Supporting Information

Hydride reduction of *o*-(fluorosilyl)benzodifluorides for subsequent C–F transformations

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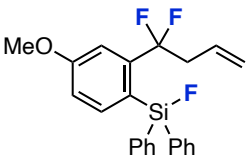
Contents

General Information

All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715. Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60, spherical, particle size 40–50 μm, Cat. No. 37562-85) by conventional manual method. Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 MHz, or a Bruker AVANCE 400 spectrometer at 400 MHz. ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 126 MHz, or a Bruker AVANCE 400 spectrometer at 101 MHz. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 ºC. $CDCl_3$ (Kanto Chemical Co. Inc., Cat. No. 07663-23) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^{+}) conditions.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzotrifluoride **4a**[S1] and difluoromethylenes **5a**–**5e**,[S1] **5g**,[S2] and **5h**–**5k**[S3] were prepared according to the reported methods. According to the procedure for the preparation of 4,4-difluoro-4-(2-(fluorodiphenylsilyl)phenyl)-3-phenyl-1-butene,[S1] (2-(1,1-difluoro-2-phenylbut-3-en-1-yl)-4-methoxyphenyl)fluorodiphenylsilane (**5f**) (294 mg, 41%) was prepared from 2-diphenylsilyl-5-methoxybenzotrifluoride (**4a**).

Structures of Difluoromethylenes 5



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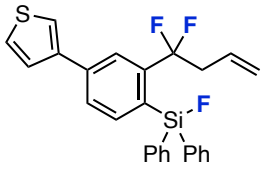

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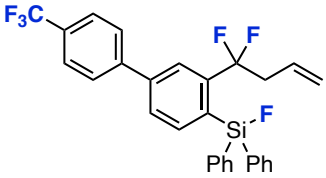

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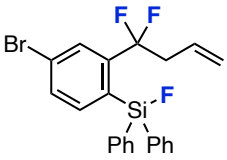

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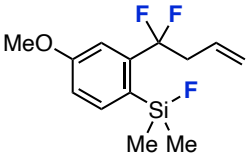

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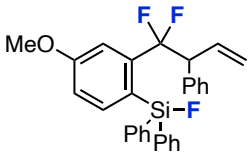

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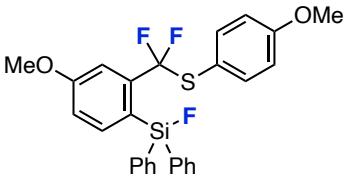

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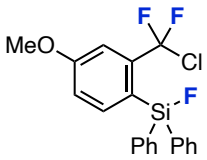

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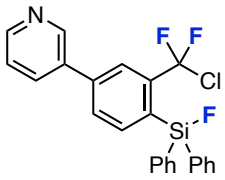

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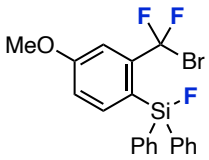

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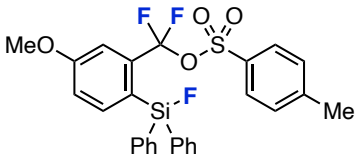
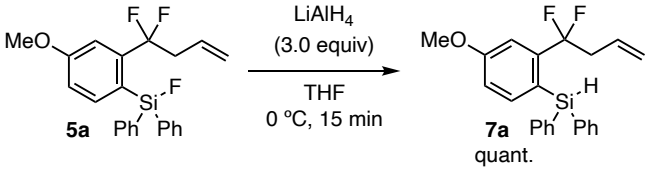


5k

Experimental Procedures

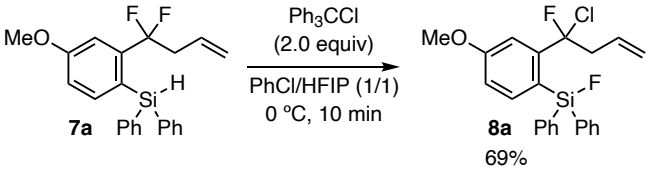
*LAH reduction of fluorosilanes **5***



To a solution of 4,4-difluoro-4-(2-(fluorodiphenylsilyl)-5-methoxyphenyl)-1-butene (**5a**) (399 mg, 1.00 mmol, 1.00 equiv) dissolved in THF (10 mL) was added $LiAlH_4$ (114 mg, 3.00 mmol, 3.00 equiv) at 0 °C. After stirring for 15 min at the same temperature, to this was slowly added EtOAc (5 mL). After stirring for 5 min at the same temperature, to this added 1 M HCl (5 mL). The mixture was extracted with EtOAc (5 mL × 3), and the combined organic extract was dried with Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure to give 4,4-difluoro-4-(5-methoxy-2-(diphenylsilyl)phenyl)-1-butene (**7a**) (395 mg, 1.04 mmol, quant.) as a colorless oil.

According to the procedure for preparing 4,4-difluoro-4-(5-methoxy-2-(diphenylsilyl)phenyl)-1-butene (**7a**), (2-(1,1-difluorobut-3-en-1-yl)-4-(thiophen-3-yl)phenyl)diphenylsilane (**7b**) (463 mg, quant.), (3-(1,1-difluorobut-3-en-1-yl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)diphenylsilane (**7c**) (407 mg, 93%), (4-bromo-2-(1,1-difluorobut-3-en-1-yl)phenyl)diphenylsilane (**7d**) (360 mg, 93%), 4,4-difluoro-4-(5-methoxy-2-(dimethylsilyl)phenyl)-1-butene (**7e**) (17.2 mg, 66%), (2-(1,1-difluoro-2-phenylbut-3-en-1-yl)-4-methoxyphenyl)diphenylsilane (**7f**) (169 mg, 86%), (2-(difluoro((4-methoxyphenyl)thio)methyl)-4-methoxyphenyl)diphenylsilane (**7g**) (18.4 mg , 77%), (2-(chlorodifluoromethyl)-4-methoxyphenyl)diphenylsilane (**7h**) (120 mg, 80%), 3-(3-(chlorodifluoromethyl)-4-(diphenylsilyl)phenyl)pyridine (**7i**) (13.0 mg, 77%), and (2-(bromodifluoromethyl)-4-methoxyphenyl)diphenylsilane (**7j**) (28.2 mg, 48%) were prepared from the corresponding fluorosilanes **5**.

*C–F chlorination of difluoromethylenes **7***

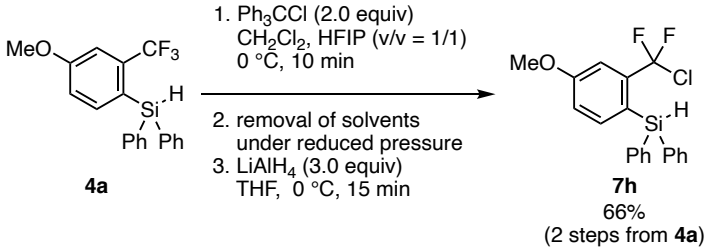


To a solution of 4,4-difluoro-4-(5-methoxy-2-(diphenylsilyl)phenyl)-1-butene (**7a**) (951 mg, 2.50 mmol, 1.00 equiv) dissolved in PhCl/HFIP (v/v = 1/1) (15.0 mL) was added trityl chloride (1.39 g, 5.00 mmol, 2.00 equiv) at 0 °C. After stirring for 10 min at the same temperature, to this was added an aqueous saturated $NaHCO_3$ (10 mL) and brine (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 20 g, *n*-hexane/CH_2Cl_2 = 10/1 to 3/1) to give 4-chloro-4-fluoro-4-(5-methoxy-2-(diphenylfluorosilyl)phenyl)-1-butene (**8a**) (717 mg, 1.73 mmol, 69%) as a colorless oil.

According to the procedure for preparing 4-chloro-4-fluoro-4-(5-methoxy-2-(diphenylfluorosilyl)phenyl)-1-butene (**8a**), (3-(1-chloro-1-fluorobut-3-en-1-yl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)fluorodiphenylsilane (**8c**) (214 mg, 59%) and (4-bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)phenyl)fluorodiphenylsilane (**8d**) (155 mg, 53%) were prepared from the corresponding difluoromethylenes **7**.

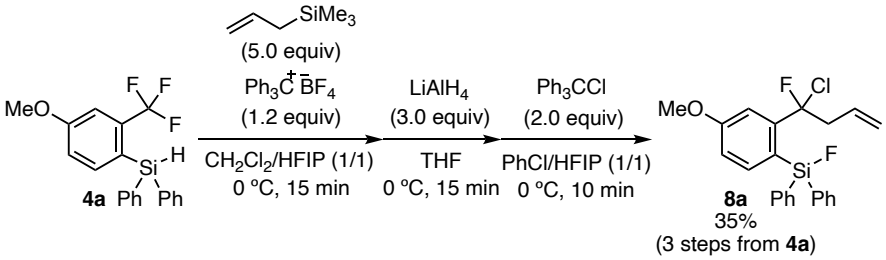
Similarly, fluoro(2-(4-fluorohepta-1,6-dien-4-yl)-4-methoxyphenyl)diphenylsilane (**8e**) (13.2 mg, 34%) was prepared from 4,4-difluoro-4-(5-methoxy-2-(diphenylsilyl)phenyl)-1-butene (**7a**) with allyltrimethylsilane (79.3 μL, 0.500 mmol, 5.00 equiv) and trityl chloride (33.4 mg, 0.120 mmol, 1.2 equiv).

*Synthesis of (2-(chlorodifluoromethyl)-4-methoxyphenyl)diphenylsilane (**7h**) from (4-methoxy-2-(trifluoromethyl)phenyl)diphenylsilane (**4a**)*



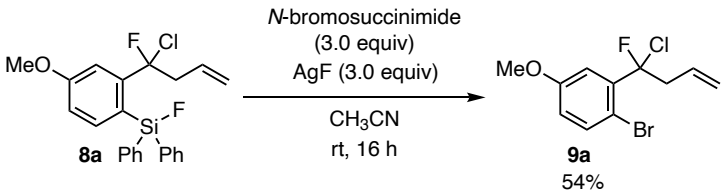
To a solution of (4-methoxy-2-(trifluoromethyl)phenyl)diphenylsilane (**4a**) (71.5 mg, 0.199 mmol) dissolved in CH_2Cl_2/HFIP (v/v = 1/1) (2.0 mL) was added trityl chloride (111.5 mg, 0.400 mmol, 2.0 equiv) at 0 ºC. After stirring for 10 min at the same temperature, the solvents were removed under reduced pressure. After filling argon, to the resulting mixture dissolved in THF (2.0 mL) was added $LiAlH_4$ (22.8 mg, 0.600 mmol, 3.0 equiv) at 0 °C. After stirring for 15 min at the same temperature, to this was slowly added EtOAc (5 mL). After stirring for 5 min at the same temperature, to this was added 1 M HCl (5 mL). The mixture was extracted with EtOAc (5 mL × 3), and the combined organic extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 10 g, *n*-hexane/CH_2Cl_2 = 20/1) to give (2-(chlorodifluoromethyl)-4-methoxyphenyl)diphenylsilane (**7h**) (49.6 mg, 0.132 mmol, 66%) as a colorless oil.

*Synthesis of 4-chloro-4-fluoro-4-(5-methoxy-2-(diphenylfluorosilyl)phenyl)-1-butene (**8a**) from (4-methoxy-2-(trifluoromethyl)phenyl)diphenylsilane (**4a**)*



To a solution of (4-methoxy-2-(trifluoromethyl)phenyl)diphenylsilane (**4a**) (71.7 mg, 0.200 mmol, 1.00 equiv) and allyltrimethylsilane (0.159 mL, 1.00 mmol, 5.00 equiv) dissolved in CH_2Cl_2/HFIP (v/v = 1/1) (1.20 mL) was added trityl tetrafluoroborate (79.2 mg, 0.240 mmol, 1.20 equiv) at 0 ºC. After stirring for 15 min at the same temperature, to this was added a saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. To the resulting mixture dissolved in THF (1.60 mL) was added $LiAlH_4$ (18.4 mg, 0.486 mmol, 3.00 equiv) at 0 °C. After stirring for 15 min at the same temperature, to this was slowly added EtOAc (0.80 mL). After stirring for 5 min at the same temperature, to this was added 1 M HCl (5 mL). The mixture was extracted with EtOAc (5 mL × 3), and the combined organic extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. To the resulting mixture dissolved in PhCl/HFIP (v/v = 1/1) (0.800 mL) was added trityl chloride (73.6 mg, 0.264 mmol, 2.00 equiv) at 0 °C. After stirring for 10 min at the same temperature, to this was added an aqueous saturated $NaHCO_3$ (5 mL) and brine (5 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 2 g, *n*-hexane/CH_2Cl_2 = 6/1 to 3/1) to give 4-chloro-4-fluoro-4-(5-methoxy-2-(diphenylfluorosilyl)phenyl)-1-butene (**8a**) (29.0 mg, 69.9 μmol, 35%) as a colorless oil.

*Synthesis of 1-bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxybenzene (**9**)*

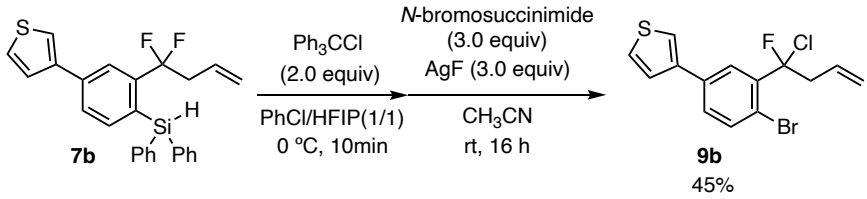


In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118) was placed a mixture of (2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxyphenyl)fluorodiphenylsilane (**8a**) (41.5 mg, 0.100 mmol, 1.00

equiv), *N*-bromosuccinimide (53.4 mg, 0.300 mmol, 3.00 equiv), and AgF (38.1 mg, 0.300 mmol, 3.00 equiv) in CH_3CN (1.00 mL) at room temperature. The mixture was stirred at the same temperature for 16 h. After completion of the reaction, the mixture was diluted with EtOAc (5 mL) and filtered through a layer of celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 5 g, *n*-hexane/CH_2Cl_2 = 10/1) to give 1-bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxybenzene (**9a**) (16.0 mg, 54.5 μmol, 54%) as a colorless oil.

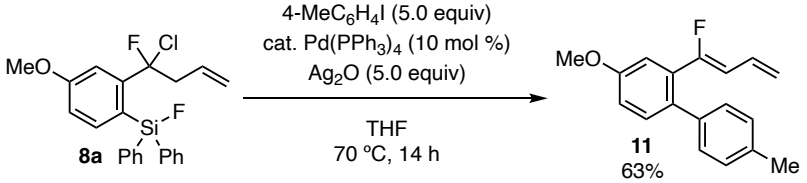
According to the procedure for preparing 1-bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxybenzene (**9a**), 4-bromo-3-(1-chloro-1-fluorobut-3-en-1-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (**9c**) (45.7 mg, 40%) and 1,4-dibromo-2-(1-chloro-1-fluorobut-3-en-1-yl)benzene (**9d**) (36.2 mg, 48%) were prepared from the corresponding benzyl fluorides **8**.

*Synthesis of 3-(4-bromo-3-(1-chloro-1-fluorobut-3-en-1-yl)phenyl)thiophene (**9b**)*



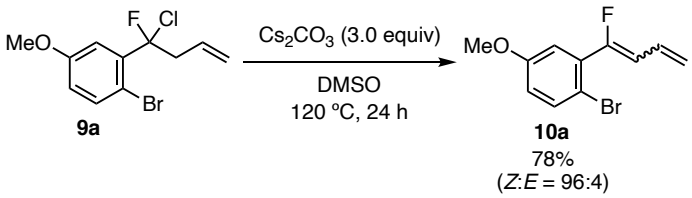
To a solution of (2-(1,1-difluorobut-3-en-1-yl)-4-(thiophen-3-yl)phenyl)diphenylsilane (**7b**) (735 mg, 1.70 mmol, 1.00 equiv) dissolved in PhCl/HFIP (v/v = 1/1) (10.2 mL) was added trityl chloride (948 mg, 3.40 mmol, 2.00 equiv) at 0 °C. After stirring for 10 min at the same temperature, to this was added an aqueous saturated $NaHCO_3$ (10 mL) and brine (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 20 g, *n*-hexane/CH_2Cl_2 = 10/1 to 3/1) to give a mixture containing (2-(1-chloro-1-fluorobut-3-en-1-yl)-4-(thiophen-3-yl)phenyl)fluorodiphenylsilane and triphenylmethane as a pale yellow oil. To the resulting mixture dissolved in CH_3CN (12.6 mL) were added *N*-bromosuccinimide (673 mg, 3.78 mmol, 3.00 equiv) and AgF (480 mg, 3.78 mmol, 3.00 equiv) at room temperature. The mixture was stirred at the same temperature for 16 h. After completion of the reaction, the mixture was diluted with EtOAc (10 mL) and filtered through a layer of celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 15 g, *n*-hexane/CH_2Cl_2 = 8/1) to give 3-(4-bromo-3-(1-chloro-1-fluorobut-3-en-1-yl)phenyl)thiophene (**9b**) (266 mg, 0.770 mmol, 45% (2 steps from **7b**)) as a pale yellow oil.

*Synthesis of (Z)-2-(1-fluorobuta-1,3-dien-1-yl)-4-methoxy-4'-methyl-1,1'-biphenyl (**11**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118) was placed a solution of (2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxyphenyl)fluorodiphenylsilane (**8a**) (41.5 mg, 0.100 mmol, 1.00 equiv) and 4-iodotoluene (109 mg, 0.500 mmol, 5.00 equiv) dissolved in THF (2.0 mL). To this were added $Pd(PPh_3)_4$ (11.6 mg, 10.0 μmol, 0.100 equiv) and Ag_2O (116 mg, 0.500 mmol, 5.00 equiv) at room temperature. The mixture was stirred at 70 °C (aluminum heating block) for 14 h. After cooling to room temperature, the mixture was filtered through a layer of silica-gel. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 5 g, *n*-hexane/CH_2Cl_2 = 10/1) to give (*Z*)-2-(1-fluorobuta-1,3-dien-1-yl)-4-methoxy-4'-methyl-1,1'-biphenyl (**11**) (17.0 mg, 63.4 μmol, 63%) as a colorless oil.

*A typical procedure for the synthesis of 1-aryl-1-fluoro-1,3-butadienes **10***



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118) was placed a solution of 1-bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxybenzene (**9a**) (14.7 mg, 50.1 μmol, 1.00 equiv) and Cs_2CO_3 (48.9 mg, 0.150 mmol, 3.00 equiv) in DMSO (0.50 mL). After stirring for 24 h at 120 °C (aluminum heating block), the mixture was cooling to room temperature. To the mixture was added an aqueous NH_4Cl (5 mL) and brine (5 mL). The mixture was extracted with EtOAc (5 mL × 3) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 10 g, *n*-hexane/CH_2Cl_2 = 5/1 to 3/1) to give (*Z*)-1-bromo-2-(1-fluorobuta-1,3-dien-1-yl)-4-methoxybenzene (**10a**) and a small amount of the *E* isomer (10.0 mg, 38.9 μmol, 78% (*Z*:*E* = 96:4)) as a colorless oil. The regiochemistry was determined by the H–F coupling constants.

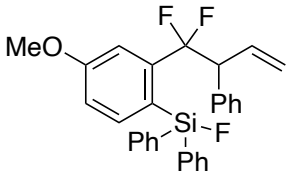
According to the procedure for preparing (*Z*)-1-bromo-2-(1-fluorobuta-1,3-dien-1-yl)-4-methoxybenzene (**10a**), (*Z*)-3-(4-bromo-3-(1-fluorobuta-1,3-dien-1-yl)phenyl)thiophene (**10b**) (38.3 mg, 0.124 mmol, 69% (*Z*:*E* = 88:12)), (*Z*)-4-bromo-3-(1-fluorobuta-1,3-dien-1-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (**10c**) (46.0 mg, 0.124 mmol, 78% (*Z*:*E* = 91:9)), and (*Z*)-1,4-dibromo-2-(1-fluorobuta-1,3-dien-1-yl)benzene (**10d**) (17.2 mg, 56.1 μmol, 71% (*Z*:*E* = 93:7)) were prepared from the corresponding benzyl fluorides **9**.

*Examinations to check the stability of 1-aryl-1-fluoro-1,3-butadienes **10** and **11***

We checked the stability of 1,3-butadiene **10a** under a variety of conditions. Complete decomposition was observed when **10a** was placed under air at room temperature for 24 h or treated with 1 M aqueous HCl in THF at room temperature for 24 h. When **10a** was treated with saturated aqueous $NaHCO_3$ in THF at room temperature for 24 h, 21% of **10a** was decomposed. When **10a** was treated with silica-gel at room temperature for 24 h, 72% of **10a** was decomposed. In further purification of 1-aryl-1-fluoro-1,3-butadienes **10c**, **10d**, and **11**, a small amount of impurities were not removed by PTLC or silica-gel column chromatograph.

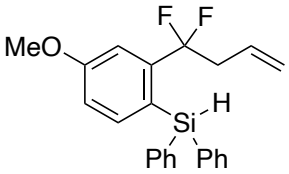
Characterization Data of New Compounds

(2-(1,1-Difluoro-2-phenylbut-3-en-1-yl)-4-methoxyphenyl)fluorodiphenylsilane (**5e**)



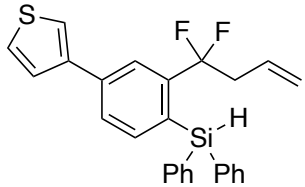
Colorless oil; TLC R_f 0.38 (*n*-hexane/CH_2Cl_2 = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45–3.57 (m, 1H), 3.59 (s, 3H), 4.66 (d, 1H, J = 17.1 Hz), 5.01 (d, 1H, J = 10.2 Hz), 5.93–6.04 (m, 1H), 6.49 (d, 1H, J = 2.0 Hz), 6.90 (dd, 1H, J = 8.3, 2.4 Hz), 6.93–6.99 (br, 2H), 7.16–7.22 (m, 3H), 7.37–7.44 (AA'BB'C, 4H), 7.45–7.50 (AA'BB'C, 2H), 7.58–7.63 (m, 2H), 7.64–7.68 (m, 2H), 7.74 (d, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.1, 58.1 (t, $J_{C–F}$ = 25.7 Hz), 113.6 (t, $J_{C–F}$ = 7.3 Hz), 114.9, 119.6, 123.4 (t, $J_{C–F}$ = 250.4 Hz), 127.3, 127.9 (d, $J_{C–F}$ = 3.6 Hz), 128.2, 129.5, 130.5 (d, $J_{C–F}$ = 3.4 Hz), 133.0 (d, $J_{C–F}$ = 6.5 Hz), 133.6 (d, $J_{C–F}$ = 17.7 Hz), 134.0 (dd, $J_{C–F}$ = 18.4, 3.3 Hz), 135.3, 136.9 (d, $J_{C–F}$ = 5.1 Hz), 138.3 (d, $J_{C–F}$ = 6.6 Hz), 144.3 (t, $J_{C–F}$ = 26.4 Hz), 160.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –91.6–(–92.5) (m, 1F), –94.5–(–95.5) (m, 1F), 160.1 (t, 1F, J = 7.1 Hz); IR (KBr, cm^{-1}) 503, 700, 716, 745, 1063, 1123, 1244, 1265, 1306, 1429, 1601; HRMS (ESI) *m/z* 475.1705 ([M + H]$^+$, $C_{29}H_{26}F_3OSi^+$ requires 475.1700).

4,4-Difluoro-4-(5-methoxy-2-(diphenylsilyl)phenyl) -1-butene (**7a**)



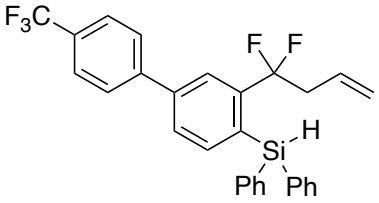
Colorless oil; TLC R_f 0.34 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.72 (dt, 2H, J = 7.0 Hz, $J_{H–F}$ = 16.6 Hz), 3.84 (s, 3H), 4.97 (d, 1H, J = 17.3 Hz), 5.11 (d, 1H, J = 10.2 Hz), 5.58 (t, 1H, $J_{H–F}$ = 10.2 Hz), 5.63–5.73 (m, 1H), 6.88 (dd, 1H, J = 8.3, 1.8 Hz), 7.06 (s, 1H), 7.30–7.45 (m, 7H), 7.47–7.53 (AA´BB´C, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 44.2 (t, $J_{C–F}$ = 27.8 Hz), 55.2, 112.8 (t, $J_{C–F}$ = 5.7 Hz), 114.0, 119.4, 120.9 (t, $J_{C–F}$ = 3.7 Hz), 122.9 (t, $J_{C–F}$ = 254.5 Hz), 127.9, 128.9 (t, $J_{C–F}$ = 4.3 Hz), 129.5, 134.3, 135.8, 139.9, 145.3 (t, $J_{C–F}$ = 25.9 Hz), 160.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –90.3 (dt, 2F, $J_{F–H}$ = 16.6, 10.2 Hz); IR (KBr, cm^{-1}) 698, 737, 795, 855, 1030, 1113, 1159, 1265, 1301, 1599; HRMS (ESI) *m/z* 403.1304 ([M + Na]$^+$, $C_{23}H_{22}F_2NaOSi^+$ requires 403.1300).

(2-(1,1-Difluorobut-3-en-1-yl)-4-(thiophen-3-yl)phenyl)diphenylsilane (**7b**)



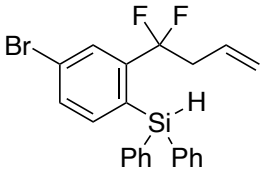
Pale yellow oil; TLC R_f 0.39 (*n*-hexane/CH_2Cl_2 = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.72 (dt, 2H, J = 7.1 Hz, $J_{H–F}$ = 16.6 Hz), 4.97 (dd, 1H, J = 17.1, 1.4 Hz,), 5.11 (d, 1H, J = 10.2 Hz), 5.60–5.75 (m, 2H), 7.22 (dd, 1H, J = 4.8, 1.6 Hz), 7.32–7.45 (m, 8H), 7.52–7.58 (m, 5H), 7.66–7.71 (m, 1H), 7.78 (d, 1H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 44.2 (t, $J_{C–F}$ = 28.2 Hz), 120.5, 121.1, 123.2 (t, $J_{C–F}$ = 350.8 Hz), 126.0, 126.5, 126.8 (t, $J_{C–F}$ = 7.5 Hz), 127.4, 128.0, 128.9 (t, $J_{C–F}$ = 3.9 Hz), 129.7, 131.1 (t, $J_{C–F}$ = 3.5 Hz), 133.7, 135.8, 135.9, 136.2, 141.1, 142.0 (t, $J_{C–F}$ = 25.6 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –89.6 (dt, 2F, $J_{F–H}$ = 16.6, 10.2 Hz); IR (KBr, cm^{-1}) 482, 698, 735, 806, 841, 993, 1067, 1107, 1161, 1300, 1429; HRMS (ESI) *m/z* 455.1072 ([M + Na]$^+$, $C_{26}H_{22}F_2NaSSi^+$ requires 455.1072).

(3-(1,1-Difluorobut-3-en-1-yl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)diphenylsilane (**7c**)



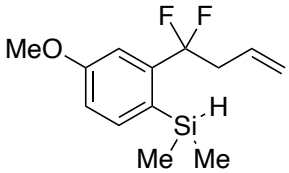
Colorless oil; TLC R_f 0.27 (*n*-hexane/CH_2Cl_2 = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.78 (dt, 2H, *J* = 7.0 Hz, $J_{H–F}$ = 16.5 Hz), 5.00 (dd, 1H, *J* = 17.1, 1.2 Hz), 5.14 (d, 1H, *J* = 10.2 Hz), 5.60–5.79 (m, 2H), 7.35–7.40 (AA'BB'C, 4H), 7.41–7.46 (AA′BB′C, 2H), 7.50–7.60 (m, 5H), 7.64 (d, 1H, *J* = 7.8 Hz), 7.68–7.72 (br, 4H), 7.73 (d, 1H, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 44.3 (t, $J_{C–F}$ = 27.8 Hz), 120.7, 123.1 (t, $J_{C–F}$ = 257.7 Hz), 125.0 (t, $J_{C–F}$ = 7.2 Hz), 125.9 (q, $J_{C–F}$ = 3.7 Hz), 127.5, 128.0, 128.7 (t, $J_{C–F}$ = 4.1 Hz), 129.1 (q, $J_{C–F}$ = 252.8 Hz), 129.8, 133.6, 135.8, 139.0, 141.0, 143.5, 144.3 (t, $J_{C–F}$ = 26.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.8 (s, 3F), –89.9 (dt, 2F, $J_{F–H}$ = 16.5, 10.2 Hz); IR (KBr, cm^{-1}) 698, 748, 793, 827, 1070, 1113, 1126, 1167, 1265, 1325; HRMS (ESI) *m/z* 517.1381 ([M + Na]$^+$, $C_{29}H_{23}F_5NaSi^+$ requires 517.1381).

(4-Bromo-2-(1,1-difluorobut-3-en-1-yl)phenyl)diphenylsilane (**7d**)



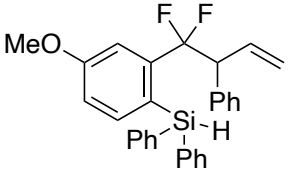
Colorless oil; TLC R_f 0.56 (*n*-hexane/CH_2Cl_2 = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.71 (dt, 2H, *J* = 7.1 Hz, $J_{H–F}$ = 16.8 Hz), 4.98 (dd, 1H, *J* = 17.1, 1.2 Hz), 5.13 (d, 1H, *J* = 10.4 Hz), 5.54–5.73 (m, 2H), 7.34–7.39 (m, 5H), 7.40–7.45 (AA′BB′C, 2H), 7.46–7.52 (m, 5H), 7.66 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 44.1 (t, $J_{C–F}$ = 27.5 Hz), 120.9, 122.3 (t, $J_{C–F}$ = 246.0 Hz), 124.7, 128.0, 128.4 (t, $J_{C–F}$ = 4.2 Hz), 129.4 (t, $J_{C–F}$ = 7.8 Hz), 129.6 (t, $J_{C–F}$ = 3.4 Hz), 129.9, 132.0, 133.2, 135.8, 139.6, 145.3 (t, $J_{C–F}$ = 26.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –90.3 (dt, 2F, $J_{F–H}$ = 16.8, 10.4 Hz); IR (KBr, cm^{-1}) 482, 698, 734, 785, 839, 991, 1028, 1117, 1304, 1427; HRMS (ESI) *m/z* 451.0296 ([M + Na]$^+$, $C_{22}H_{19}BrF_2NaSi^+$ requires 451.0300).

(2-(1,1-Difluorobut-3-en-1-yl)-4-methoxyphenyl)dimethylsilane (**7e**)



Colorless oil; TLC R_f 0.35 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.34 (d, 6H, *J* = 3.6 Hz), 2.90 (dt, 2H, *J* = 7.0 Hz, $J_{H–F}$ = 16.8 Hz), 3.84 (s, 3H), 4.44–4.55 (m, 1H), 5.13–5.26 (m, 2H), 5.83 (dddd, 1H, *J* = 17.1, 10.3, 7.0, 7.0 Hz), 6.93 (dd, 1H, *J* = 8.3, 2.5 Hz), 7.00 (d, 1H, *J* = 2.5 Hz), 7.58 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ −2.1 (t, $J_{C–F}$ = 3.3 Hz), 44.2 (t, $J_{C–F}$ = 28.0 Hz), 55.2, 112.2 (t, $J_{C–F}$ = 7.9 Hz), 114.0, 120.5, 123.0 (t, $J_{C–F}$ = 244.6 Hz), 125.3 (t, $J_{C–F}$ = 4.0 Hz), 129.1 (t, $J_{C–F}$ = 4.3 Hz), 137.6, 144.1 (t, $J_{C–F}$ = 25.9 Hz), 160.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −90.9 (dt, $J_{C–F}$ = 16.8, 8.3 Hz); IR (KBr, cm^{-1}) 838, 886, 904, 993, 1012, 1033, 1062, 1095, 1158, 1233, 1249, 1302, 1601; HRMS (ESI) *m/z* 535.2094 ([2M + Na]$^+$, $C_{26}H_{36}F_4NaSi_2^+$ requires 535.2088).

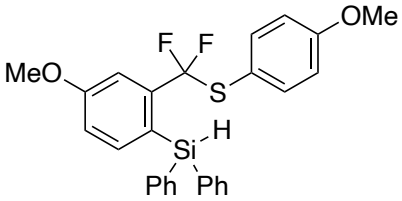
(2-(1,1-Difluoro-2-phenylbut-3-en-1-yl)-4-methoxyphenyl)diphenylsilane (**7f**)



Colorless oil; TLC R_f 0.45 (*n*-hexane/CH_2Cl_2 = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.62 (s, 3H), 3.80–3.94 (m, 1H), 4.88 (d, 1H, *J* = 17.0 Hz), 5.14 (d, 1H, *J* = 10.2 Hz), 5.59 (dd, 1H, *J* = 12.8, 9.0 Hz), 6.11–6.27 (m, 1H), 6.64 (d, 1H, *J* = 2.4 Hz), 6.80 (dd, 1H, *J* = 8.3, 2.4 Hz), 7.02–7.11 (m, 2H), 7.18–7.23 (m, 3H), 7.39–7.44 (m, 7H), 7.46–7.57 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.1, 58.5 (t, $J_{C–F}$ = 25.9 Hz), 113.5 (t, $J_{C–F}$ = 7.8 Hz), 114.6, 119.7, 121.0 (t, $J_{C–F}$ = 3.6 Hz), 123.4 (t, $J_{C–F}$ = 250.7 Hz), 127.3, 127.93, 127.94, 128.2, 129.56, 129.58, 133.4 (t,

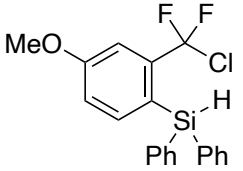
J_{C-F} = 3.4 Hz), 135.8, 135.9, 139.4, 144.2 (t, J_{C-F} = 26.1 Hz), 160.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –92.6–(–93.5) (m, 1F), –94.9–(–95.8) (m, 1F); IR (KBr, cm^{-1}) 698, 737, 810, 1030, 1063, 1109, 1242, 1302, 1427, 1599; HRMS (ESI) *m/z* 479.1612 ($[M + Na]^+$, $C_{29}H_{26}F_2NaOSi^+$ requires 479.1613).

