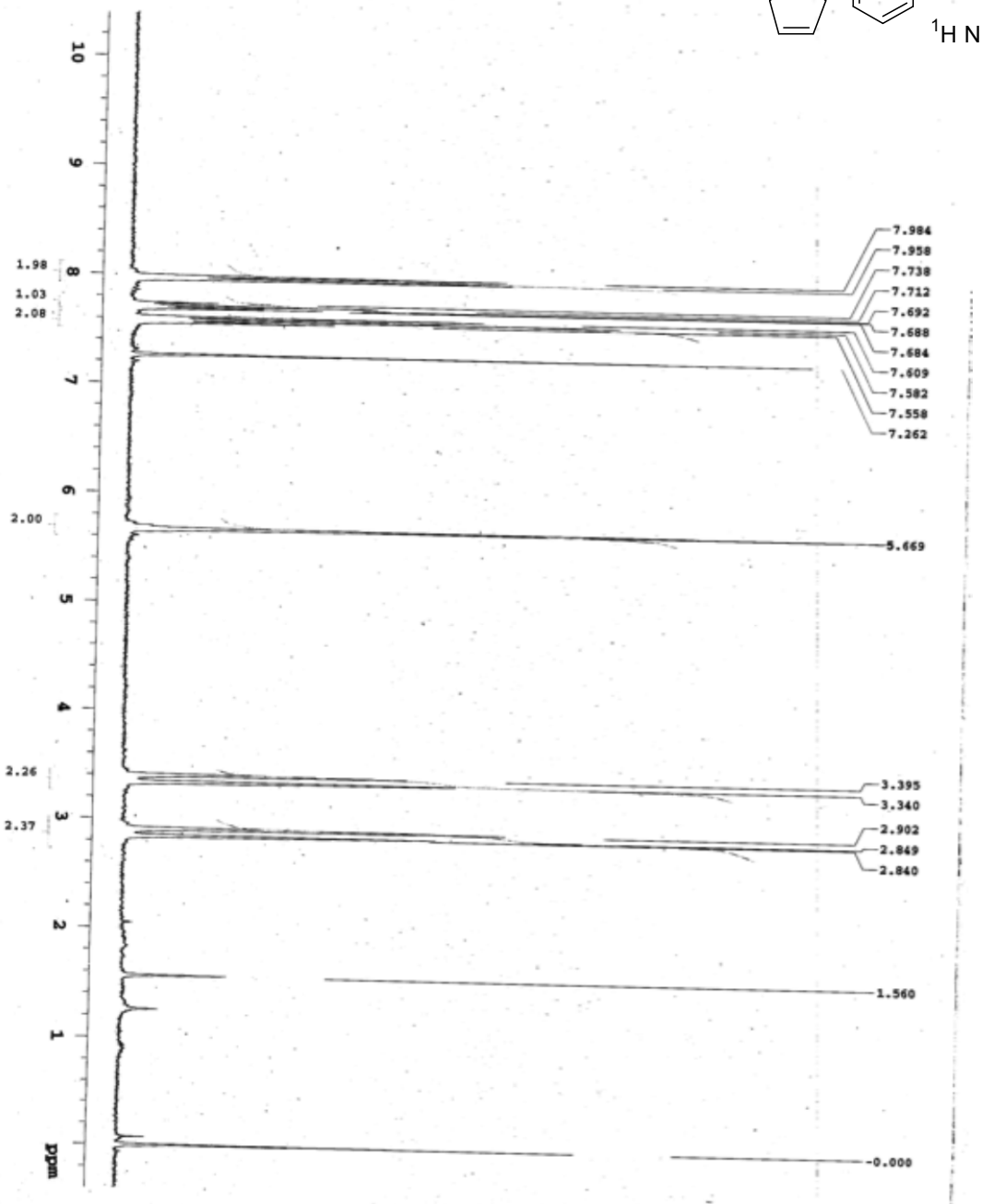

0.000
-122.845
-122.901
-123.048
-123.104
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

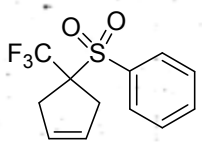

6b
CHF2
13C NMR
142.007
128.334
125.821
122.091
118.882
115.673
104.990
77.425
77.000
76.575
42.108
41.859
41.617
36.063
28.641
27.402
27.344
27.285
220
200
180
160
140
120
100
80
60
40
20
0
ppm