(2-(Difluoro((4-methoxyphenyl)thio)methyl)-4-methoxyphenyl)diphenylsilane (**7g**)



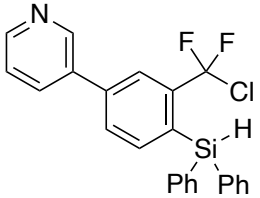
Colorless solid; Mp 121–123 °C; TLC R_f 0.17 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.81 (s, 3H), 3.82 (s, 3H), 5.80 (t, 1H, J_{H-F} = 10.1 Hz), 6.82–6.87 (AA´BB´, 2H), 6.90 (dd, 1H, *J* = 8.3, 2.5 Hz,), 7.18 (d, 1H, *J* = 2.5 Hz), 7.31–7.38 (AA´BB´C, 4H), 7.38–7.43 (m, 5H), 7.38–7.43 (AA´BB´C, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.29, 55.33, 112.5 (t, J_{C-F} = 5.4 Hz), 114.4, 115.3, 118.0, 121.8, 127.8, 128.2 (t, J_{C-F} = 280.4 Hz), 129.5, 134.4, 135.9, 138.3, 139.6, 143.6 (t, J_{C-F} = 24.5 Hz), 160.6, 161.2;^{19}F NMR ($CDCl_3$, 376 MHz) δ –68.5 (d, 2F, J_{F-H} = 10.1 Hz); IR (KBr, cm^{-1}) 698, 735, 787, 829, 1030, 1061, 1250, 1290, 1302, 1493, 1591; HRMS (ESI) *m/z* 501.1122 ($[M + Na]^+$, $C_{27}H_{24}F_2NaO_2SSi^+$ requires 501.1127).

(2-(Chlorodifluoromethyl)-4-methoxyphenyl)diphenylsilane (**7h**)



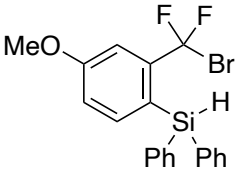
Colorless oil; TLC R_f 0.52 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.85 (s, 3H), 5.70 (t, 1H, J_{H-F} = 9.5 Hz), 6.93 (dd, 1H, *J* = 8.4, 2.5 Hz), 7.26–7.28 (br, 1H), 7.33–7.38 (AA'BB'C, 4H), 7.39–7.44 (m, 3H), 7.48–7.53 (AA´BB´C, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.4, 111.8 (t, J_{C-F} = 6.8 Hz), 115.5, 121.3 (t, J_{C-F} = 2.7 Hz), 126.6 (t, J_{C-F} = 292.0 Hz), 128.0, 129.7, 133.5, 135.8, 139.9, 143.9 (t, J_{C-F} = 25.7 Hz), 160.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –45.9 (d, 2F, J_{F-H} = 9.5 Hz); IR (KBr, cm^{-1}) 698, 746, 764, 791, 827, 941, 1042, 1107, 1277, 1304, 1599; HRMS (ESI) *m/z* 397.0596 ($[M + Na]^+$, $C_{20}H_{17}ClF_2NaOSi^+$ requires 397.0597).

3-(3-(Chlorodifluoromethyl)-4-(diphenylsilyl)phenyl)pyridine (**7i**)



Colorless oil; TLC R_f 0.58 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.81 (t, 1H, *J* = 7.0 Hz, J_{H-F} = 9.4 Hz), 7.29–7.48 (m, 7H), 7.52–7.60 (AA´BB´C, 4H), 7.68–7.78 (m, 3H), 7.85 (d, 1H, *J* = 8.1 Hz), 8.59 (dd, 1H, *J* = 4.8, 1.8 Hz), 8.68 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 123.7, 126.0 (t, J_{C-F} = 6.4 Hz), 126.8 (t, J_{C-F} = 291.5 Hz), 128.1, 128.5, 130.1, 132.5 (t, J_{C-F} = 2.8 Hz), 132.6, 134.4, 135.1, 135.8, 136.8, 139.5, 142.0 (t, J_{C-F} = 25.9 Hz), 148.2, 149.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –45.7 (d, 2F, J_{F-H} = 9.4 Hz); IR (KBr, cm^{-1}) 700, 746, 787, 802, 841, 907, 1038, 1111, 1265, 1429; HRMS (ESI) *m/z* 422.0937 ($[M + H]^+$, $C_{24}H_{19}ClF_2NSi^+$ requires 422.0938).

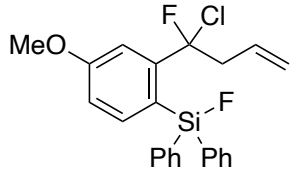
(2-(Bromodifluoromethyl)-4-methoxyphenyl)diphenylsilane (**7j**)



Colorless oil; TLC R_f 0.56 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.86 (s, 3H), 5.75 (t, 1H, J_{H-F} = 9.9 Hz), 6.93 (dd, 1H, *J* = 8.3, 2.5 Hz), 7.24 (d, 1H, *J* = 2.5 Hz), 7.33–7.45 (m, 7H), 7.48–7.54 (AA'BB'C, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.4, 111.4 (t, J_{C-F} = 6.9 Hz), 115.6, 118.3 (t, J_{C-F} = 306.0 Hz), 120.9 (t, J_{C-F} = 2.6 Hz), 128.0, 129.7, 133.4, 135.8, 139.9, 145.7 (t, J_{C-F} = 23.0 Hz), 160.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –

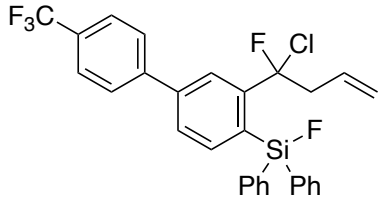
40.9 (d, 2F, $J_{F–H}$ = 9.9 Hz); IR (KBr, cm^{-1}) 698, 735, 787, 812, 924, 1038, 1101, 1225, 1304, 1427, 1599; HRMS (ESI) *m/z* 441.0095 ([M + Na]$^+$, $C_{20}H_{17}BrF_2NaOSi^+$ requires 441.0092).

4-Chloro-4-fluoro-4-(5-methoxy-2-(diphenylfluorosilyl)phenyl)-1-butene (**8a**)



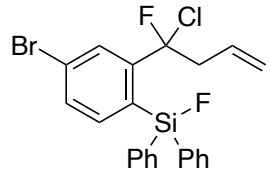
Colorless oil; TLC R_f 0.30 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.68 (ddd, 1H, *J* = 15.6, 7.1 Hz, J_{H-F} = 15.6 Hz), 2.80 (ddd, 1H, *J* = 15.6, 7.1 Hz, J_{H-F} = 15.6 Hz), 3.86 (s, 3H), 4.75 (d, 1H, *J* = 17.1 Hz), 4.95 (d, 1H, *J* = 10.1 Hz), 5.37–5.48 (m, 1H), 7.00 (dd, 1H, *J* = 8.5, 2.4 Hz), 7.07 (s, 1H), 7.31–7.47 (m, 6H), 7.56–7.70 (AA′BB′C, 2H), 7.63–7.69 (AA′BB′C, 2H), 7.92 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 49.7 (d, $J_{C–F}$ = 24.2 Hz), 55.3, 113.6 (d, $J_{C–F}$ = 6.4 Hz), 113.8, 115.2 (d, $J_{C–F}$ = 244.7 Hz), 118.7 (dd, $J_{C–F}$ = 15.3, 5.8 Hz), 120.7, 127.6, 127.7, 129.4 (d, $J_{C–F}$ = 2.8 Hz), 130.2, 130.3, 113.4 (dd, $J_{C–F}$ = 17.5, 5.6 Hz), 134.4 (dd, $J_{C–F}$ = 19.2, 6.4 Hz), 135.0, 135.2, 138.3 (d, $J_{C–F}$ = 8.1 Hz), 149.1 (d, $J_{C–F}$ = 24.7, 2.2 Hz), 161.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –96.7 (ddd, $J_{F–H}$ = 15.6, 15.6 Hz, *J* = 9.6 Hz), –158.4 (d, *J* = 9.6 Hz); IR (KBr, cm^{-1}) 492, 507, 698, 743, 1094, 1123, 1240, 1304, 1429, 1599; HRMS (ESI) *m/z* 437.0910 ([M + Na]$^+$, $C_{23}H_{21}ClF_2NaOSi^+$ requires 437.0910).

(3-(1-Chloro-1-fluorobut-3-en-1-yl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)fluorodiphenylsilane (**8c**)



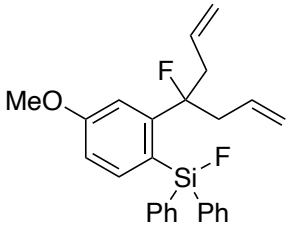
Colorless oil; TLC R_f 0.28 (*n*-hexane/CH_2Cl_2 = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.63–2.90 (m, 2H), 4.77 (d, 1H, *J* = 17.1 Hz), 4.98 (d, 1H, *J* = 10.1 Hz), 5.39–5.51 (m, 1H), 7.36–7.49 (m, 6H), 7.63 (d, 2H, *J* = 7.4 Hz), 7.68–7.75 (m, 8H), 8.14 (d, 1H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 49.8 (d, $J_{C–F}$ = 23.9 Hz), 115.4 (d, $J_{C–F}$ = 244.7 Hz), 120.9, 124.1 (q, $J_{C–F}$ = 272.1 Hz), 125.8 (d, $J_{C–F}$ = 6.0 Hz), 126.0 (q, $J_{C–F}$ = 3.7 Hz), 127.6 (d, $J_{C–F}$ = 7.8 Hz), 127.8 (d, $J_{C–F}$ = 10.7 Hz), 129.3 (d, $J_{C–F}$ = 3.1 Hz), 130.4 (d, $J_{C–F}$ = 10.2 Hz), 132.7 (dd, $J_{C–F}$ = 17.3, 5.6 Hz), 133.8 (dd, $J_{C–F}$ = 19.0, 6.5 Hz), 135.0, 135.2, 137.2, 137.3, 142.2, 143.3, 148.1 (d, $J_{C–F}$ = 24.4, 2.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.8 (s, 3F), –96.7 (ddd, 1F, $J_{F–H}$ = 16.1, 16.1 Hz, *J* = 8.2 Hz), –158.4 (d, 1F, *J* = 8.2 Hz); IR (KBr, cm^{-1}) 509, 698, 718, 741, 827, 1070, 1115, 1123, 1169, 1325, 1429; HRMS (ESI) *m/z* 551.0992 ([M + Na]$^+$, $C_{29}H_{22}ClF_5NaSi^+$ requires 551.0992).

(4-Bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)phenyl)fluorodiphenylsilane (**8d**)



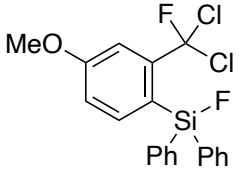
Colorless oil; TLC R_f 0.55 (*n*-hexane/CH_2Cl_2 = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (ddd, 1H, *J* = 15.5, 7.0 Hz, J_{H-F} = 15.5 Hz), 2.77 (ddd, 1H, *J* = 15.5, 7.0 Hz, J_{H-F} = 15.5 Hz), 4.75 (d, 1H, *J* = 17.1 Hz), 4.96 (d, 1H, *J* = 10.2 Hz), 5.31–5.43 (m, 1H), 7.33–7.49 (m, 6H), 7.55–7.70 (m, 6H), 7.89 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 49.6 (d, $J_{C–F}$ = 23.8 Hz), 114.4 (d, $J_{C–F}$ = 245.0 Hz), 121.1, 127.0 (dd, $J_{C–F}$ = 15.5, 5.4 Hz), 127.8 (d, $J_{C–F}$ = 10.3 Hz), 129.0 (d, $J_{C–F}$ = 2.9 Hz), 130.0 (d, $J_{C–F}$ = 6.0 Hz), 130.6 (d, $J_{C–F}$ = 15.8 Hz), 132.0, 132.4 (dd, $J_{C–F}$ = 17.4, 6.2 Hz), 133.4 (dd, $J_{C–F}$ = 19.1, 6.8 Hz), 135.1 (d, $J_{C–F}$ = 24.2 Hz), 137.9 (d, $J_{C–F}$ = 8.6 Hz), 149.1 (d, $J_{C–F}$ = 24.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –97.5 (ddd, $J_{F–H}$ = 15.5, 15.5 Hz, *J* = 8.2 Hz), –158.4 (d, *J* = 8.2 Hz); IR (KBr, cm^{-1}) 513, 565, 698, 716, 741, 822, 854, 1090, 1123, 1429, 1576; HRMS (ESI) *m/z* 484.9910 ([M + Na]$^+$, $C_{22}H_{18}BrClF_2NaSi^+$ requires 484.9910).

Fluoro(2-(4-fluorohepta-1,6-dien-4-yl)-4-methoxyphenyl)diphenylsilane (**8e**)



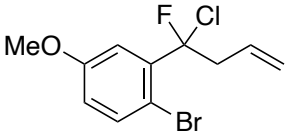
Colorless oil; TLC R_f 0.25 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36–2.48 (m, 4H), 3.85 (s, 3H), 4.80–4.97 (m, 4H), 5.35–5.48 (m, 2H), 6.60–6.65 (br, 1H), 6.93 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.31–7.37 (AA'BB'C, 4H), 7.38–7.43 (AA'BB'C, 2H), 7.61–7.68 (AA'BB'C, 4H), 8.02 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 44.3 (d, $J_{C–F}$ = 23.0 Hz), 55.2, 102.4 (d, $J_{C–F}$ = 176.3 Hz), 111.3, 112.2 (d, $J_{C–F}$ = 7.6 Hz), 119.1, 127.4, 129.9, 131.7 (d, $J_{C–F}$ = 4.2 Hz), 135.11, 135.13, 135.2, 138.8 (d, $J_{C–F}$ = 8.2 Hz), 151.3 (dd, $J_{C–F}$ = 23.7, 2.6 Hz), 161.2 (d, J_{C-F} = 2.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –140.3 (td, $J_{F–H}$ = 23.4 Hz, *J* = 8.8 Hz), –156.2 (d, *J* = 8.8 Hz); IR (KBr, cm^{-1}) 500, 517, 698, 718, 743, 806, 1123, 1233, 1429, 1597; HRMS (ESI) *m/z* 443.1615 ([M + Na]$^+$, $C_{26}H_{26}F_2NaOSi^+$ requires 443.1613).

Fluoro(2-(dichlorofluoromethyl)-4-methoxyphenyl)diphenylsilane (**8g**)



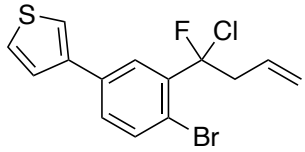
Colorless oil; TLC R_f 0.22 (*n*-hexane/CH_2Cl_2 = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.90 (s, 3H), 7.02 (dd, 1H, *J* = 8.5, 2.5 Hz), 7.35–7.42 (m, 5H), 7.44–7.50 (AA'BB'C, 2H), 7.57–7.62 (AA'BB'C, 4H),7.77 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 55.5, 113.9 (d, $J_{C–F}$ = 5.5 Hz), 115.4, 116.6 (d, $J_{C–F}$ = 245 Hz), 117.9, 127.8, 133.0 (dd, $J_{C–F}$ = 17.9, 4.6 Hz), 130.6, 135.0, 138.4 (d, $J_{C–F}$ = 7.1 Hz), 149.1 (d, $J_{C–F}$ = 26.4 Hz), 161.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –49.7 (d, *J* = 14.5 Hz), –159.8 (d, *J* = 14.5 Hz); IR (KBr, cm^{-1}) 818, 937, 1056, 1123, 1243, 1266, 1305, 1429, 1601; HRMS (ESI) *m/z* 431.0220 ([M + Na]$^+$, $C_{20}H_{16}Cl_2F_2NaOSi^+$ requires 431.0213).

1-Bromo-2-(1-chloro-1-fluorobut-3-en-1-yl)-4-methoxybenzene (**9a**)



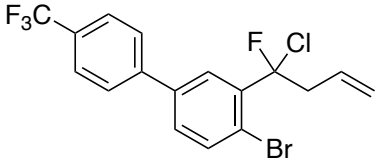
Colorless oil; TLC R_f 0.52 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.34–3.47 (m, 1H), 3.52–3.67 (m, 1H), 3.81 (s, 3H), 5.09–5.24 (m, 2H), 5.61–5.75 (m, 1H), 6.77 (dd, 1H, *J* = 8.7, 3.1 Hz), 7.21 (d, 1H, *J* = 3.1 Hz), 7.53 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 46.1 (d, $J_{C–F}$ = 23.6 Hz), 55.6, 111.6 (d, $J_{C–F}$ = 245.4 Hz), 113.1, 113.3, 116.0, 120.4, 128.9 (d, $J_{C–F}$ = 145.6 Hz), 129.9 (d, $J_{C–F}$ = 2.5 Hz), 136.1 (d, $J_{C–F}$ = 1.7 Hz), 158.7 (d, $J_{C–F}$ = 2.9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –101.5 (dd, $J_{F–H}$ = 26.9, 21.9 Hz); IR (KBr, cm^{-1}) 706, 748, 764, 818, 1024, 1240, 1265, 1292, 1470, 1574; HRMS (ESI) *m/z* 314.9558 ([M + Na]$^+$, $C_{11}H_{11}BrClFNaO^+$ requires 314.9558).

3-(4-Bromo-3-(1-chloro-1-fluorobut-3-en-1-yl)phenyl)thiophene (**9b**)



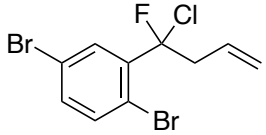
Pale yellow oil; TLC R_f 0.55 (*n*-hexane/CH_2Cl_2 = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (ddd, 1H, *J* = 15.1, 15.1, 7.0 Hz), 3.63 (ddd, 1H, *J* = 15.1, 15.1, 7.0 Hz), 5.09–5.26 (m, 2H), 5.63–5.78 (m, 1H), 7.34–7.53 (m, 4H),7.68 (d, 1H, *J* = 8.2 Hz), 7.88 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 46.3 (d, $J_{C–F}$ = 23.7 Hz), 111.8 (d, $J_{C–F}$ = 245.3 Hz), 117.8 (d, $J_{C–F}$ = 4.4 Hz), 120.5, 121.4, 125.0 (d, $J_{C–F}$ = 17.6 Hz), 126.0, 126.8, 128.3, 129.9 (d, $J_{C–F}$ = 2.3 Hz), 135.2 (d, $J_{C–F}$ = 2.7 Hz), 135.8 (d, $J_{C–F}$ = 1.7 Hz), 139.0 (d, $J_{C–F}$ = 22.9 Hz), 140.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –101.8 (dd, $J_{F–H}$ = 26.4, 22.9 Hz); IR (KBr, cm^{-1}) 687, 760, 779, 822, 847, 870, 928, 988, 1030, 1296, 1418, 1470; HRMS (ESI) *m/z* 344.9510 ([M + H]$^+$, $C_{14}H_{12}BrClFS^+$ requires 344.9510).

4-Bromo-3-(1-chloro-1-fluorobut-3-en-1-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (**9c**)



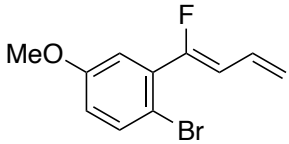
Colorless oil; TLC R_f 0.56 (*n*-hexane/CH_2Cl_2 = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.46 (ddd, 1H, *J* = 15.0, 15.0, 6.9 Hz), 3.65 (ddd, 1H, *J* = 15.0, 15.0, 6.9 Hz), 5.13–5.26 (m, 2H), 5.64–5.78 (m, 1H), 7.45 (dd, 1H, *J* = 8.2, 2.1 Hz), 7.66–7.73 (m, 4H), 7.77 (d, 1H, *J* = 8.2 Hz), 7.88 (d, 1H, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 46.3 (d, $J_{C–F}$ = 23.7 Hz), 111.7 (d, $J_{C–F}$ = 245.2 Hz), 120.7, 124.1 (q, $J_{C–F}$ = 272.1 Hz), 125.8, 125.9 (q, $J_{C–F}$ = 2.6 Hz), 127.4, 129.1, 129.8 (d, $J_{C–F}$ = 2.2 Hz), 130.1 (d, $J_{C–F}$ = 32.4 Hz), 136.1 (d, $J_{C–F}$ = 2.1 Hz), 139.08, 139.10, 139.4 (d, $J_{C–F}$ = 23.0 Hz), 142.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.8 (s, 3F), –101.7 (dd, $J_{F–H}$ = 26.8, 21.8 Hz); IR (KBr, cm^{-1}) 822, 847, 1016, 1028, 1072, 1113, 1126, 1167, 1325, 1469; HRMS (ESI) *m/z* 428.9639 ([M + Na]$^+$, $C_{17}H_{12}BrClF_4Na^+$ requires 428.9639).

1,4-Dibromo-2-(1-chloro-1-fluorobut-3-en-1-yl)benzene (**9d**)



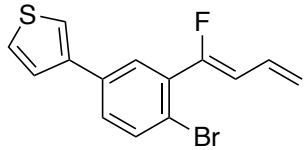
Colorless oil; TLC R_f 0.59 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (ddd, 1H, *J* = 15.0, 15.0, 7.1 Hz), 3.58 (ddd, 1H, *J* = 15.0, 15.0, 7.1 Hz), 5.11–5.26 (m, 2H), 5.59–5.73 (m, 1H), 7.35 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.52 (d, 1H, *J* = 8.4 Hz), 7.79 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 46.0 (d, $J_{C–F}$ = 23.7 Hz), 110.9 (d, $J_{C–F}$ = 245.7 Hz), 118.2 (d, $J_{C–F}$ = 4.2 Hz), 120.9, 121.6 (d, $J_{C–F}$ = 2.8 Hz), 129.5 (d, $J_{C–F}$ = 2.2 Hz), 130.2 (d, $J_{C–F}$ = 18.8 Hz), 133.6, 136.7 (d, $J_{C–F}$ = 1.7 Hz), 140.4 (d, $J_{C–F}$ = 23.7 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –101.8 (dd, $J_{F–H}$ = 27.1, 21.6 Hz); IR (KBr, cm^{-1}) 816, 854, 928, 986, 999, 1034, 1107, 1265, 1281, 1377, 1456; HRMS (ESI) *m/z* 362.8546 ([M + Na]$^+$, $C_{10}H_8Br_2ClFNa^+$ requires 362.8558).

(*Z*)-1-Bromo-2-(1-fluorobuta-1,3-dien-1-yl)-4-methoxybenzene (**10a**)



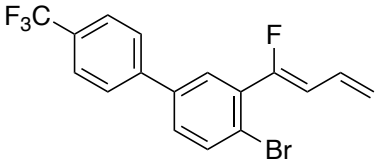
Colorless oil; TLC R_f 0.48 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (s, 3H), 5.19–5.24 (m, 1H), 5.32–5.40 (m, 1H), 6.05 (dd, 1H, *J* = 34.5, 10.8 Hz), 6.73–6.84 (m, 2H), 7.01 (d, 1H, *J* = 3.0 Hz), 7.49 (dd, 1H, *J* = 8.8, 0.6 Hz);^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.6, 112.6 (d, $J_{C–F}$ = 13.1 Hz), 115.3 (d, $J_{C–F}$ = 5.3 Hz), 116.6, 118.5 (d, $J_{C–F}$ = 3.7 Hz), 128.3, 128.4 (d, $J_{C–F}$ = 5.3 Hz), 129.4, 134.5, 155.4 (d, $J_{C–F}$ = 258.9 Hz), 158.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –103.1 (d, $J_{F–H}$ = 34.5 Hz); IR (KBr, cm^{-1}) 750, 763, 1028, 1215, 1242, 1261, 1277, 1288, 1456, 1472; HRMS (ESI) *m/z* 256.9970 ([M + H]$^+$, $C_{11}H_{11}BrFO^+$ requires 256.9972).

(*Z*)-3-(4-Bromo-3-(1-fluorobuta-1,3-dien-1-yl)phenyl)thiophene (**10b**)



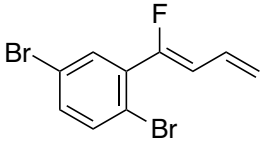
Pale yellow oil; TLC R_f 0.56 (*n*-hexane/CH_2Cl_2 = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (d, 1H, *J* = 10.6 Hz), 5.37 (d, 1H, *J* = 17.2 Hz), 6.06 (dd, 1H, *J* = 34.3, 10.6 Hz), 6.74–6.89 (m, 1H), 7.34–7.38 (m, 1H), 7.39–7.45 (m, 2H), 7.46–7.50 (m, 1H), 7.60–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 112.7 (d, $J_{C–F}$ = 13.3 Hz), 118.6 (d, $J_{C–F}$ = 3.7 Hz), 121.2, 126.0, 126.1 (d, $J_{C–F}$ = 252.3 Hz), 128.1 (d, $J_{C–F}$ = 4.7 Hz), 128.3, 128.4 (d, $J_{C–F}$ = 5.1 Hz), 134.2, 135.2, 140.4, 154.5, 156.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –102.8 (d, $J_{F–H}$ = 34.3 Hz); IR (KBr, cm^{-1}) 704, 741, 779, 905, 1007, 1034, 1069, 1263, 1304, 1418, 1468; HRMS (ESI) *m/z* 308.9736 ([M + H]$^+$, $C_{14}H_{11}BrFS^+$ requires 308.9743).

(*Z*)-4-Bromo-3-(1-fluorobuta-1,3-dien-1-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (**10c**)



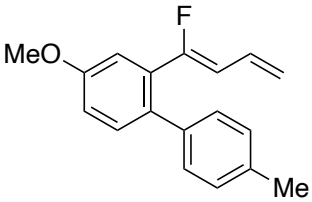
Colorless oil; TLC R_f 0.29 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.25 (d, 1H, J = 10.4 Hz), 5.39 (d, 1H, J = 17.1 Hz), 6.10 (dd, 1H, J = 34.3, 10.4 Hz), 6.74–6.88 (m, 1H), 7.43 (dd, 1H, J = 8.2, 2.1 Hz), 7.64–7.78 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 113.0 (d, $J_{C–F}$ = 13.4 Hz), 118.9 (d, $J_{C–F}$ = 3.7 Hz), 121.3 (d, $J_{C–F}$ = 1.3 Hz), 124.1 (d, $J_{C–F}$ = 272.1 Hz), 124.8 (q, $J_{C–F}$ = 346.4 Hz), 125.9 (q, $J_{C–F}$ = 3.7 Hz), 127.3, 128.3 (d, $J_{C–F}$ = 5.0 Hz), 128.9 (d, $J_{C–F}$ = 4.9 Hz), 129.0, 134.5, 139.1, 142.8, 154.1, 156.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.8 (s, 3F), –103.2 (d, $J_{F–H}$ = 34.3 Hz); IR (KBr, cm^{-1}) 748, 822, 1015, 1072, 1113, 1125, 1167, 1263, 1325, 1470; HRMS (ESI) *m/z* 392.9878 ([M + Na]$^+$, $C_{17}H_{11}BrF_4Na^+$ requires 392.9872).

(*Z*)-1,4-Dibromo-2-(1-fluorobuta-1,3-dien-1-yl)benzene (**10d**)



Colorless oil; TLC R_f 0.57 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.25 (d, 1H, J = 10.7 Hz), 5.38 (d, 1H, J = 17.2 Hz), 6.05 (dd, 1H, J = 34.1, 10.7 Hz), 6.77 (ddd, 1H, J = 17.2, 17.2, 10.7 Hz), 7.33 (dd, 1H, J = 8.4, 2.4 Hz), 7.48 (d, 1H, J = 8.4 Hz), 7.61 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 113.4 (d, $J_{C–F}$ = 12.9 Hz), 117.8 (d, $J_{C–F}$ = 304.6 Hz), 119.3 (d, $J_{C–F}$ = 3.8 Hz), 120.5 (d, $J_{C–F}$ = 151.9 Hz), 128.2 (d, $J_{C–F}$ = 5.0 Hz), 132.8 (d, $J_{C–F}$ = 5.3 Hz), 133.3, 135.2, 153.1, 155.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –104.1 (d, $J_{F–H}$ = 34.1 Hz); IR (KBr, cm^{-1}) 814, 1003, 1024, 1043, 1086, 1279, 1456, 1682, 1697; HRMS (ESI) *m/z* 326.8792 ([M + Na]$^+$, $C_{10}H_7Br_2FNa^+$ requires 326.8791).

(*Z*)-2-(1-Fluorobuta-1,3-dien-1-yl)-4-methoxy-4'-methyl-1,1'-biphenyl (**11**)



Colorless oil; TLC R_f 0.42 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.38 (s, 3H), 3.86 (s, 3H), 5.00–5.14 (m, 2H), 5.50 (dd, 1H, J = 34.7, 11.0 Hz), 6.56–6.68 (m, 1H), 6.95 (dd, 1H, J = 8.5, 2.7 Hz), 7.06 (d, 1H, J = 2.7 Hz), 7.15–7.24 (m, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.2, 55.5, 111.8 (d, $J_{C–F}$ = 13.1 Hz), 113.7 (d, $J_{C–F}$ = 5.9 Hz), 115.0, 117.1 (d, $J_{C–F}$ = 3.6 Hz), 119.8, 128.5, 128.8 (d, $J_{C–F}$ = 5.7 Hz), 129.0, 132.0, 133.3 (d, $J_{C–F}$ = 18.7 Hz), 136.5, 138.1, 157.3 (d, $J_{C–F}$ = 259.5 Hz), 158.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –102.4 (d, $J_{F–H}$ = 34.8 Hz); IR (KBr, cm^{-1}) 814, 1003, 1024, 1045, 1213, 1233, 1288, 1319, 1418, 1487, 1607; HRMS (ESI) *m/z* 291.1155 ([M + H]$^+$, $C_{18}H_{17}FNaO^+$ requires 291.1156).

References for Supporting Information

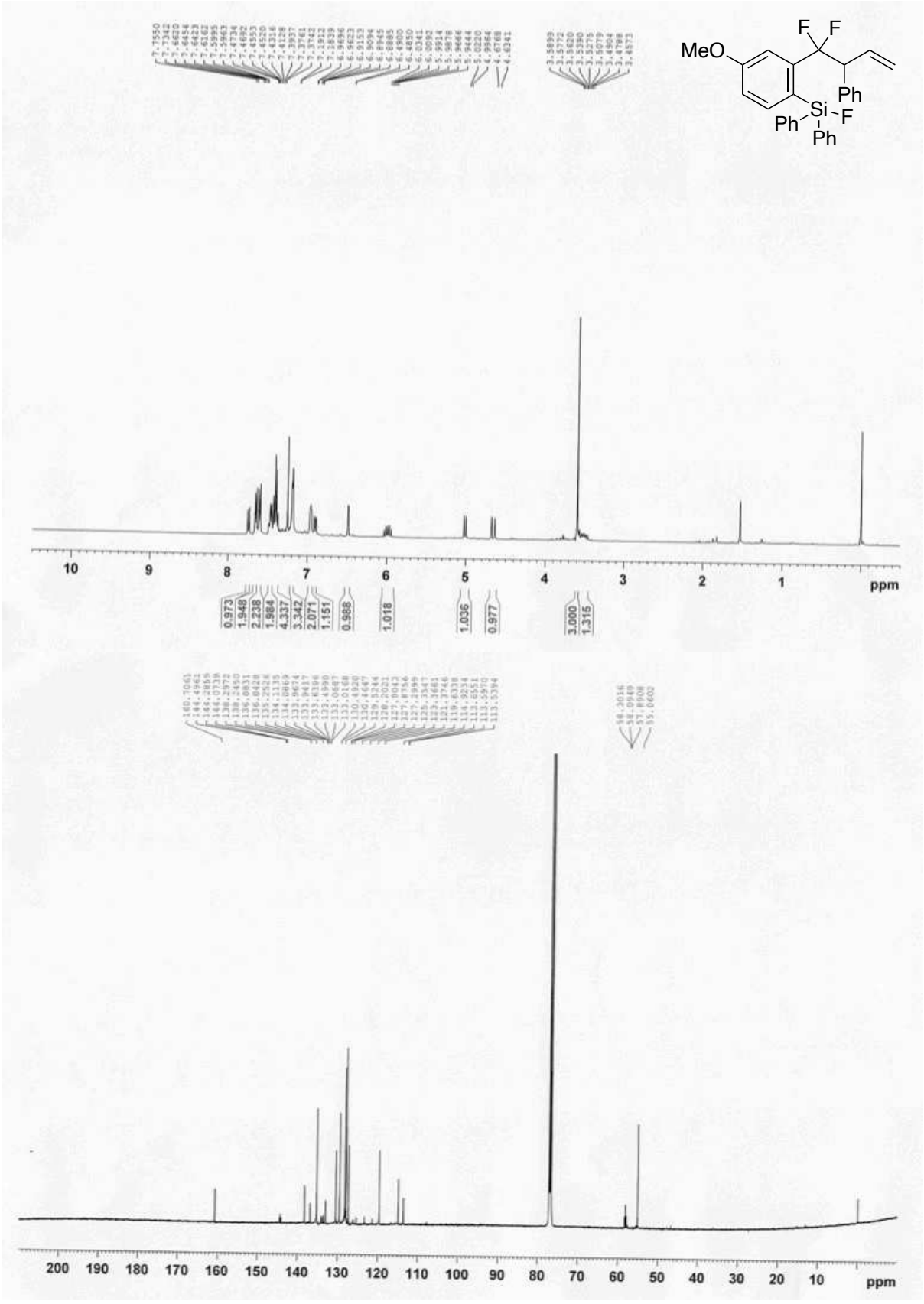
S1 S. Yoshida, K. Shimomori, Y. Kim and T. Hosoya, *Angew. Chem., Int. Ed.*, 2016, **55**, 10406.

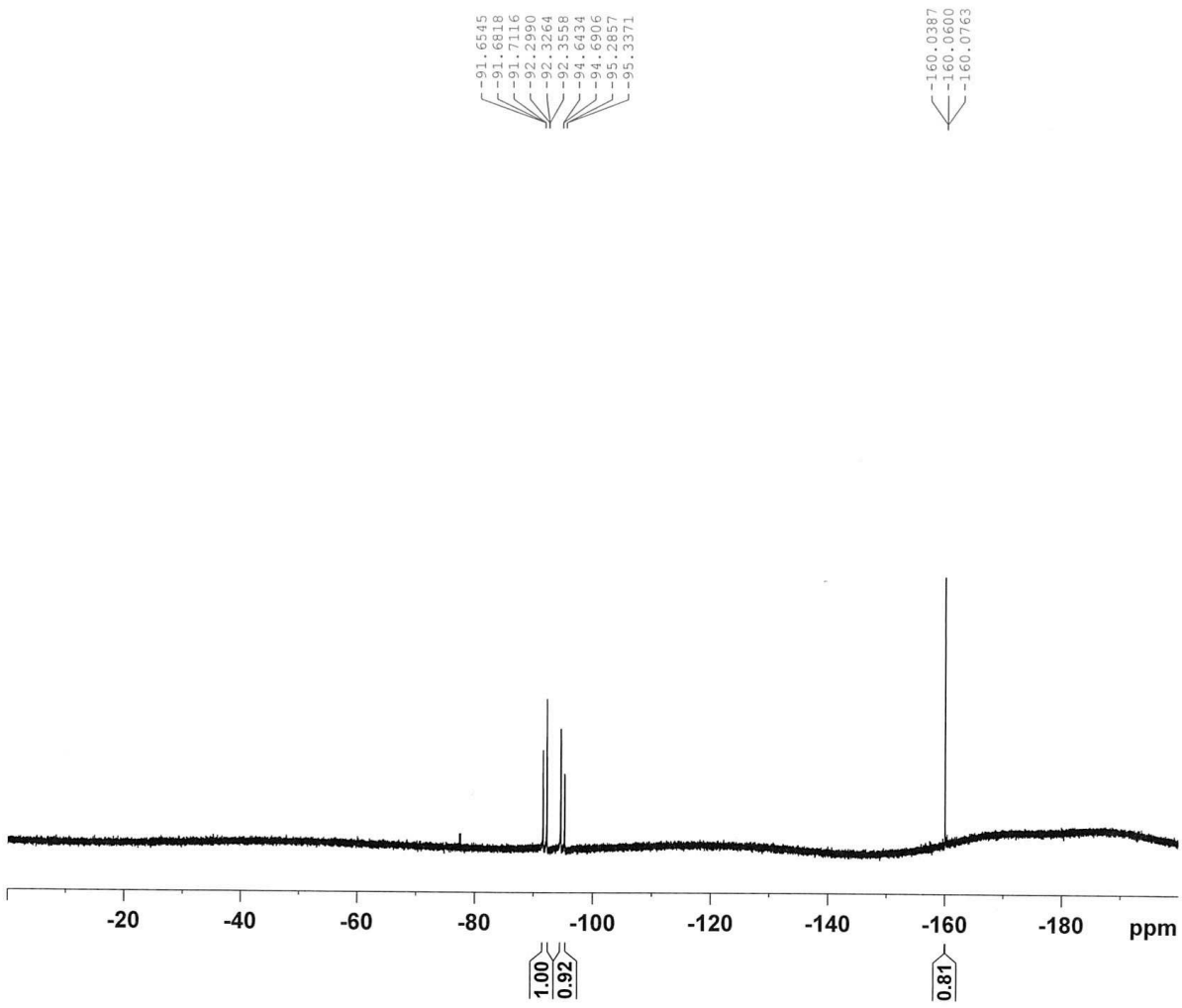
S2 Y. Kim, K. Kanemoto, K. Shimomori, T. Hosoya and S. Yoshida, *Chem. Eur. J.*, 2020, **26**, 6136.

S3 R. Idogawa, Y. Kim, K. Shimomori, T. Hosoya and S. Yoshida, *Org. Lett.*, 2020, **22**, 9292.

^{1}H and ^{13}C NMR Spectra of Compounds

^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **5e** ($CDCl_3$)

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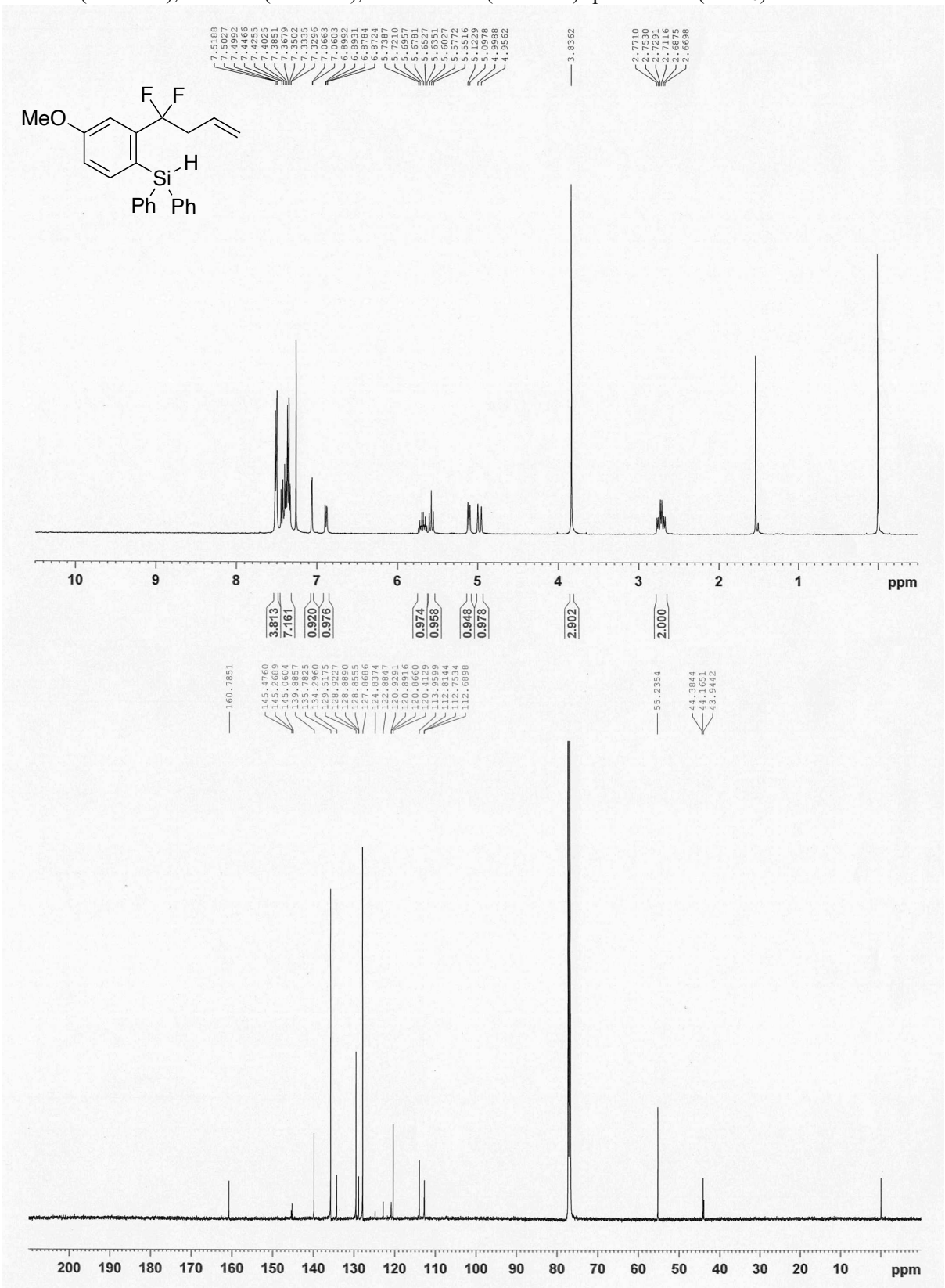
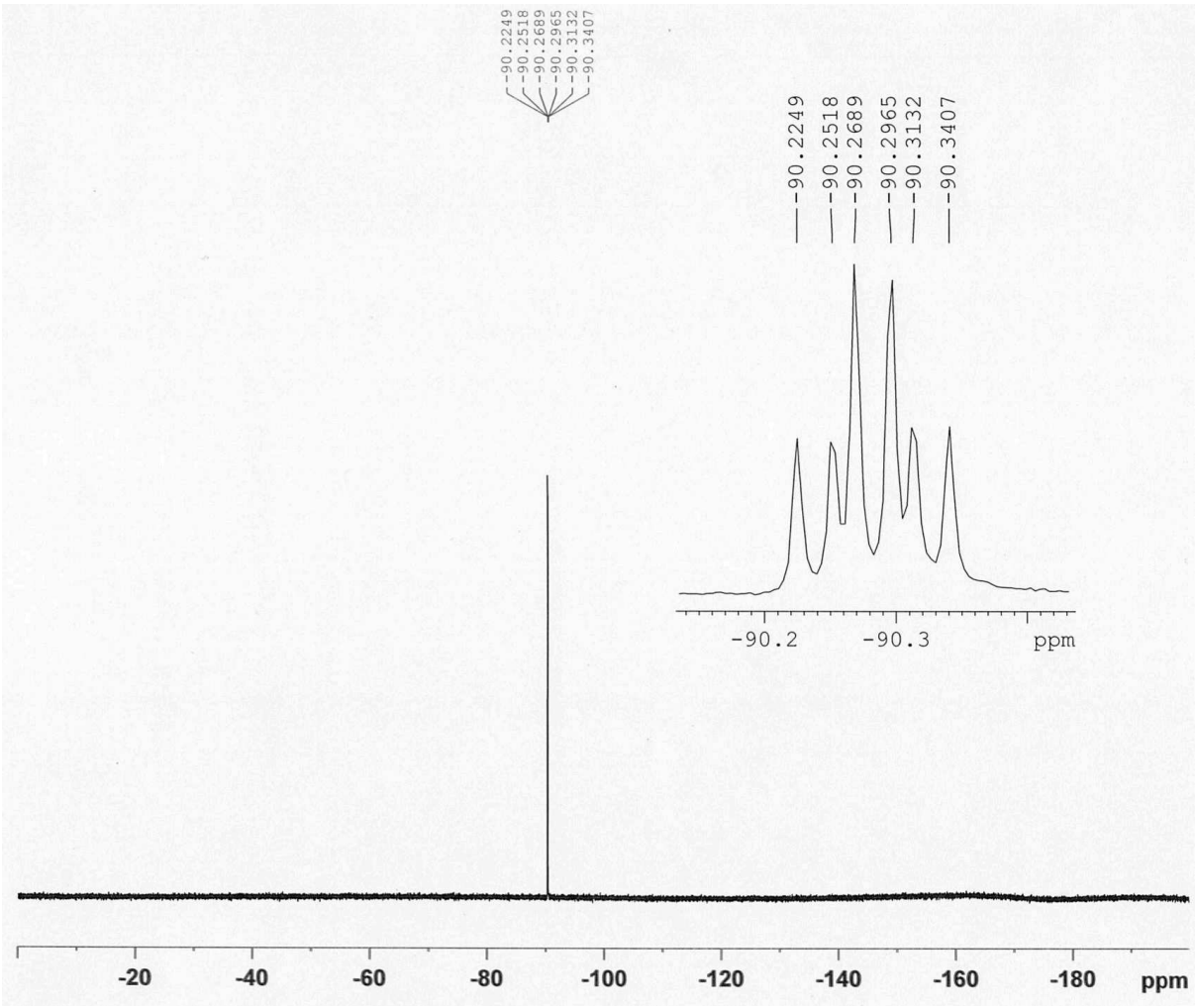
-92.2990
-92.3264
-92.3558
-94.6434
-94.6906
-95.2857
-95.3371
-160.0387
-160.0600
-160.0763
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
1.00
0.92
0.81

^{1}H NMR (500 MHz),^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7a** ($CDCl_3$)

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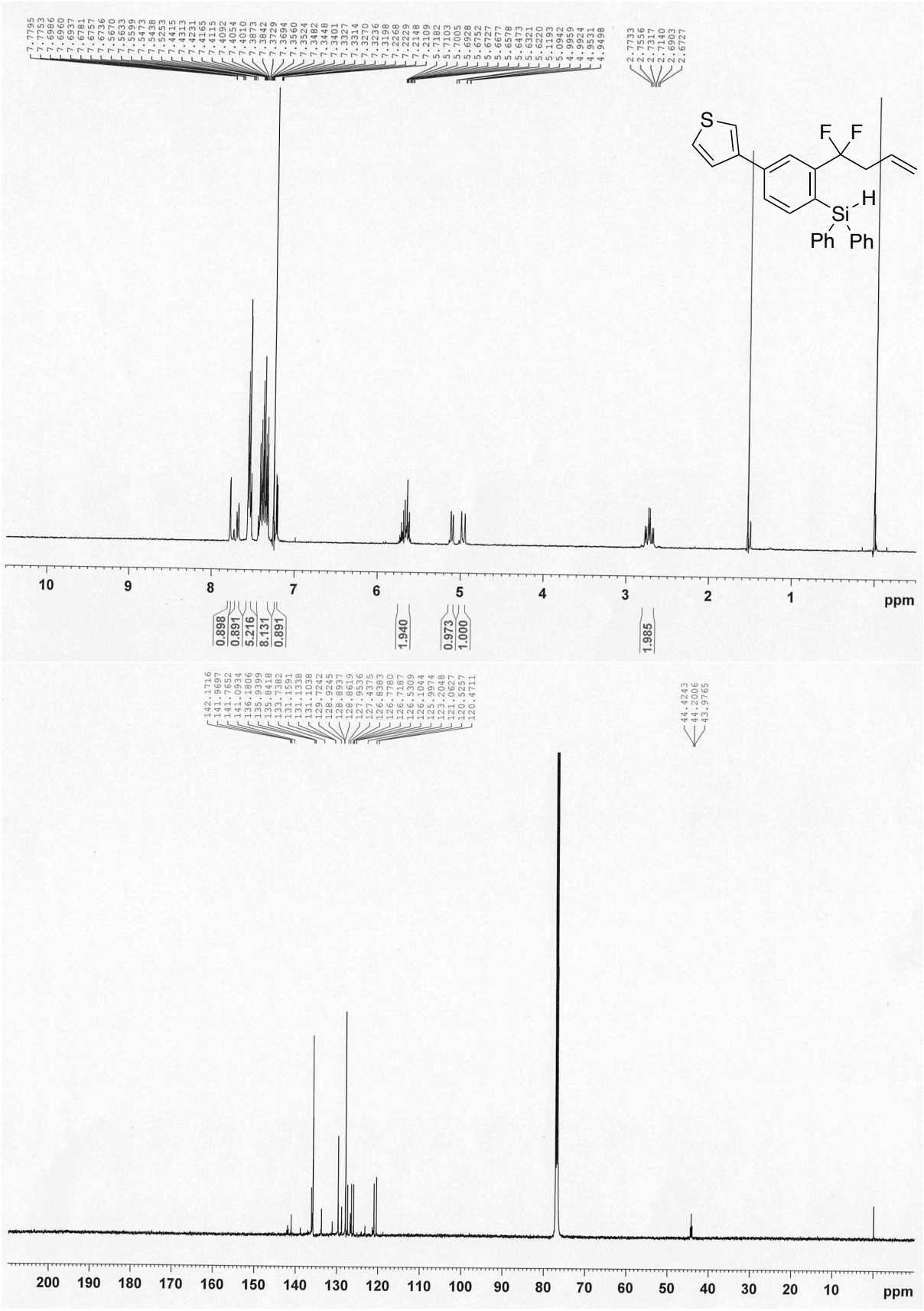
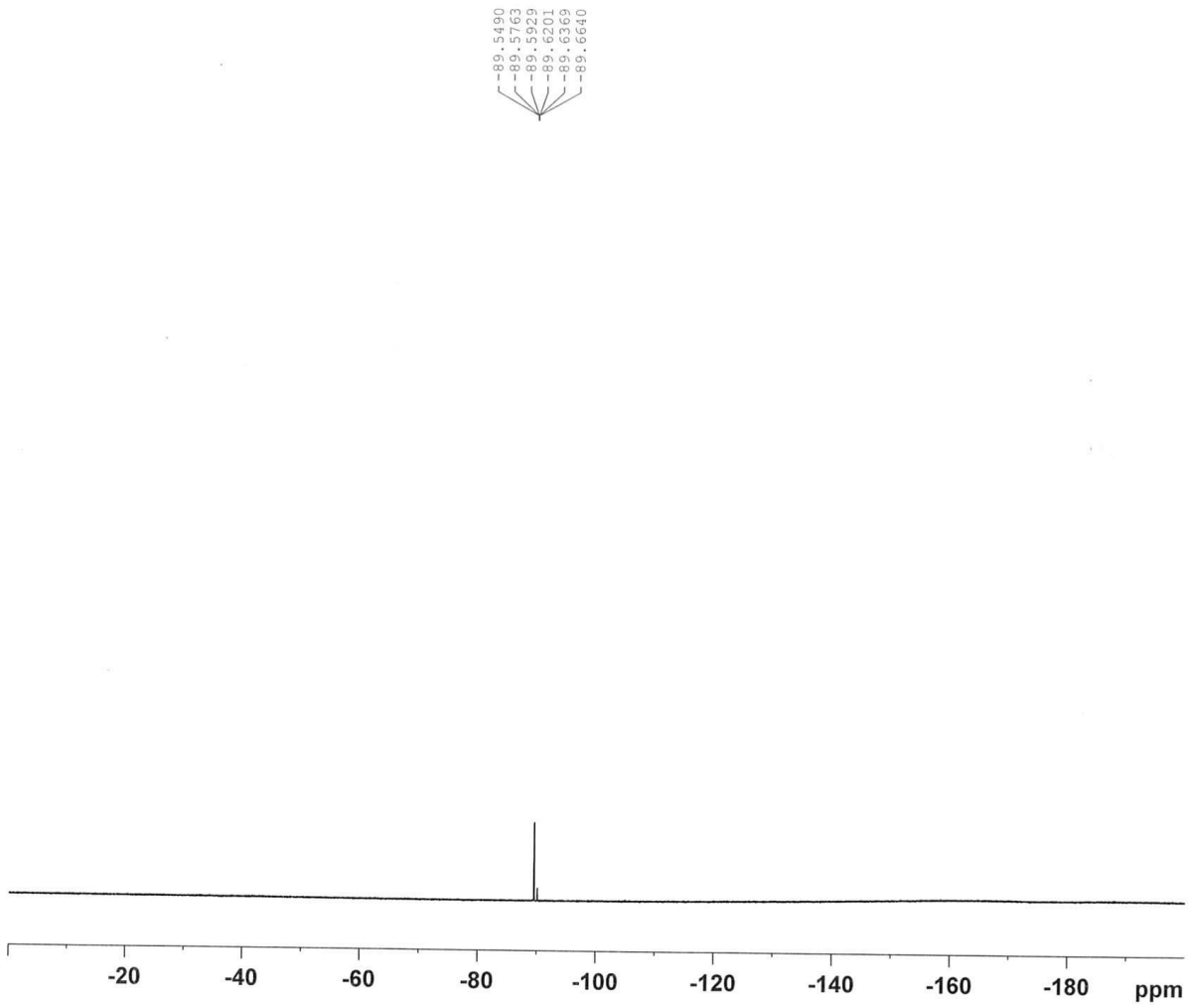
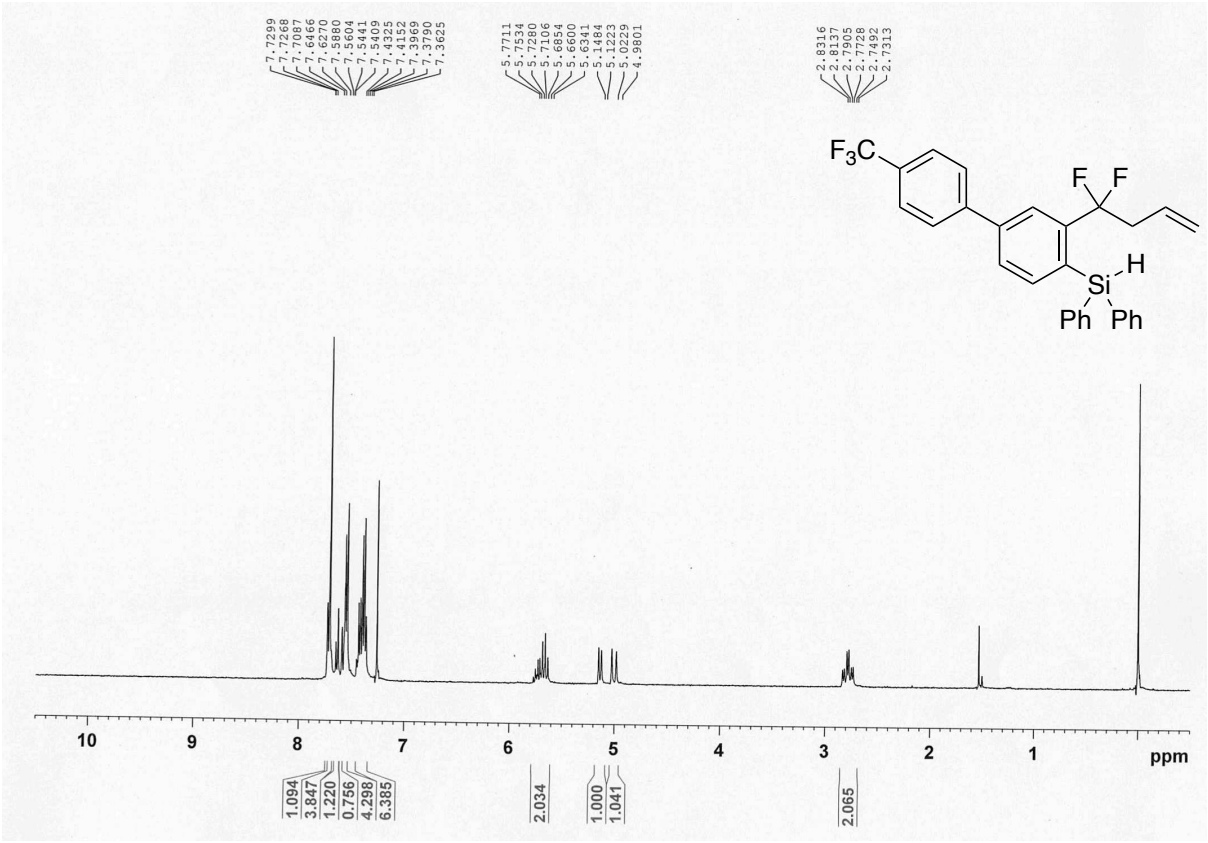
-90.2689
-90.2965
-90.3132
-90.3407
-90.2
-90.3
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

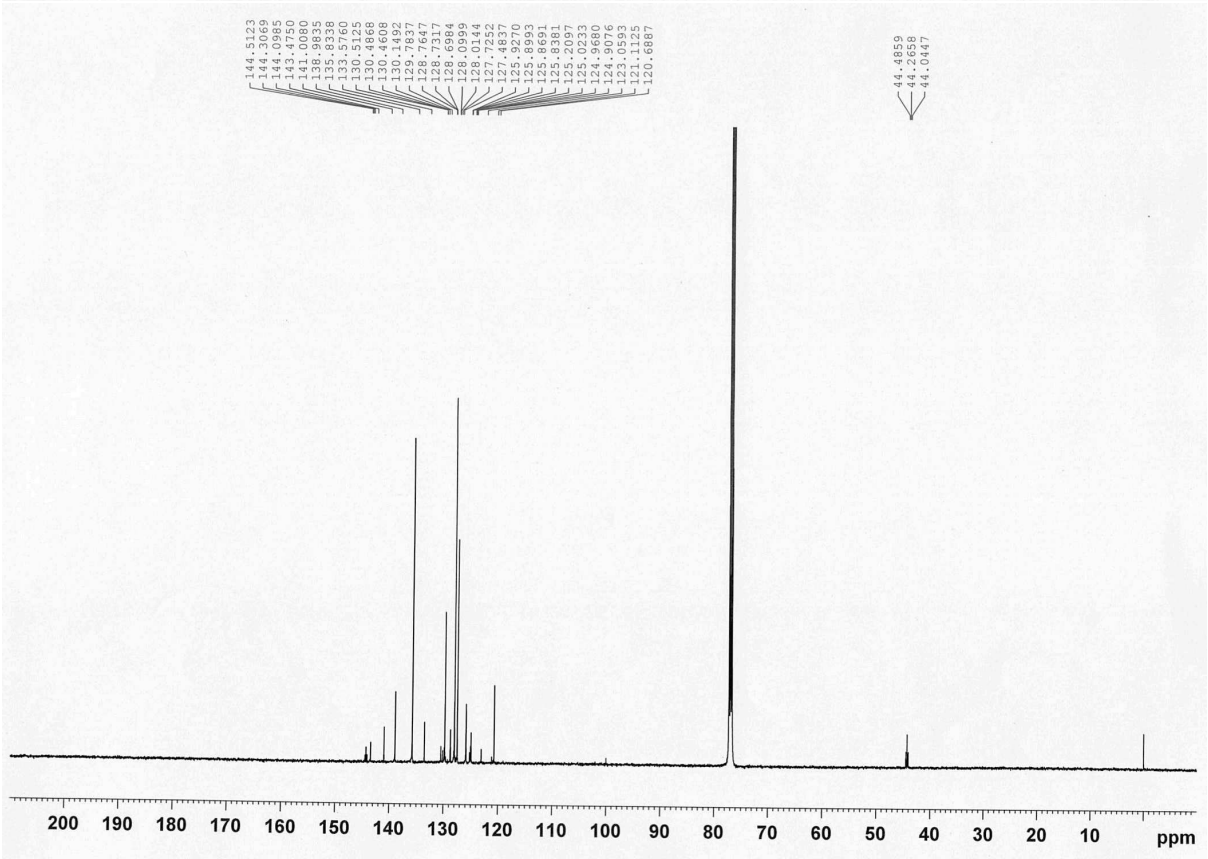
^{1}H NMR (400 MHz),^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7b** ($CDCl_3$)

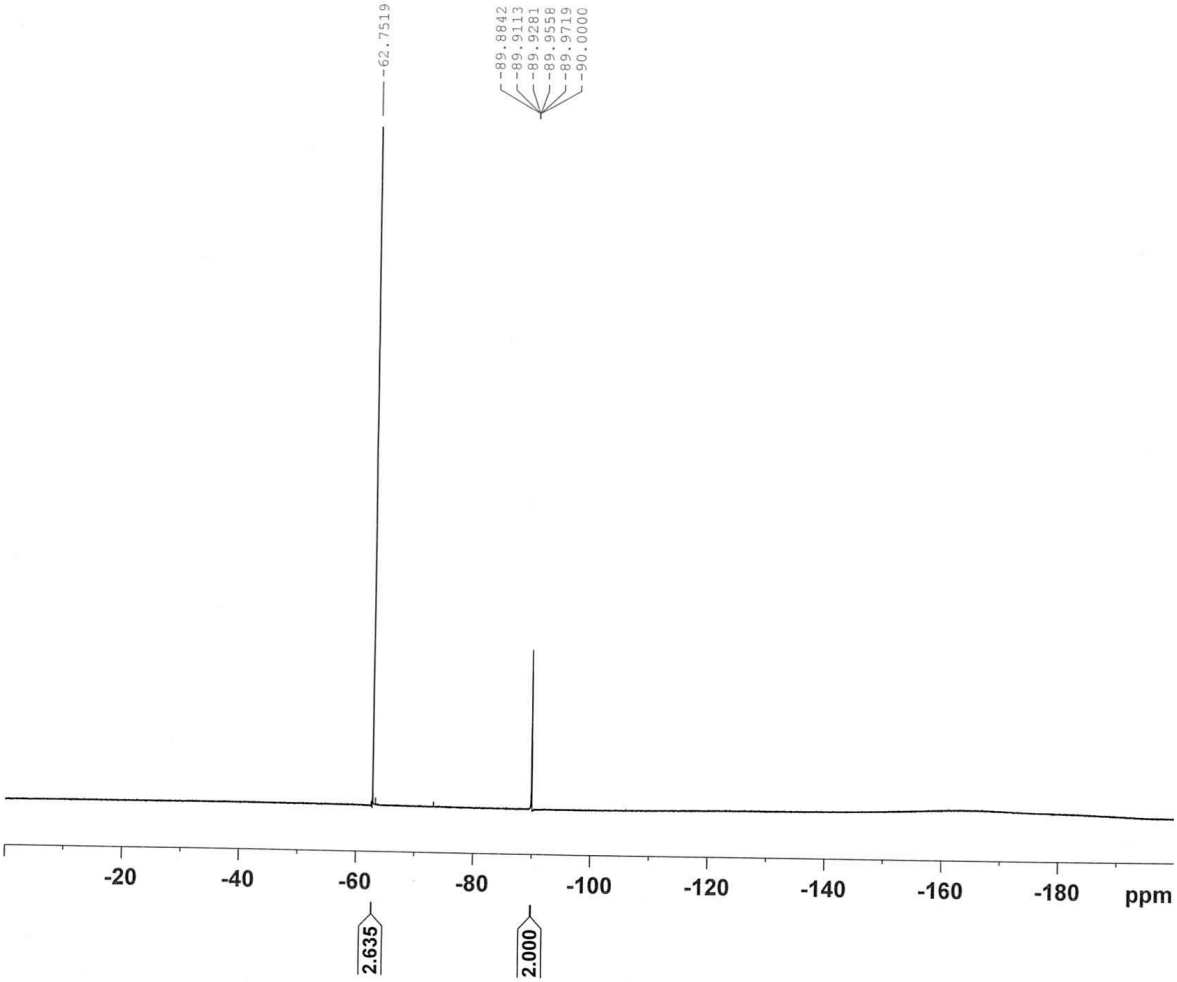



-89.5490
-89.5763
-89.5929
-89.6201
-89.6369
-89.6640
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7c** ($CDCl_3$)