F3C
O
O
S

4

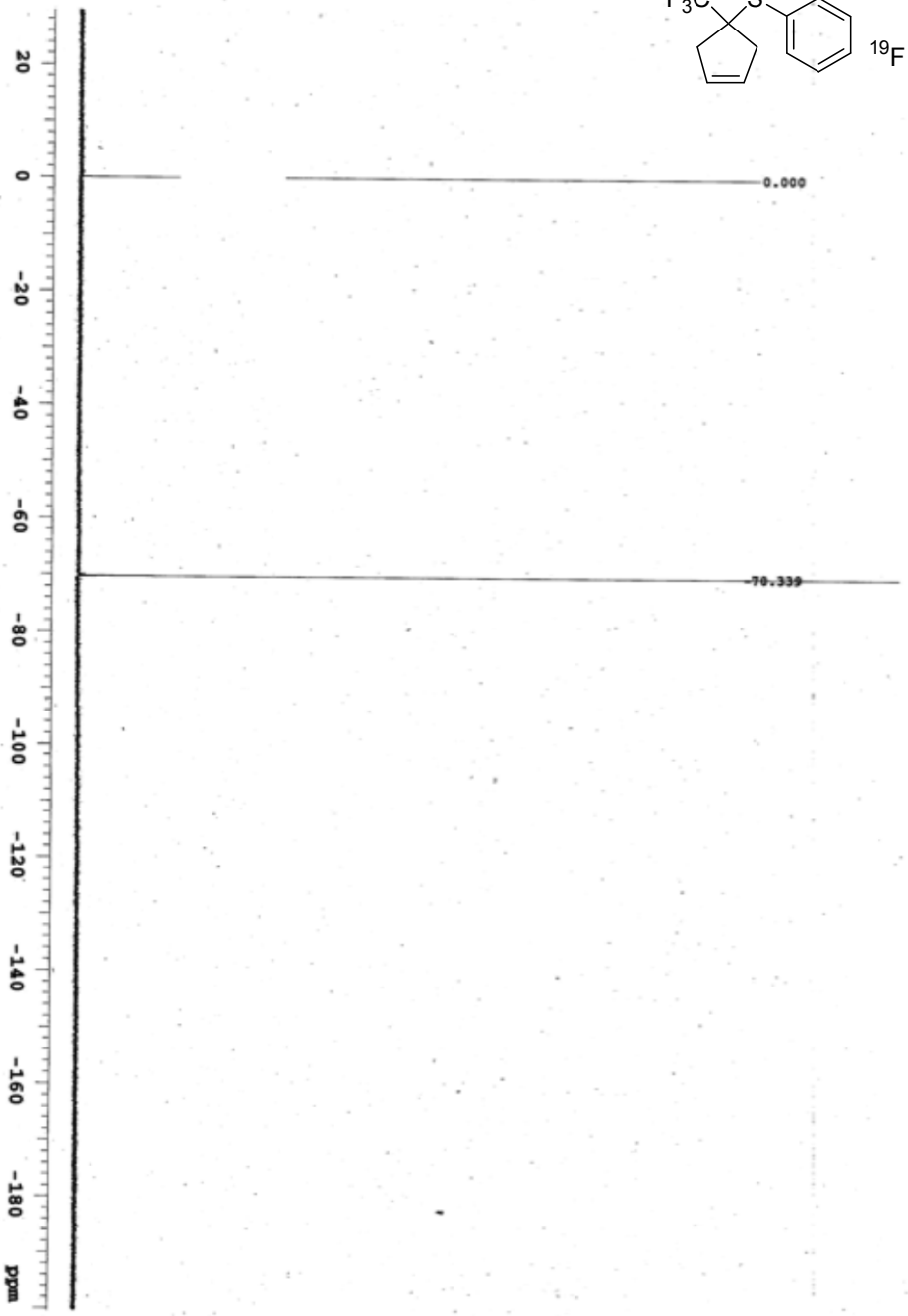
^{1}H NMR

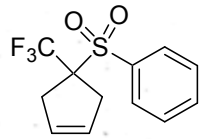

7.984
7.958
7.738
7.712
7.692
7.688
7.684
7.609
7.582
7.558
7.262
5.669
3.395
3.340
2.902
2.849
2.840
1.560
-0.000
1.98
1.03
2.08
2.00
2.26
2.37
10
9
8
7
6
5
4
3
2
1
ppm



4

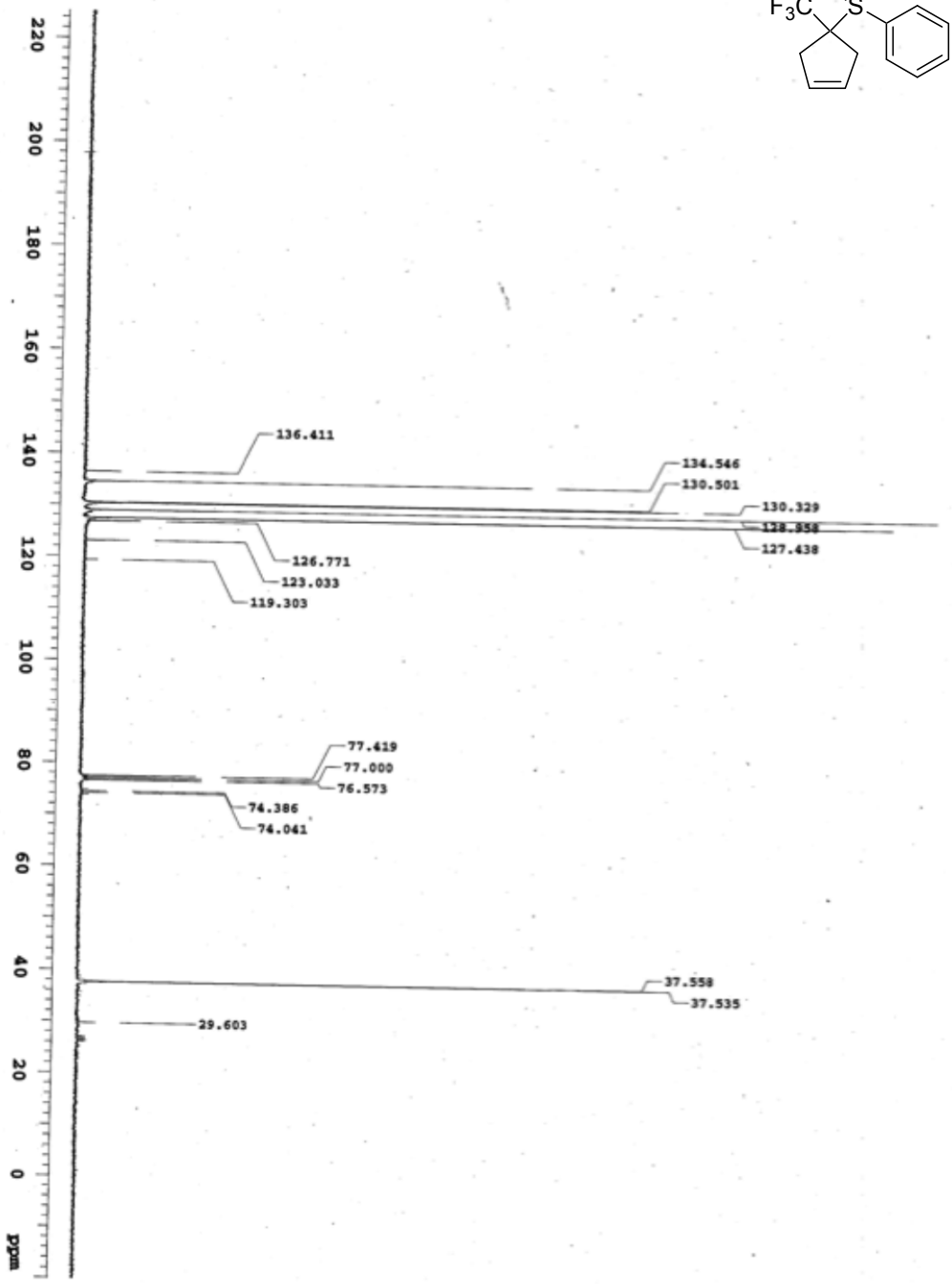
^{19}F NMR




F3C
O
O
S

4

^{13}C NMR


220
200
180
160
140
120
100
80
60
40
20
0
ppm
136.411
134.546
130.501
130.329
128.958
127.438
126.771
123.033
119.303
77.419
77.000
76.573
74.386
74.041
37.558
37.535
29.603