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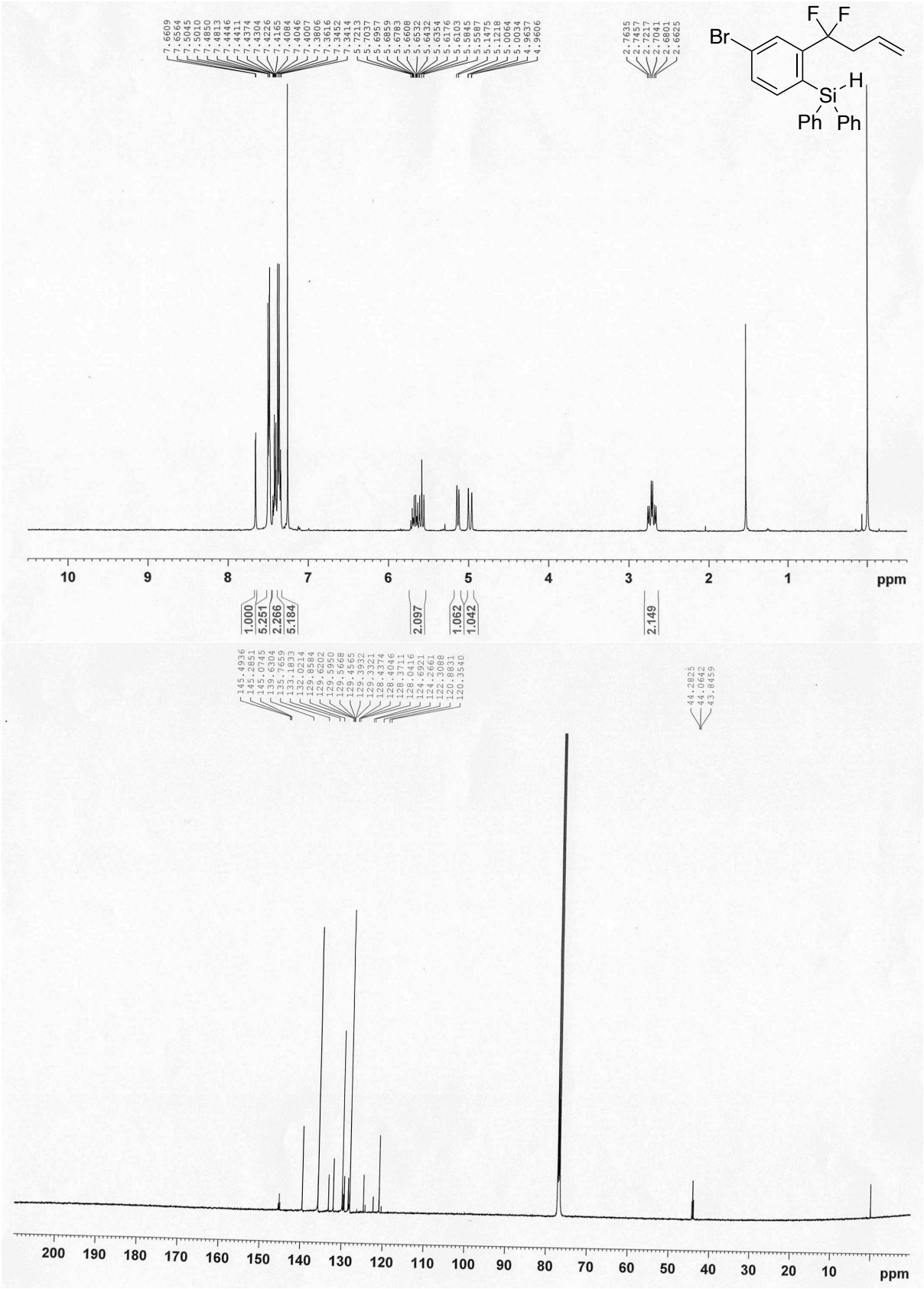
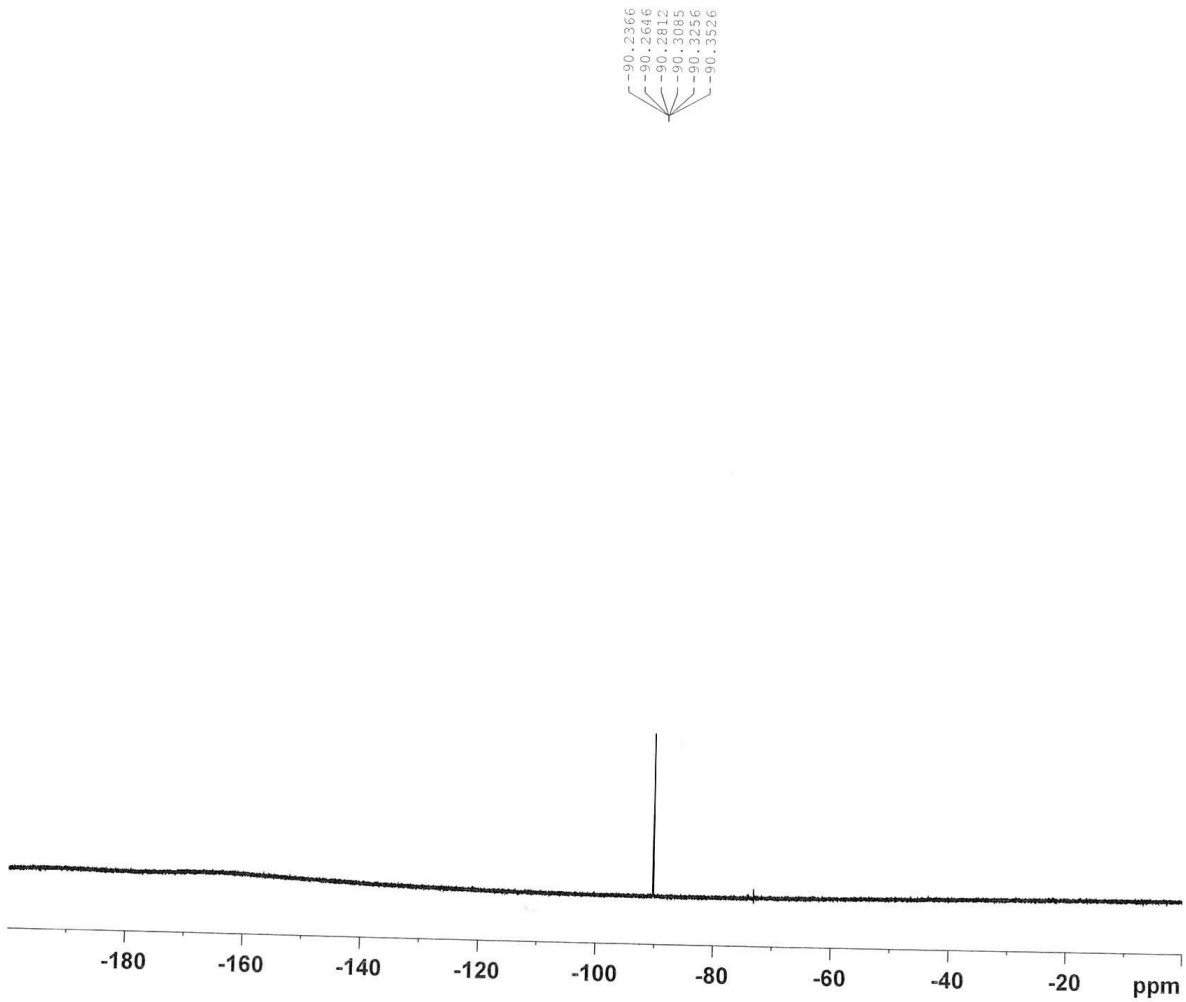
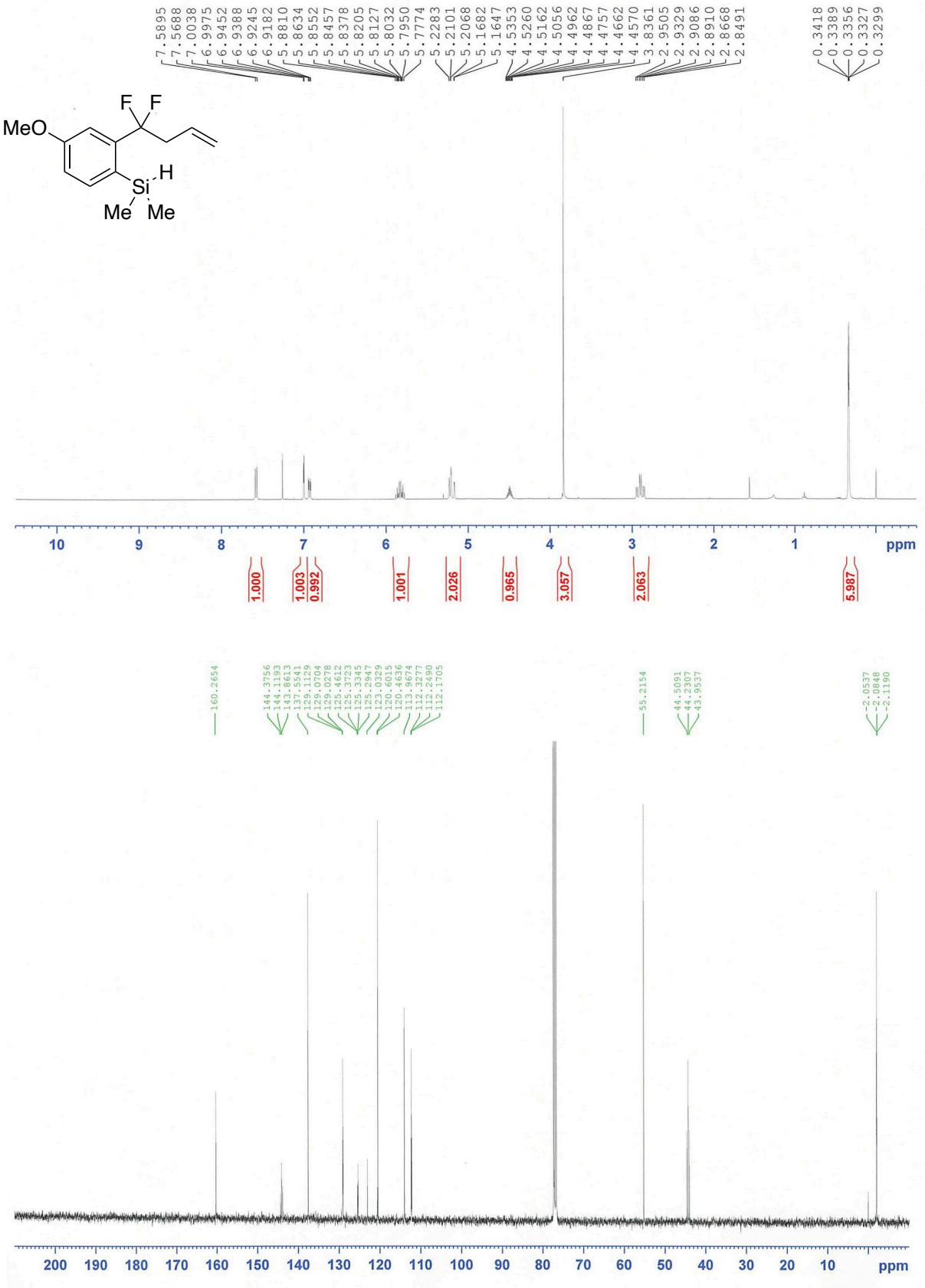
-89.8842
-89.9113
-89.9281
-89.9558
-89.9719
-90.0000
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.635
2.000

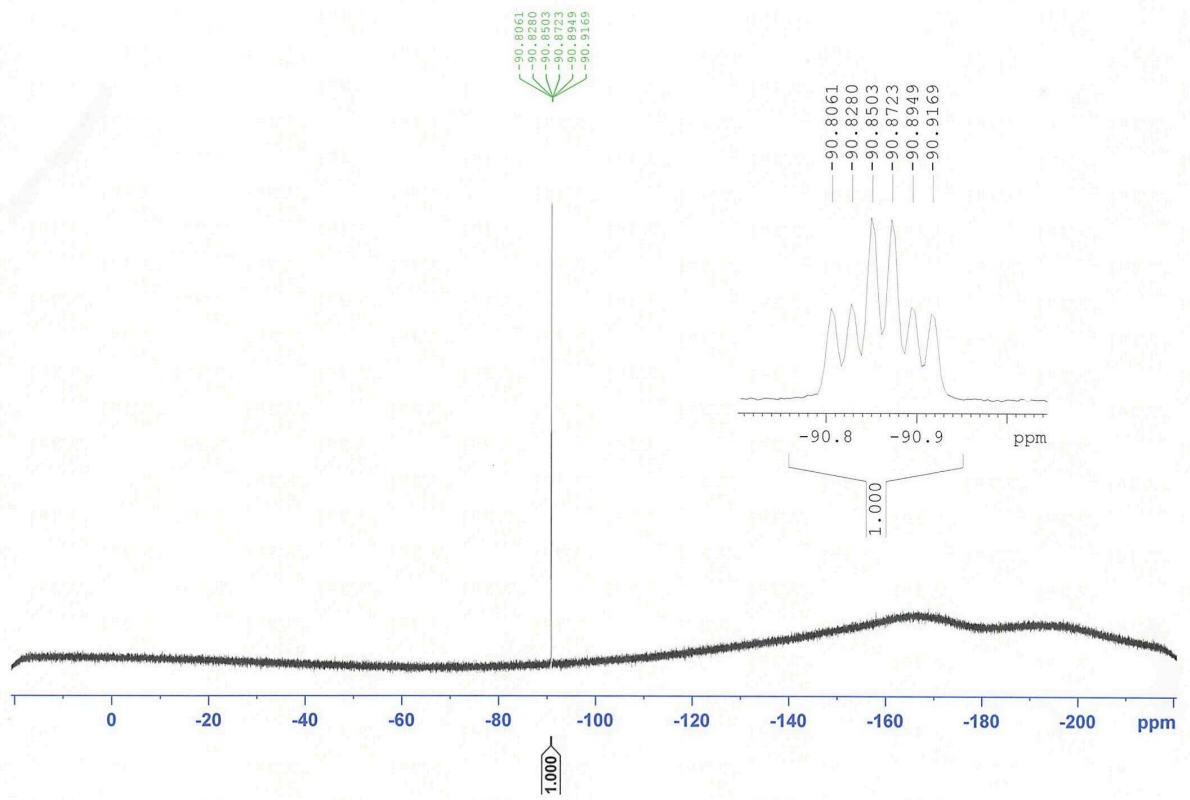
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7d** ($CDCl_3$)



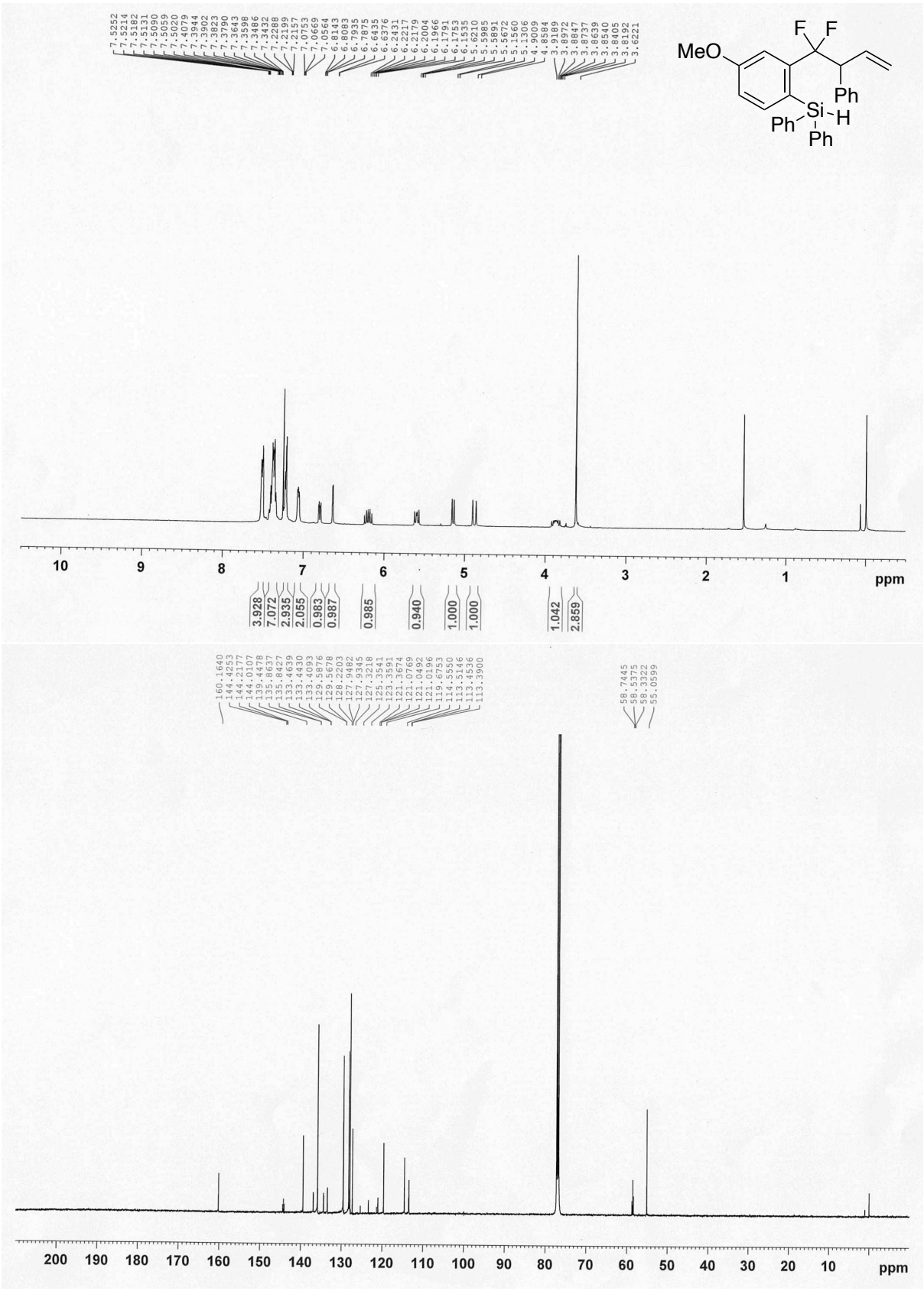

-90.2366
-90.2646
-90.2812
-90.3085
-90.3256
-90.3526
-180
-160
-140
-120
-100
-80
-60
-40
-20
ppm

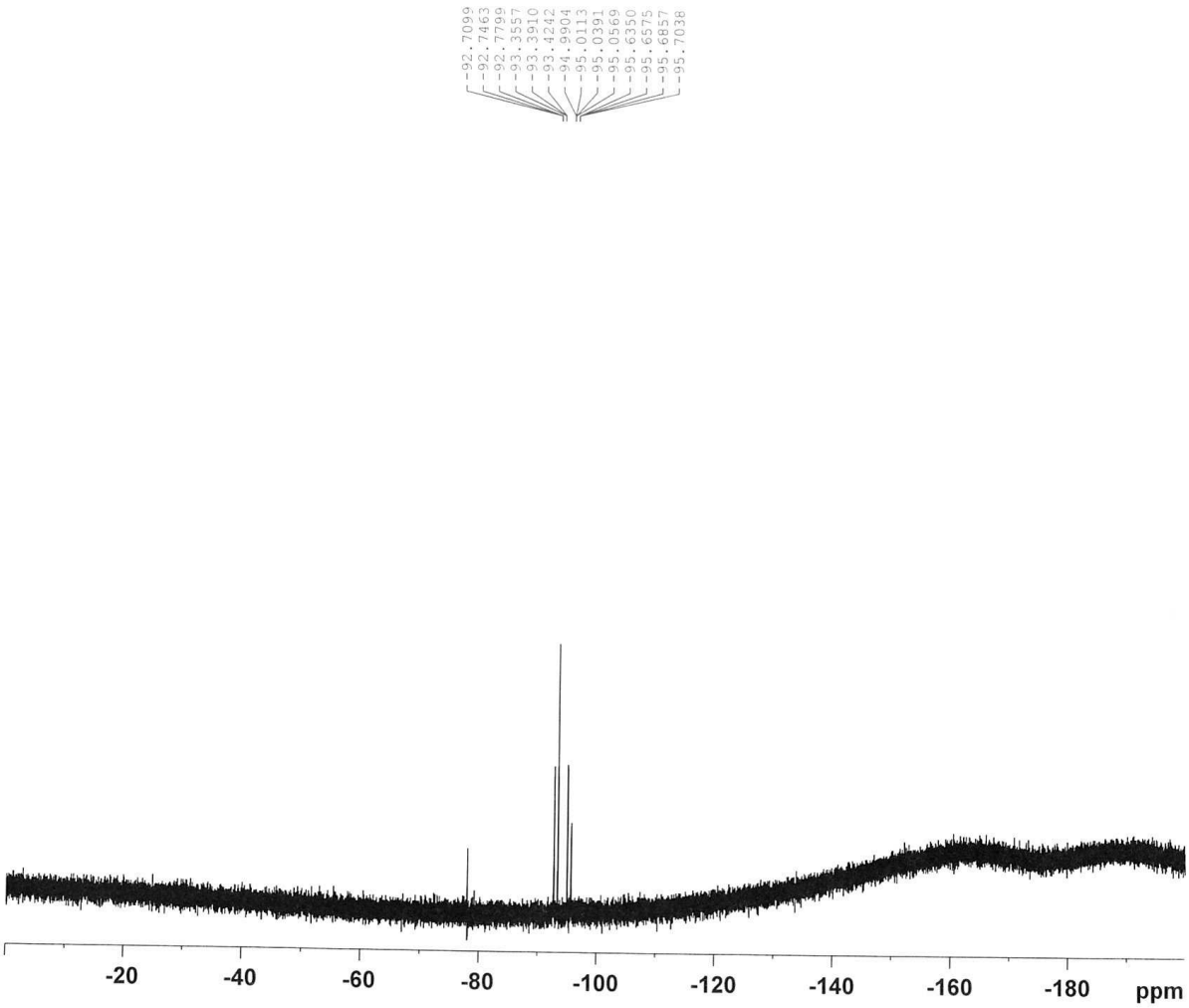
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7e** ($CDCl_3$)



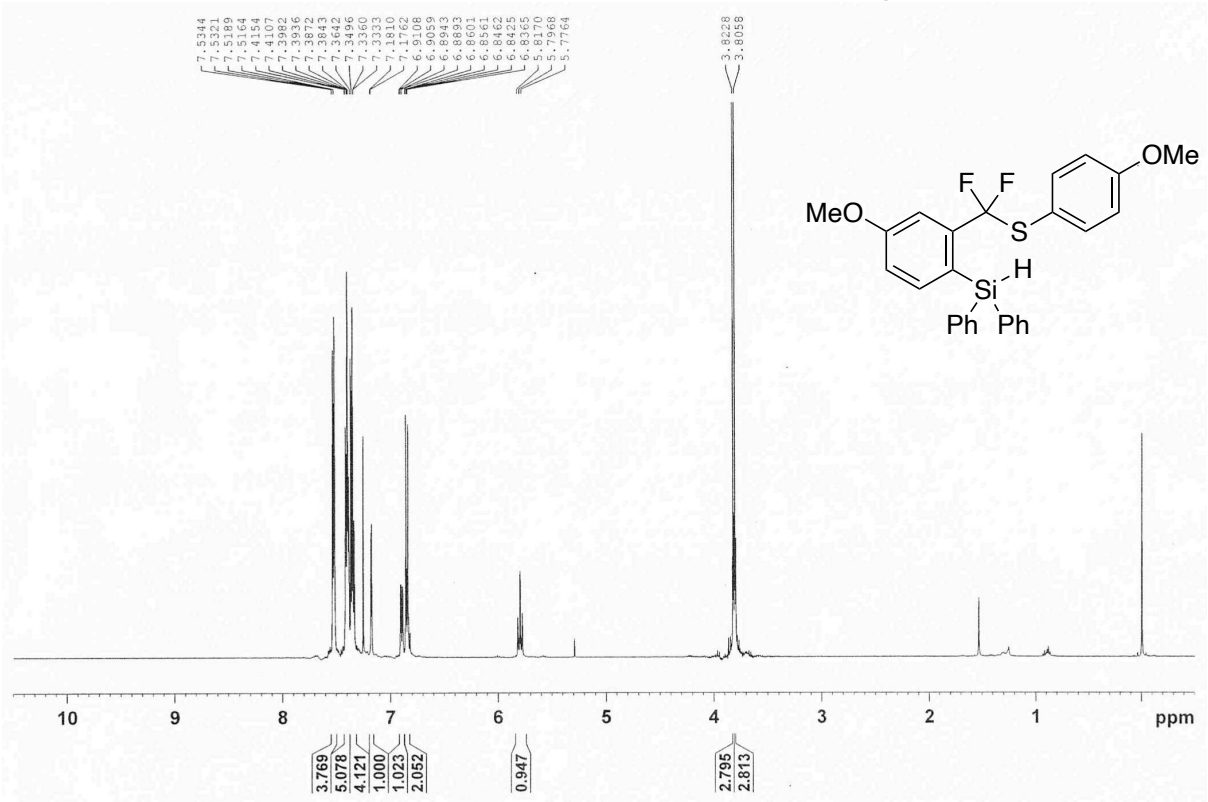

-90.8061
-90.8280
-90.8503
-90.8723
-90.8949
-90.9169
-90.8
-90.9
ppm
1.000
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.000

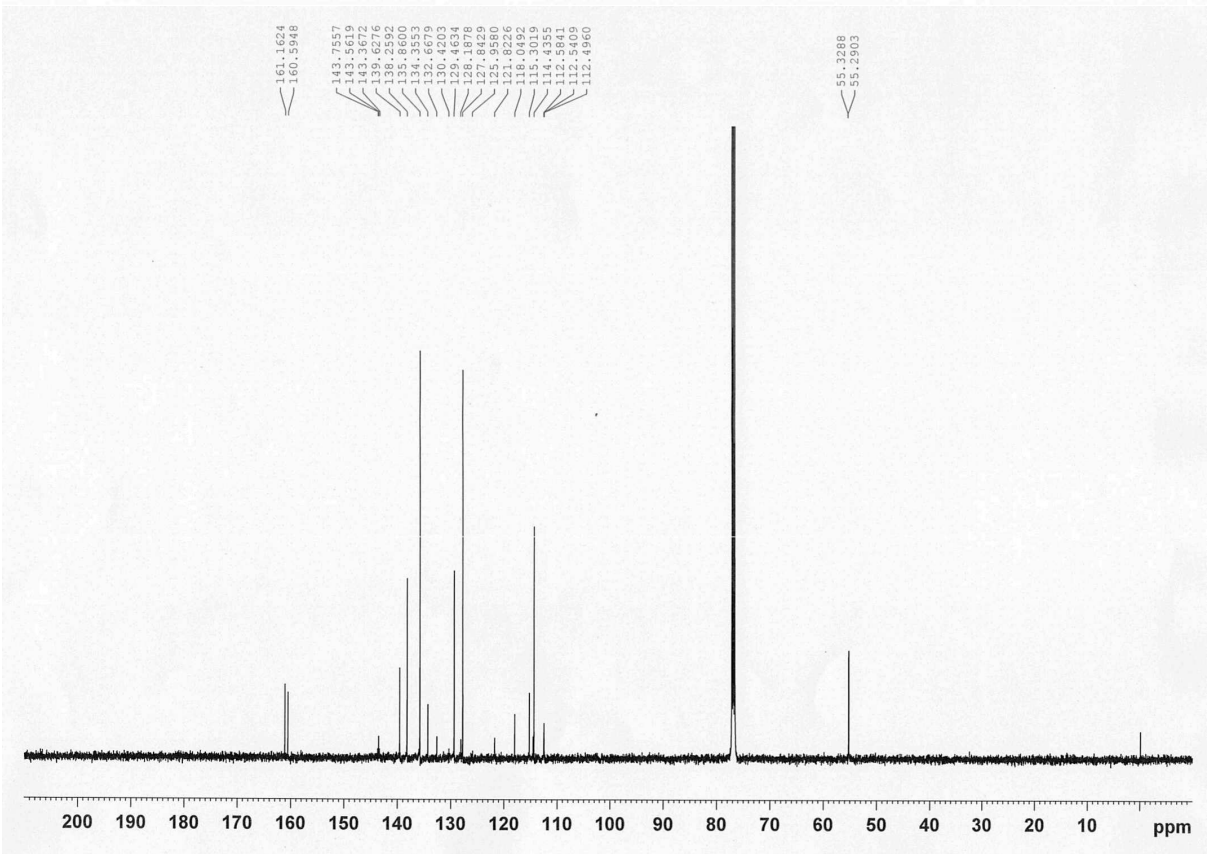
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7f** ($CDCl_3$)

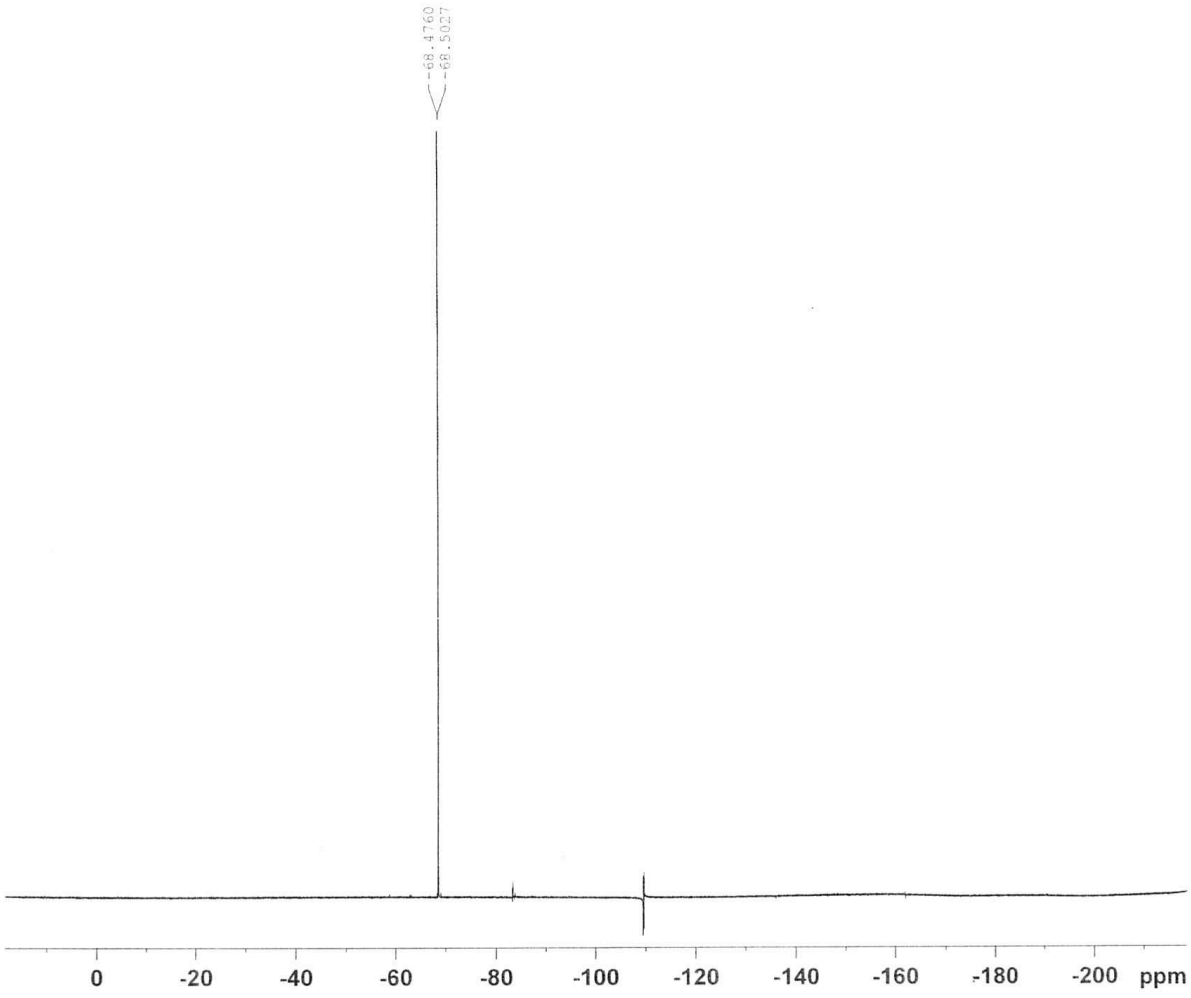



-92.7099
-92.7463
-92.7799
-93.3557
-93.3910
-93.4242
-94.9904
-95.0113
-95.0391
-95.0569
-95.6350
-95.6575
-95.6857
-95.7038
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

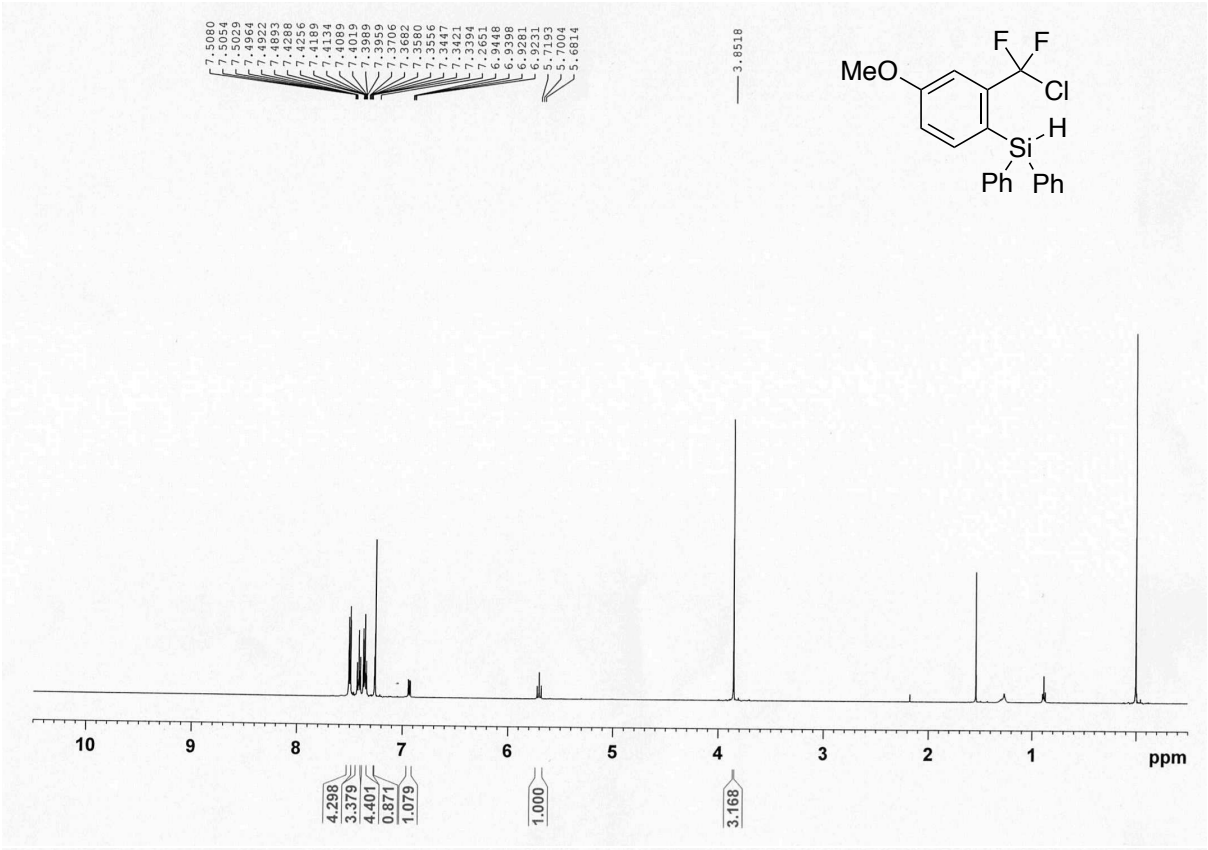
^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7g** ($CDCl_3$)

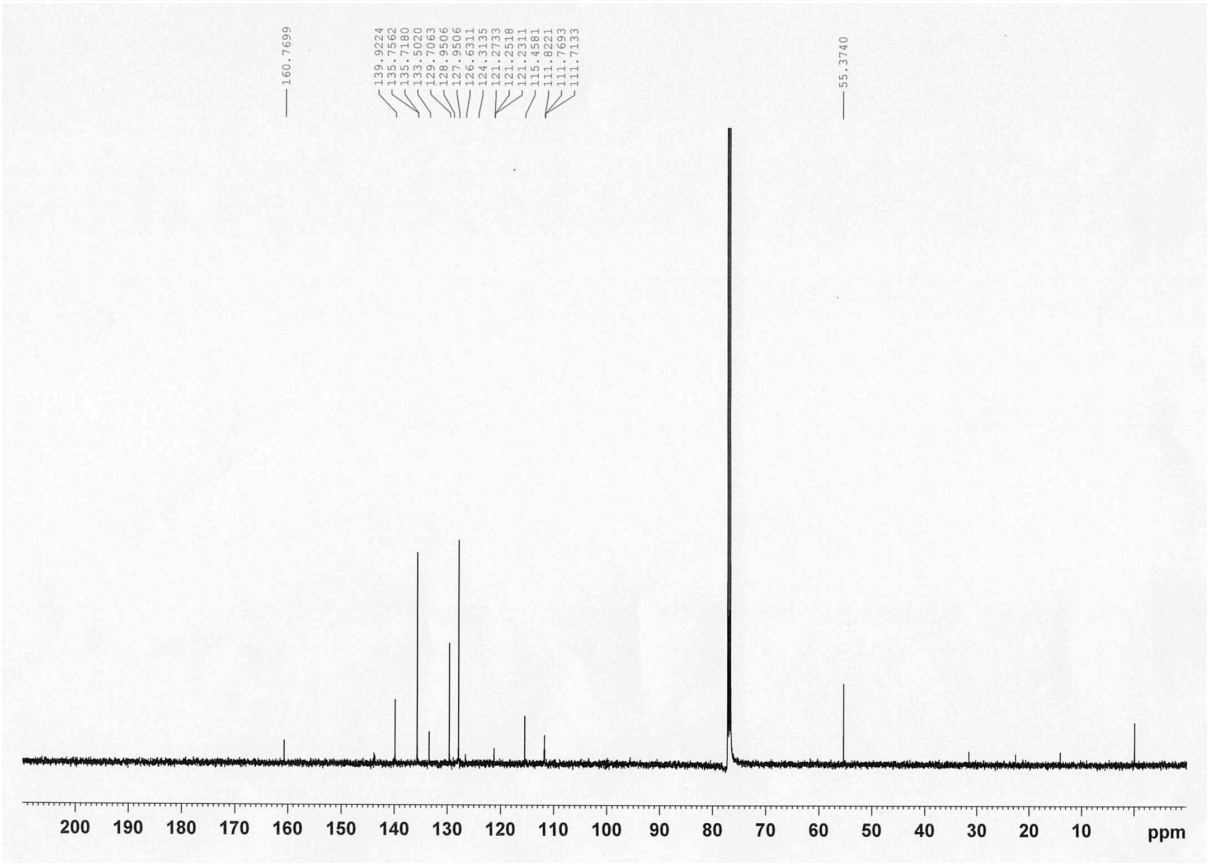


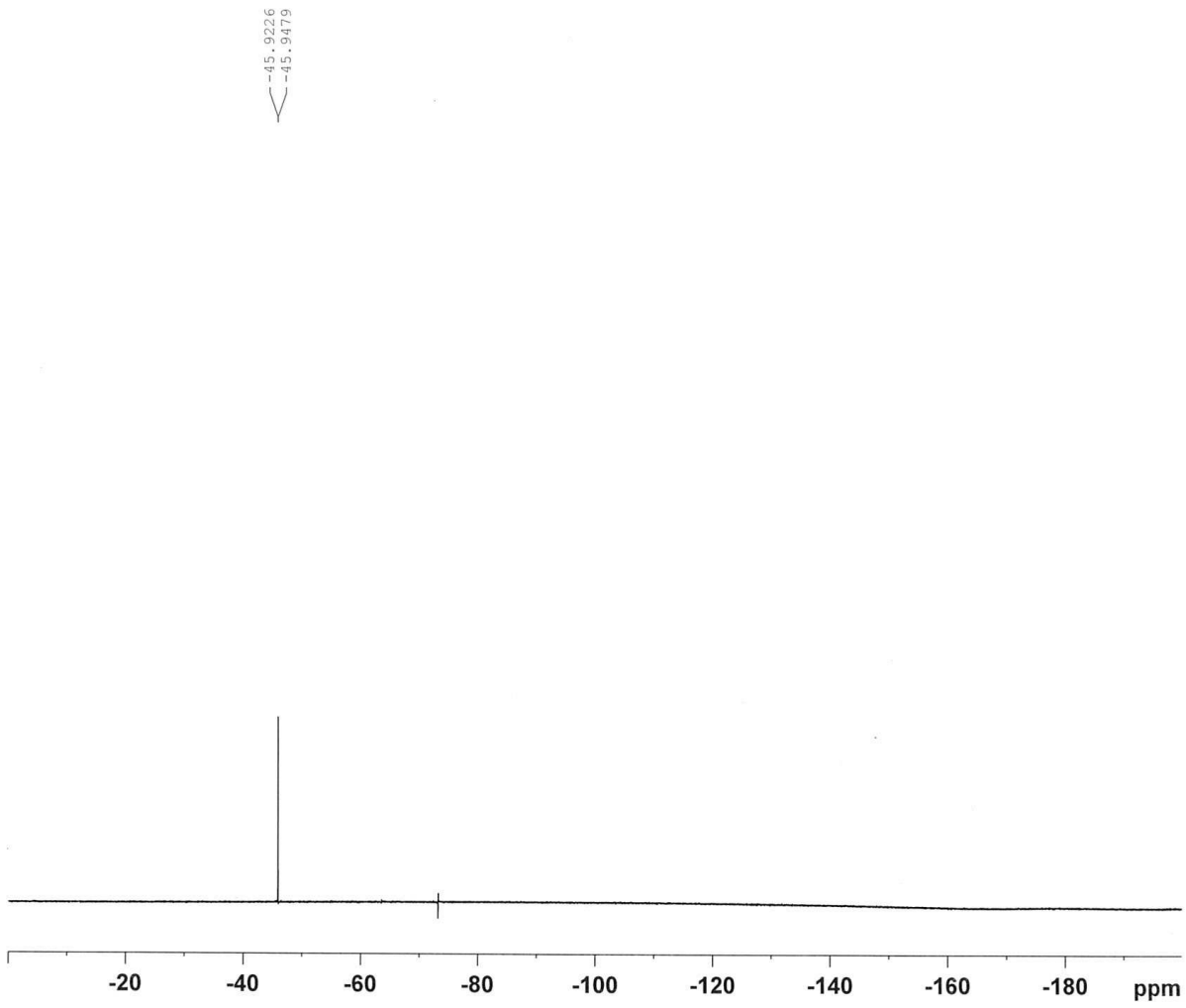



-68.4760
-68.5027
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

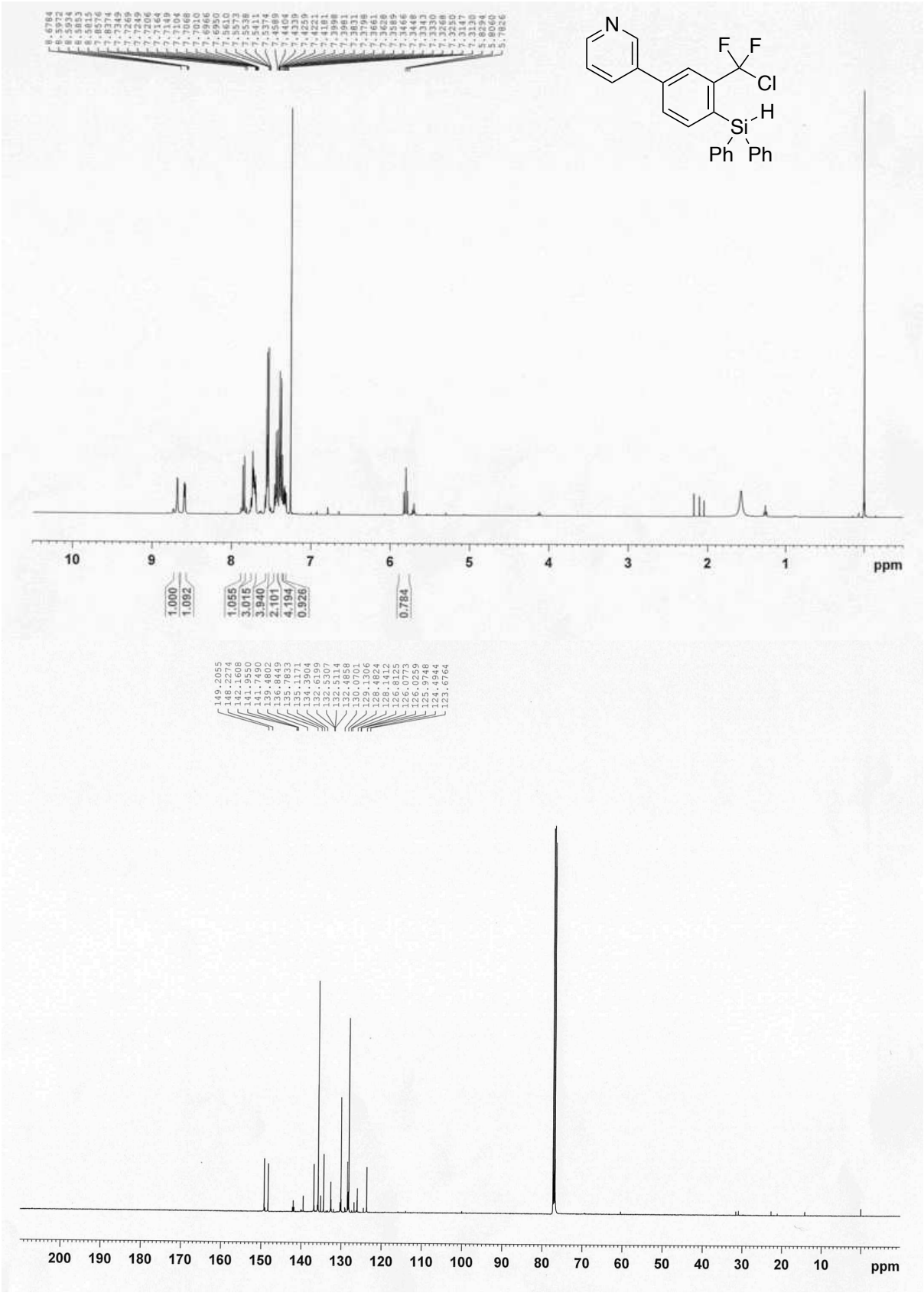
^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7h** ($CDCl_3$)

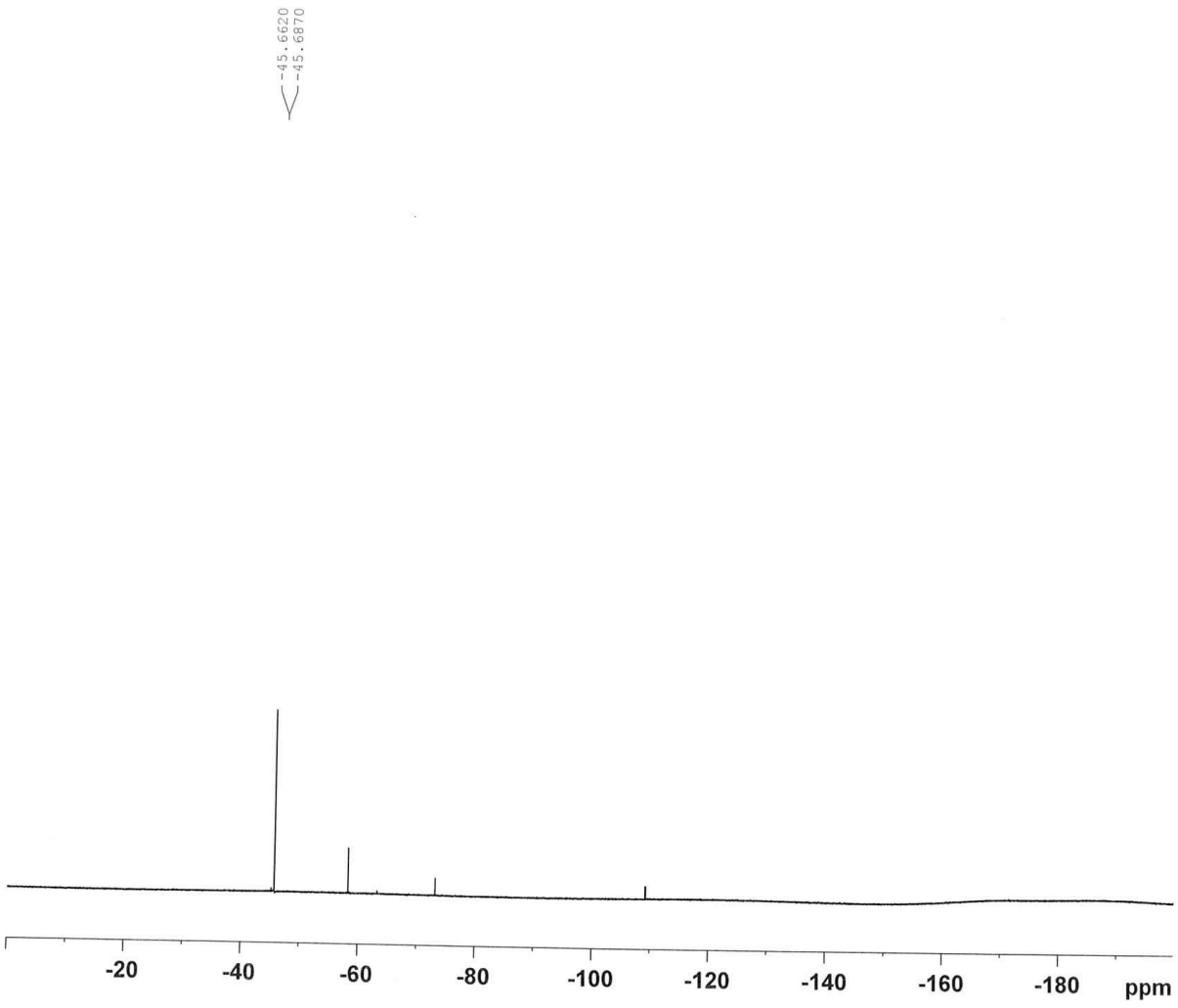




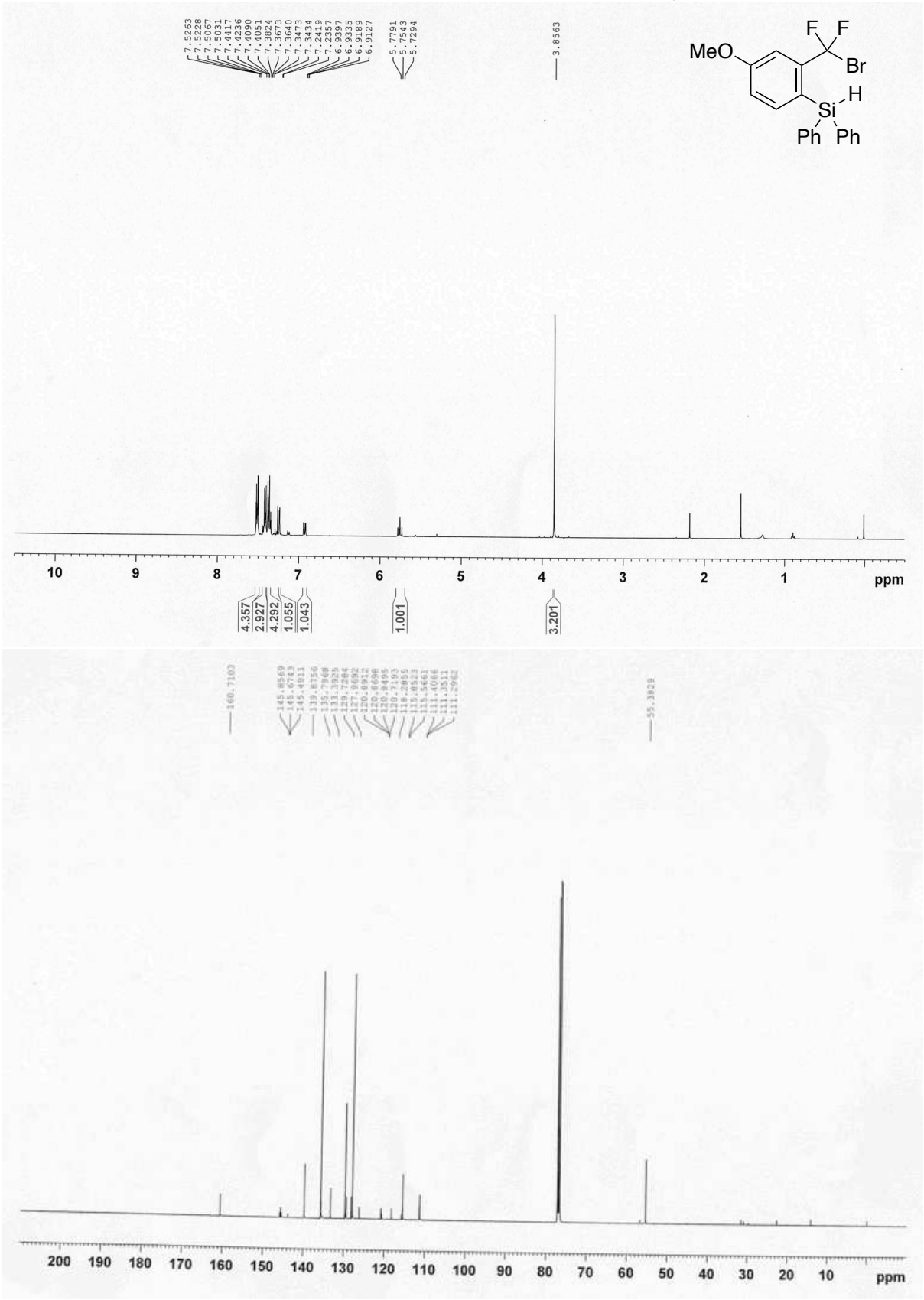

-45.9226
-45.9479
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

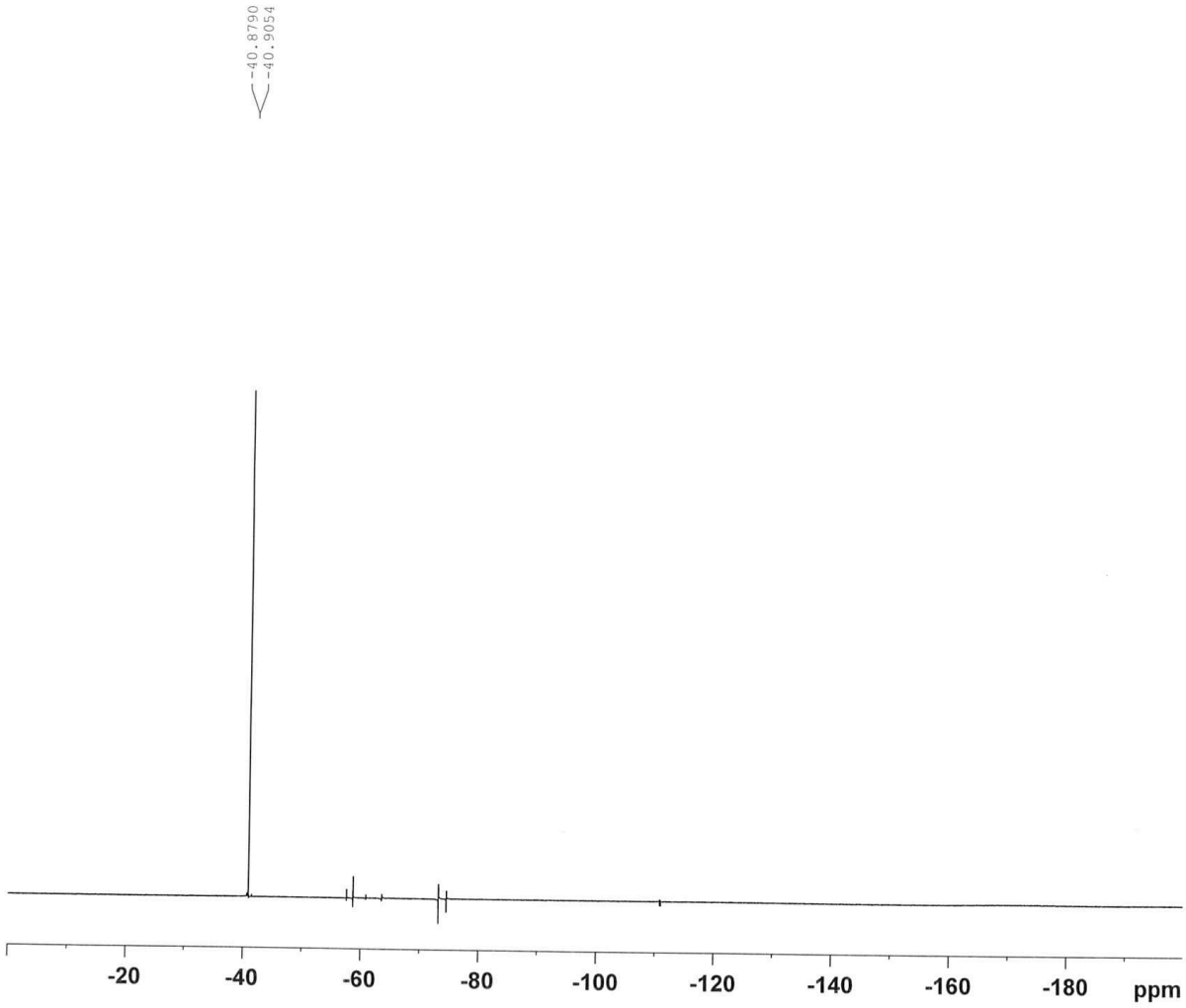
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7i** ($CDCl_3$)



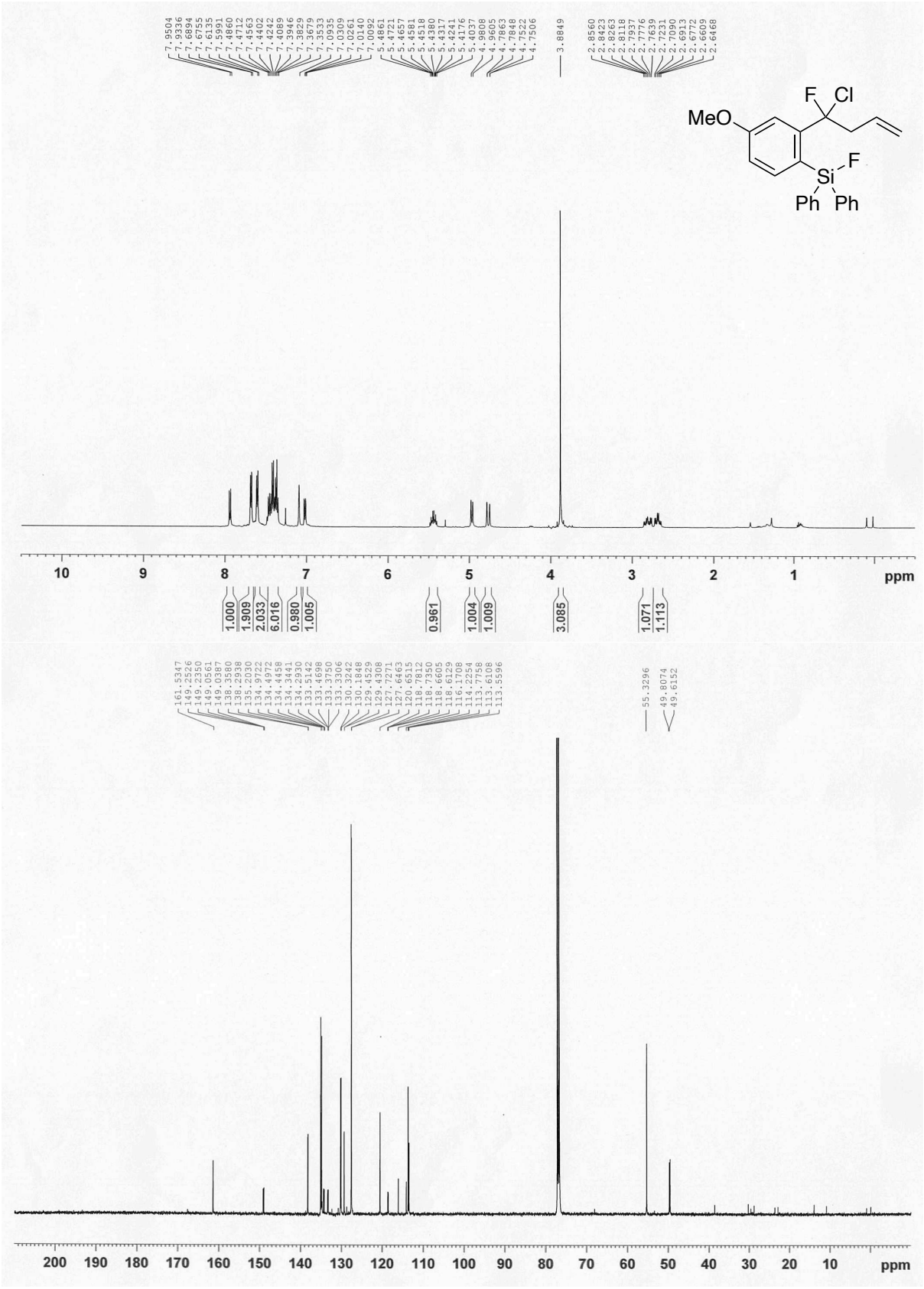

-45.6620
-45.6870
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

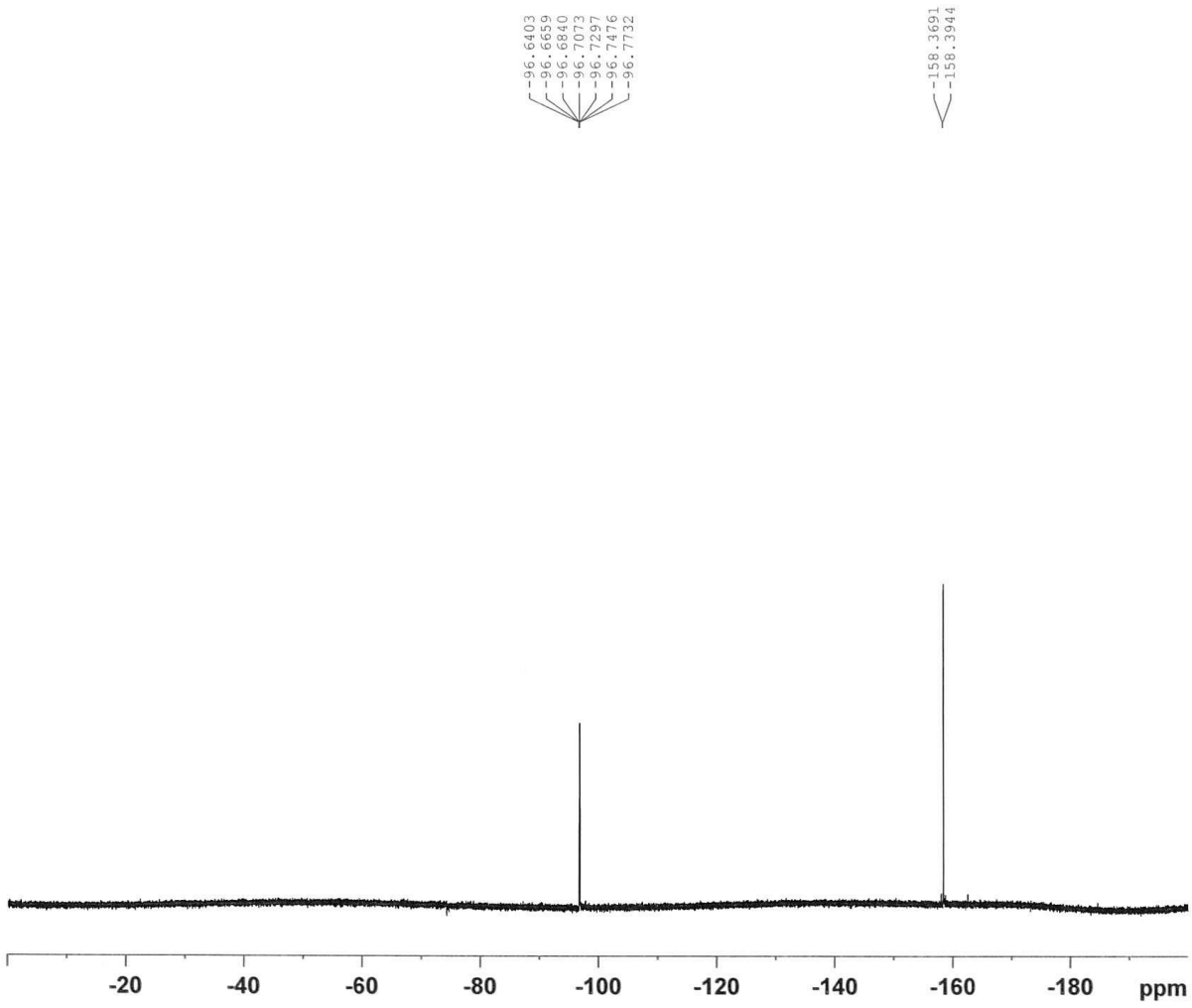
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **7j** ($CDCl_3$)



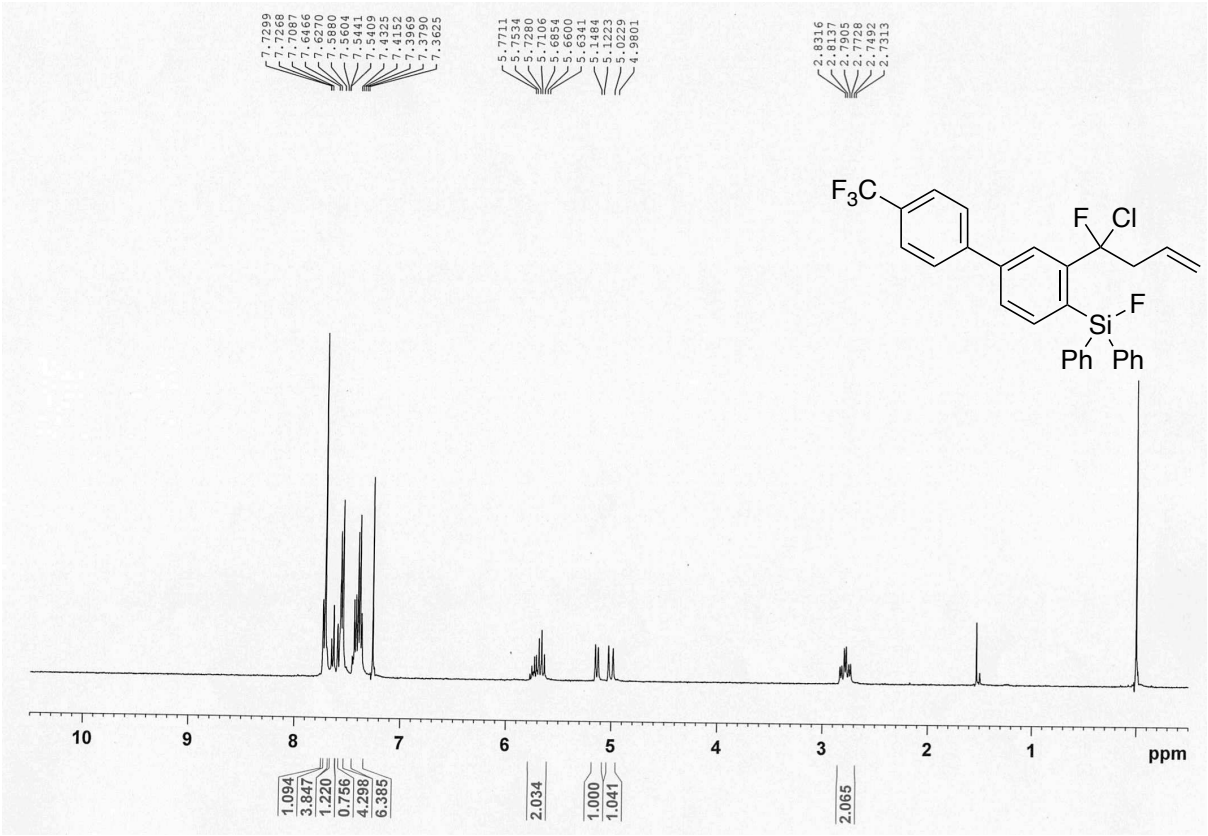

-40.8790
-40.9054
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

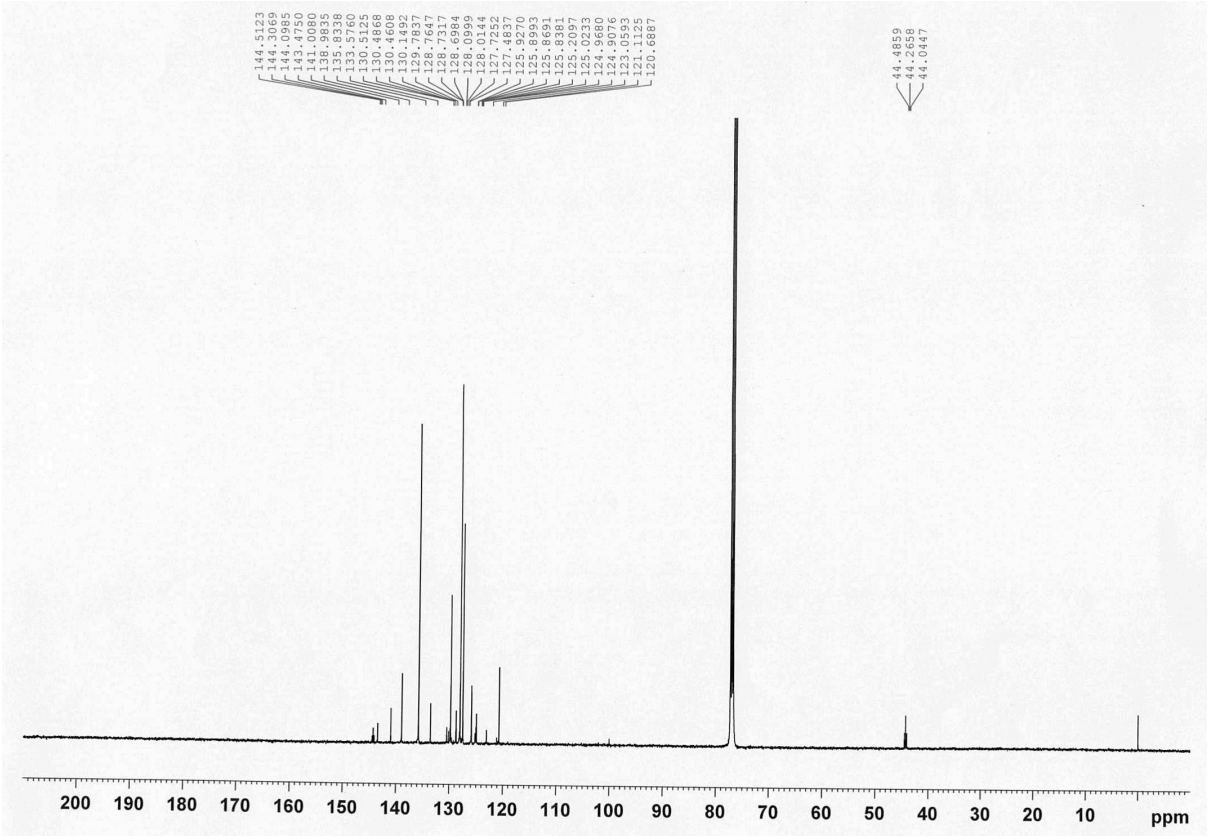
^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **8a** ($CDCl_3$)

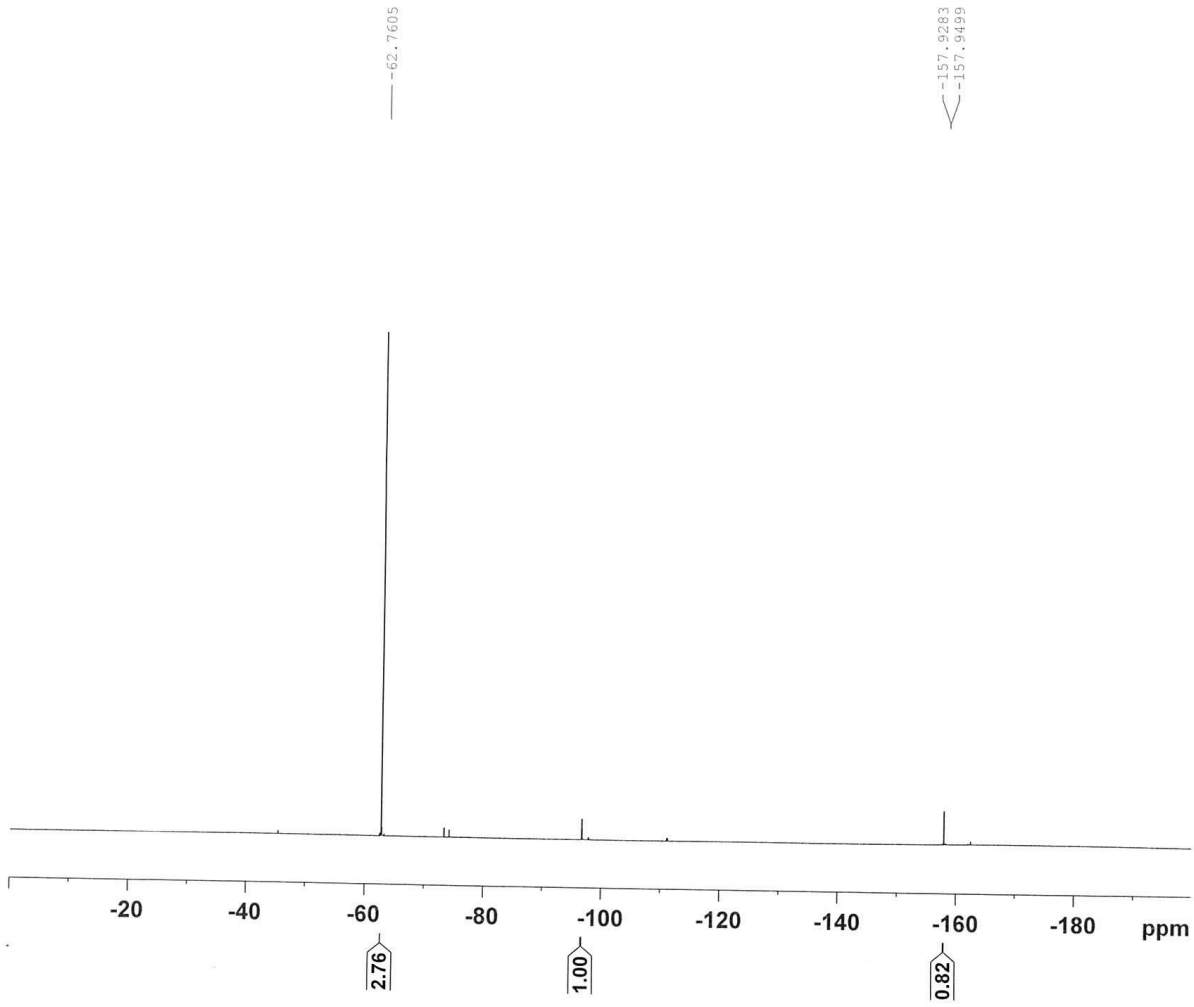



-96.6403
-96.6659
-96.6840
-96.7073
-96.7297
-96.7476
-96.7732
-158.3691
-158.3944
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

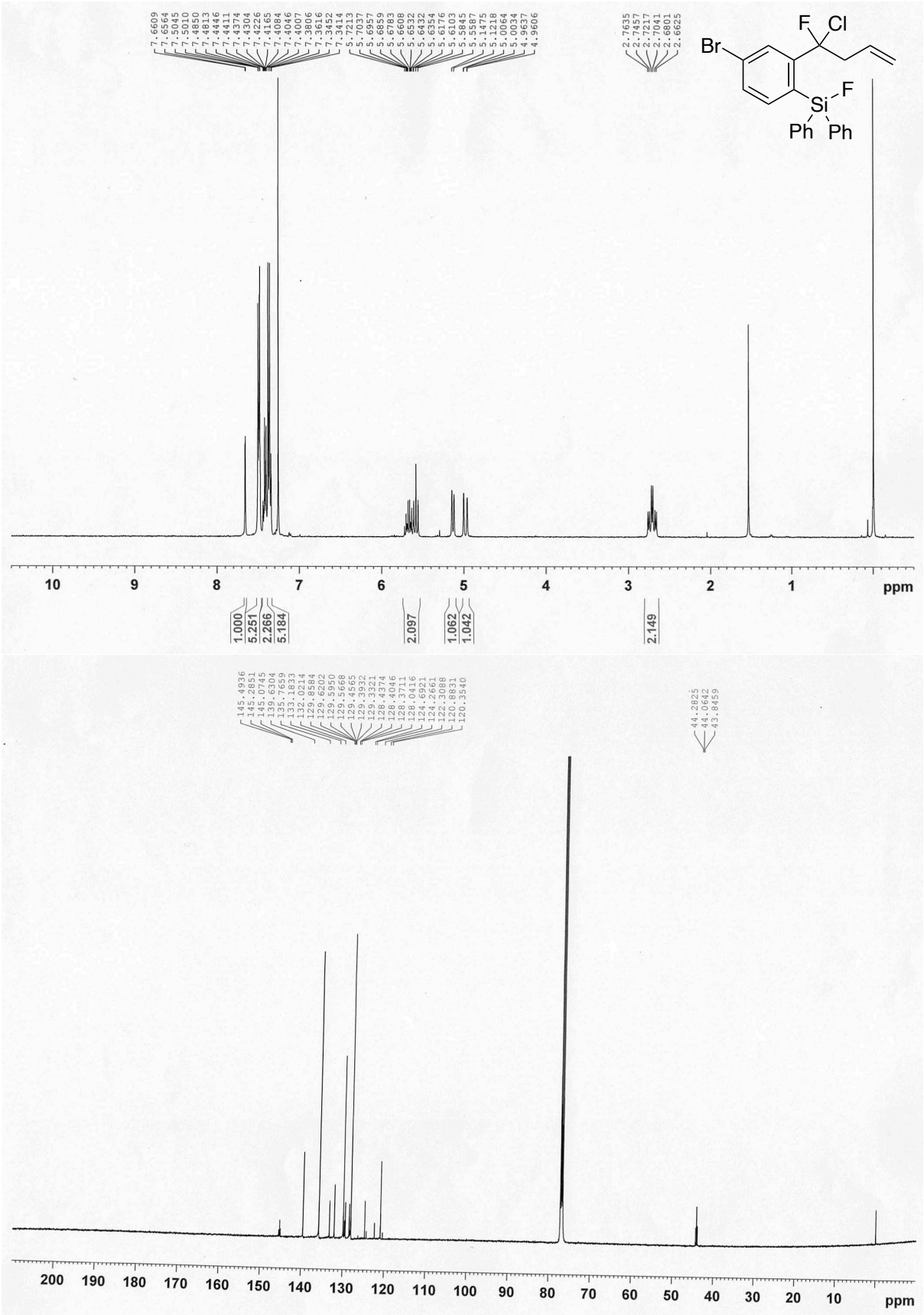
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **8c** ($CDCl_3$)

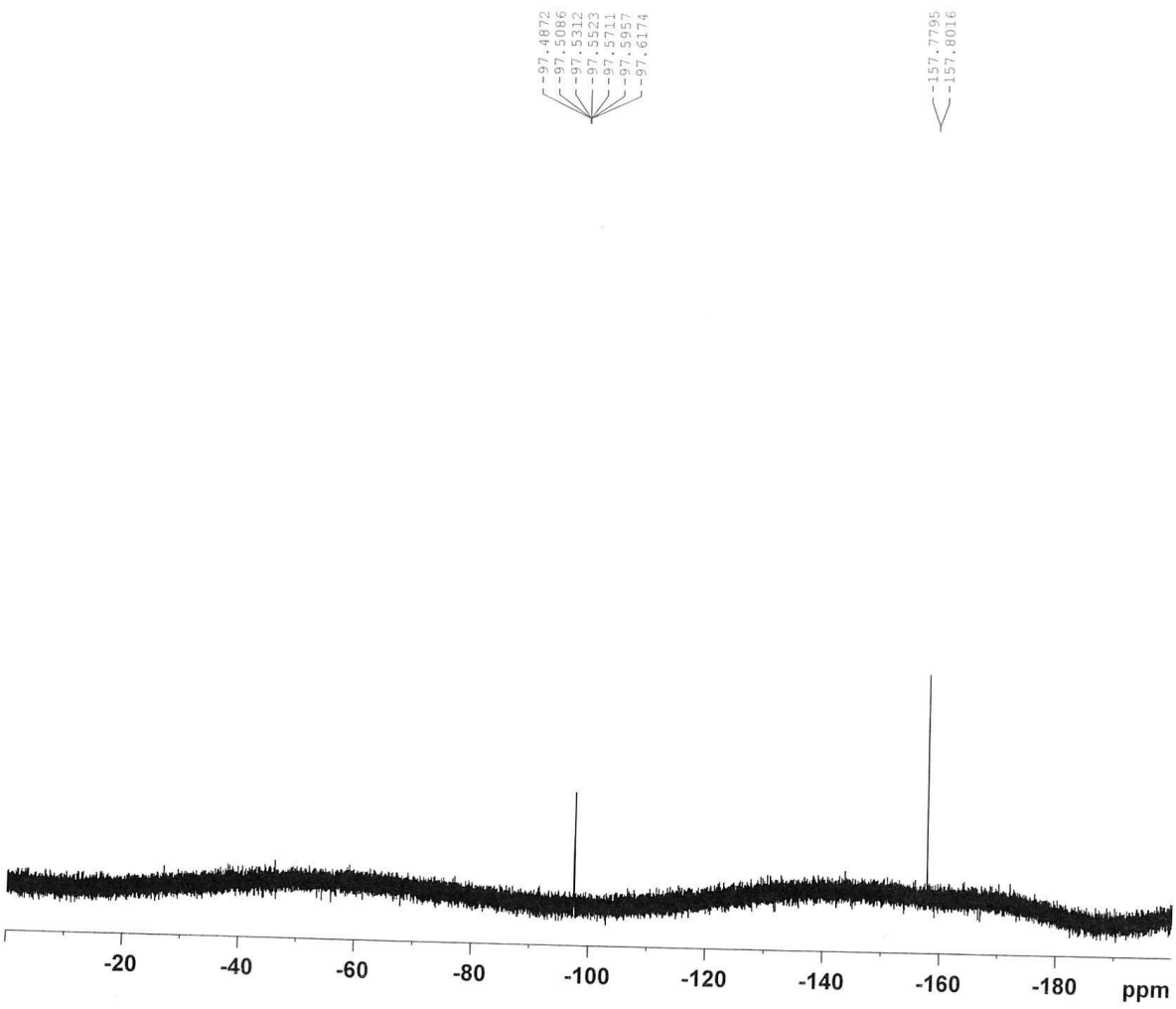




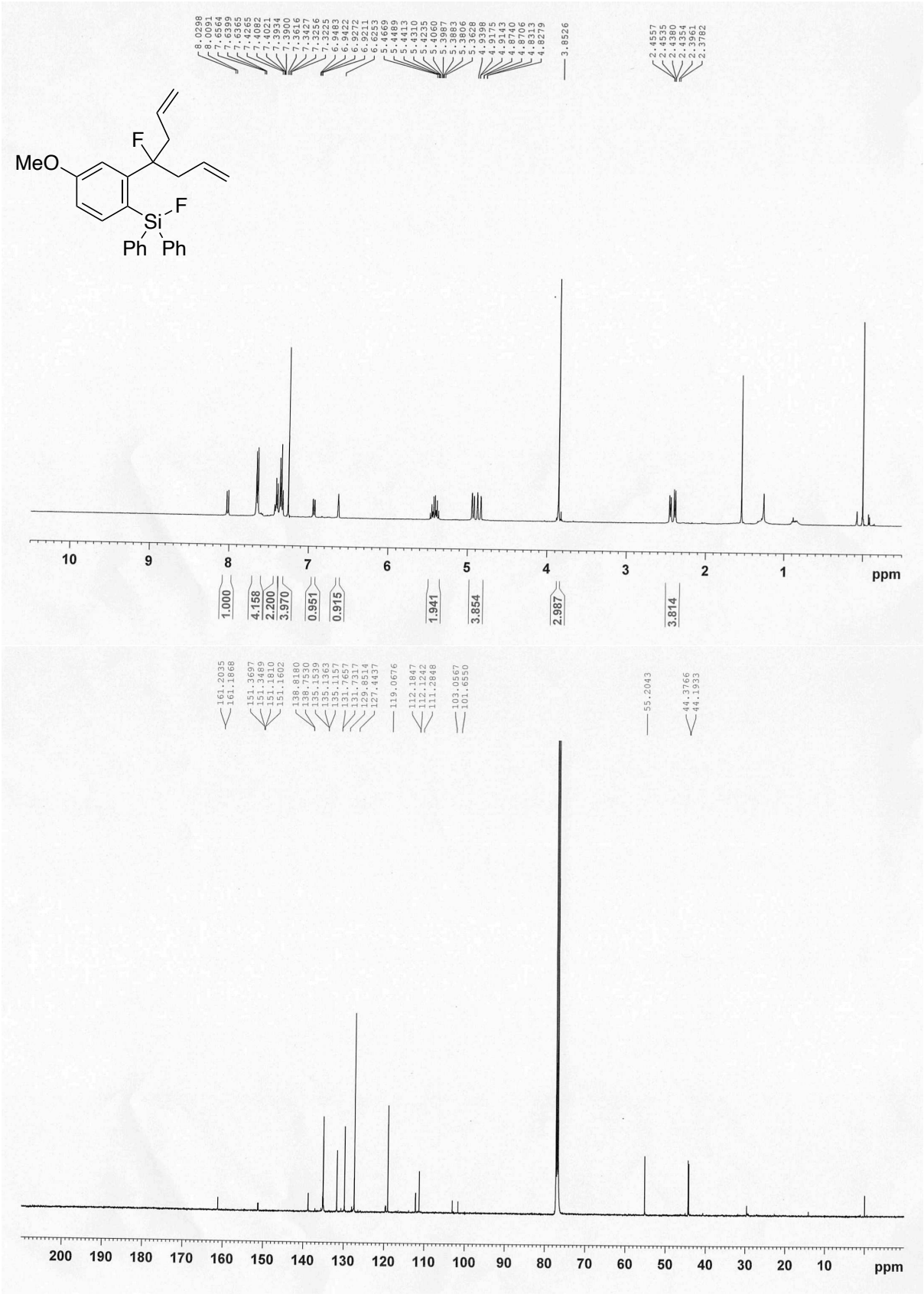

-62.7605
-157.9283
-157.9499
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
2.76
1.00
0.82

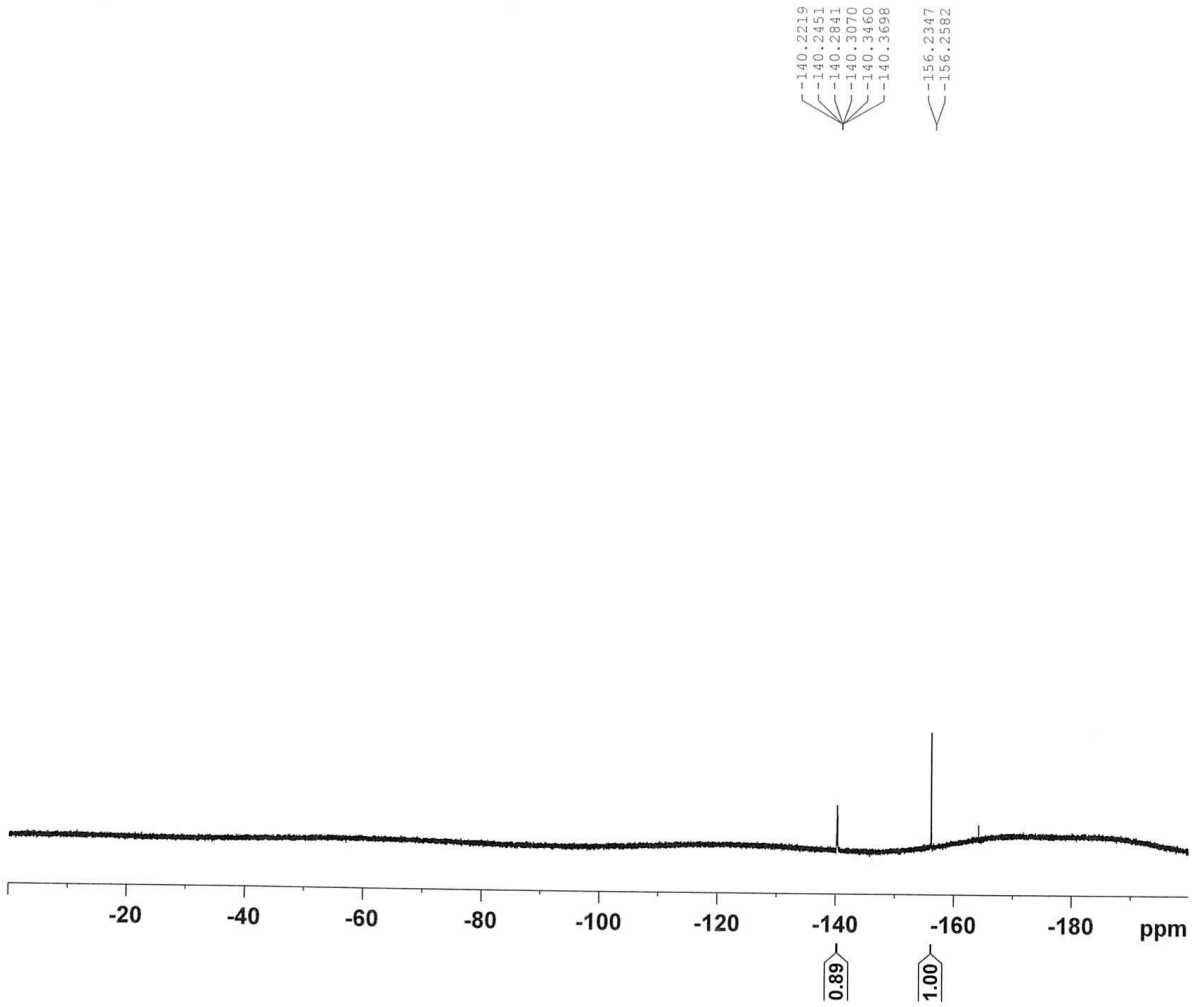
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **8d** ($CDCl_3$)



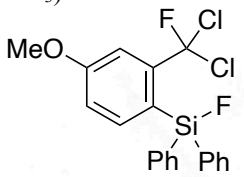

-97.4872
-97.5086
-97.5312
-97.5523
-97.5711
-97.5957
-97.6174
-157.7795
-157.8016
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

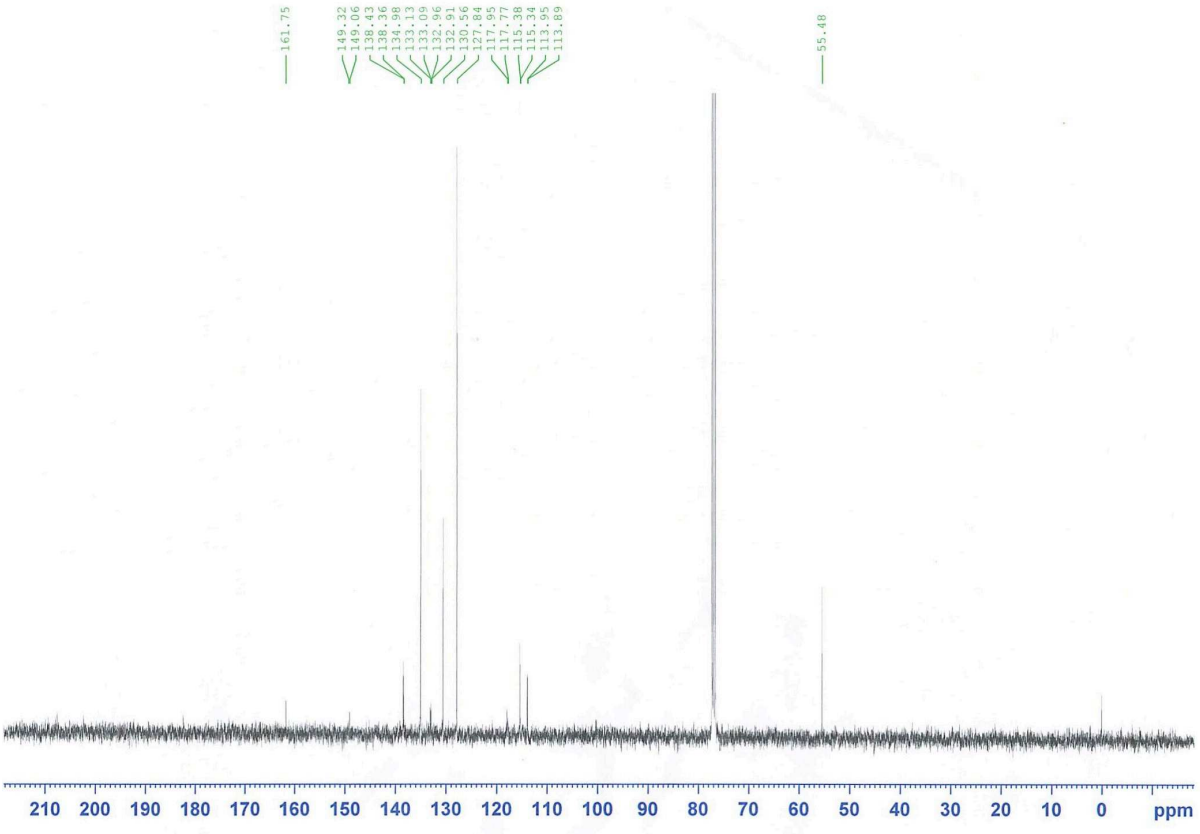
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **8e** ($CDCl_3$)

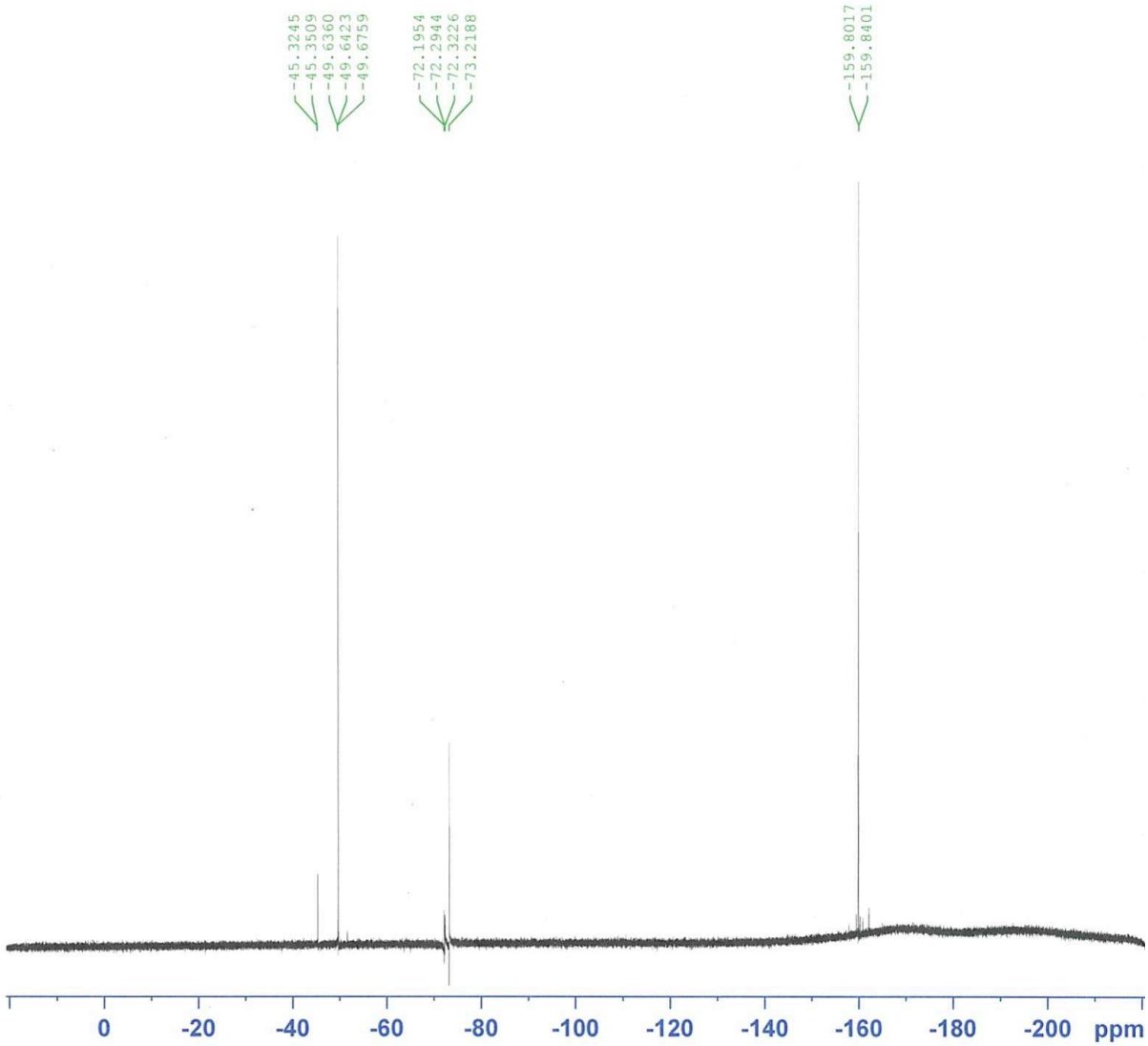



-140.2219
-140.2451
-140.2841
-140.3070
-140.3460
-140.3698
-156.2347
-156.2582
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.89
1.00

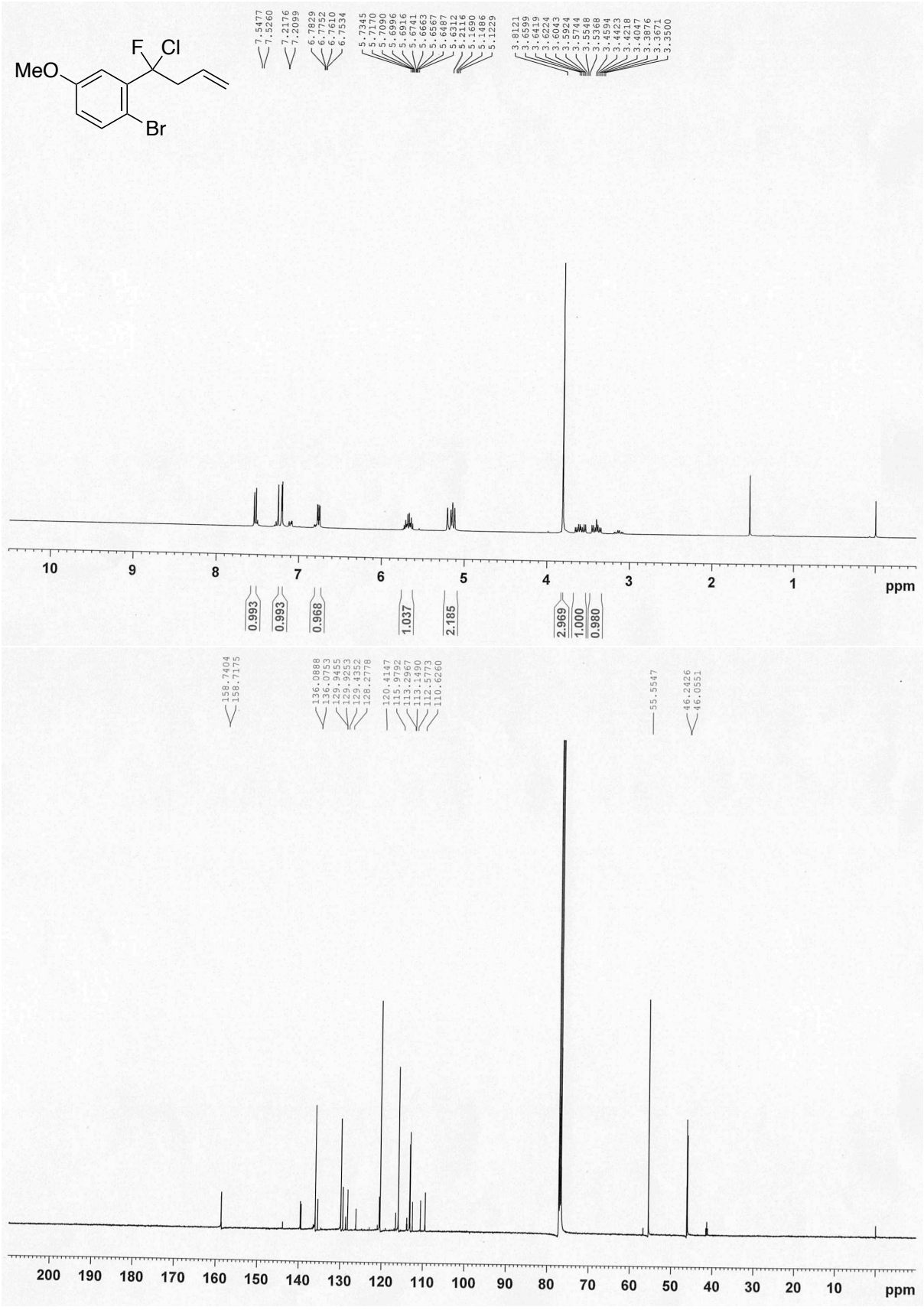
^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and ^{19}F NMR (376 MHz) spectra of **8g** ($CDCl_3$)

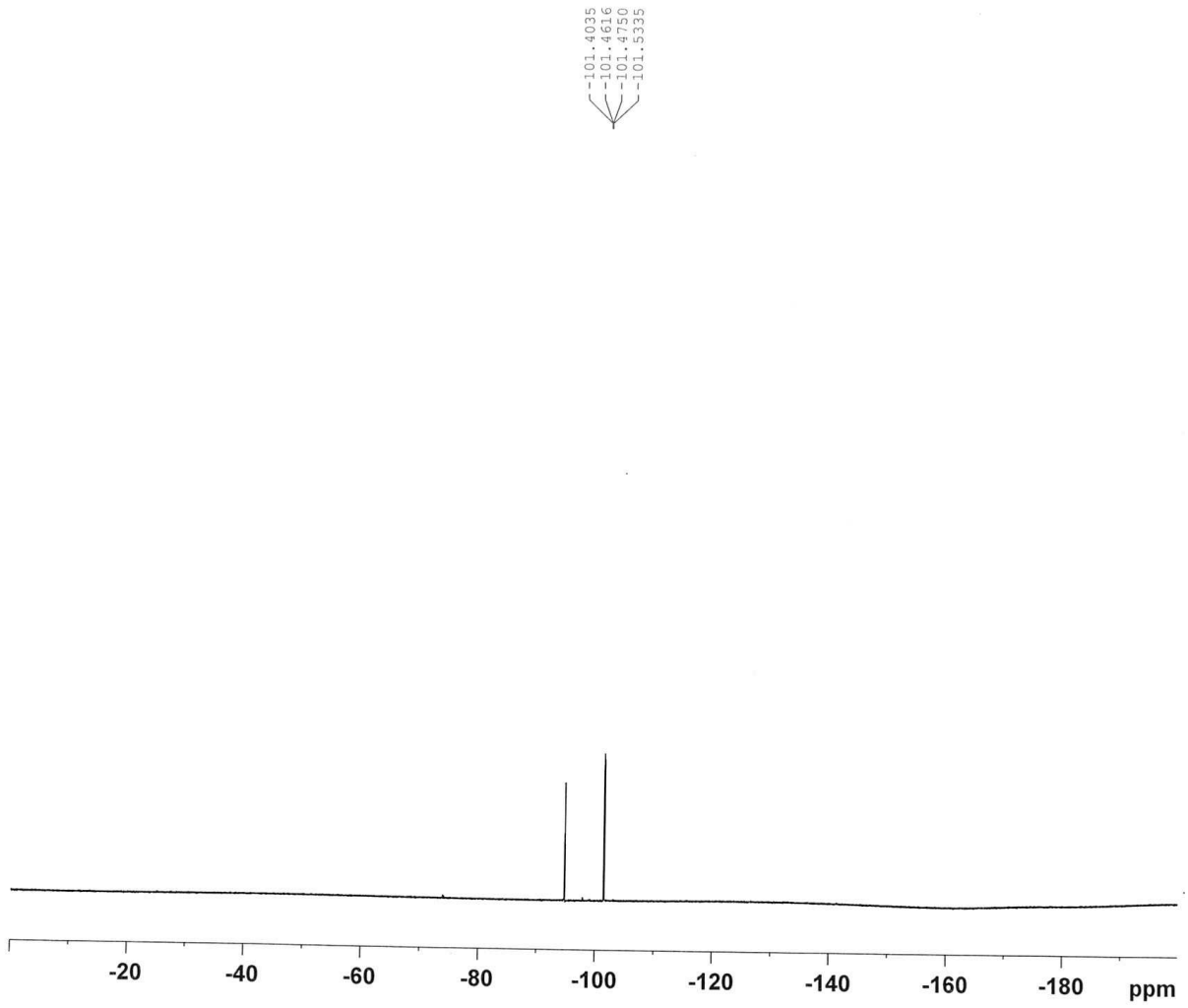




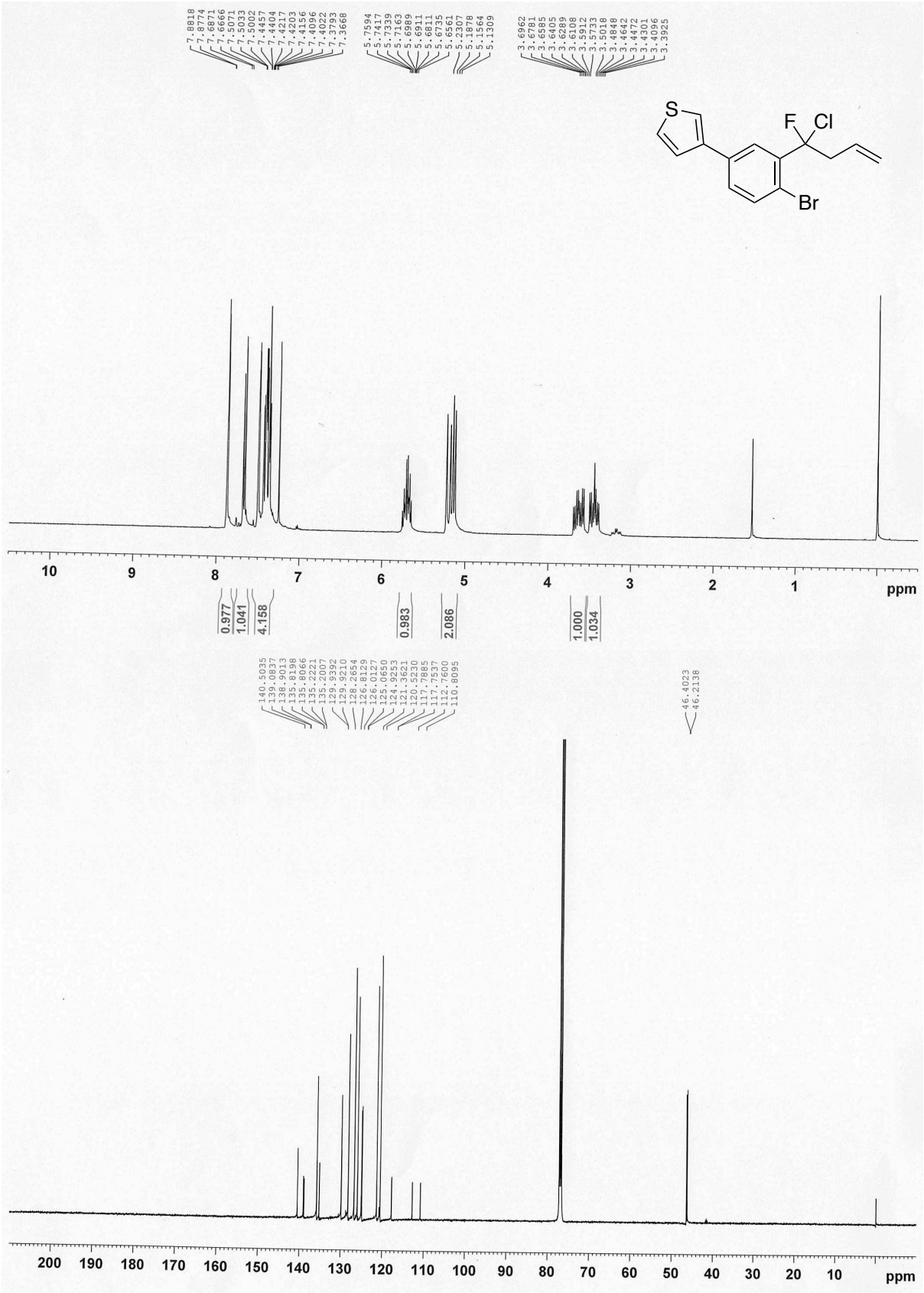

-45.3245
-45.3509
-49.6360
-49.6423
-49.6759
-72.1954
-72.2944
-72.3226
-73.2188
-159.8017
-159.8401
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

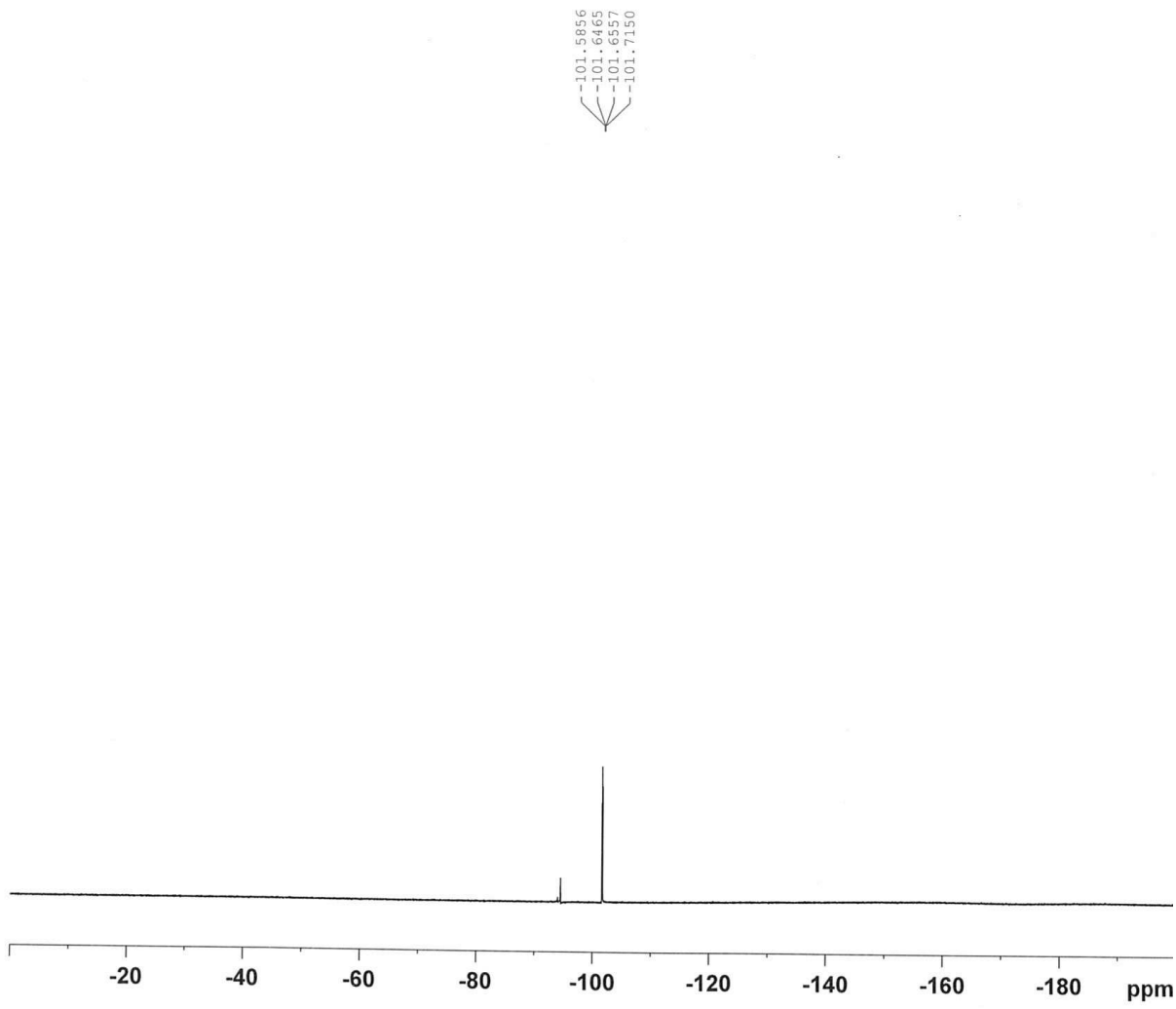
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **9a** ($CDCl_3$)



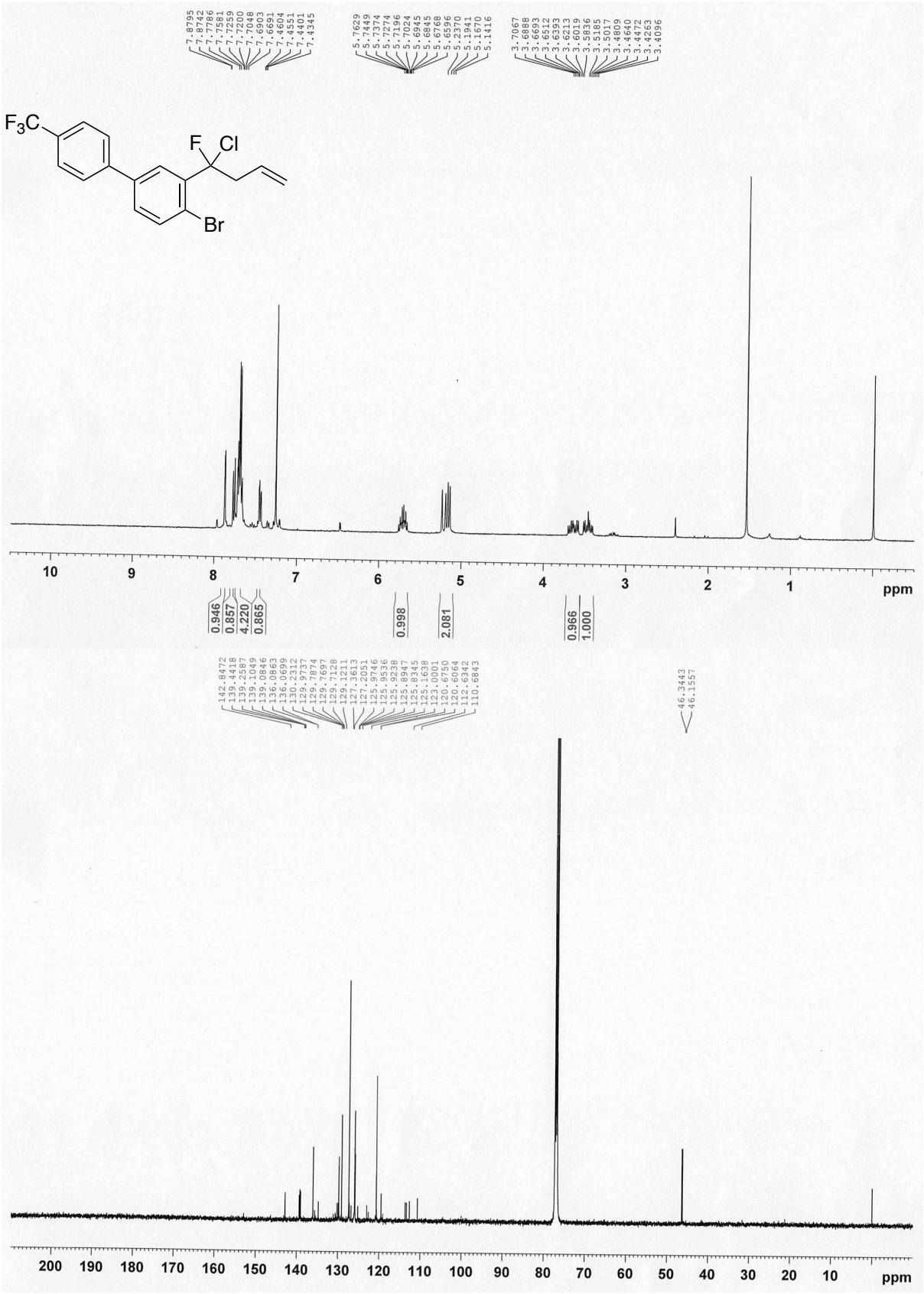

-101.4035
-101.4616
-101.4750
-101.5335
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

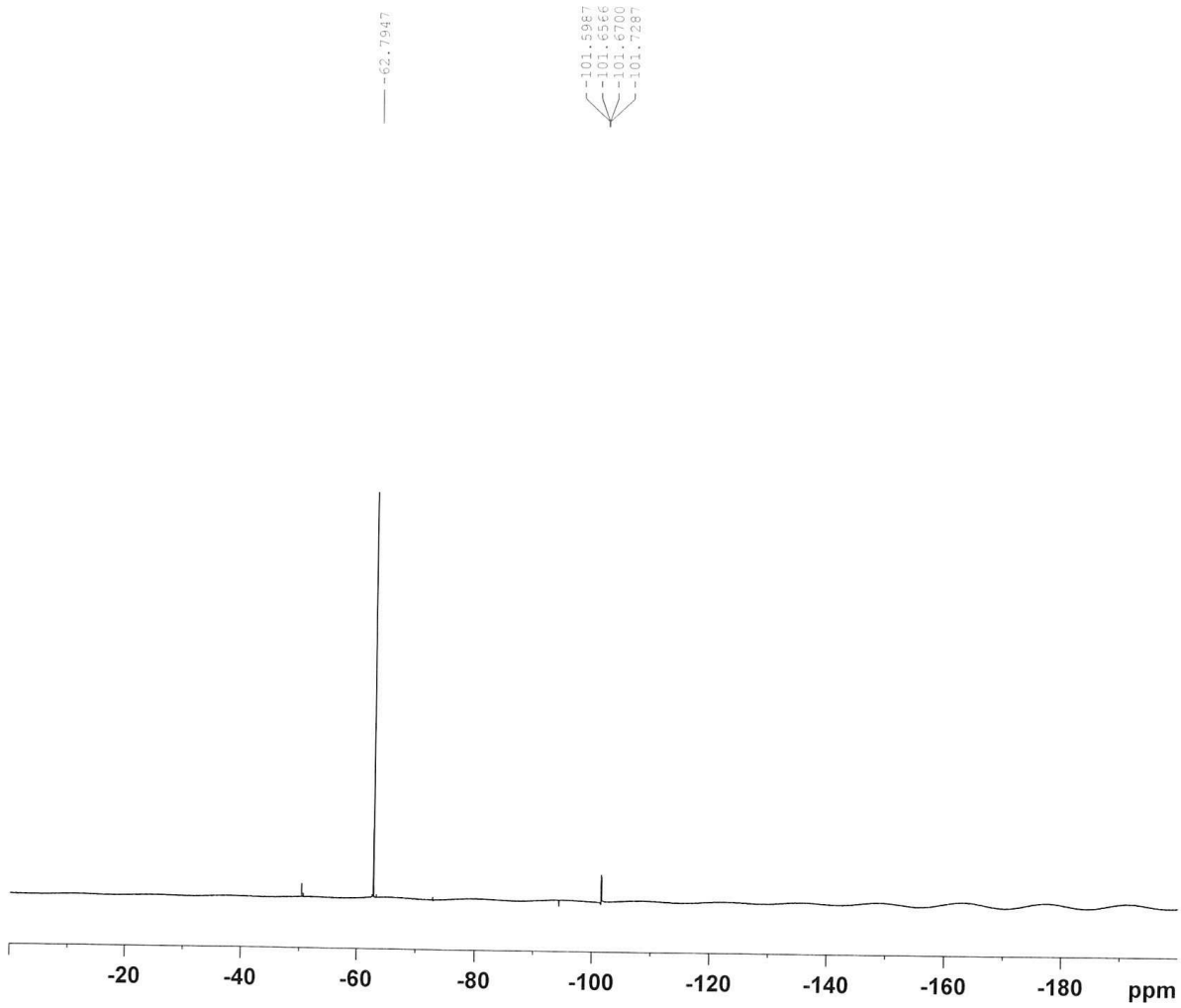
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **9b** ($CDCl_3$)



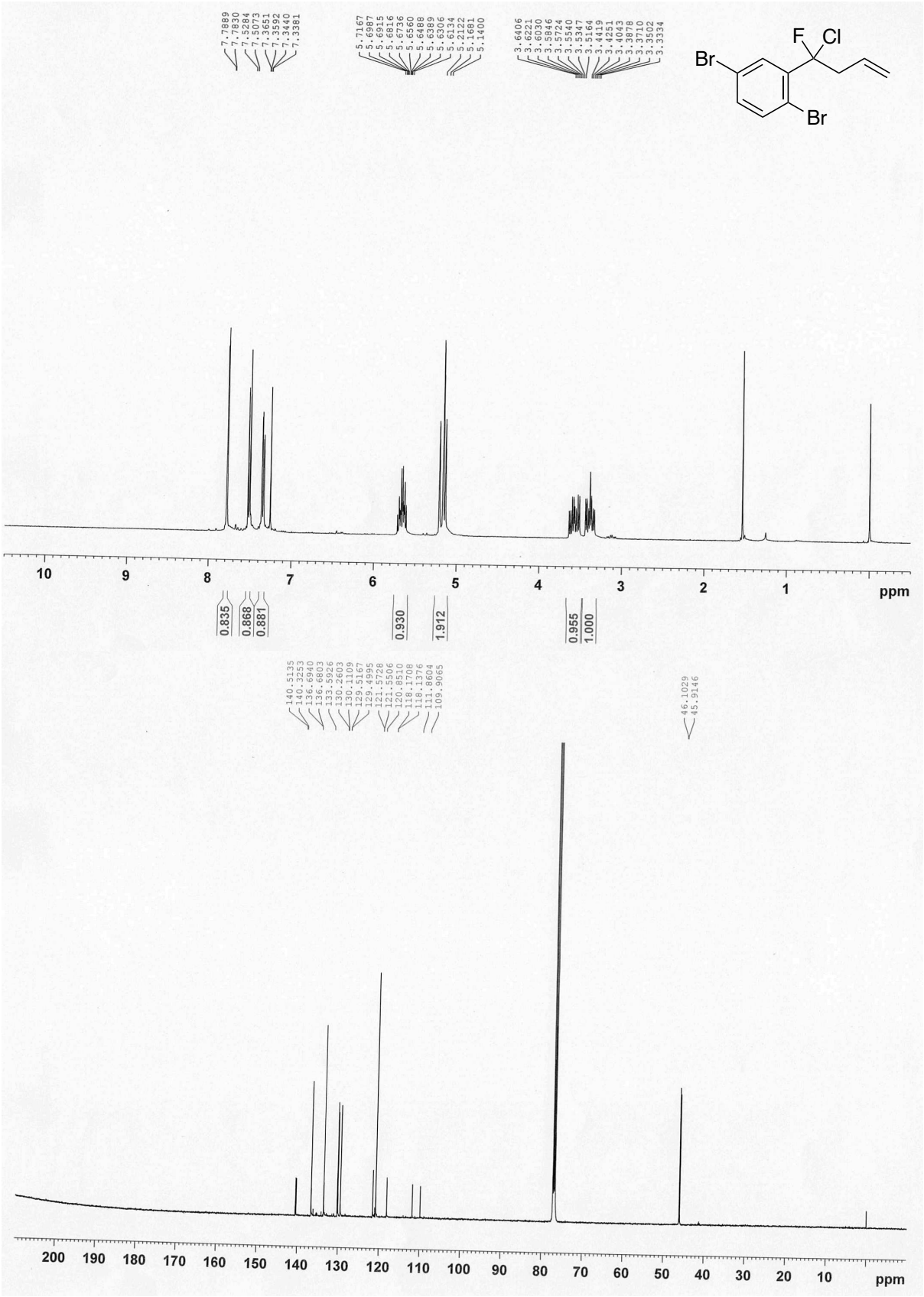

-101.5856
-101.6465
-101.6557
-101.7150
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

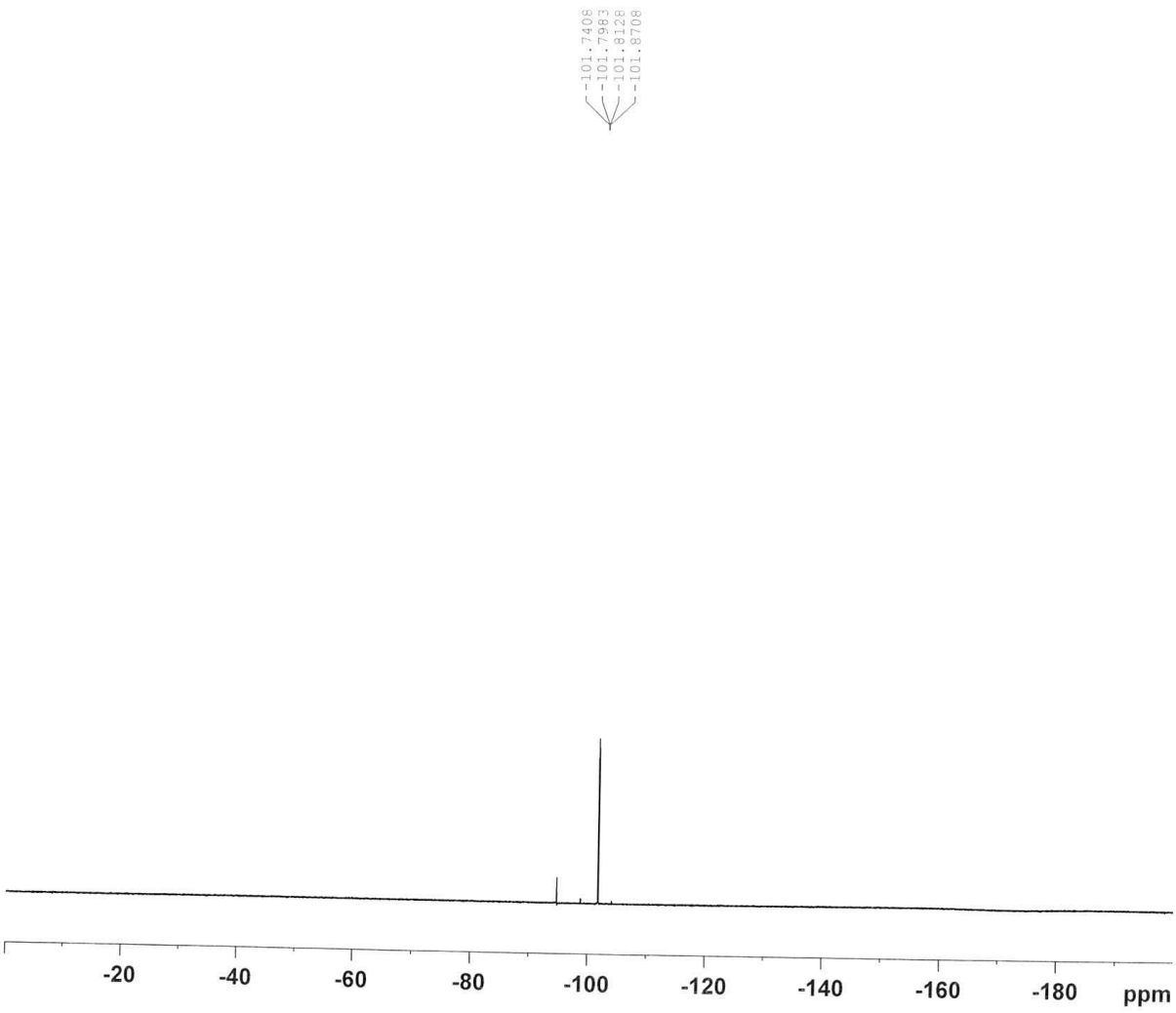
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **9c** ($CDCl_3$)



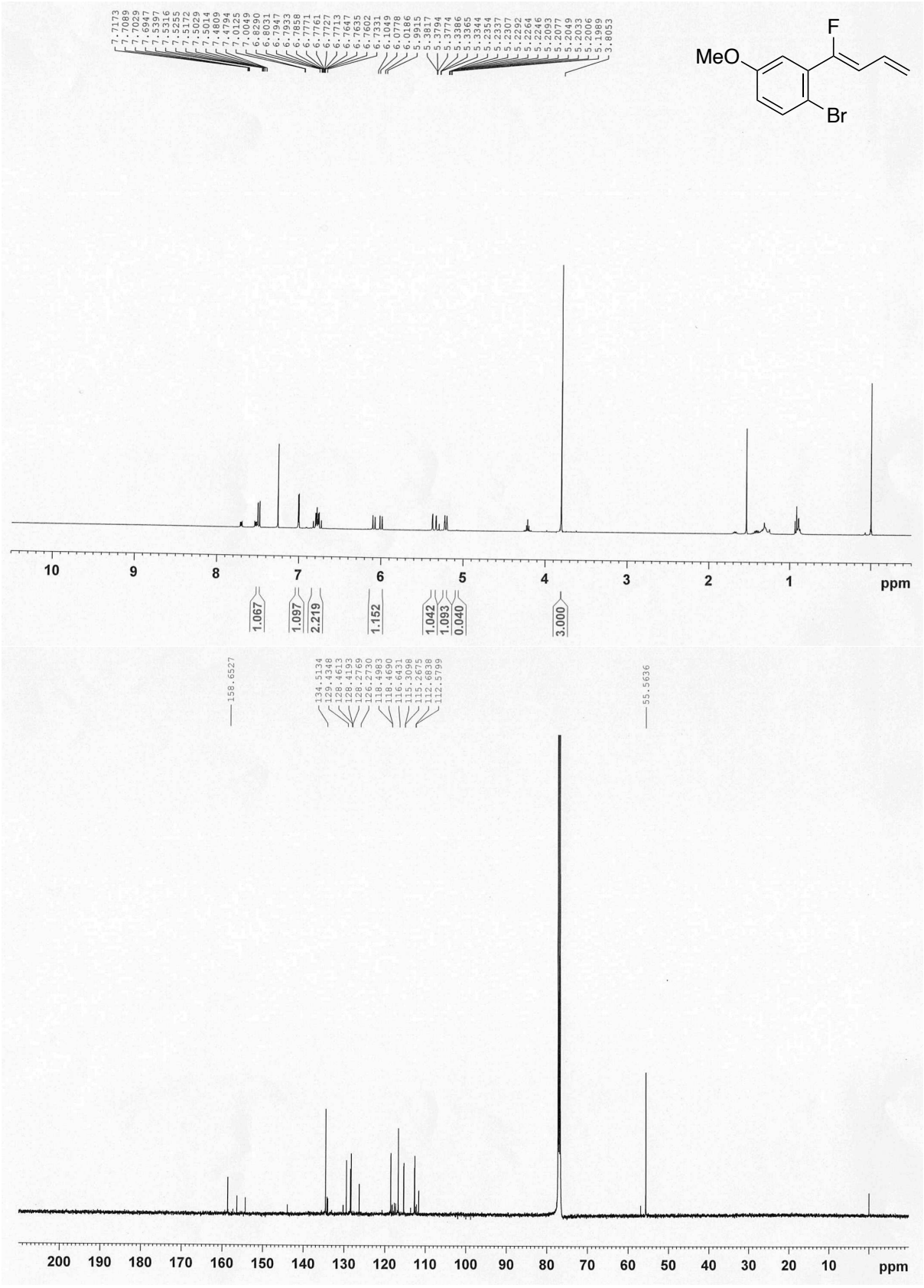

-62.7947
-101.5967
-101.6566
-101.6700
-101.7287
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

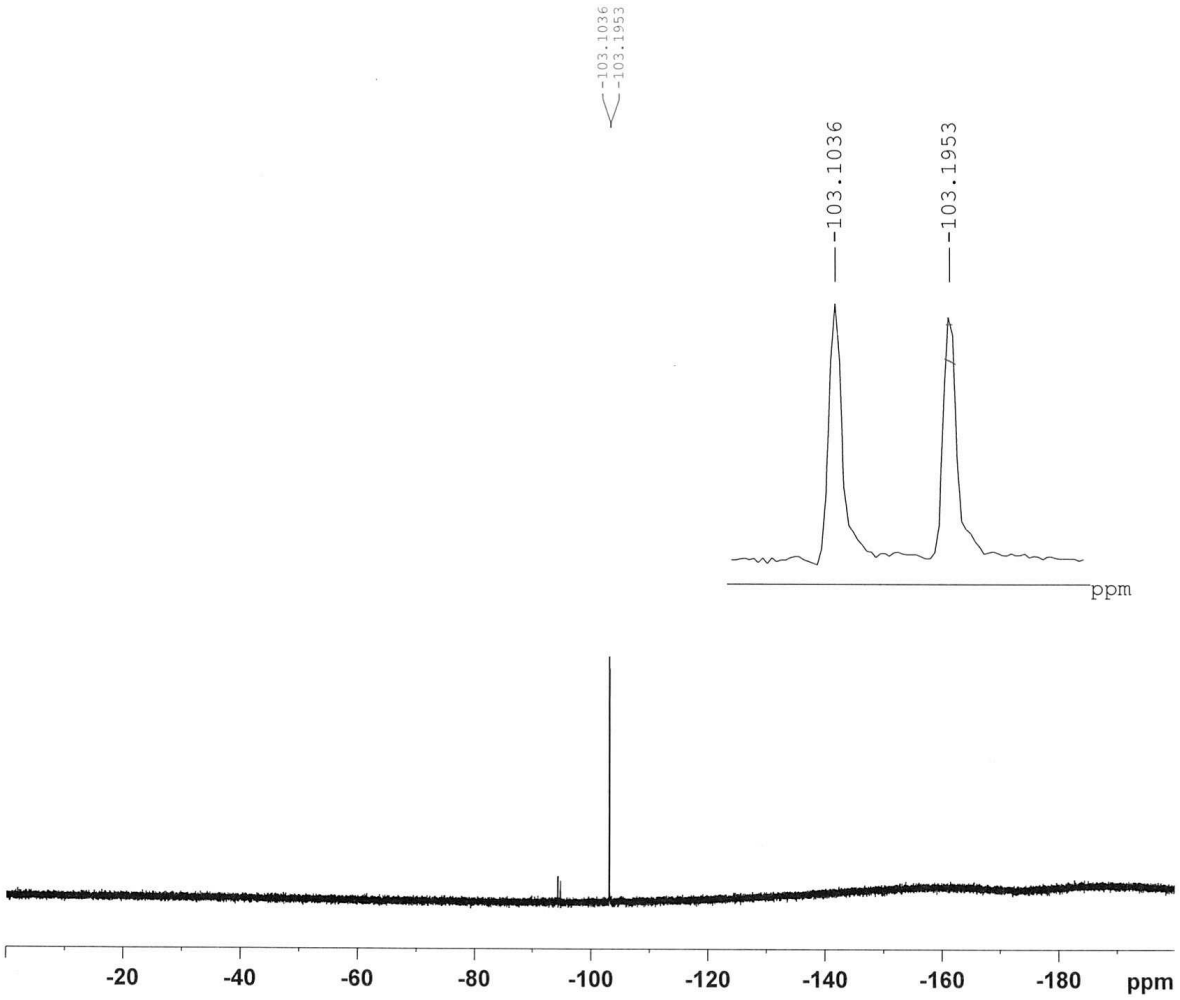
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **9d** ($CDCl_3$)



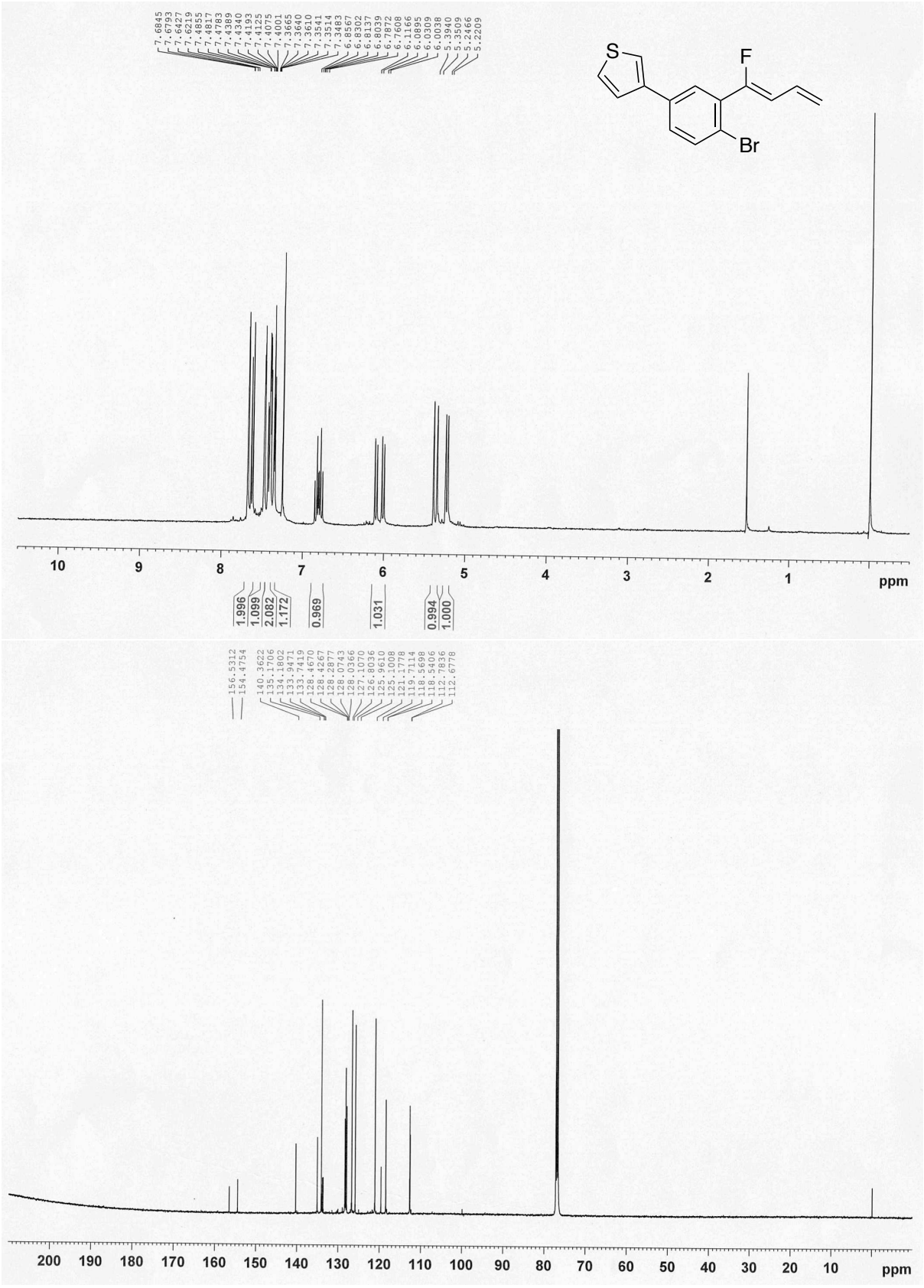

-101.7408
-101.7983
-101.8128
-101.8708
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

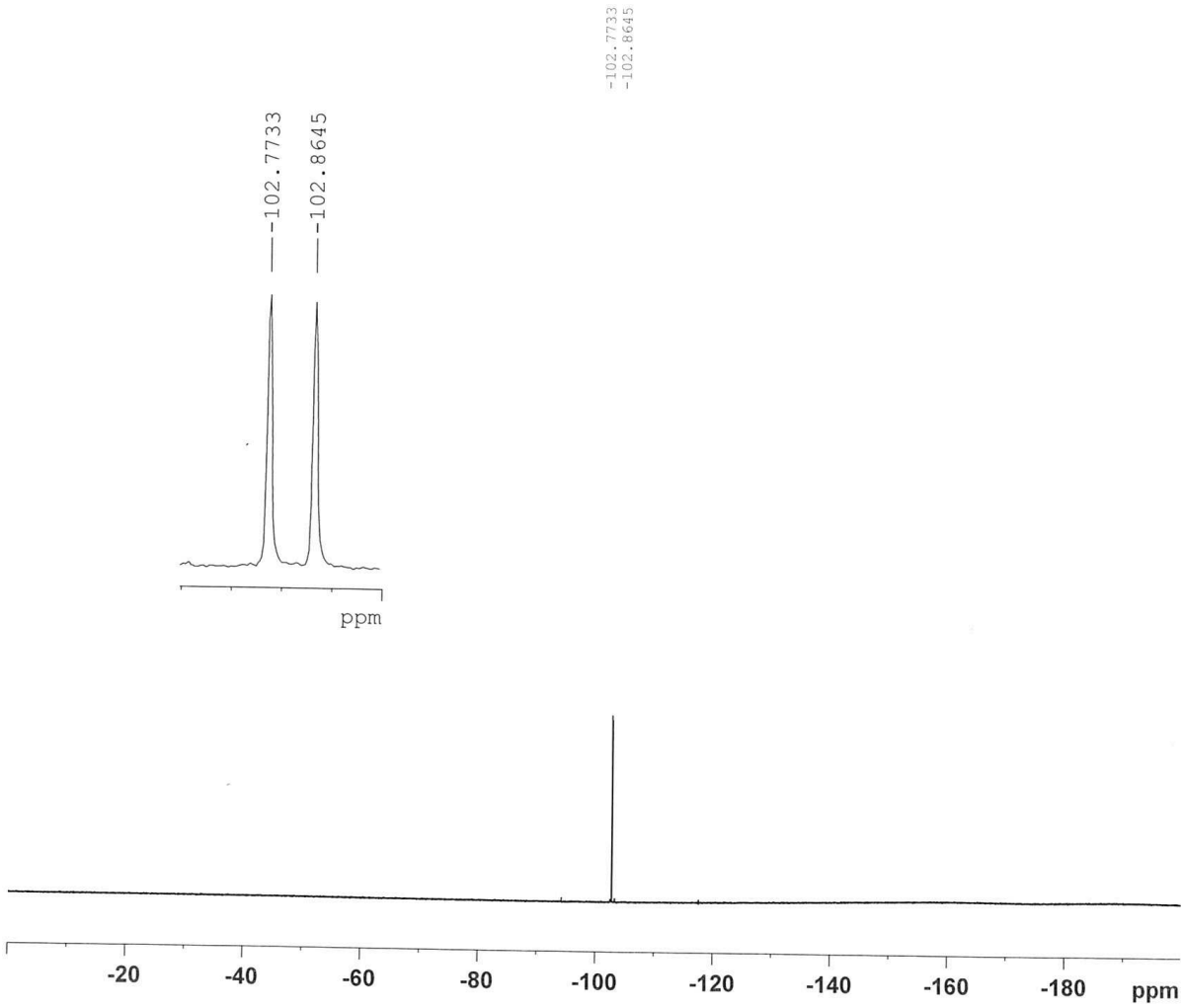
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **10a** ($CDCl_3$)



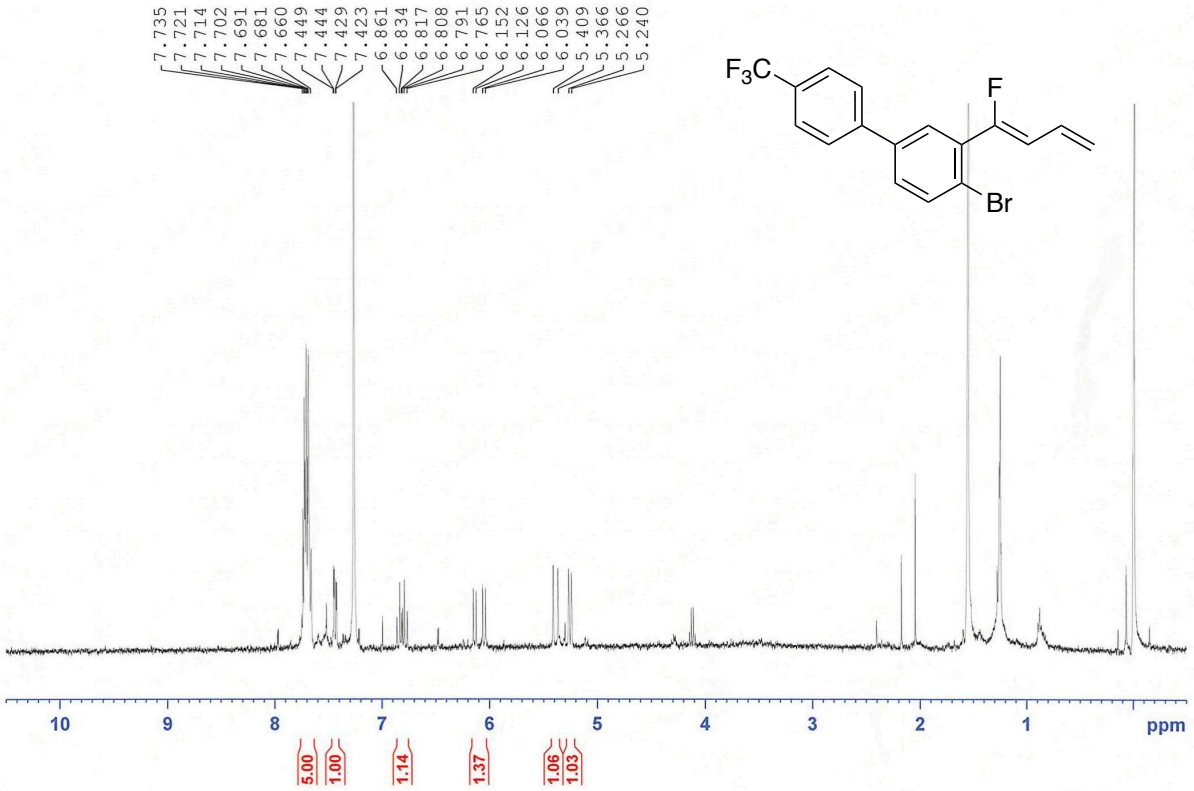

-103.1036
-103.1953
-103.1036
-103.1953
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

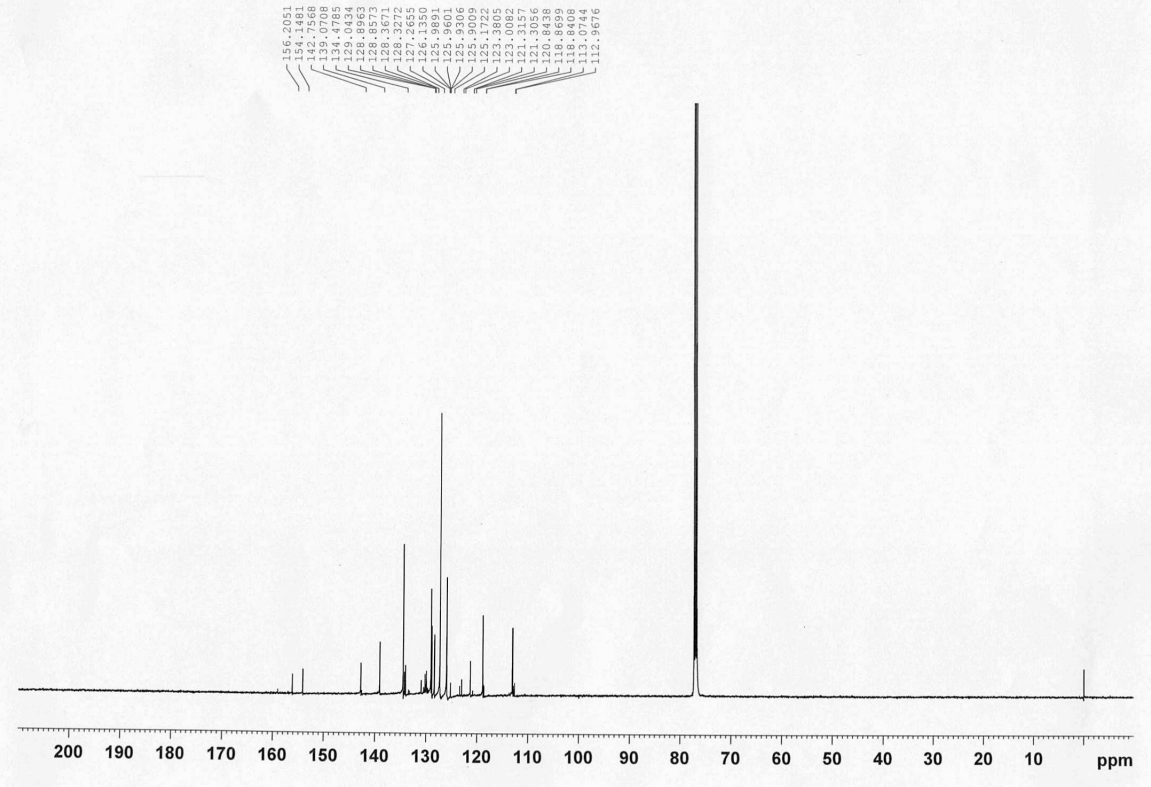
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **10b** ($CDCl_3$)

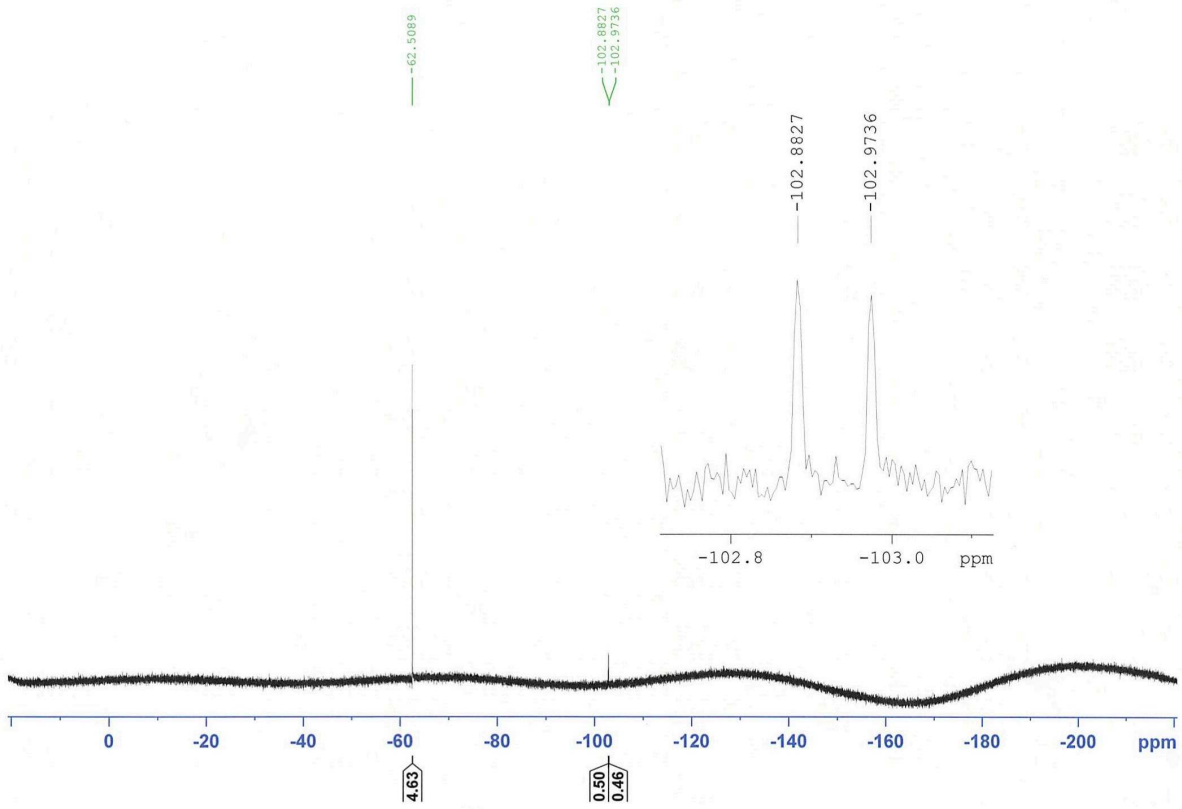



-102.7733
-102.8645
-102.7733
-102.8645
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

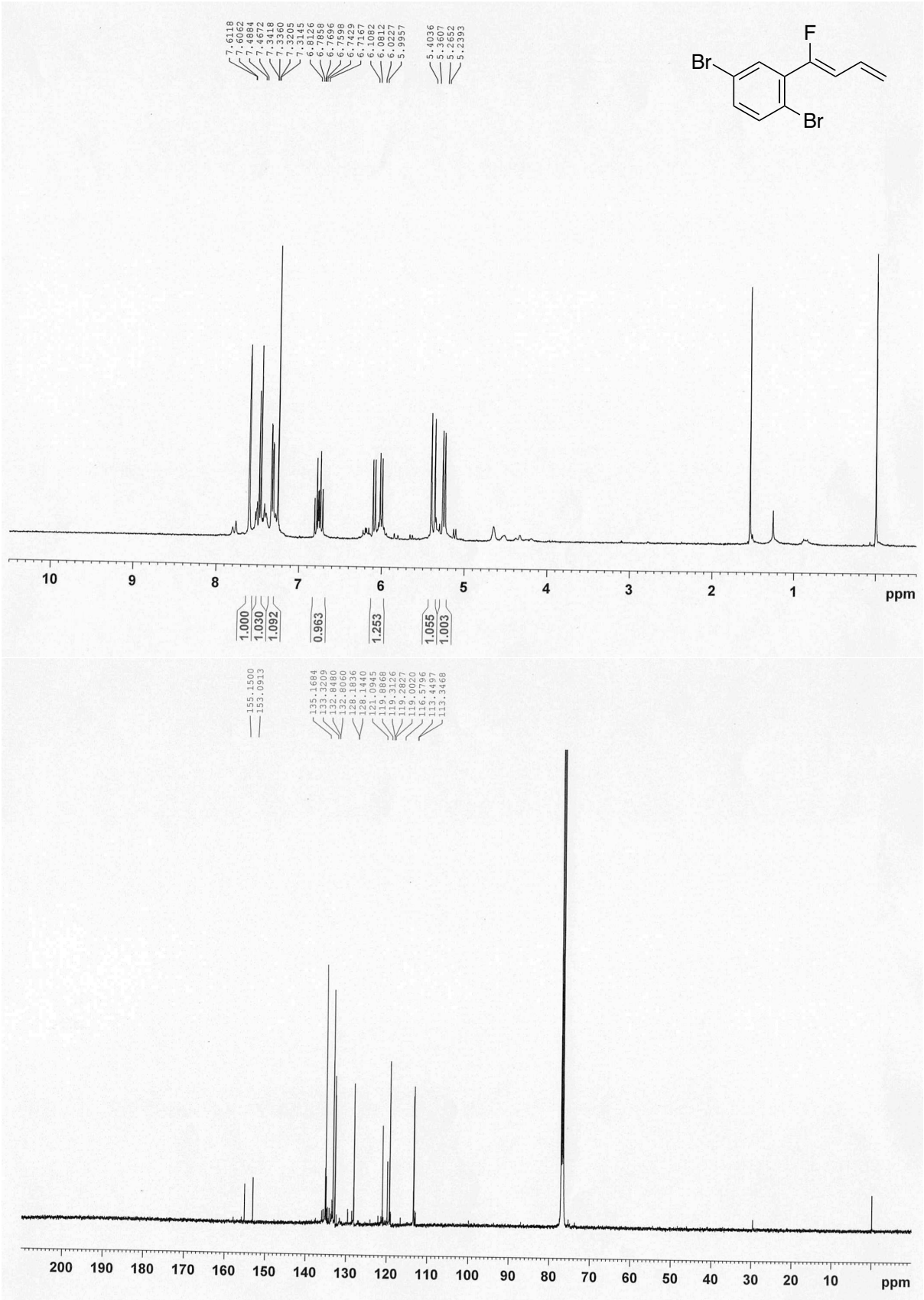
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **10c** ($CDCl_3$)

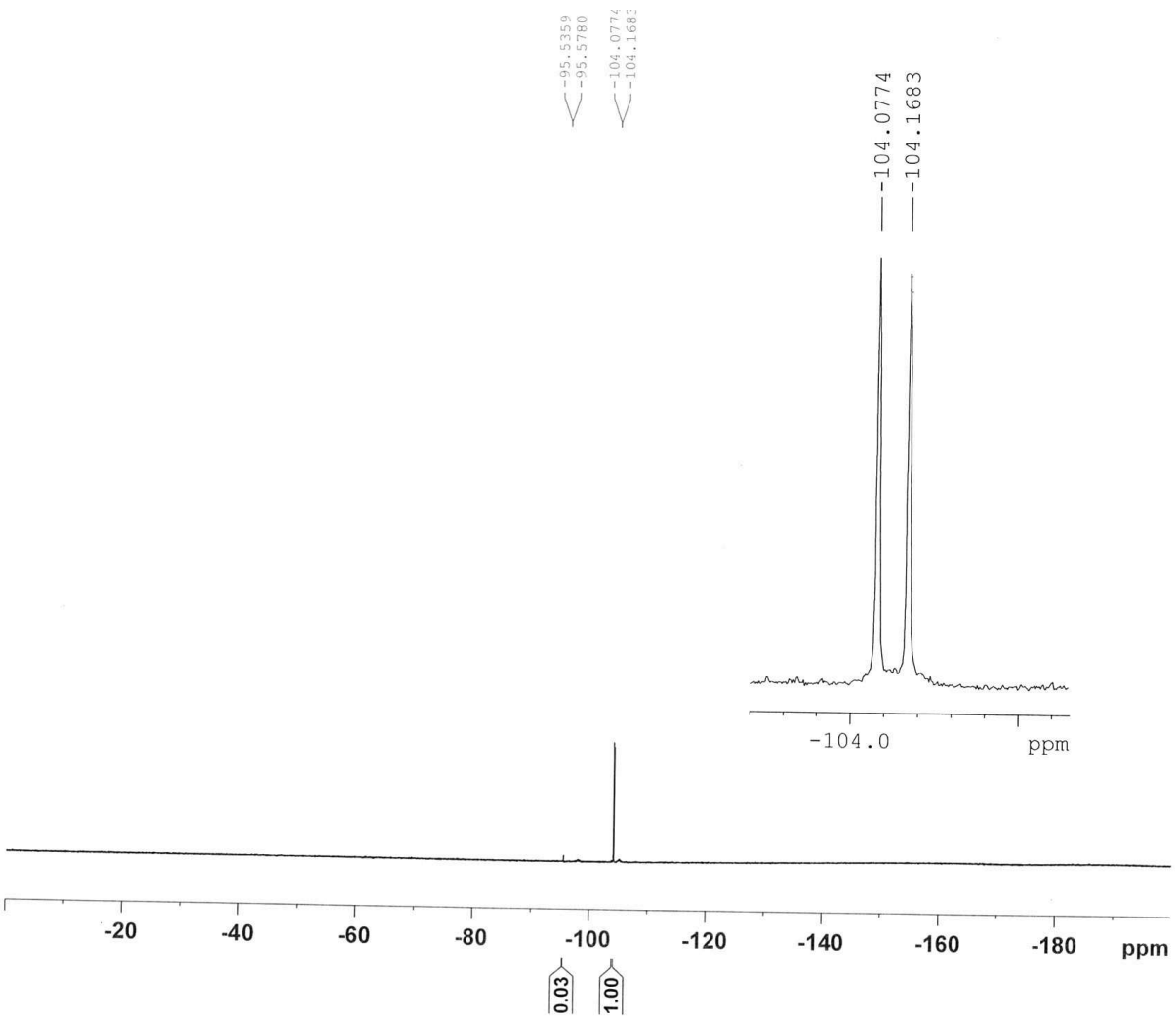




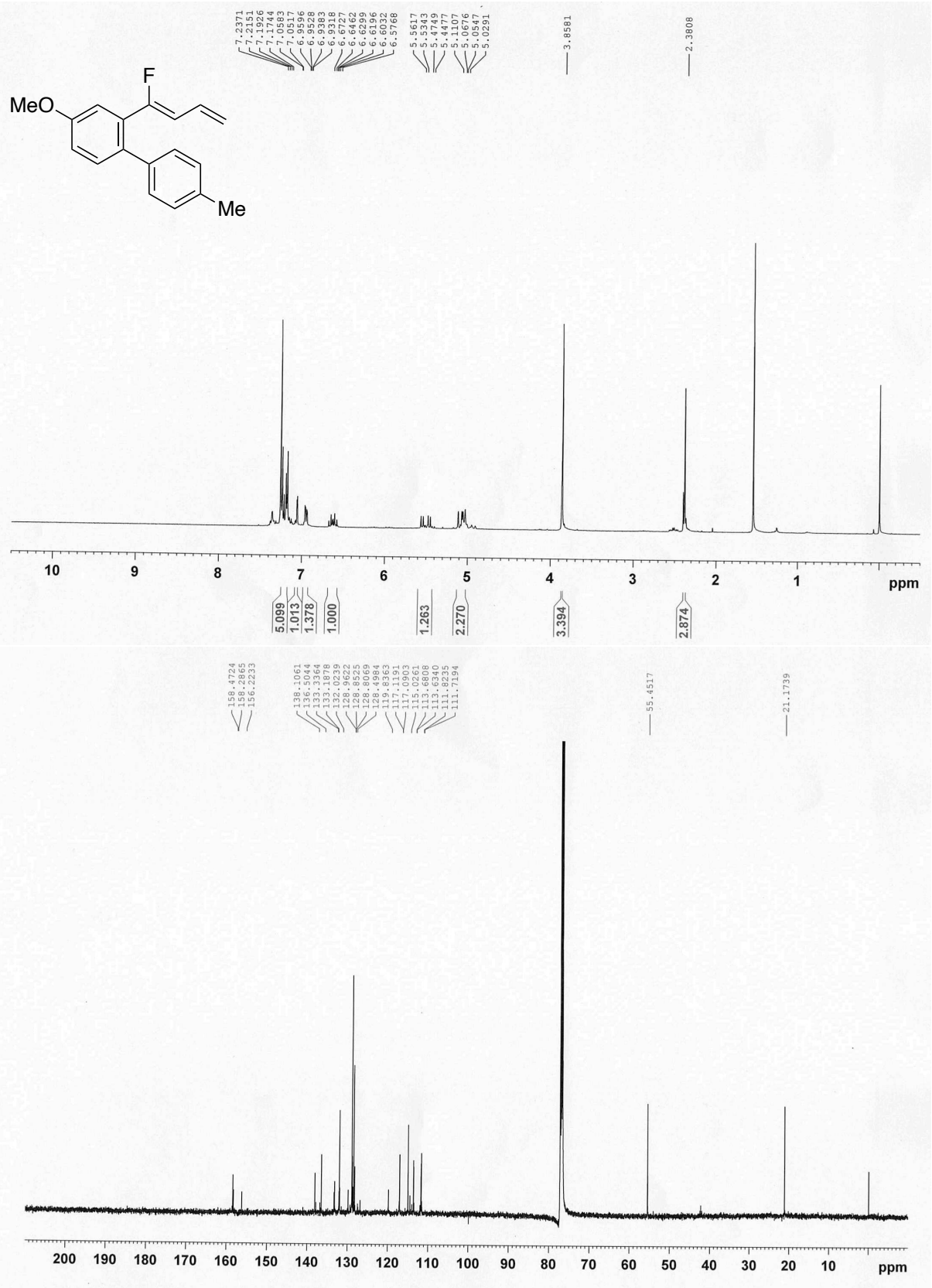

-62.5089
-102.8827
-102.9736
-102.8827
-102.9736
-102.8
-103.0
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
4.63
0.50
0.46

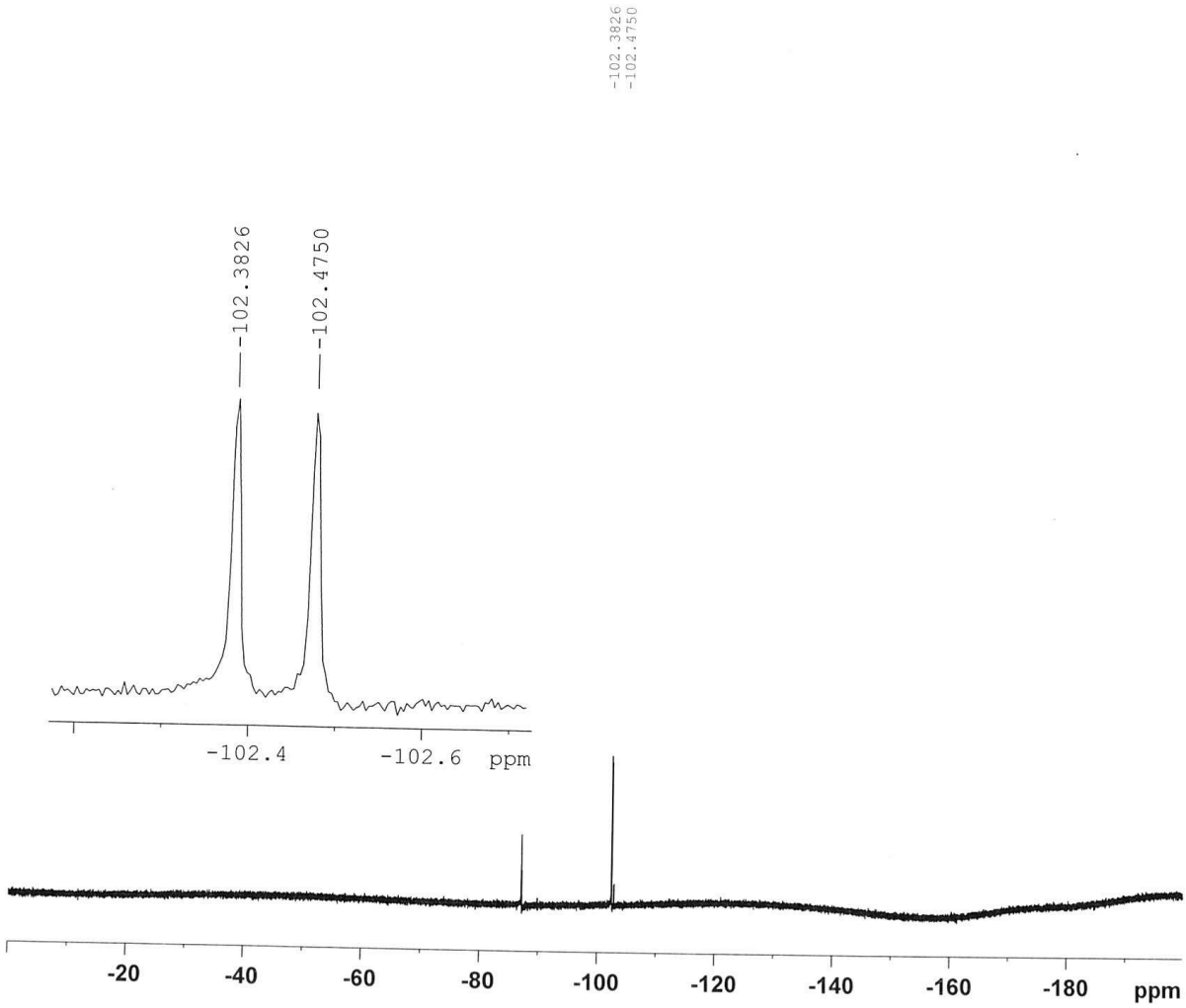
^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **10d** ($CDCl_3$)




-95.5359
-95.5780
-104.0774
-104.1683
-104.0774
-104.1683
-104.0
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
0.03
1.00

^{1}H NMR (400 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (376 MHz) spectra of **11** ($CDCl_3$)




-102.3826
-102.4750
-102.3826
-102.4750
-102.4
-102.6
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm