Supporting Information

Stereoselective Synthesis of Both Stereoisomers of β-Fluorostyrene Derivatives from a Common Intermediate

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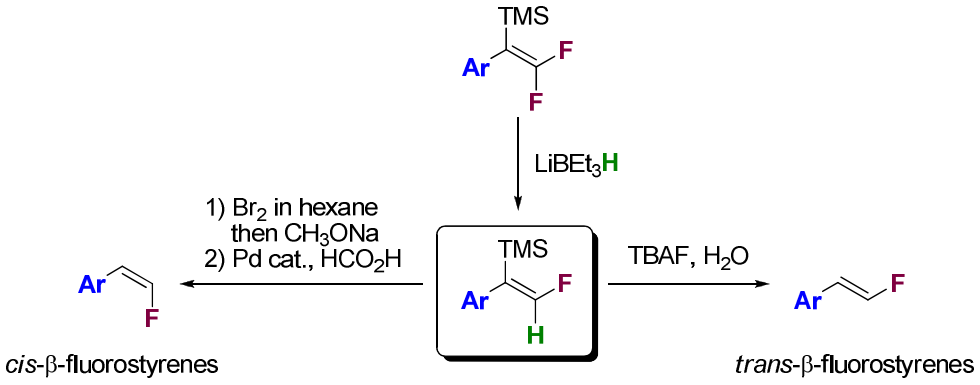
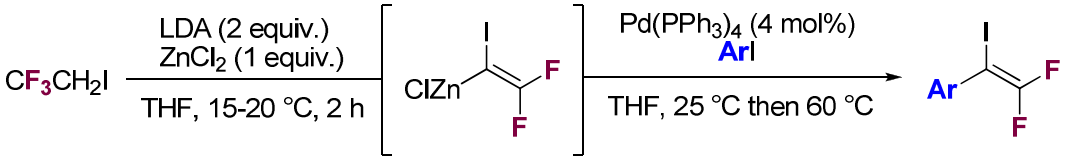


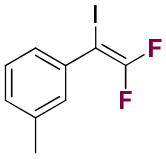
Table of content

1. General information: The following includes general experimental procedures, specific details for representative reactions and spectroscopic information for the new compounds prepared. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a VARIAN Inova 400 MHz or BRUKER Avance 300 MHz in $CDCl_3$ at ambient temperature using tetramethylsilane (^{1}H NMR) or residual $CHCl_3$ (^{1}H and ^{13}C NMR) as the internal standard, or $CFCl_3$ (^{19}F NMR) as the external standard. Infrared spectra were recorded on a Bomem FT-IR MB-Series spectrometer. High-resolution mass spectra were obtained on a LC/MS-TOF Agilent 6210 using atmospheric pressure photoionization ionization (APPI). Low-resolution mass spectra were obtained on a ThermoFisher Scientific Trace GC Ultra with a ITQ 900 Ion Trap mass spectrometer.

2. Synthesis of the α-iodo-β,β-difluorostyrenes

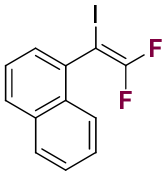


All the α-iodo-β,β-difluorostyrenes were prepared according to the protocol reported by Burton[1,2] The data for the α-iodo-β,β-difluorostyrenes not described previously are given below.



S1

1-(2,2-difluoro-1-iodovinyl)-3-methylbenzene (S1). Following Burton's protocol[1] on a 7.7 mmol scale of 3-iodotoluene, the desired product (1.82 g, 85%) was isolated as a pink oil by flash chromatography using 100% hexane. IR (neat) ν = 3038, 2861, 1706, 1485, 1258, 1178, 981, 695 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 3H), 7.12 (m, 1H), 2.37 (s, 3H) ; ^{13}C (75 MHz, $CDCl_3$) δ 152.8 (dd, $J_{C\text{-}F}$ = 298 Hz, $J_{C\text{-}F}$ = 282 Hz), 138.3, 133.8, 130.3, 129.5, 128.4, 126.8, 48.4 (dd, J = 29 Hz, J = 27 Hz), 21.3 ; ^{19}F (282 MHz, $CDCl_3$) δ -70.8 (d, 1F, J = 26 Hz), -77.8 (d, 1F, J = 26 Hz); GC/MS cald for $C_9H_7F_2I$ $[M]^+$ 280.05, found 280.93.



S2

1-(2,2-difluoro-1-iodovinyl)naphthalene (S2). Following Burton's protocol[1] on a 6 mmol scale of 1-iodonaphthalene, the desired product (1.65 g, 87%) was isolated as a pink oil by flash chromatography using 100% hexane. IR (neat) ν = 3059, 1720, 1508, 1262, 1241, 1095, 968, 780 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d,1H, J = 9 Hz), 7.92 (t, 2H, J = 9 Hz), 7.65 (t, 1H, J = 7 Hz), 7.60-7.53 (2H, m),

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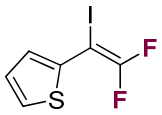
[1] Anilkumar, R.; Burton, D. J. *J. Fluorine Chem.* **2005**, *126*, 457.
[2] Landelle, G.; Champagne, P.-A.; Barbeau, X.; Paquin, J.-F. *Org. Lett.* **2009**, *11*, 681.

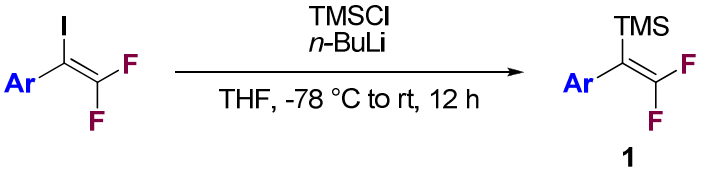
7.48 (t,1H, J = 7 Hz); ^{13}C (100 MHz, $CDCl_3$) δ 153.3 (dd, $J_{C\text{-}F}$ = 295 Hz, $J_{C\text{-}F}$ = 285 Hz), 150.4, 134.2, 131.3 (dd, J = 9 Hz, J = 2 Hz), 130.1, 128.8, 128.5 (m), 126.9, 126.8, 125.8, 125.2, 43.1 (d, J = 31 Hz) ; ^{19}F (376 MHz, $CDCl_3$) -73.6 (d, 1F, J = 24 Hz), -75.6 (d, 1F, J = 24 Hz).; HRMS-APPI cald for $C_{12}H_7F_2I$ $[M^*]^+$ 315.9561, found 315.9558.



S3

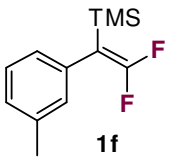
2-(2,2-difluoro-1-iodovinyl)thiophene (S3). Following Burton's protocol[1] on a 7.7 mmol scale of 2-iodothiophene, the desired product (1.42 g, 68%) was isolated as a colorless oil by flash chromatography using 100% hexane. IR (neat) ν = 3106, 1698, 1517, 1424, 1275, 1197, 979, 699 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, 1H, J = 5.1 Hz, J = 0.9 Hz), 7.24 (m, 1H), 7.05 (m, 1H) ; ^{13}C (75 MHz, $CDCl_3$) δ 153.1 (dd, $J_{C\text{-}F}$ = 302 Hz, $J_{C\text{-}F}$ = 284 Hz), 140.2 (d, J = 14 Hz), 129.7, 127.2, 127.0, 42.1 (dd, J = 36 Hz, J = 27 Hz) ; ^{19}F (282 MHz, $CDCl_3$) δ -71.0 (d, 1F, J = 18 Hz), -72.4 (d, 1F, J = 18 Hz); GC/MS cald for $C_6H_3F_2IS$ $[M]^+$ 272.05, found 272.99.

3. Synthesis of the α-silylated-β,β-difluoroalkenes



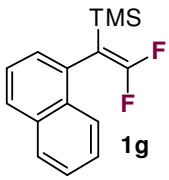
1

All the α-silylated-β,β-difluoroalkenes were prepared according to the protocol reported previously.[2] The data for the α-silylated-β,β-difluoroalkenes not described previously are given below.



1f

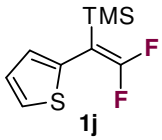
(2,2-difluoro-1-*m*-tolylvinyl)trimethylsilane (1f). Following the reported procedure[2] on a 6 mmol scale using TMSCl, the desired product (1.07 g, 79%) was isolated as a colorless oil by flash chromatography using 100% hexane. IR (neat) ν = 3038, 2959, 1692, 1606, 1269, 1225, 1021, 842 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 1H), 7.07 (m, 1H), 6.90 (m, 2H), 2.37 (s, 3H), 0.17 (s, 9H) ; ^{13}C (75 MHz, $CDCl_3$) δ 155.5 (dd, $J_{C\text{-}F}$ = 306 Hz, $J_{C\text{-}F}$ = 286 Hz), 137.9, 134.5 (d, J = 9 Hz), 129.7, 128.2, 127.2, 126.1, 87.7 (dd, $J_{C\text{-}F}$ = 33 Hz, $J_{C\text{-}F}$ = 4 Hz), 21.4, 0.9 ; ^{19}F (376 MHz, $CDCl_3$) δ -71.0 (d, 1F, J = 28 Hz), -78.4 (d, 1F, J = 28 Hz) ; HRMS-APPI cald for $C_{12}H_{16}F_2Si$ $[M^*]^+$ 226.0989, found 226.1028



1g

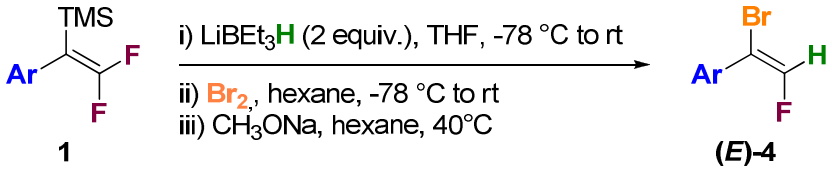
(2,2-difluoro-1-(naphthalen-1-yl)vinyl)trimethylsilane (1g). Following the reported procedure[2] on a 1.57 mmol scale using TMSCl, the desired product (407 mg, 98%) was isolated as a colorless oil by flash chromatography using 100% hexane. IR (neat) ν = 3060, 2959, 1691, 1270, 1252, 1017, 916, 843 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.95 (m, 2H), 7.84 (d, 1H, *J* = 8 Hz), 7.62-7.46 (m, 3H), 7.28 (d, 1H, *J* = 7 Hz), 0.23 (s, 9H), 0.17 (s, 9H) ; ^{13}C (100 MHz, $CDCl_3$) δ 155.2 (dd, $J_{C\text{-}F}$ = 308 Hz, $J_{C\text{-}F}$ = 287 Hz), 134.1, 132.3 (m, 2C), 129.0, 128.8, 127.5, 126.7 (m, 2C), 126.3, 126.2, 125.7, 124.0, 85.7 (dd, *J* = 35 Hz, *J* = 3Hz), -0.8 ; ^{19}F (376 MHz, $CDCl_3$) δ -68.0 (d, 1F, *J* = 25 Hz), -77.2 (d, 1F, *J* = 25 Hz) ; HRMS-APPI cald for $C_{15}H_{16}F_2Si$ $[M^*]^+$ 262.0989, found 262.0990

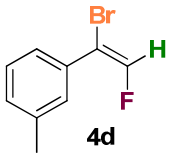


(2,2-difluoro-1-(thiophen-2-yl)vinyl)trimethylsilane (1j). Following the reported procedure[2] on a 4.3 mmol scale using TMSCl, the desired product (655 mg, 70%) was isolated as a colorless oil by flash chromatography using 100% hexane. IR (neat) ν = 3075, 2959, 1682, 1524, 1434, 1251, 1014, 845 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, 1H, *J* = 4.8 Hz), 6.99 (dd, 1H, *J* = 4.8 Hz, *J* = 3.6 Hz), 6.79 (d, 1H, *J* = 3.4 Hz), 0.22 (s, 9H) ; ^{13}C (75 MHz, $CDCl_3$) δ 155.8 (dd, $J_{C\text{-}F}$ = 311 Hz, $J_{C\text{-}F}$ = 288 Hz), 135.2 (d, *J* = 13 Hz), 126.9, 126.2, 124.7, 81.6, -0.9 ; ^{19}F (282 MHz, $CDCl_3$) δ -66.5 (d, 1F, *J* = 19 Hz), -74.6 (d, 1F, *J* = 18 Hz) ; HRMS-APPI cald for $C_9H_{12}F_2SSi$ $[M^*]^+$ 218.0397 found 218.0424

4. General procedure for the addition/elimination reaction of hydride followed by a bromination/desilicobromination reaction



All the 1-aryl-1-bromo-2-fluoroethenes were prepared according to the protocol reported previously.[3] The data for the 1-aryl-1-bromo-2-fluoroethenes not described previously are given below.

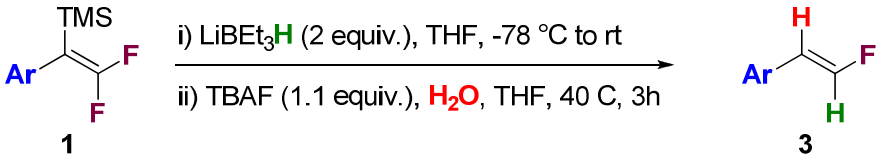


(*E*)-1-(1-bromo-2-fluorovinyl)-3-methylbenzene (4d). Following the general procedure on a 3.16 mmol scale of **1f**, the desired product (472 mg, 70%) was isolated as a colorless oil by flash chromatography using 100% hexane. IR (neat) ν = 3097, 2922, 1704, 1603, 1486, 1166, 1086, 782 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.26 (m, 1H), 7.15 (m, 1H), 7.08 (d, 1H, $J_{H\text{-}F}$ = 82 Hz), 2.39 (s, 3H) ; ^{13}C (75 MHz, $CDCl_3$) δ 145.4 (d, $J_{C\text{-}F}$ = 277 Hz), 138.1, 132.8, 129.9, 129.6 (d, *J* = 5 Hz), 128.2, 126.2 (d, *J* = 5 Hz), 110.4 (d, *J* =

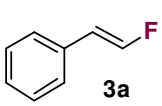
[3] Landelle, G.; Turcotte-Savard, M.-O.; Marterer, J.; Champagne, P. A.; Paquin, J.-F. *Org. Lett.* **2009**, *11*, 5406.

19 Hz), 21.4 ; ^{19}F (376 MHz, $CDCl_3$) δ -113.1 (d, 1F, J_{F-H} = 83 Hz) ; HRMS-APPI cald for C_9H_8BrF $[M^*]^+$ 213.9793, found 213.9818

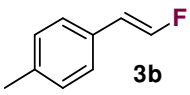
5. General procedure for the addition/elimination reaction of hydride followed by a protodesilylation reaction



(*E*)-Fluorostyrene derivatives – General protocol: To a stirred solution of α-silylated-β,β-difluoroalkenes **1** (1 mmol) and THF (9 mL) at -78 °C was added dropwise $LiBEt_3H$ (1 M in THF, 2 mmol) under N_2. After 20 min at -78 °C, the reaction mixture was allowed to warm to rt over 1 h. H_2O and Et_2O were added and the layers were separated. The aqueous layer was extracted with Et_2O (3×). The aqueous phase was neutralized with saturated aqueous NH_4Cl and extracted further with Et_2O (2×). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The crude material was directly used without purification for the protodesilylation reaction. To a stirred solution of the crude material in THF (9 mL) and H_2O (2 mmol) at rt was added tetrabutylammonium fluoride (1 M in THF, 1.1 equiv). The reaction mixture was heated to 40 °C for 3 h and then cooled down to rt (For substrate bearing an electron-rich aryl group, TBAF was added slowly over 1 h at 40 °C in order to reduce the formation of the corresponding alkyne). H_2O (10 mL) and Et_2O (10 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3×) and pentane (1×). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The crude material was purified with flash chromatography to give the desired product.

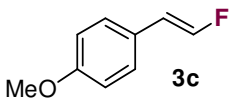


(*E*)-(2-fluorovinyl)benzene (3a). Following the general procedure on a 1.4 mmol scale of (2,2-difluoro-1-phenylvinyl)trimethylsilane, the desired product (104 mg, 61%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3296, 3063, 2856, 1658, 1447, 1095, 920, 675 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 5H), 7.21 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 11 Hz), 6.43 (dd, 1H, J_{H-F} = 19 Hz, J_{H-H} = 11 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 150.4 (d, J_{C-F} = 259 Hz), 132.2, 128.8, 127.5, 126.2, 113.9 (d, J = 16 Hz) ; ^{19}F (376 MHz, $CDCl_3$) δ -130.3 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 19 Hz) ; HRMS-APPI cald for C_8H_7F $[M^*]^+$ 122.0532, found 122.0538

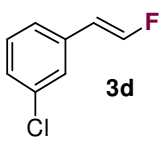


(*E*)-1-(2-fluorovinyl)-4-methylbenzene (3b). Following the general procedure on a 1.1 mmol scale of (2,2-difluoro-1-*p*-tolylvinyl)trimethylsilane, the desired product (95 mg, 64%) was isolated as a colorless oil by flash chromatography using 100% pentane.

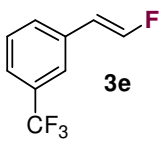
IR (neat) ν = 3298, 2924, 1663, 1514, 1454, 1089, 911, 798 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.16 (m, 4H), 7.17 (dd, 1H, J_{H-F} = 84 Hz, J_{H-H} = 11 Hz), 6.40 (dd, 1H, J_{H-F} = 20 Hz, J_{H-H} = 11 Hz), 2.37 (s, 3H) ; ^{13}C (100 MHz, $CDCl_3$) δ 150.0 (d, J_{C-F} = 260 Hz), 137.5 (d, J_{C-F} = 3 Hz), 132.3, 129.7, 126.3 (d, J_{C-F} = 3 Hz), 113.9 (d, J_{C-F} = 16 Hz), 21.4 ; ^{19}F (400 MHz, $CDCl_3$) δ -131.7 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 20 Hz) ; HRMS-APPI cald for C_9H_9F $[M^*]^+$ 136.0688, found 136.0737



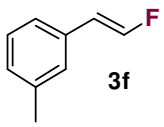
(*E*)-1-(2-fluorovinyl)-4-methoxybenzene (3c). Following the general procedure on a 1.03 mmol scale of (2,2-difluoro-1-(4-methoxyphenyl)vinyl)trimethylsilane, the desired product (100 mg, 64% contaminated with ca. 2% of 4-ethynylanisole) was isolated as a colorless oil by flash chromatography using diethyl ether/pentane (2:98). IR (neat) ν = 3294, 2958, 1661, 1511, 1465, 1085, 911, 835 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, 2H, J = 8 Hz), 7.11 (dd, 1H, J_{H-F} = 84 Hz, J_{H-H} = 12 Hz), 6.86 (d, 2H, J = 8 Hz), 6.36 (dd, 1H, J_{H-F} = 20 Hz, J_{H-H} = 11 Hz), 3.81 (s, 3H) ; ^{13}C (75 MHz, $CDCl_3$) δ 159.1, 149.1 (d, J_{C-F} = 256 Hz), 133.6, 127.3 (d, J = 3 Hz), 114.3, 113.3 (d, J = 15 Hz), 55.3 ; ^{19}F (376 MHz, $CDCl_3$) δ -133.1 (dd, 1F, J_{F-H} = 84 Hz, J_{F-H} = 20 Hz) ; HRMS-APPI cald for C_9H_9FO $[M^*]^+$ 152.0637, found 152.0656



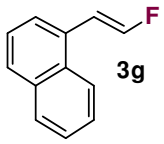
(*E*)-1-chloro-3-(2-fluorovinyl)benzene (3d). Following the general procedure on a 0.81 mmol scale of (1-(3-chlorophenyl)-2,2-difluorovinyl)trimethylsilane, the desired product (61 mg, 48%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3298, 2959, 1660, 1596, 1476, 1105, 915, 779 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 3H), 7.17 (dd, 1H, J_{H-F} = 82 Hz, J_{H-H} = 11 Hz), 7.13 (m, 1H), 6.35 (dd, 1H, J_{H-F} = 19 Hz, J_{H-H} = 12 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 151.0 (d, J_{C-F} = 263 Hz), 134.7 (d, J = 8 Hz), 134.4, 130.0, 127.5 (d, J = 2 Hz), 126.1 (d, J = 2 Hz), 124.4 (d, J = 3 Hz), 112.9 (d, J = 17 Hz) ; ^{19}F (376 MHz, $CDCl_3$) δ -127.8 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 19 Hz) ; HRMS-APPI cald for C_8H_6ClF $[M^*]^+$ 156.0142, found 156.0153



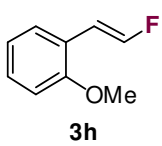
(*E*)-1-(2-fluorovinyl)-3-(trifluoromethyl)benzene (3e). Following the general procedure on a 0.89 mmol scale of (2,2-difluoro-1-(3-(trifluoromethyl)phenyl)vinyl)trimethylsilane, the desired product (49 mg, 30%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3083, 2931, 1663, 1593, 1448, 1337, 1200, 913 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.40 (m, 4H), 7.23 (dd, 1H, J_{H-F} = 82 Hz, J_{H-H} = 11 Hz), 6.44 (dd, 1H, J_{H-F} = 19 Hz, J_{H-H} = 12 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 151.2 (d, J_{C-F} = 263 Hz), 133.6 (d, J = 13 Hz), 129.3, 128.9, 125.9 (d, J = 21 Hz), 124.1 (m), 122.9 (m), 122.1, 113.0 (d, J = 16 Hz) ; ^{19}F (282 MHz, $CDCl_3$) δ -63.1 (s, 3F), -127.0 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 19 Hz) ; HRMS-APPI cald for $C_9H_6F_4$ $[M^*]^+$ 190.0406, found 190.0380



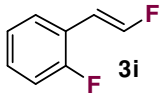
(*E*)-1-(2-fluorovinyl)-3-methylbenzene (3f). Following the general procedure on a 1.1 mmol scale of (2,2-difluoro-1-*m*-tolylvinyl)trimethylsilane (**1f**), the desired product (95 mg, 64%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3034, 2922, 1703, 1659, 1606, 1489, 1075, 917 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.22 (m, 1H), 7.24 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 11 Hz), 7.13 (m, 3H), 6.43 (dd, 1H, J_{H-F} = 19 Hz, J_{H-H} = 11 Hz), 2.4 (s, 3H) ; ^{13}C (75 MHz, $CDCl_3$) δ 150.1 (d, J_{C-F} = 258 Hz), 138.4, 132.6 (d, J = 13 Hz), 128.7, 128.3, 126.9 (d, J = 3 Hz), 123.3 (d, J = 3 Hz), 113.9 (d, J = 16 Hz), 21.4 ; ^{19}F (282 MHz, $CDCl_3$) δ -130.5 (d, 1F, J_{F-H} = 84 Hz, J_{F-H} = 19 Hz) ; HRMS-APPI cald for C_9H_9F $[M^*]^+$ 136.0688, found 136.0697



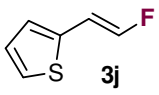
(*E*)-1-(2-fluorovinyl)naphthalene (3g). Following the general procedure on a 0.70 mmol scale of (2,2-difluoro-1-(naphthalen-1-yl)vinyl)trimethylsilane (**1g**), the desired product (103 mg, yield of **3g** is 62%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3297, 3059, 1654, 1590, 1508, 1102, 916, 775 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (m, 1H), 7.88 (d, 2H, J = 8 Hz), 7.54 (m, 2H), 7.44 (m, 2H), 7.01 (dd, 1H, J_{H-F} = 29 Hz, J_{H-F} = 11 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 150.8 (d, J_{C-F} = 263 Hz), 133.6 (d, J = 10 Hz), 131.3, 129.3, 128.6, 128.3, 126.3, 126.1, 125.6, 124.1, 119.8, 111.5 (d, J = 15 Hz) ; ^{19}F (282 MHz, $CDCl_3$) δ -123.8 (d, 1F, J_{F-H} = 87 Hz, J_{F-H} = 16 Hz) ; HRMS-APPI cald for $C_{12}H_9F$ $[M^*]^+$ 172.0688, found 172.0704



(*E*)-1-(2-fluorovinyl)-2-methoxybenzene (3h). Following the general procedure on a 0.83 mmol scale of (2,2-difluoro-1-(2-methoxyphenyl)vinyl)trimethylsilane, the desired product (74 mg, 60%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3005, 2838, 1657, 1599, 1493, 1246, 1077, 915 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (dd, 1H, J_{H-F} = 86 Hz, J_{H-H} = 11 Hz), 7.24 (m, 2H), 6.94 (m, 2H), 6.54 (dd, 1H, J_{H-F} = 22 Hz, J_{H-H} = 11 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 156.8, 151.6 (d, J_{C-F} = 258 Hz), 128.4 (dd, J = 9 Hz, J = 2 Hz), 121.6 (d, J = 11 Hz), 131.4, 120.8, 110.8, 110.5 (d, J = 18 Hz), 55.3 ; ^{19}F (282 MHz, $CDCl_3$) δ -125.2 (dd, 1F, J = 87 Hz, J = 23 Hz) ; HRMS-APPI cald for C_9H_9FO $[M^*]^+$ 152.0637, found 152.0648



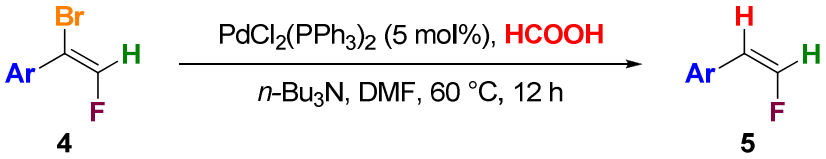
(*E*)-1-fluoro-2-(2-fluorovinyl)benzene (3i). Following the general procedure on a 1.05 mmol scale of (2,2-difluoro-1-(2-fluorophenyl)vinyl)trimethylsilane, the desired product (76 mg, 52%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3085, 2959, 1660, 1489, 1455, 1118, 915, 753 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, 1H, J_{H-F} = 84 Hz, J_{H-H} = 11 Hz), 7.14-6.86 (m, 4H), 6.27 (dd, 1H, J_{H-F} = 21 Hz, J_{H-H} = 11 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 161.3 (dd, J_{C-F} = 250 Hz, J_{C-F} = 3 Hz), 153.6 (dd, J_{C-F} = 260 Hz, J_{C-F} = 11 Hz), 129.9, 129.8 (m), 125.5 (d, J = 3Hz), 117.2, 116.9, 109.5 (d, J = 20 Hz) ; ^{19}F (282 MHz, $CDCl_3$) δ -113.8 (m, 1H), -123.0 (dm, 1F, J_{F-H} = 84 Hz) ; HRMS-APPI cald for $C_8H_6F_2$ $[M^*]^+$ 140.0438, found 140.0444



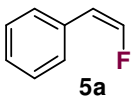
3j

(*E*)-2-(2-fluorovinyl)thiophene (3j). Following the general procedure on a 1.01 mmol scale of (2,2-difluoro-1-(thiophen-2-yl)vinyl)trimethylsilane (**1j**), the desired product (49 mg, 35%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3073, 2959, 1659, 1465, 1201, 1103, 905, 694 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 11 Hz), 7.15 (d, 1H, J = 5 Hz), 7.03-6.90 (m, 2H), 6.55 (dd, 1H, J_{H-F} = 17 Hz, J_{H-H} = 11 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 149.7 (d, J_{C-F} = 261 Hz), 134.9 (d, J = 13 Hz), 127.4, 125.8 (d, J = 6 Hz), 123.8 (d, J = 3 Hz), 108.1 (d, J = 20 Hz) ; ^{19}F (282 MHz, $CDCl_3$) δ -129.6 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 18 Hz) ; HRMS-APPI cald for C_6H_5FS $[M^*]^+$ 128.0096, found 128.0104

6. Procedure for the reduction with formic acid

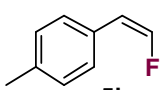


(*Z*)-Fluorostyrene derivatives – General protocol: To a stirred solution of $PdCl_2(PPh_3)_2$ (0.1 mmol) and *n*-Bu_3N (4.5 mmol) in DMF (7 mL) was added a solution of 1-aryl-1-bromo-2-fluoroethene **4** (1 mmol) in DMF (2 mL) under N_2. After 5 min at rt, formic acid (3 mmol) was added and the reaction mixture was heated for 12 h at 60 °C. Et_2O (10 mL) and H_2O (20 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3×). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The crude material was purified with flash chromatography to give the desired product.



5a

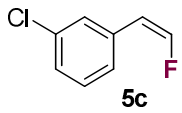
(*Z*)-(2-fluorovinyl)benzene (5a). Following the general procedure on a 0.34 mmol scale of (*E*)-(1-bromo-2-fluorovinyl)benzene, the desired product (31 mg, 73%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3085, 2856, 1644, 1590, 1432, 1058, 923, 693 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H, J = 7 Hz), 7.36 (t, 2H, J = 7 Hz), 7.28 (d, 1H, J = 7 Hz), 6.67 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 5 Hz), 5.62 (dd, 1H, J_{H-F} = 45 Hz, J_{H-H} = 5 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 148.2 (d, J_{C-F} = 270 Hz), 128.9, 128.8, 128.5, 127.5, 110.8 ; ^{19}F (376 MHz, $CDCl_3$) δ -122.6 (dd, 1F, J_{F-H} = 82 Hz, J_{F-H} = 45 Hz) ; HRMS-APPI cald for C_8H_7F $[M^*]^+$ 122.0531, found 122.0510



5b

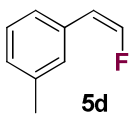
(*Z*)-1-(2-fluorovinyl)-4-methylbenzene (5b). Following the general procedure on a 0.58 mmol scale of (*E*)-1-(1-bromo-2-fluorovinyl)-4-methylbenzene, the desired product (38 mg, 52%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR

(neat) ν = 3026, 2923, 1663, 1514, 1387, 1236, 1017, 824 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, *J* = 8 Hz), 7.17 (d, 2H, *J* = 8 Hz), 6.64 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 5 Hz), 5.61 (dd, 1H, J_{H-F} = 45 Hz, J_{H-H} = 5 Hz), 2.37 (s, 3H) ; ^{13}C (100 MHz, $CDCl_3$) δ 147.8 (d, J_{C-F} = 269 Hz), 137.4, 129.8, 129.2, 128.8 (d, *J* = 7 Hz), 110.7, 21.3 ; ^{19}F (376 MHz, $CDCl_3$) δ -123.4 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 45 Hz) ; HRMS-APPI cald for C_9H_9F $[M^*]^+$ 136.0688, found 136.0696



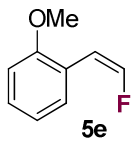
5c

(*Z*)-1-chloro-3-(2-fluorovinyl)benzene (5c). Following the general procedure on a 0.81 mmol scale of (*E*)-1-(1-bromo-2-fluorovinyl)-3-chlorobenzene, the desired product (64 mg, 51%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 2926, 2854, 1660, 1597, 1566, 1235, 1026, 791 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.38 (d, 1H, *J* = 7 Hz), 7.26 (m, 2H), 6.68 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 5 Hz), 5.59 (dd, 1H, J_{H-F} = 44 Hz, J_{H-H} = 5 Hz) ; ^{13}C (75 MHz, $CDCl_3$) δ 149.2 (d, J_{C-F} = 274 Hz), 134.3 (d, *J* = 8 Hz), 129.7, 128.8, 127.6, 126.9, 126.1, 109.8 ; ^{19}F (282 MHz, $CDCl_3$) δ -120.2 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 45 Hz) ; HRMS-APPI cald for C_8H_6ClF $[M^*]^+$ 156.0142, found 156.0160



5d

(*Z*)-1-(2-fluorovinyl)-3-methylbenzene (5d). Following the general procedure on a 0.47 mmol scale of (*E*)-1-(1-bromo-2-fluorovinyl)-3-methylbenzene (**4d**), the desired product (35 mg, 56%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 3052, 2923, 1662, 1606, 1491, 1235, 1027, 794 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.25 (m, 1H), 7.10 (d, 1H, *J* = 8 Hz), 6.65 (dd, 1H, J_{H-F} = 83 Hz, J_{H-H} = 5 Hz), 5.60 (dd, 1H, J_{H-F} = 45 Hz, J_{H-H} = 5 Hz), 2.37 (s, 3H) ; ^{13}C (100 MHz, $CDCl_3$) δ 148.4 (d, J_{C-F} = 267 Hz), 138.3, 132.7, 129.8 (d, *J* = 7 Hz), 128.6, 128.5 (d, *J* = 2 Hz), 126.2 (d, *J* = 7 Hz), 111.1, 21.7 ; ^{19}F (376 MHz, $CDCl_3$) δ -122.6 (dd, 1F, J_{F-H} = 83 Hz, J_{F-H} = 45 Hz) ; HRMS-APPI cald for C_9H_9F $[M^*]^+$ 136.0688, found 136.0691

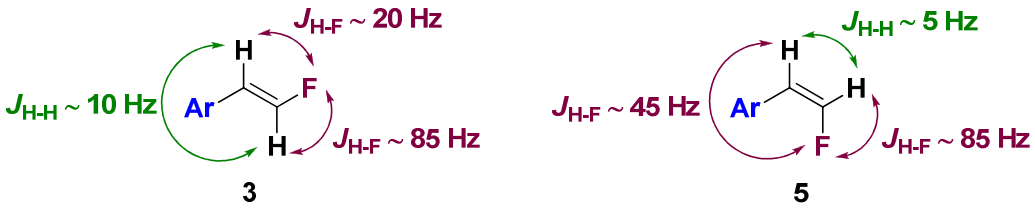


5e

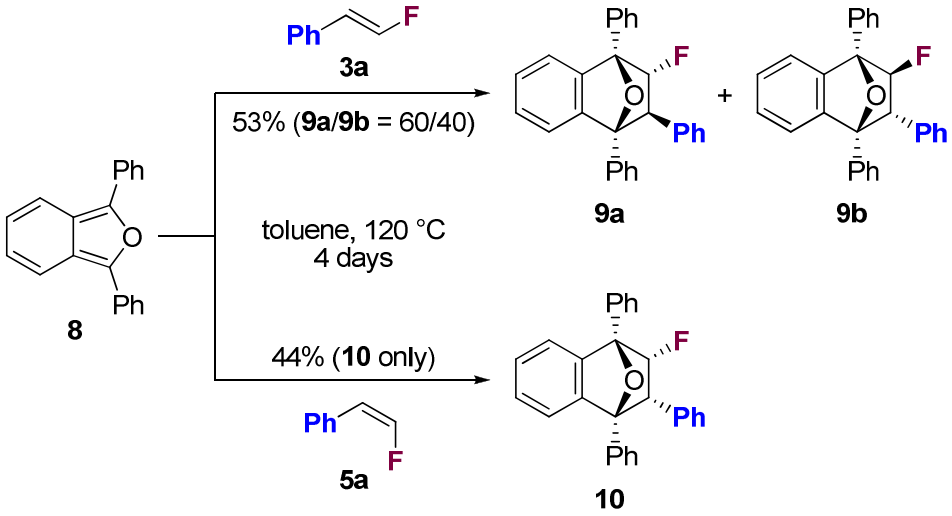
(*Z*)-1-(2-fluorovinyl)-2-methoxybenzene (5e). Following the general procedure on a 0.62 mmol scale of (*E*)-1-(1-bromo-2-fluorovinyl)-2-methoxybenzene, the desired product (49 mg, 52%) was isolated as a colorless oil by flash chromatography using diethyl ether/pentane (1:99). IR (neat) ν = 3073, 2838, 1661, 1599, 1488, 1247, 1016, 771 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 1H, *J* = 8 Hz), 7.26 (t, 1H, *J* = 7 Hz), 6.98 (t, 1H, *J* = 7 Hz), 6.89 (d, 1H, *J* = 9Hz), 6.70 (dd, 1H, J_{H-F} = 84 Hz, J_{H-H} = 6 Hz), 6.08 (dd, 1H, J_{H-F} = 46 Hz, J_{H-H} = 6 Hz), 3.85 (s, 3H) ; ^{13}C (100 MHz, $CDCl_3$) δ 156.3, 148.5 (d, J_{C-F} = 270 Hz), 134.0 (d, *J* = 19 Hz), 130.6 (d, *J* = 11 Hz), 128.9, 120.9, 110.7, 104.5, 55.8 ; ^{19}F (376 MHz, $CDCl_3$) δ -124.3 (dd, 1F, J_{F-H} = 84 Hz, J_{F-H} = 47 Hz) ; HRMS-APPI cald for C_9H_9FO $[M^*]^+$ 152.0637, found 152.0640

7. Determination of the stereochemistry

The stereochemistry of the two isomers of β-fluorostyrenes **3** and **5** was unambiguously determined by examination of the coupling constants in ^{1}H and ^{19}F NMR.



8. Diels-Alder reaction with 1,3-diphenylisobenzofuran



The β-fluorostyrene (**3a** or **5a**, 0.2 mmol) and 1,3-diphenylisobenzofuran **8** (0.2 mmol) in toluene (1 mL) were heated in a sealed glass tube at 120 °C for 4 days. The solvent was removed under reduced pressure. After taking a ^{19}F NMR spectrum of the crude product, in order to determine the ratio of diastereoisomers, the desired product was isolated as a light yellow oil by flash chromatography using 8% ethyl acetate/hexane. The spectroscopic data were in agreement with the literature.[4]

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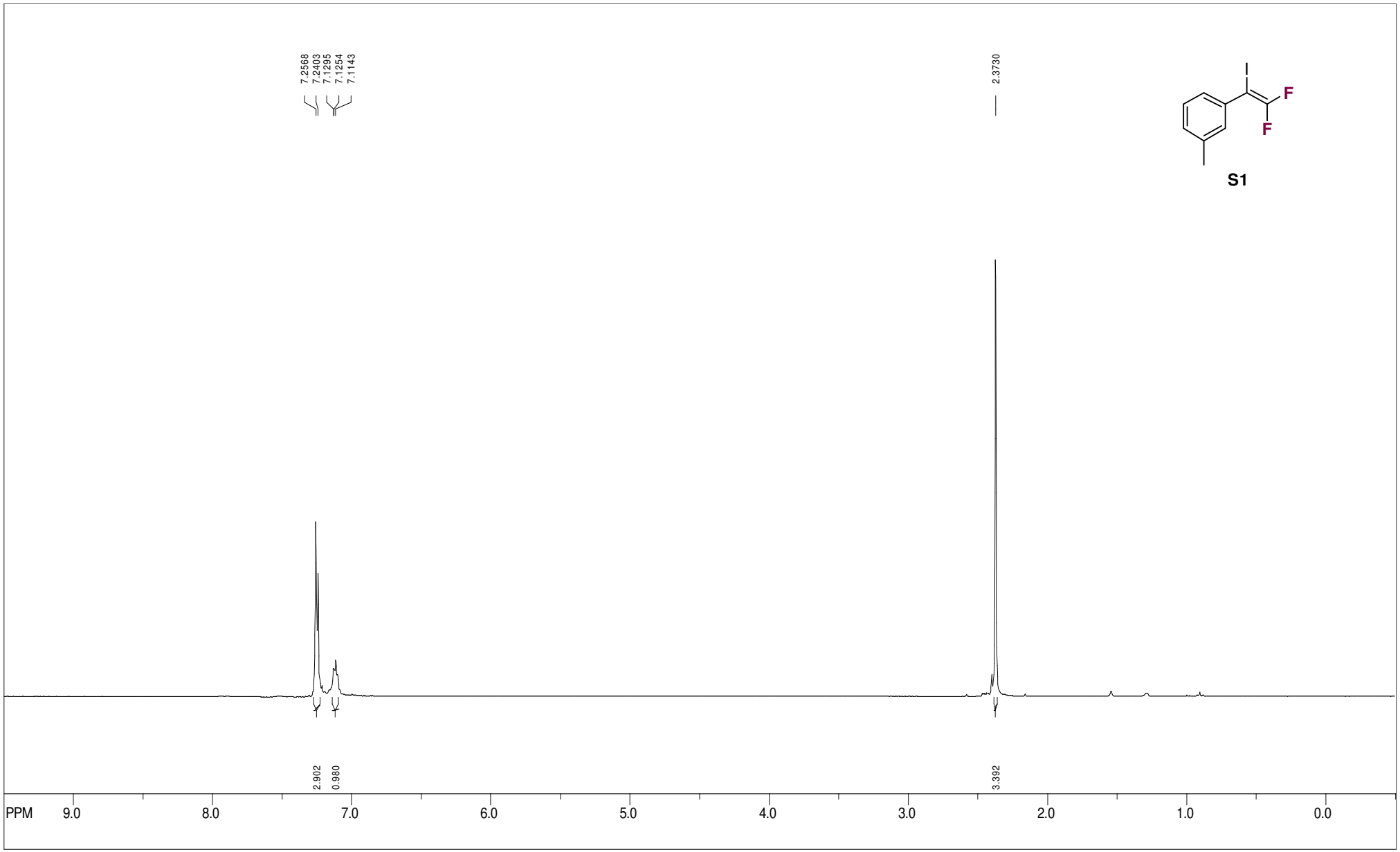
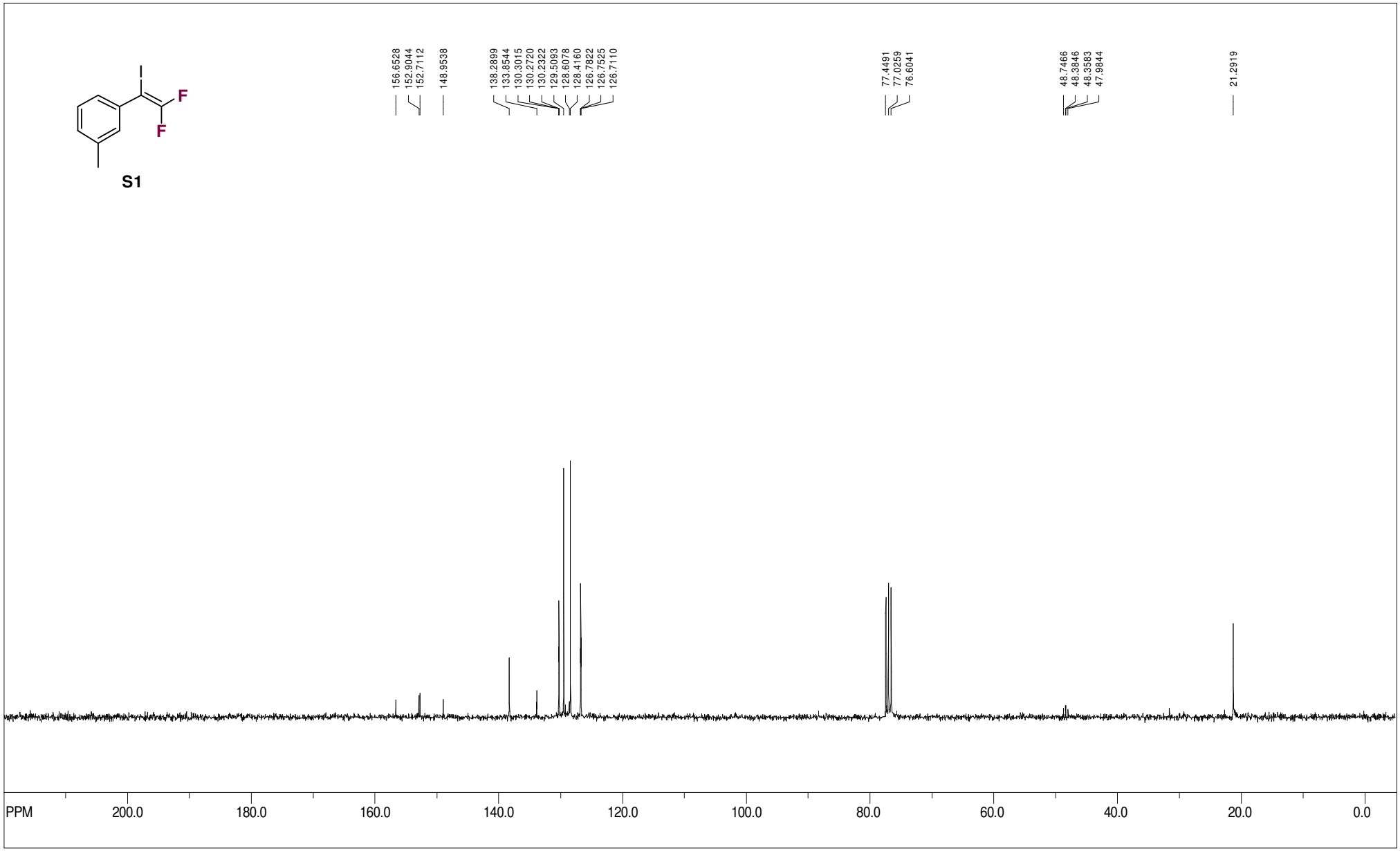
[4] Ernet, T.; Maulitz, A. H.; Würthwein, E.-U.; Haufe, G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1929.

9. ^{1}H and ^{13}C spectrum

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129.5093
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128.4160
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126.7525
126.7110
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21.2919
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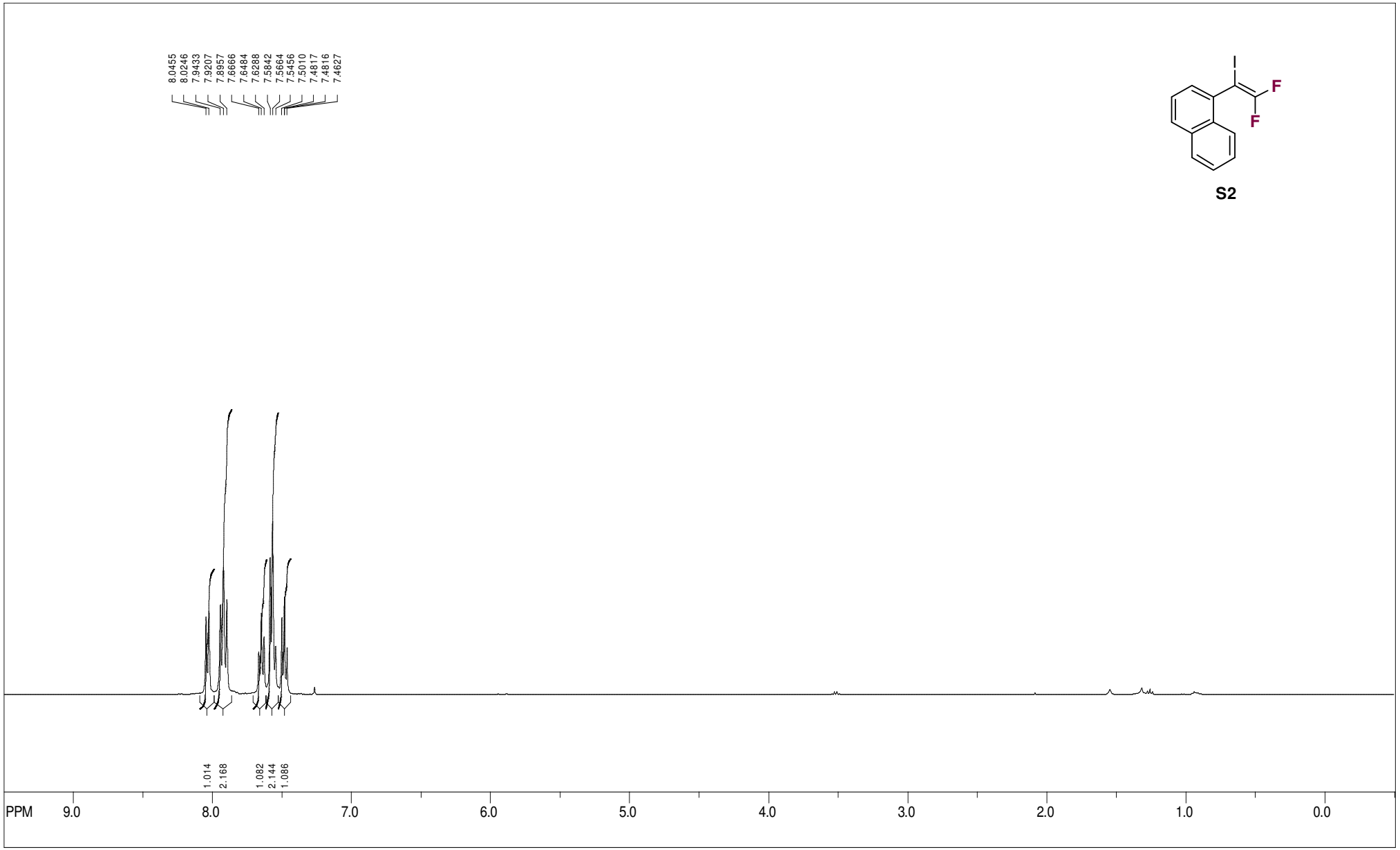
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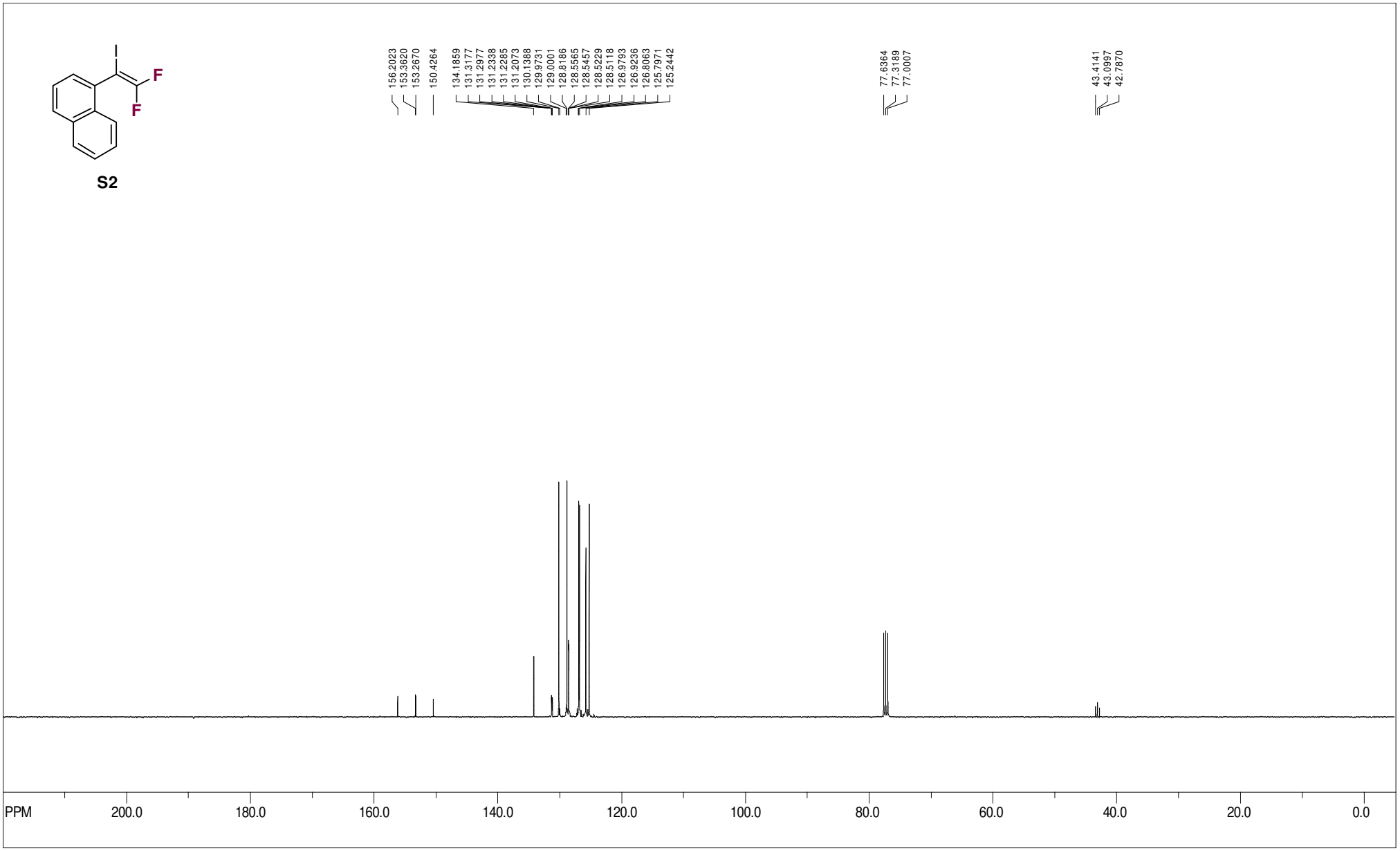
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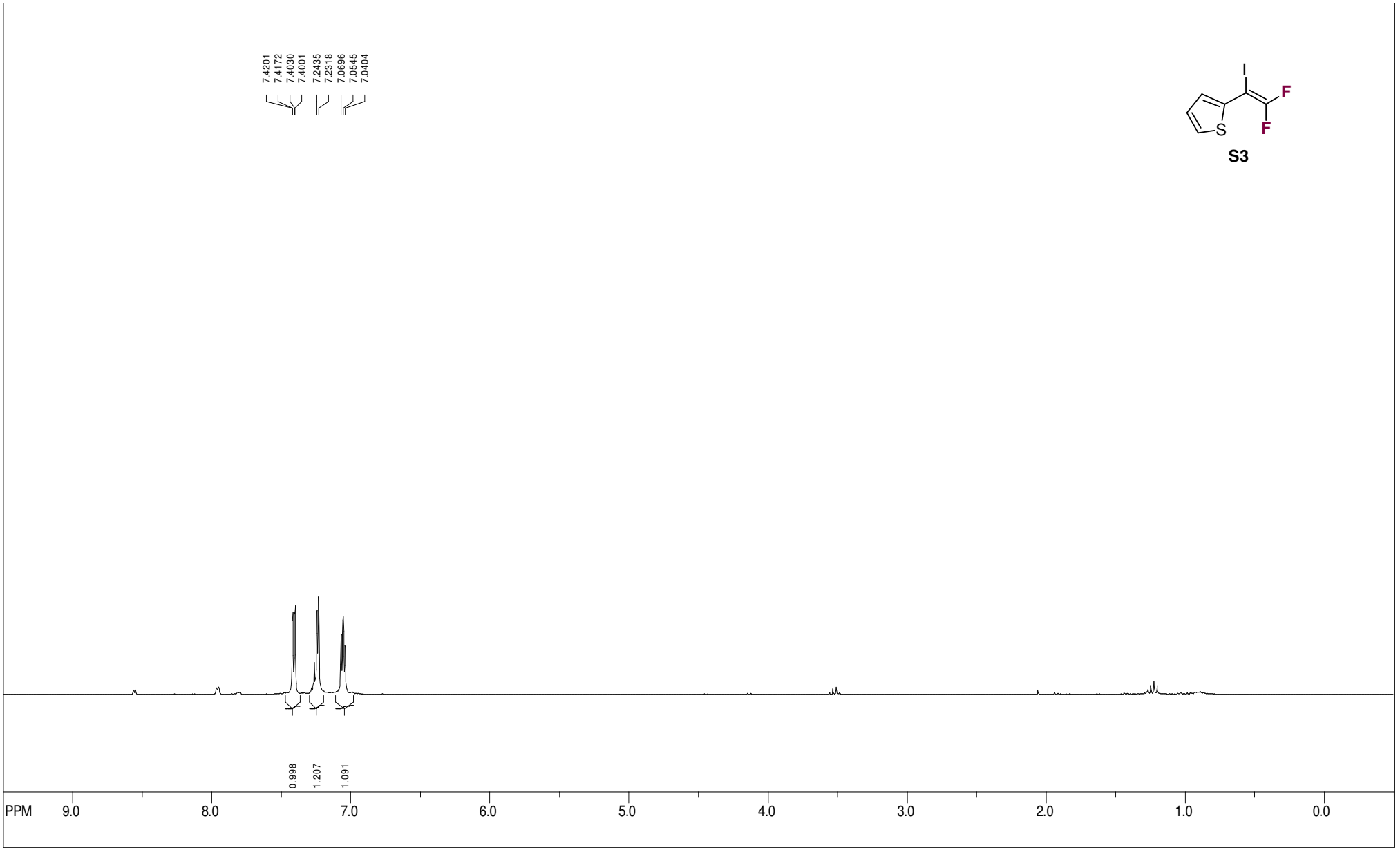
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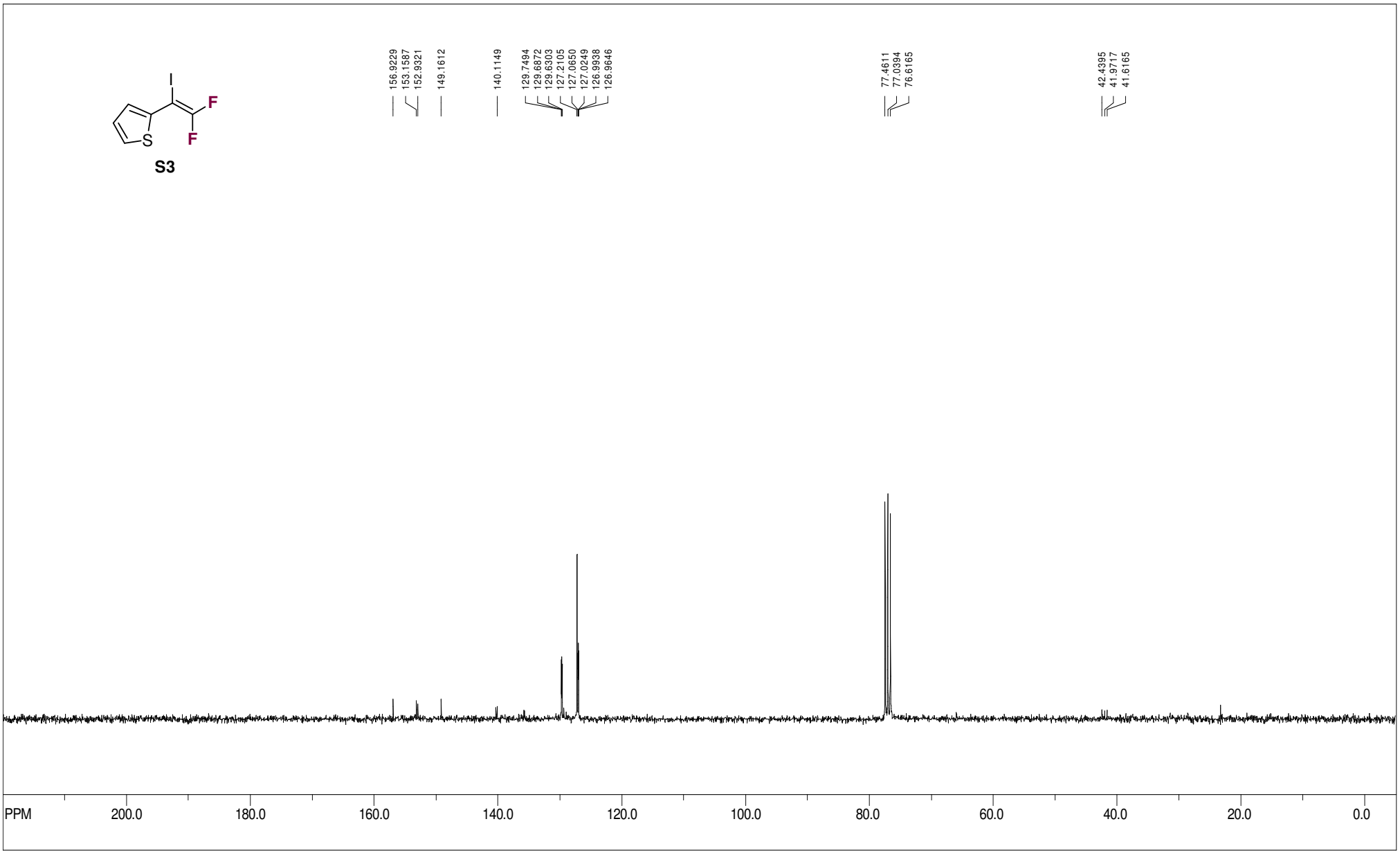
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41.9717
41.6165
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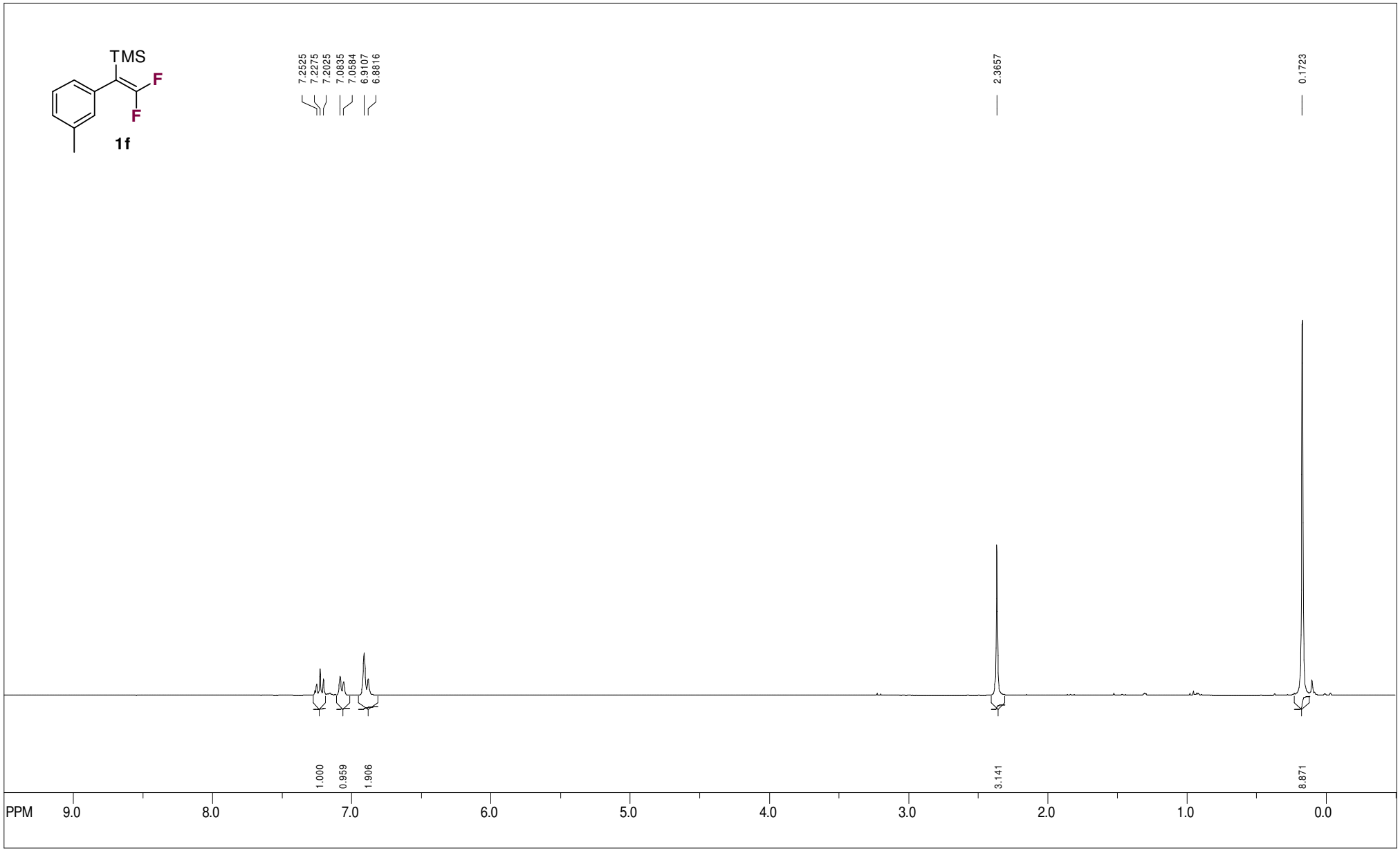
TMS
F
F
1f
7.2525
7.2275
7.2025
7.0835
7.0584
6.9107
6.8816
2.3657
0.1723
1.000
0.959
1.906
3.141
8.871
PPM
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8.0
7.0
6.0
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4.0
3.0
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1.0
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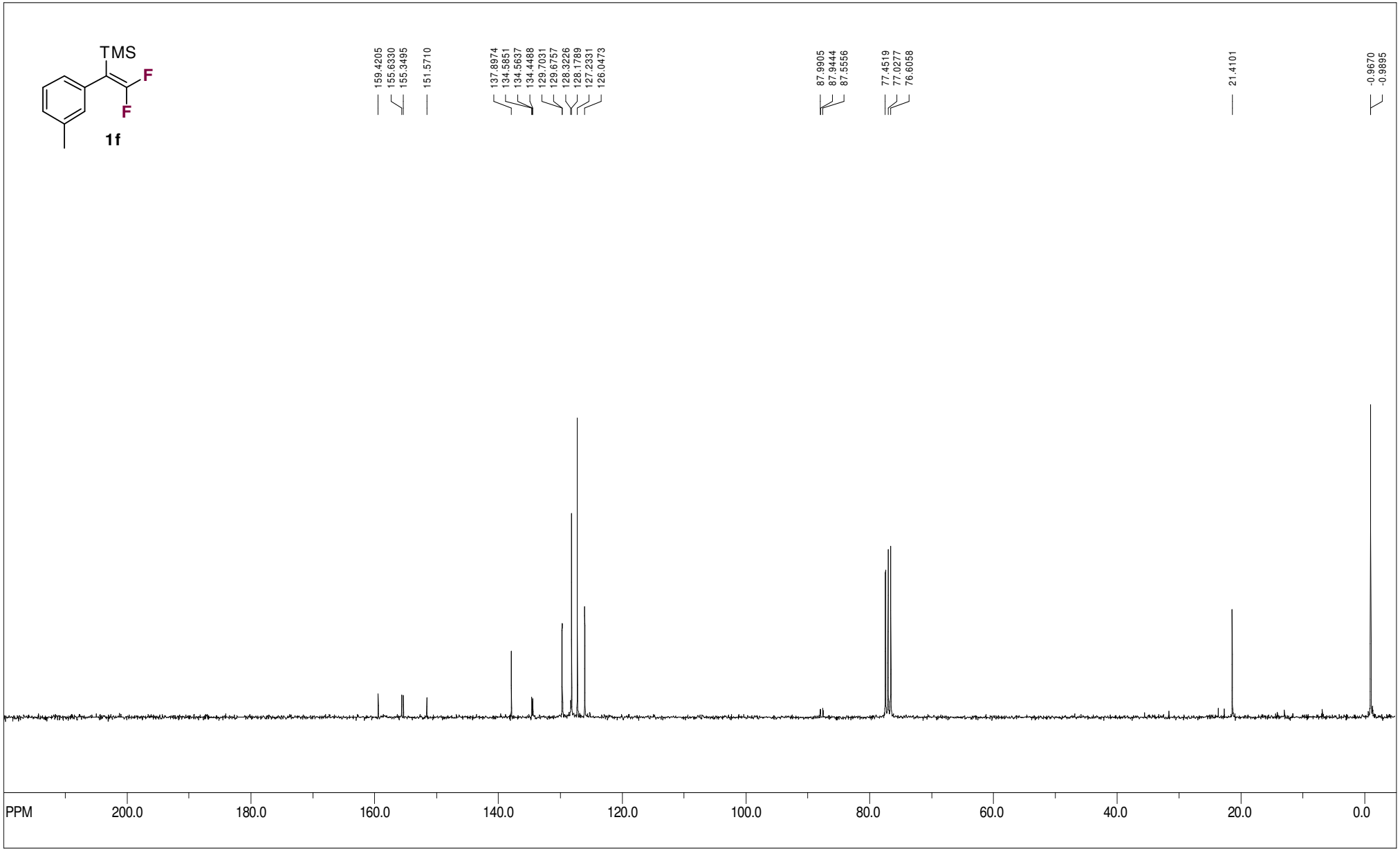
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F
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155.3495
151.5710
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134.5851
134.5637
134.4488
129.7031
129.6757
128.3226
128.1789
127.2331
126.0473
87.9905
87.9444
87.5556
77.4519
77.0277
76.6058
21.4101
-0.9670
-0.9895
PPM
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120.0
100.0
80.0
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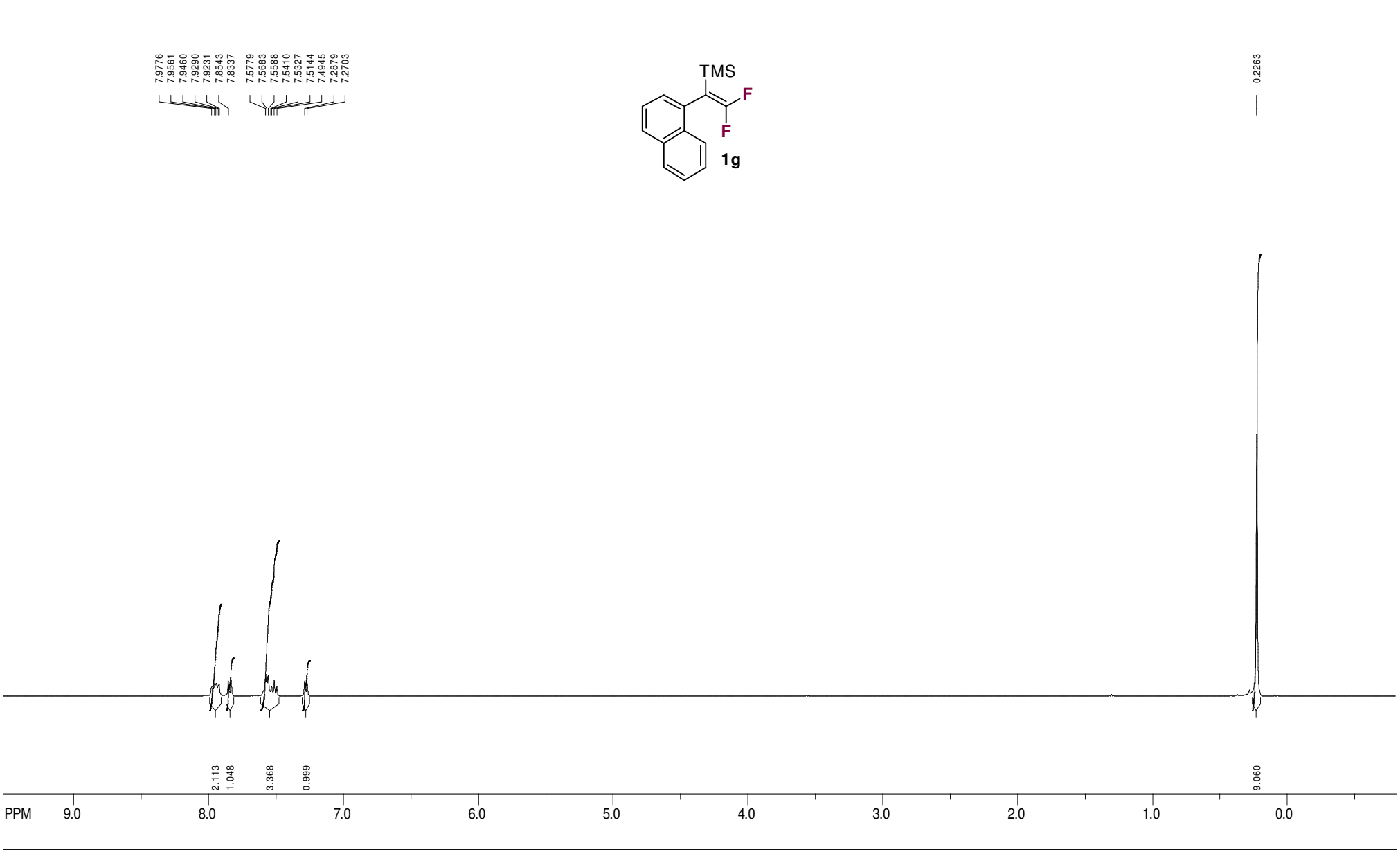
0.0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7.9460
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7.9231
7.8543
7.8337
7.5779
7.5683
7.5588
7.5410
7.5327
7.5144
7.4945
7.2879
7.2703
TMS
F
F
1g
0.2263
2.113
1.048
3.368
0.999
9.060
PPM
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8.0
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6.0
5.0
4.0
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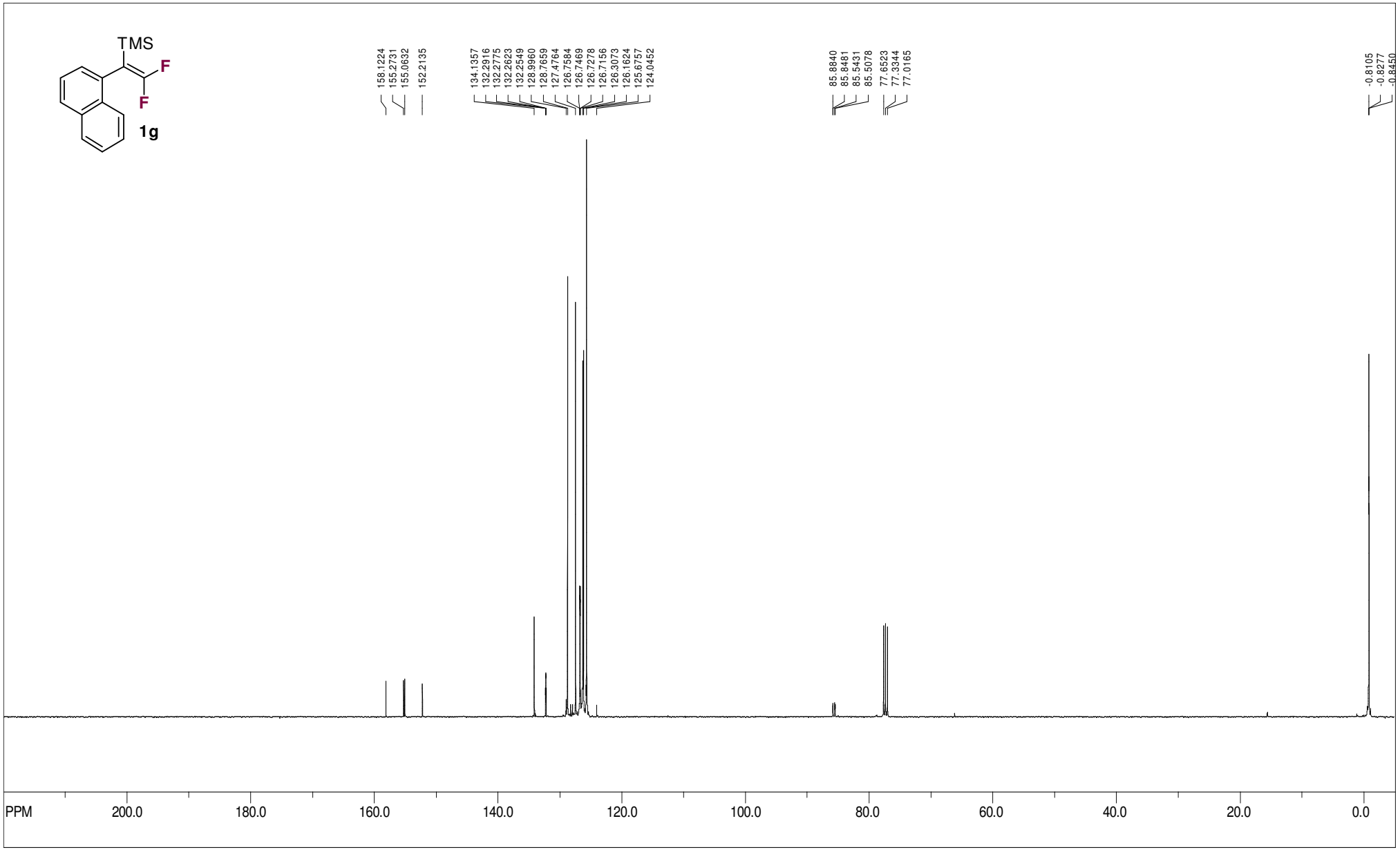
TMS
F
F
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155.2731
155.0632
152.2135
134.1357
132.2916
132.2775
132.2623
132.2549
128.9960
128.7659
127.4764
126.7584
126.7469
126.7278
126.7156
126.3073
126.1624
125.6757
124.0452
85.8840
85.8481
85.5431
85.5078
77.6523
77.3344
77.0165
-0.8105
-0.8277
-0.8450
PPM
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160.0
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120.0
100.0
80.0
60.0
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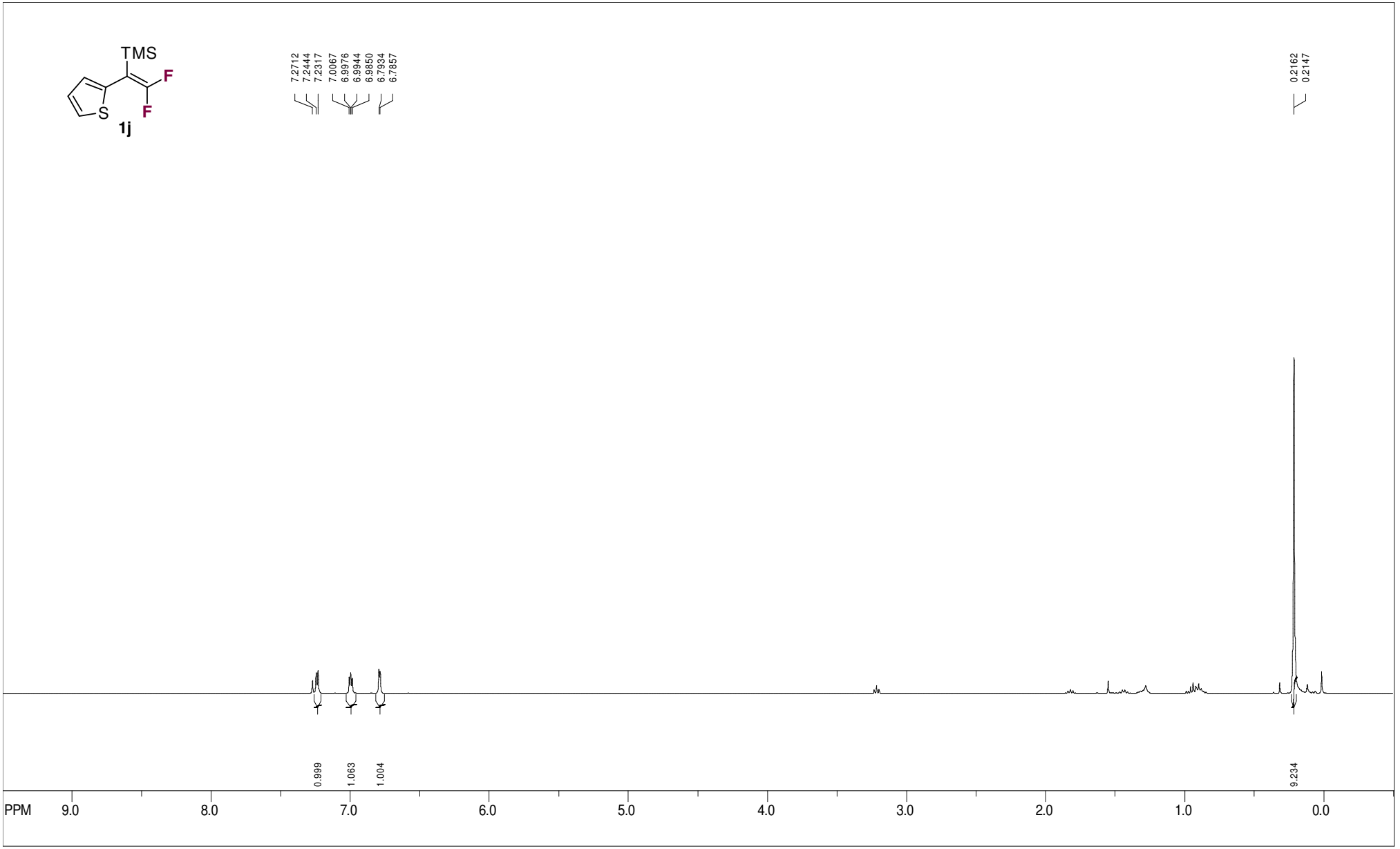
0.0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F
F
S
1j
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7.2444
7.2317
7.0067
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6.9944
6.9850
6.7934
6.7857
0.2162
0.2147
0.999
1.063
1.004
9.234
PPM
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8.0
7.0
6.0
5.0
4.0
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2.0
1.0
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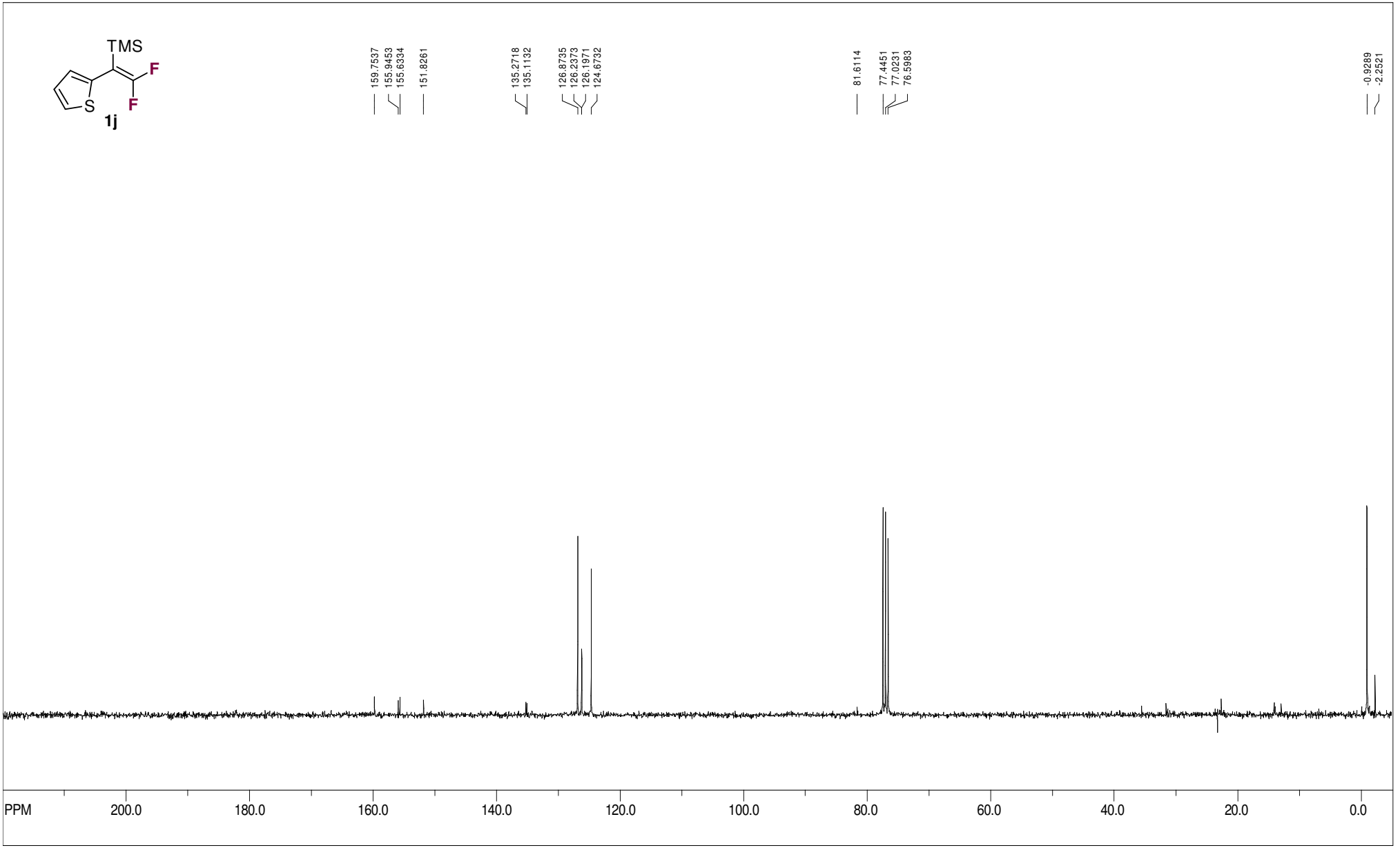
TMS
F
F
S
1j
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155.9453
155.6334
151.8261
135.2718
135.1132
126.8735
126.2373
126.1971
124.6732
81.6114
77.4451
77.0231
76.5983
-0.9289
-2.2521
PPM
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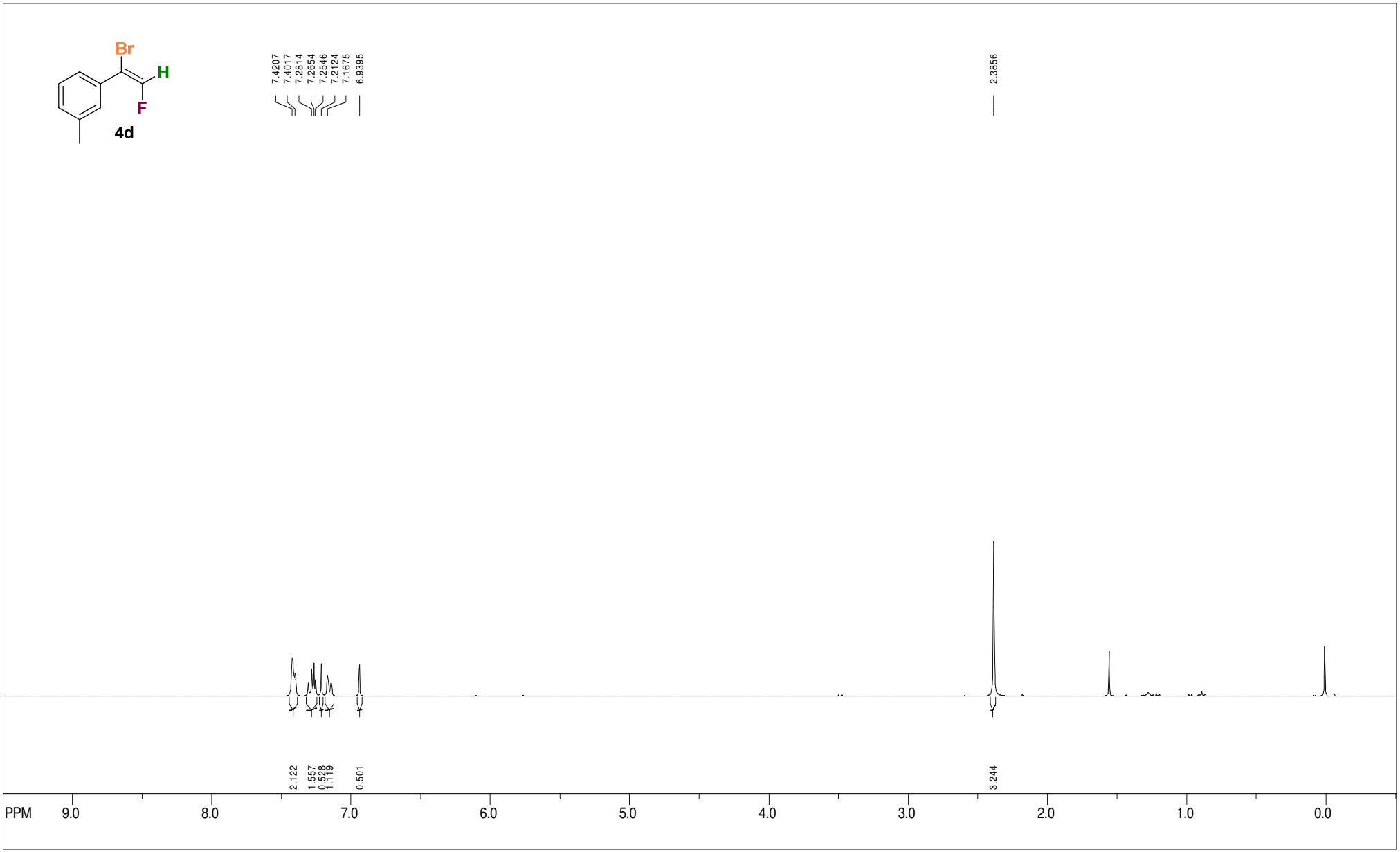
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


Br
H
F
4d
7.4207
7.4017
7.2814
7.2654
7.2546
7.2124
7.1675
6.9395
2.3856
2.122
1.557
0.528
1.119
0.501
3.244
PPM
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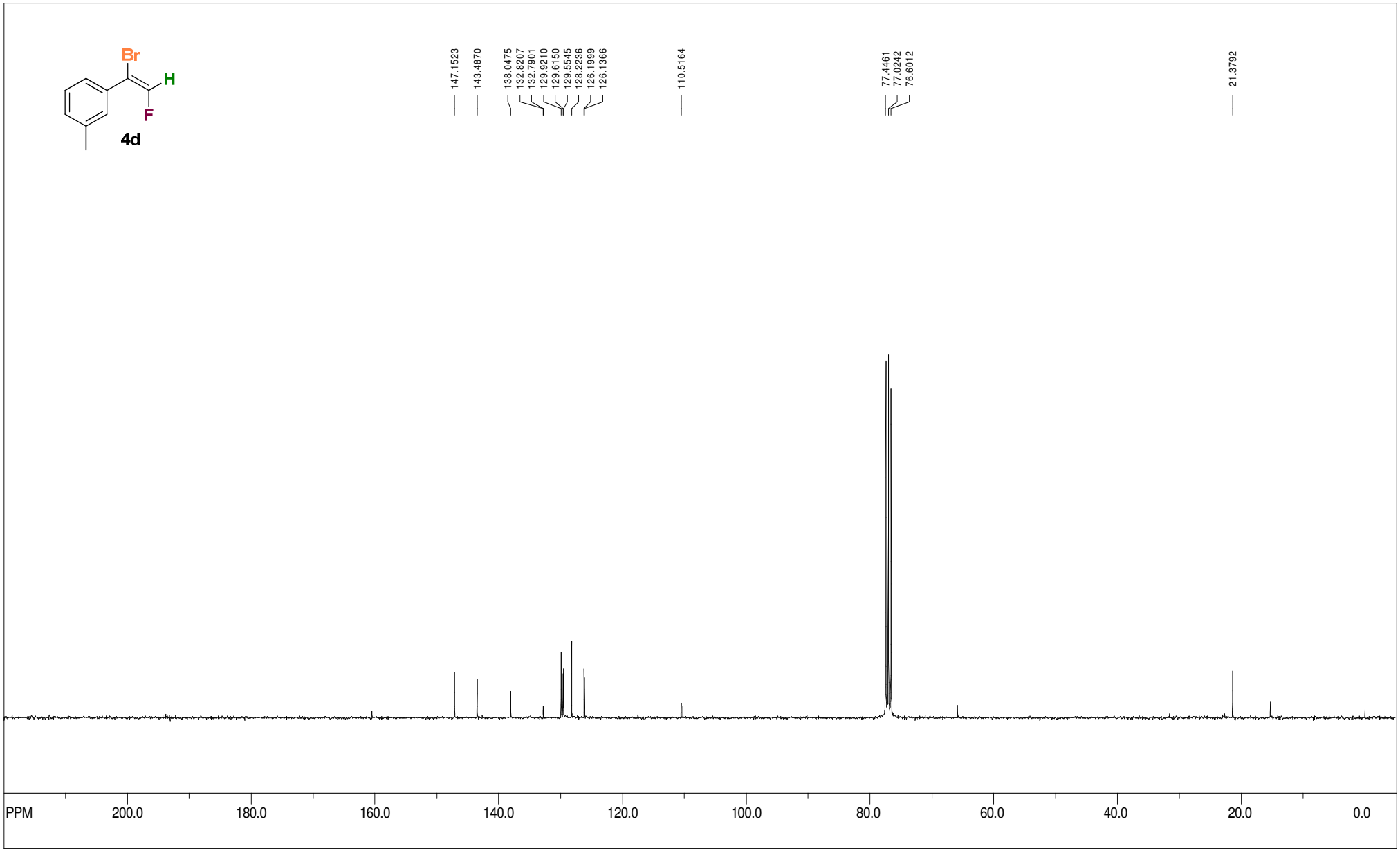
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


Br
H
F
4d
147.1523
143.4870
138.0475
132.8207
132.7901
129.9210
129.6150
129.5545
128.2236
126.1999
126.1366
110.5164
77.4461
77.0242
76.6012
21.3792
PPM
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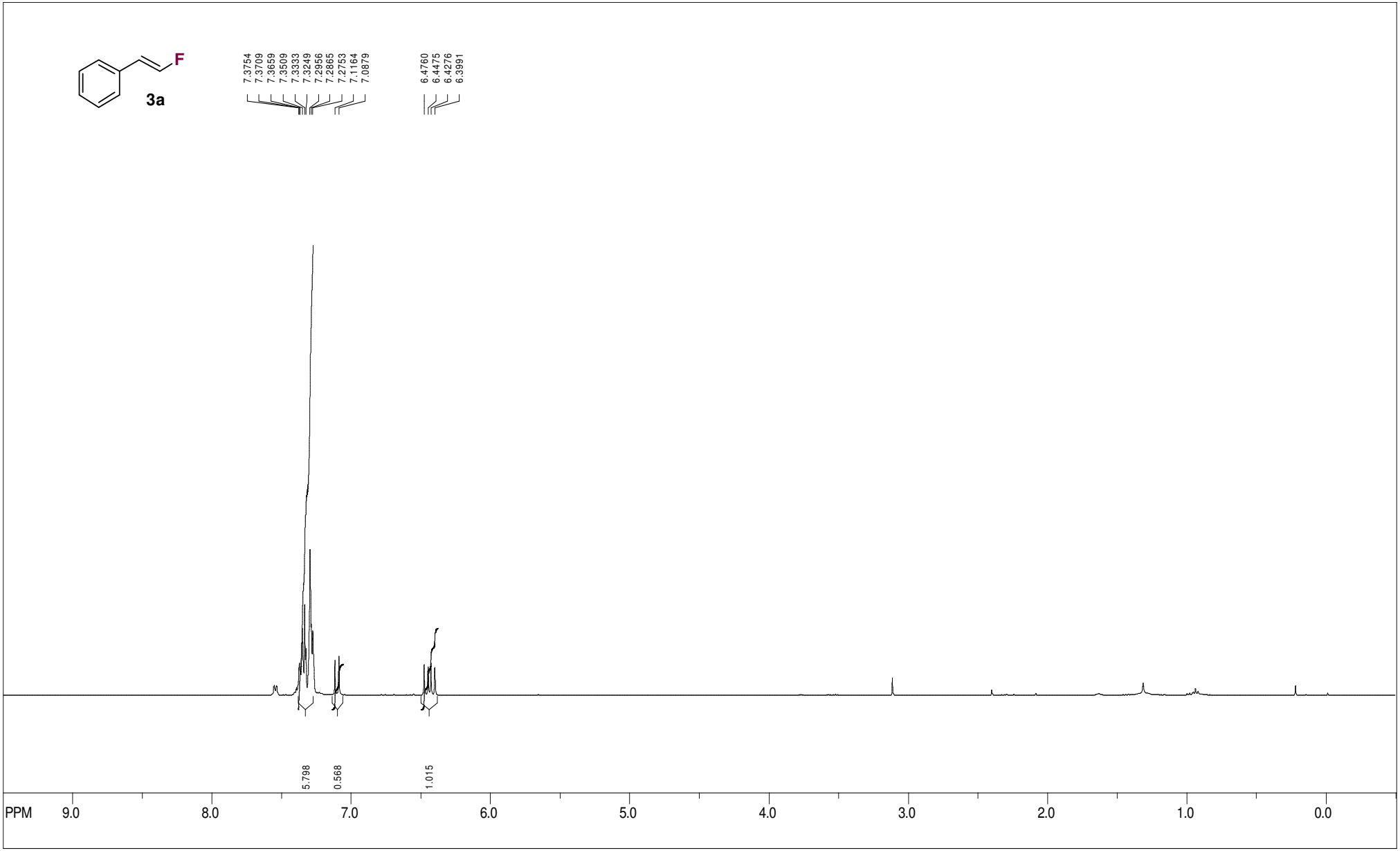
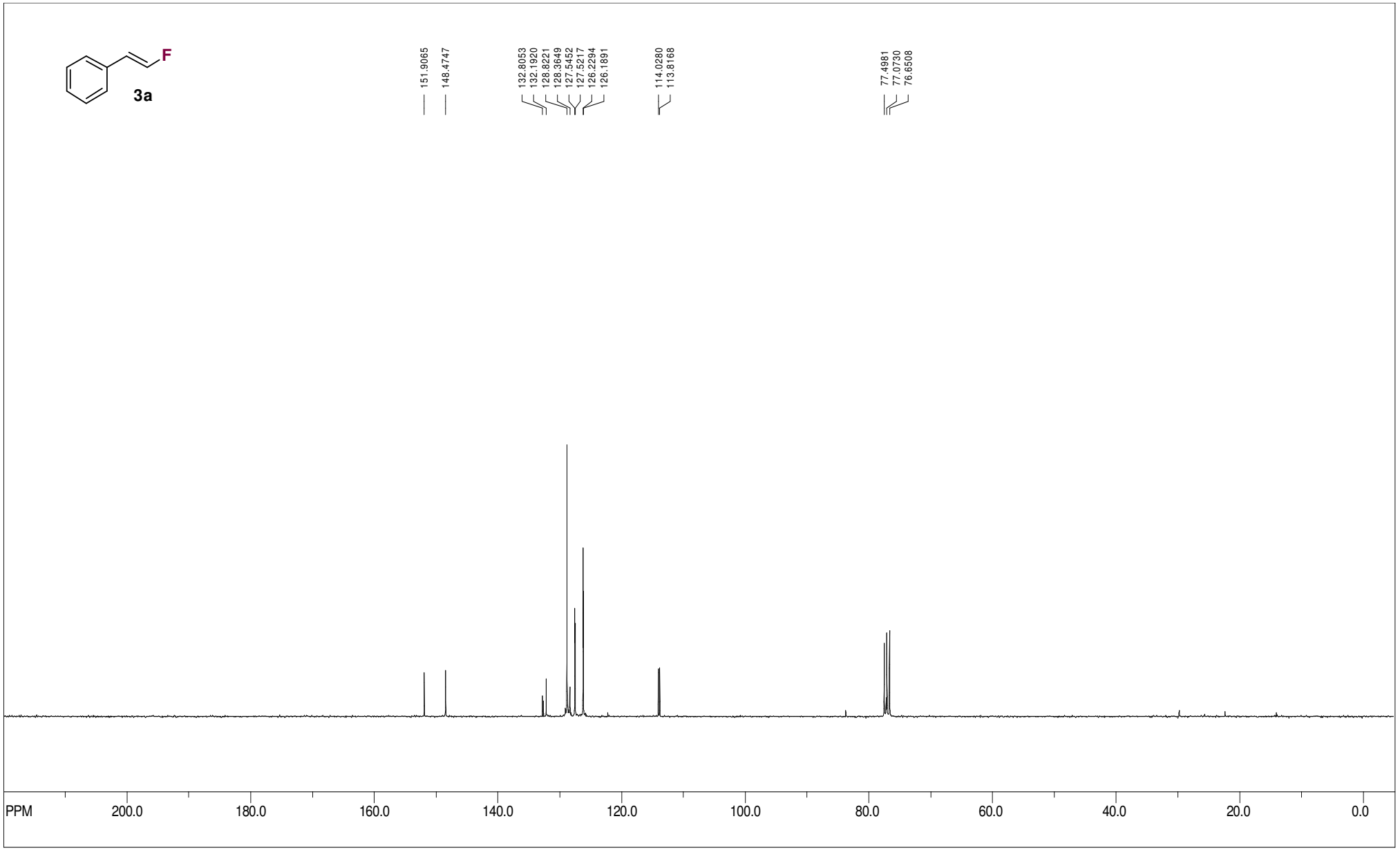
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
3a
7.3754
7.3709
7.3659
7.3509
7.3333
7.3249
7.2956
7.2865
7.2753
7.1164
7.0879
6.4760
6.4475
6.4276
6.3991
5.798
0.568
1.015
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


F
3a
151.9065
148.4747
132.8053
132.1920
128.8221
128.3649
127.5452
127.5217
126.2294
126.1891
114.0280
113.8168
77.4981
77.0730
76.6508
PPM
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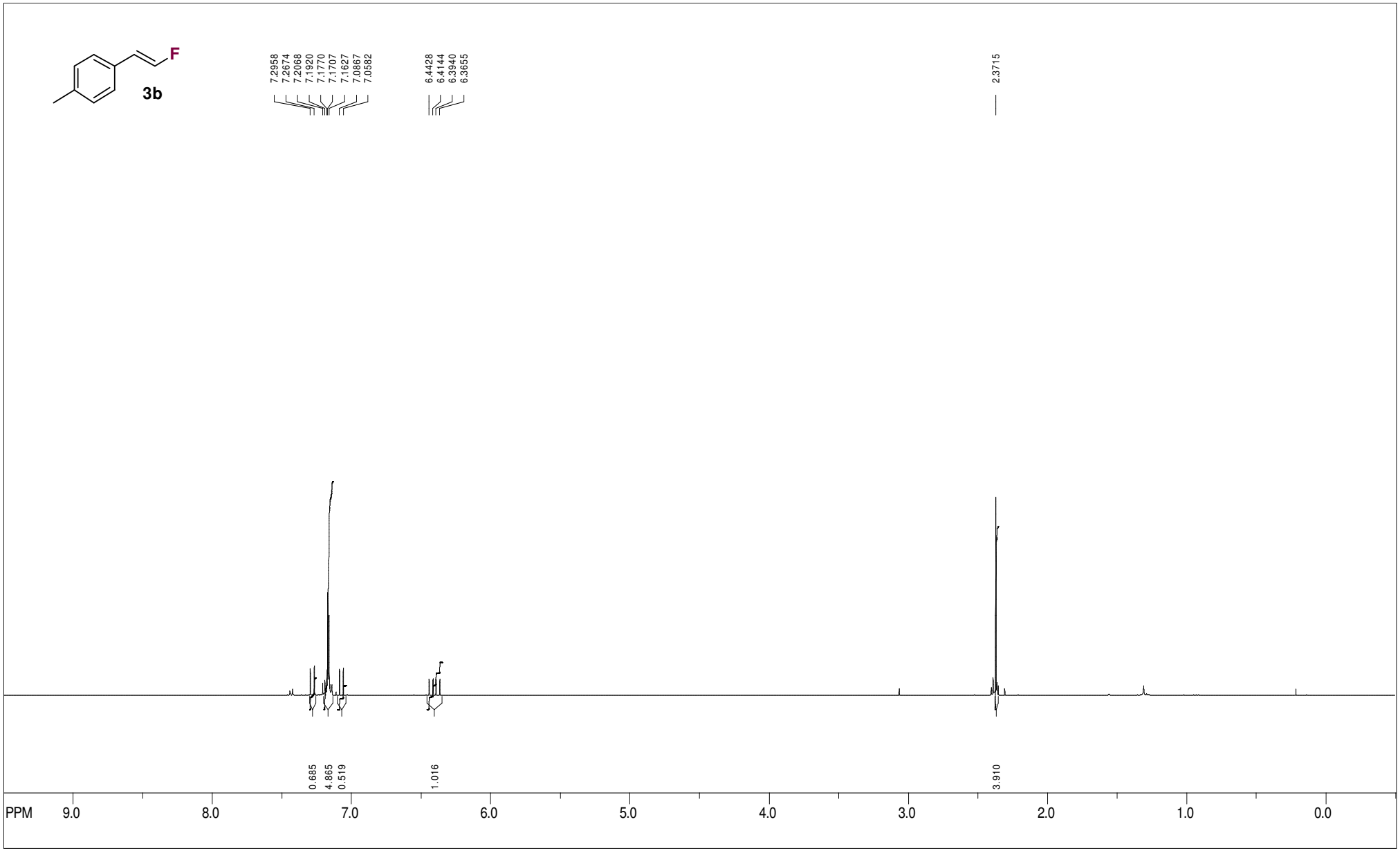
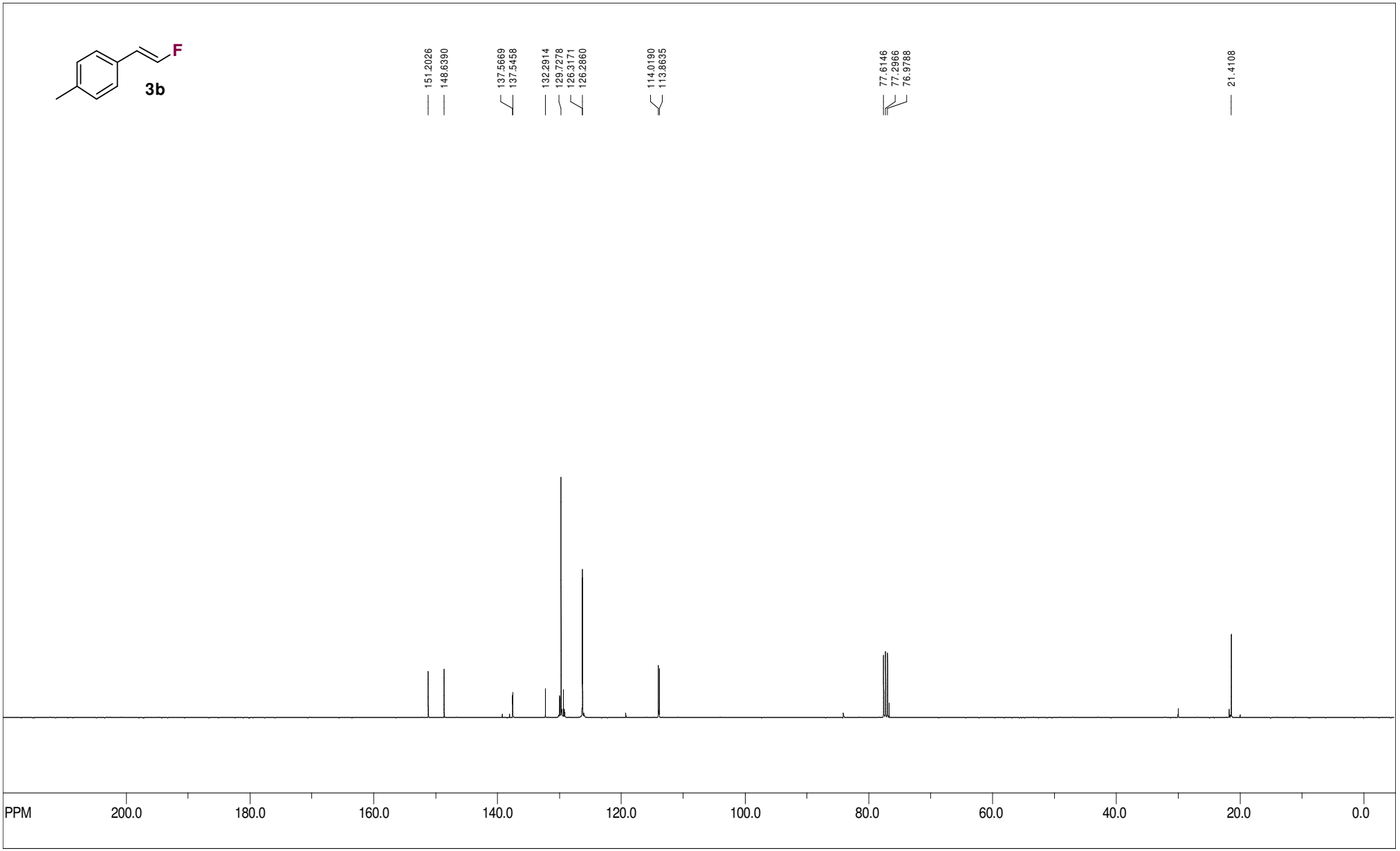
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
3b
7.2958
7.2674
7.2068
7.1920
7.1770
7.1707
7.1627
7.0867
7.0582
6.4428
6.4144
6.3940
6.3655
2.3715
0.685
4.865
0.519
1.016
3.910
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


F
3b
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148.6390
137.5669
137.5458
132.2914
129.7278
126.3171
126.2860
114.0190
113.8635
77.6146
77.2966
76.9788
21.4108
PPM
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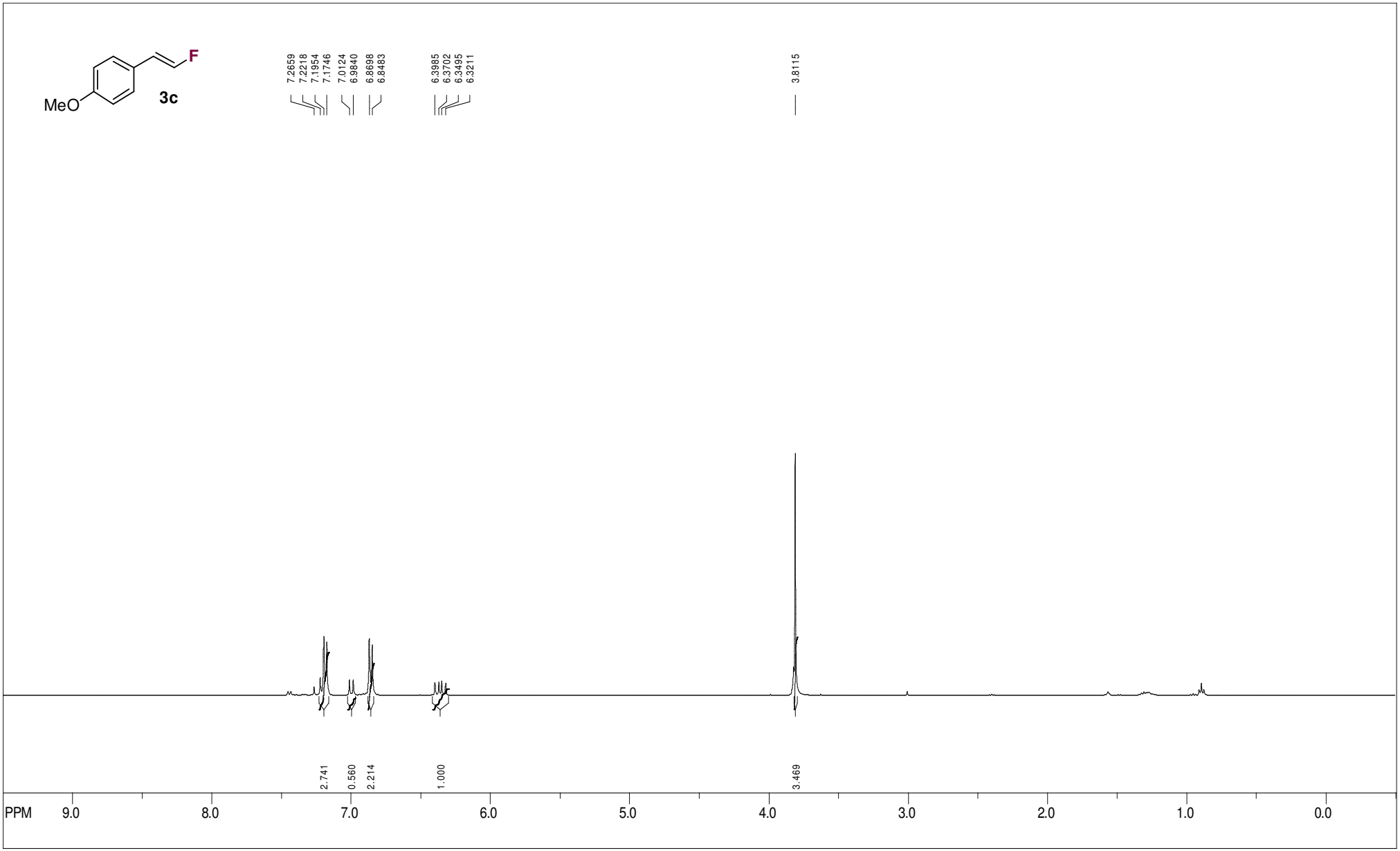
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
MeO
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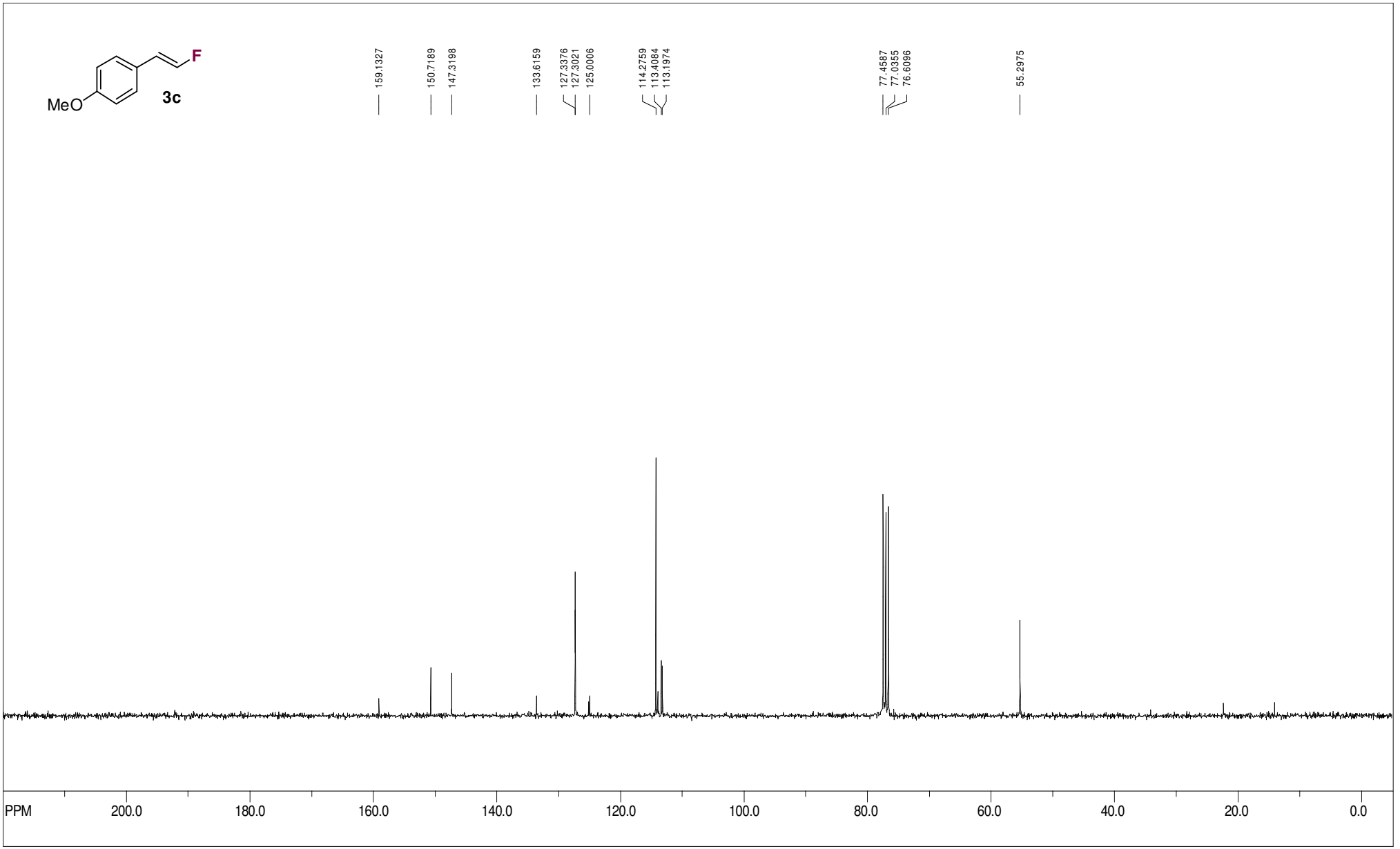
7.2218
7.1954
7.1746
7.0124
6.9840
6.8698
6.8483
6.3985
6.3702
6.3495
6.3211
3.8115
2.741
0.560
2.214
1.000
3.469
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


MeO
F
3c
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133.6159
127.3376
127.3021
125.0006
114.2759
113.4084
113.1974
77.4587
77.0355
76.6096
55.2975
PPM
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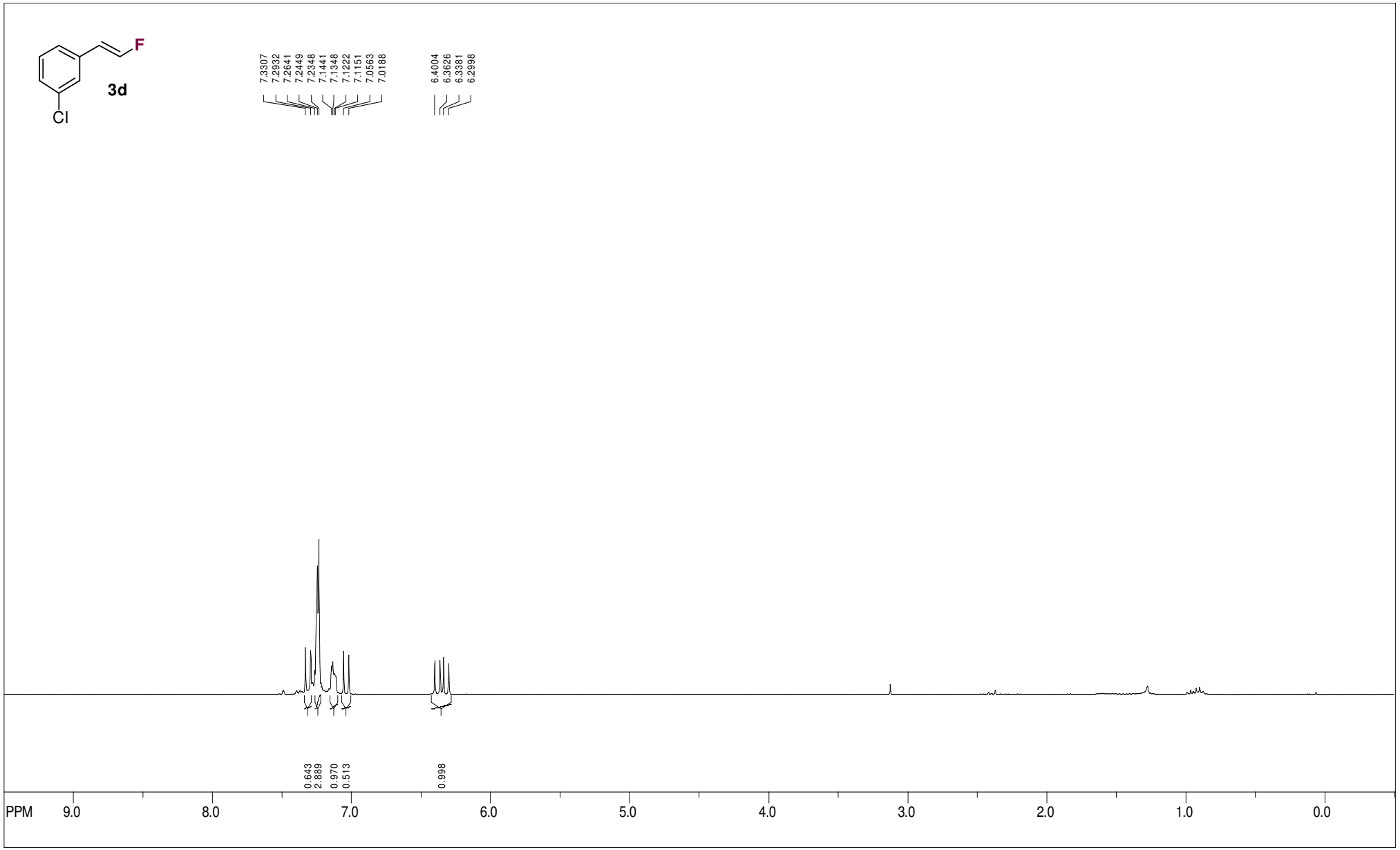
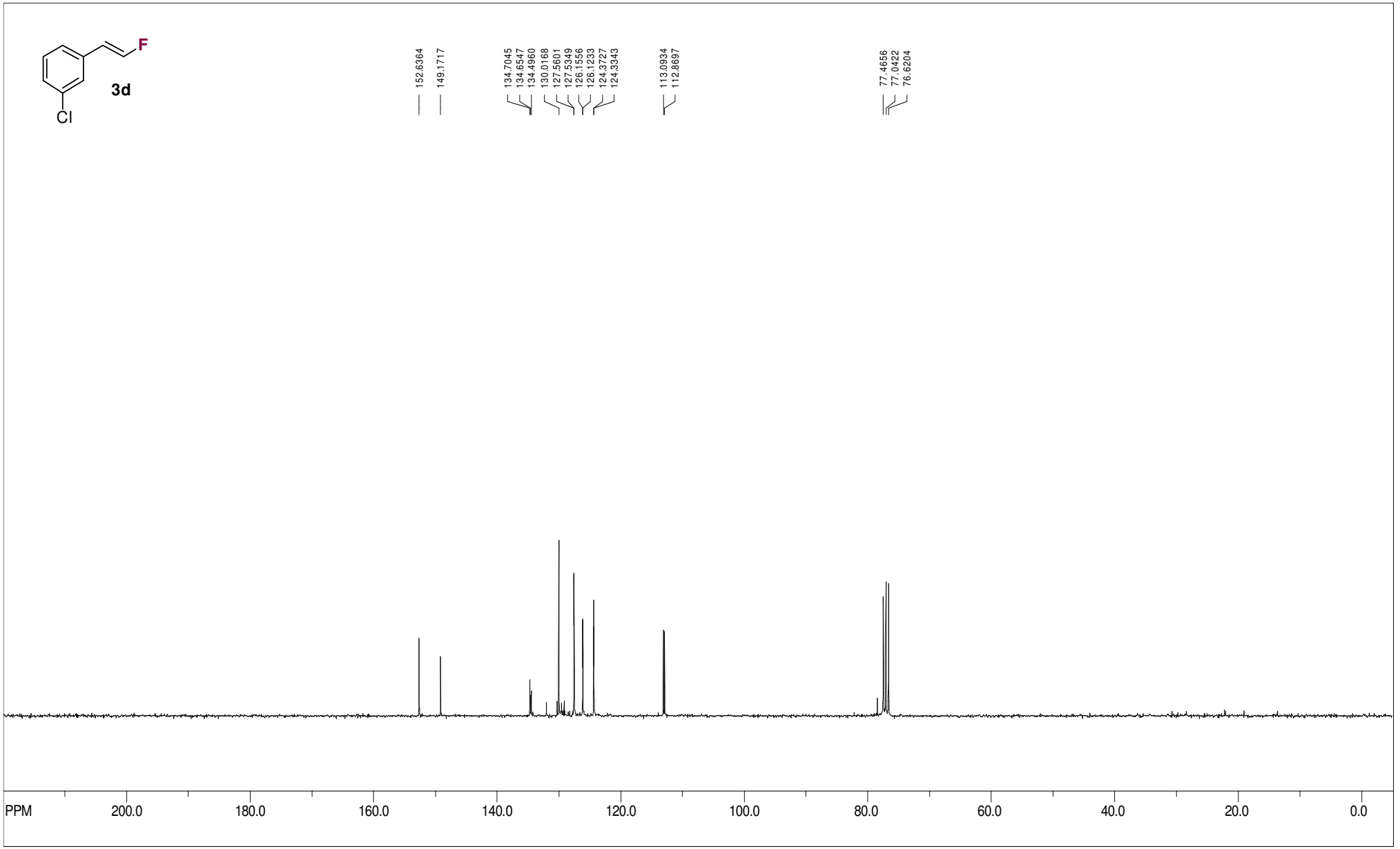
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
Cl
3d
7.3307
7.2932
7.2641
7.2449
7.2348
7.1441
7.1348
7.1222
7.1151
7.0563
7.0188
6.4004
6.3626
6.3381
6.2998
0.643
2.889
0.970
0.513
0.998
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


F
Cl
3d
152.6364
149.1717
134.7045
134.6547
134.4960
130.0168
127.5601
127.5349
126.1556
126.1233
124.3727
124.3343
113.0934
112.8697
77.4656
77.0422
76.6204
PPM
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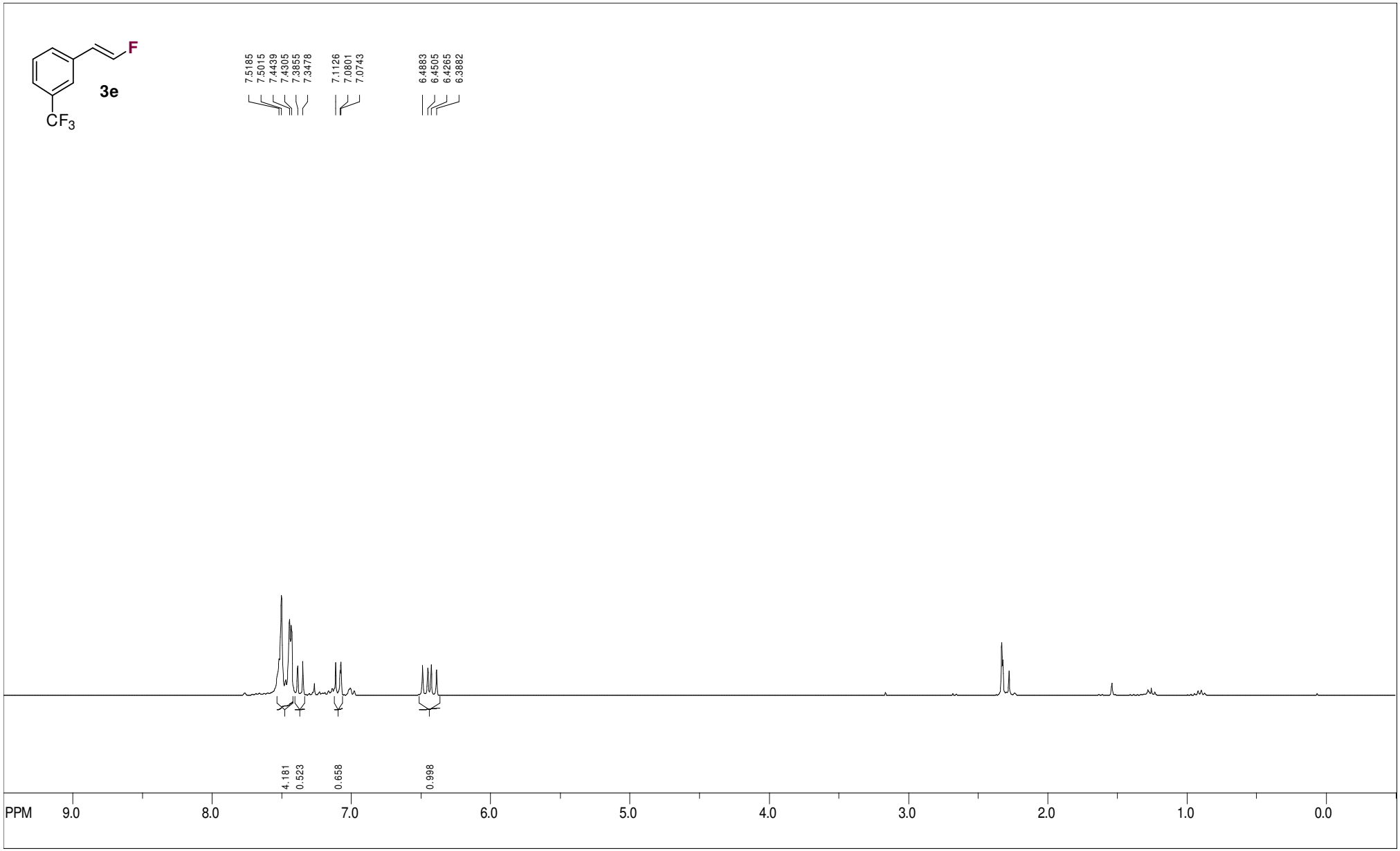
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
3e
CF3
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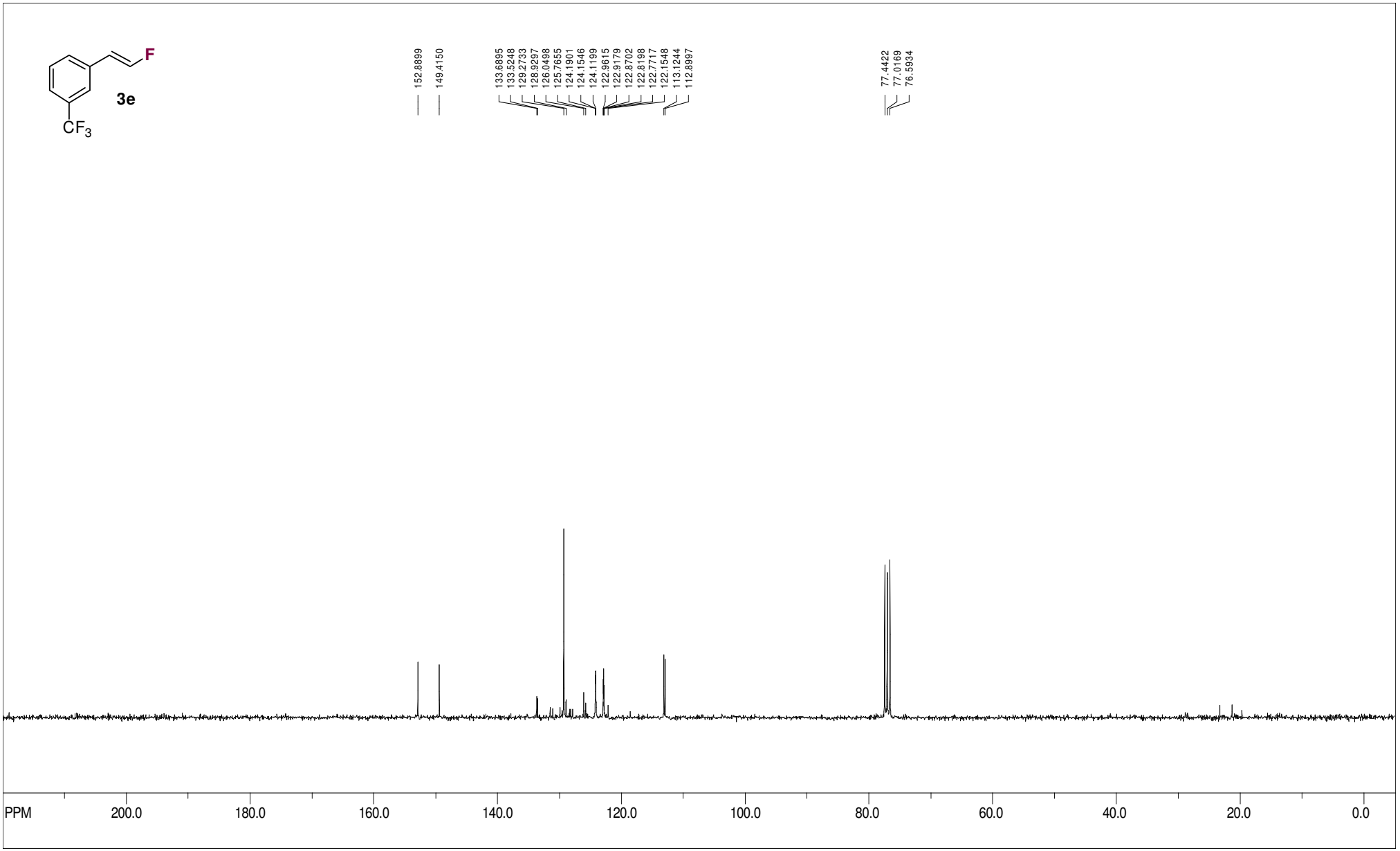
7.5015
7.4439
7.4305
7.3855
7.3478
7.1126
7.0801
7.0743
6.4883
6.4505
6.4265
6.3882
4.181
0.523
0.658
0.998
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


F
3e
CF3
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133.6895
133.5248
129.2733
128.9297
126.0498
125.7655
124.1901
124.1546
124.1199
122.9615
122.9179
122.8702
122.8198
122.7717
122.1548
113.1244
112.8997
77.4422
77.0169
76.5934
PPM
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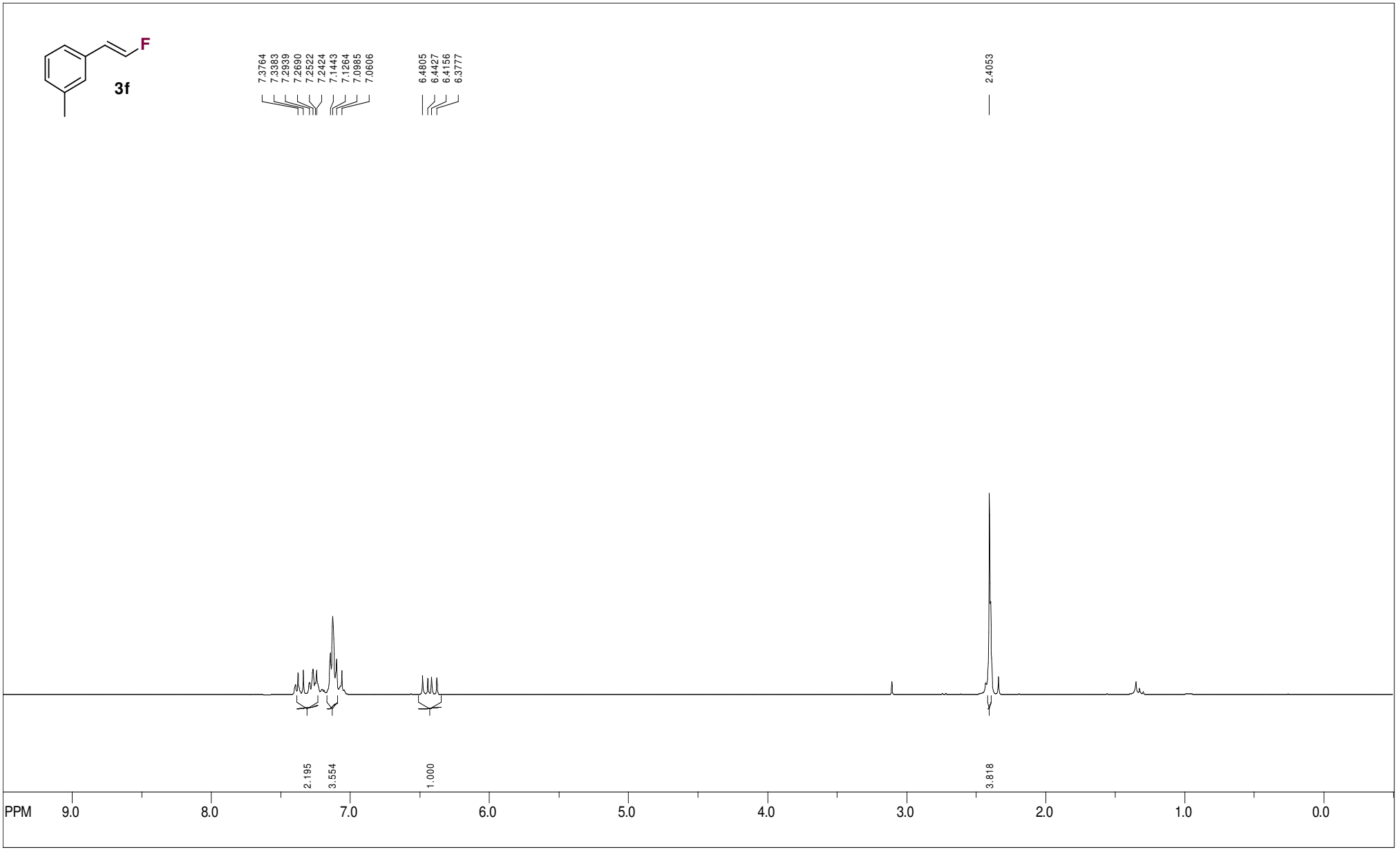
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
3f
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7.3383
7.2939
7.2690
7.2522
7.2424
7.1443
7.1264
7.0985
7.0606
6.4805
6.4427
6.4156
6.3777
2.4053
2.195
3.554
1.000
3.818
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9.0
8.0
7.0
6.0
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4.0
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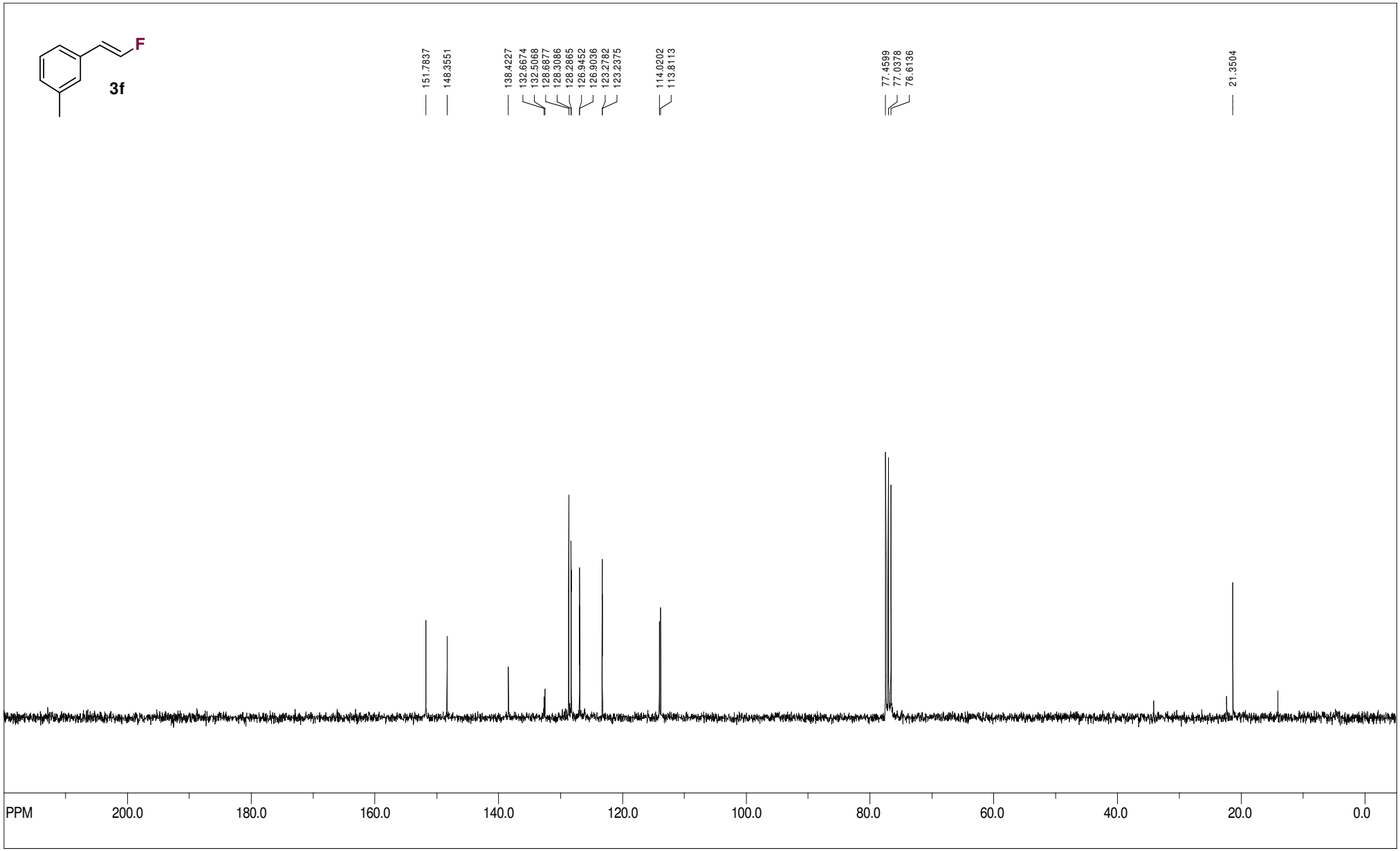
2.0
1.0
0.0


F
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148.3551
138.4227
132.6674
132.5068
128.6877
128.3086
128.2865
126.9452
126.9036
123.2782
123.2375
114.0202
113.8113
77.4599
77.0378
76.6136
21.3504
PPM
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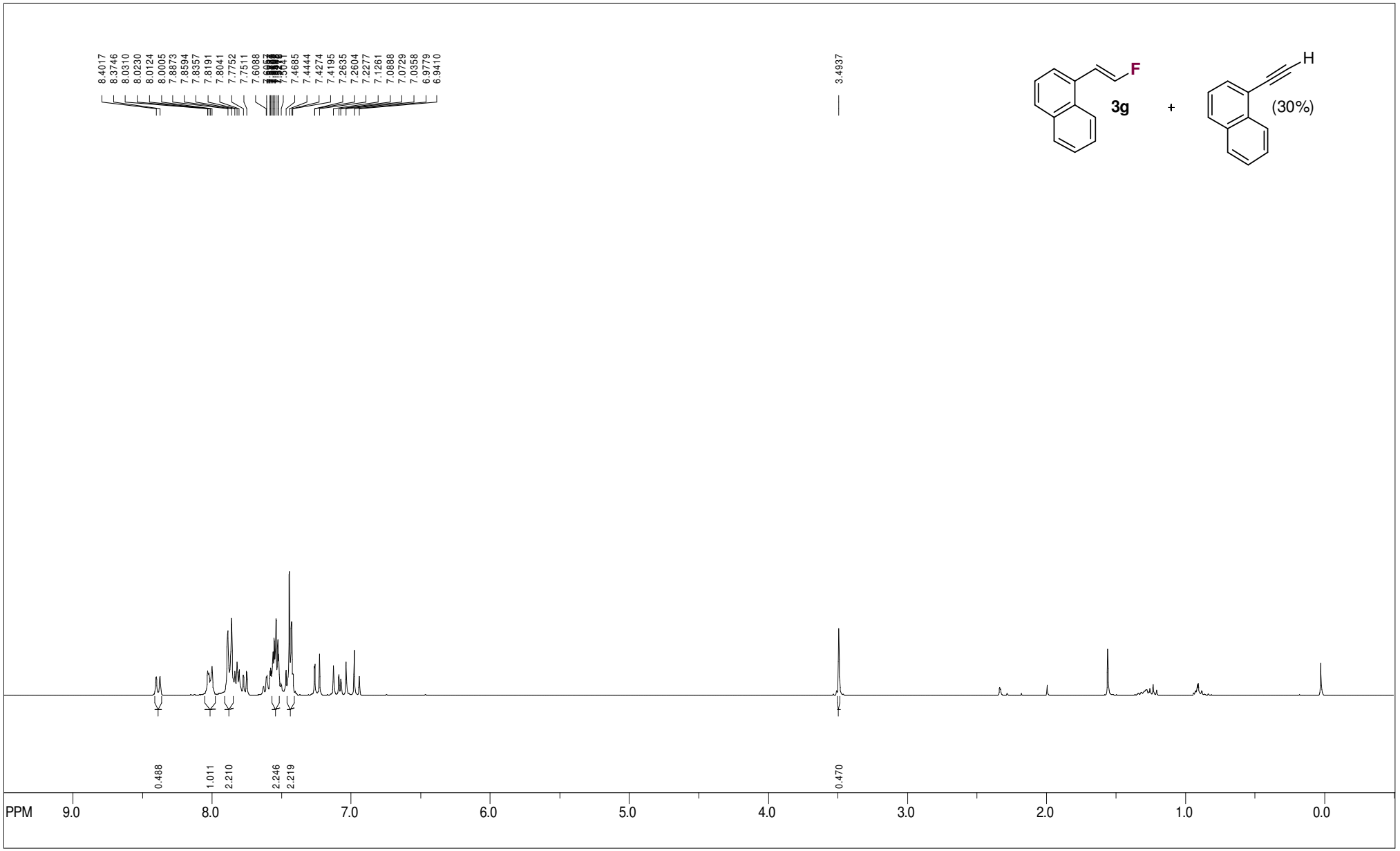
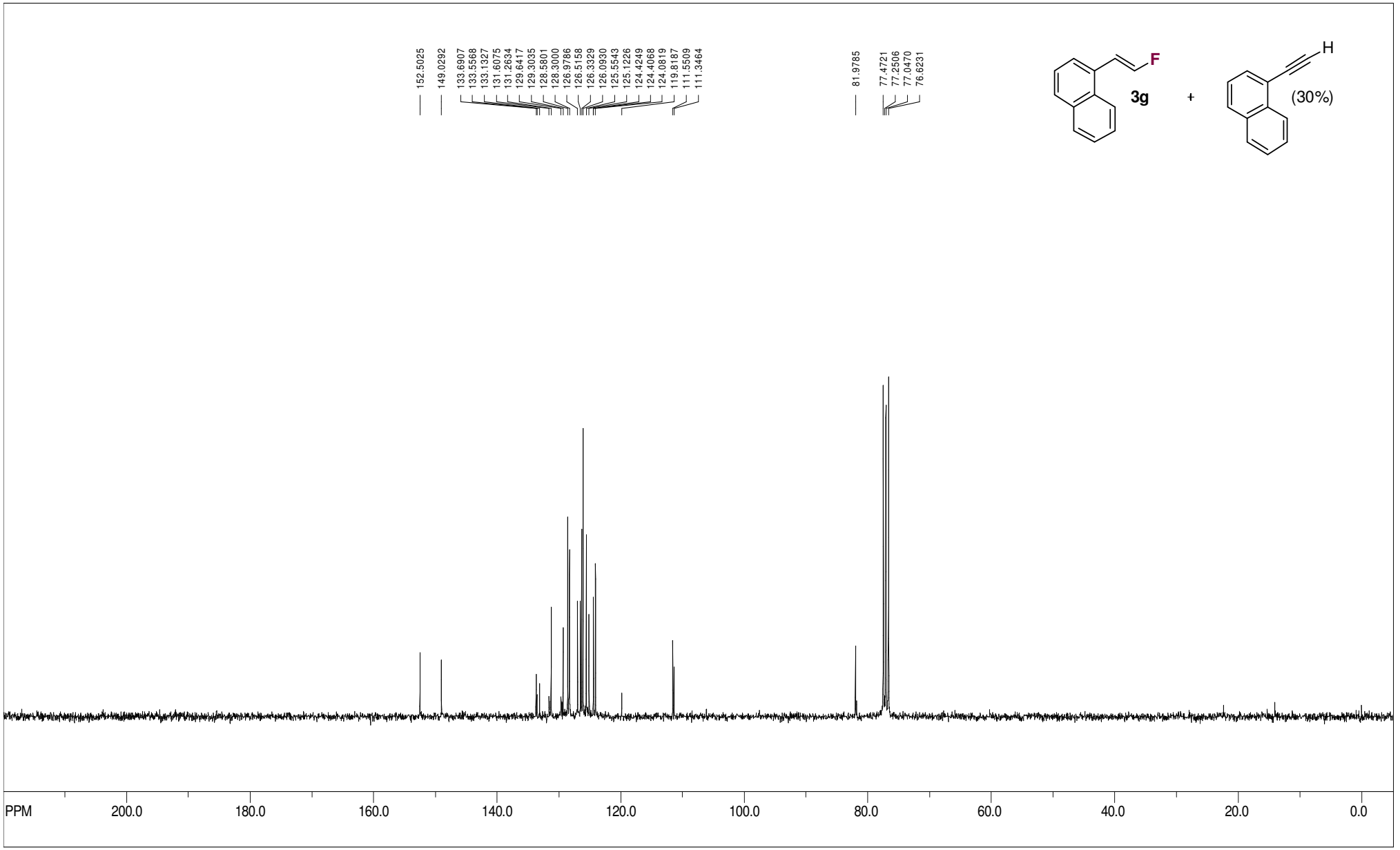
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


8.4017
8.3746
8.0310
8.0230
8.0124
8.0005
7.8873
7.8594
7.8357
7.8191
7.8041
7.7752
7.7511
7.6088
7.4685
7.4444
7.4274
7.4195
7.2635
7.2604
7.2277
7.1261
7.0888
7.0729
7.0358
6.9779
6.9410
3.4937
F
3g
+
H
(30%)
0.488
1.011
2.210
2.246
2.219
0.470
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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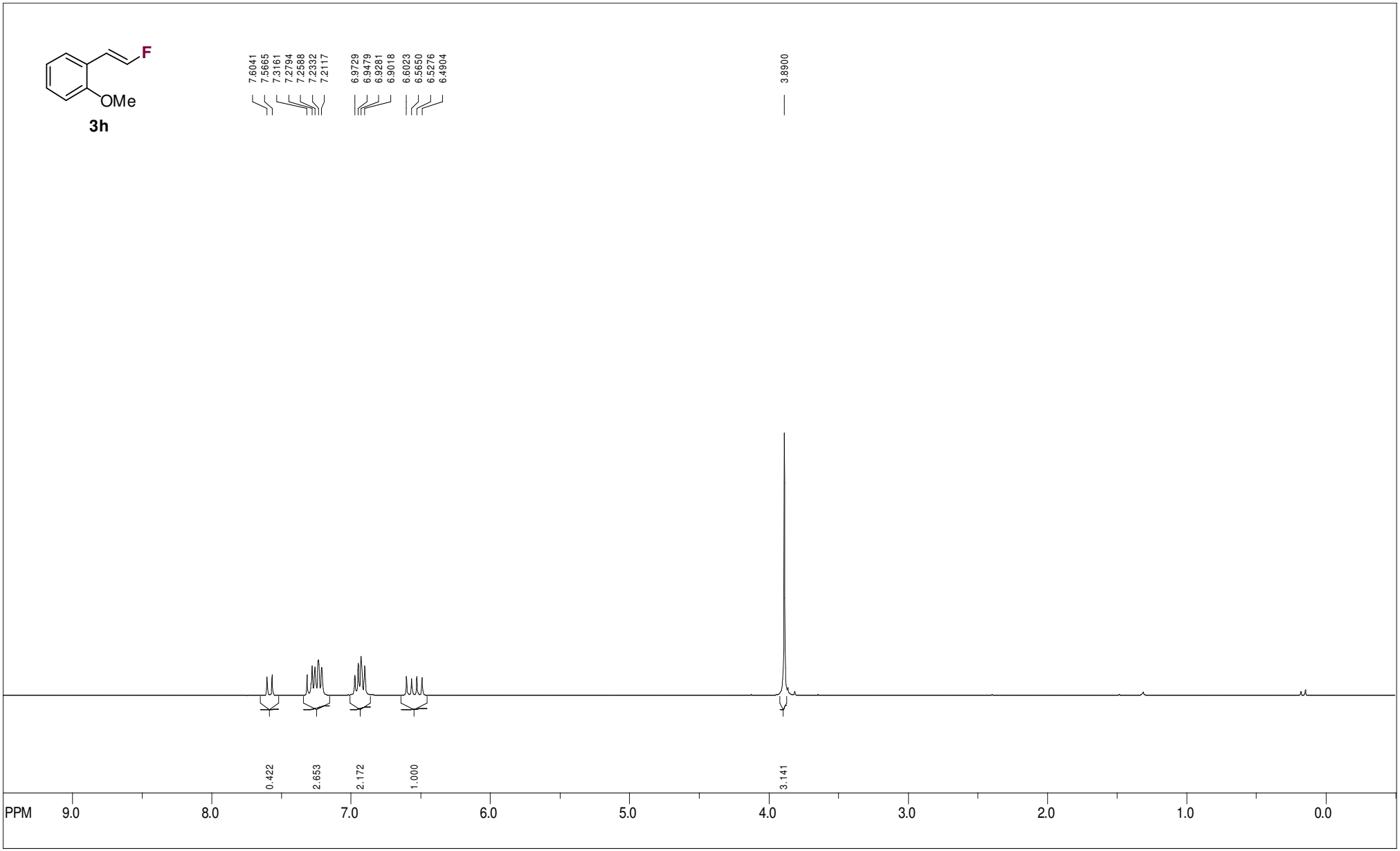
149.0292
133.6907
133.5568
133.1327
131.6075
131.2634
129.6417
129.3035
128.5801
128.3000
126.9786
126.5158
126.3329
126.0930
125.5543
125.1226
124.4249
124.4068
124.0819
119.8187
111.5509
111.3464
81.9785
77.4721
77.2506
77.0470
76.6231
F
3g
+
H
(30%)
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
OMe
3h
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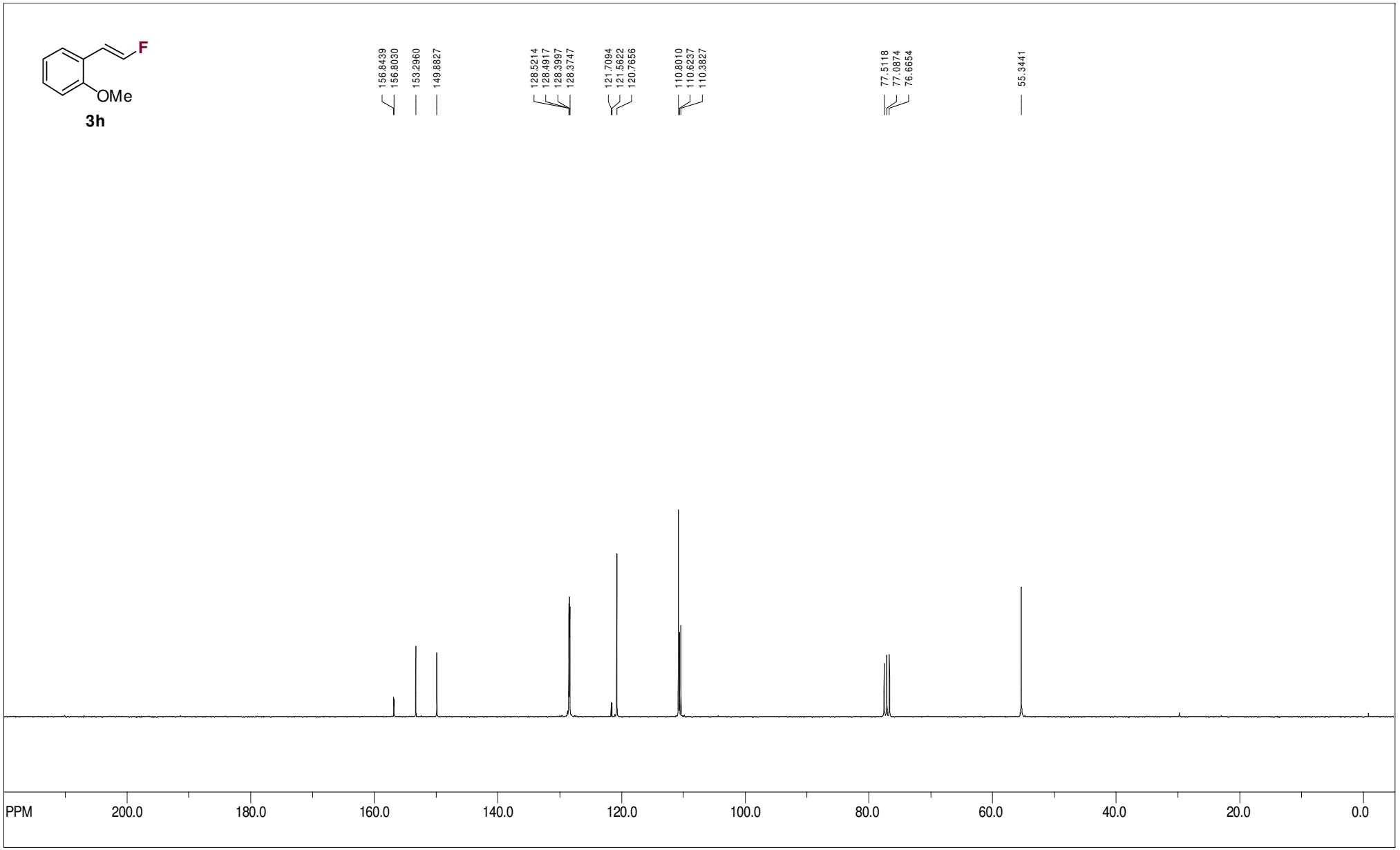
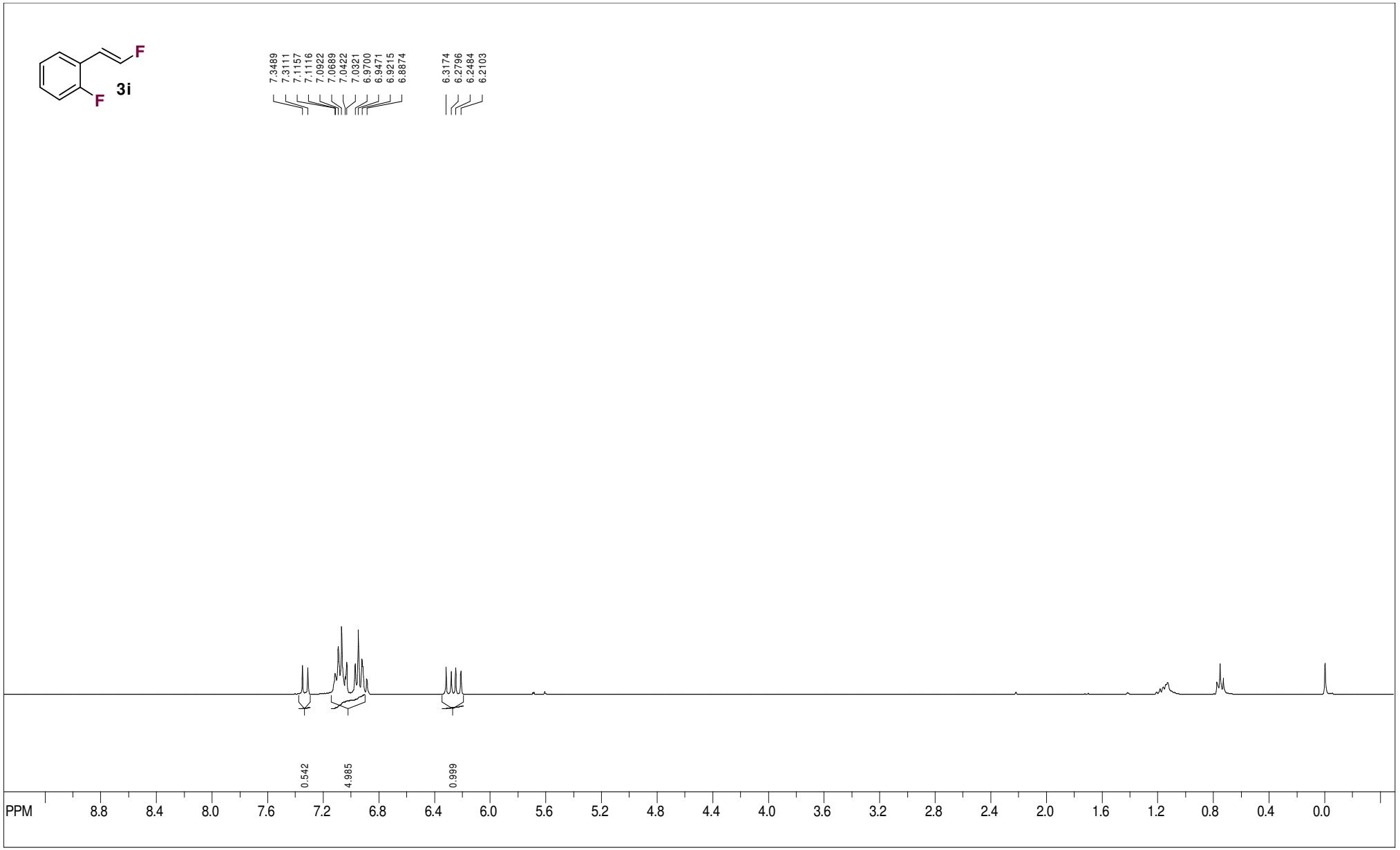
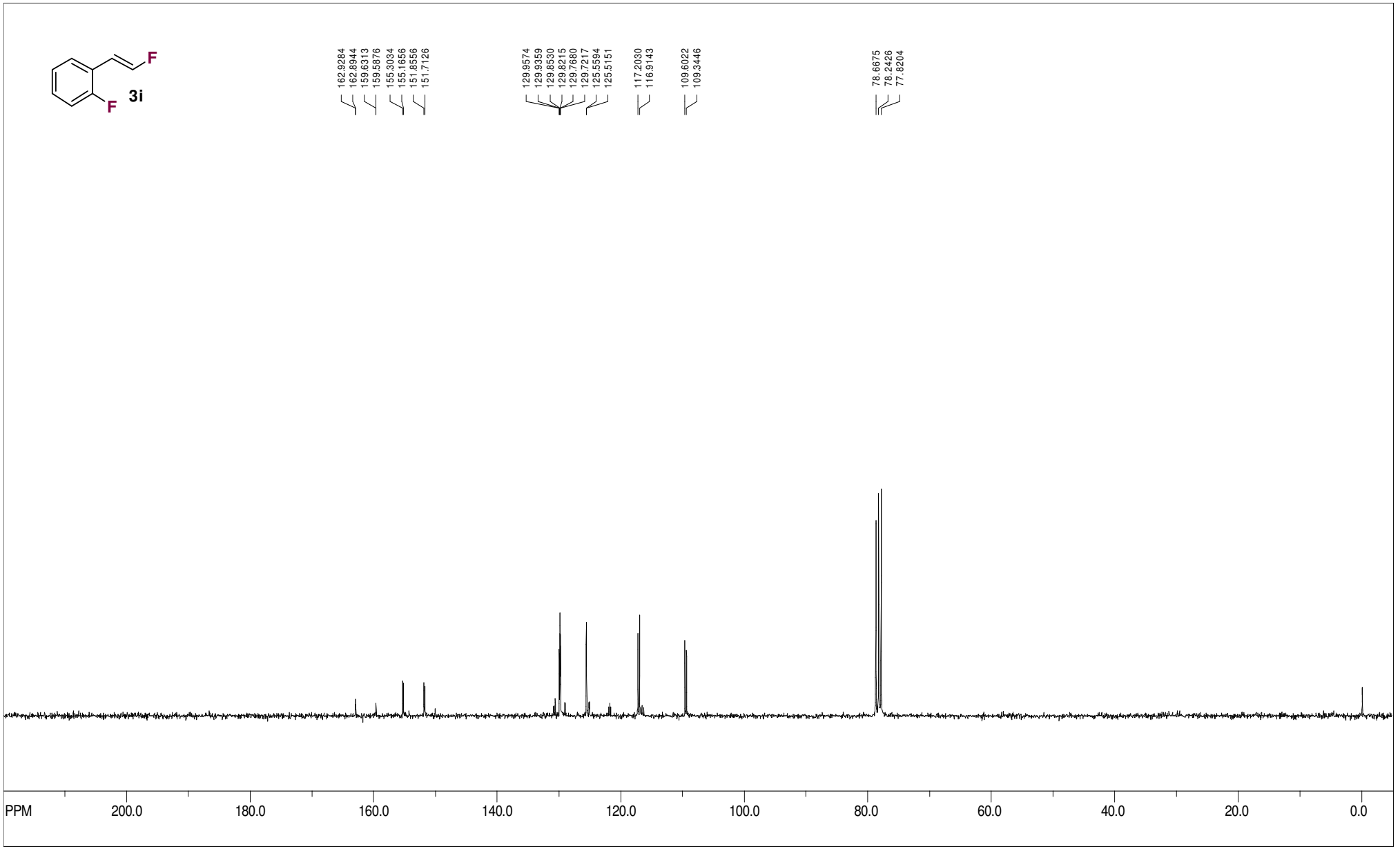
7.5665
7.3161
7.2794
7.2588
7.2332
7.2117
6.9729
6.9479
6.9281
6.9018
6.6023
6.5650
6.5276
6.4904
3.8900
0.422
2.653
2.172
1.000
3.141
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


F
OMe
3h
156.8439
156.8030
153.2960
149.8827
128.5214
128.4917
128.3997
128.3747
121.7094
121.5622
120.7656
110.8010
110.6237
110.3827
77.5118
77.0874
76.6654
55.3441
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


F
F
3i
7.3489
7.3111
7.1157
7.1116
7.0922
7.0689
7.0422
7.0321
6.9700
6.9471
6.9215
6.8874
6.3174
6.2796
6.2484
6.2103
0.542
4.985
0.999
PPM
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0


F
F
3i
162.9284
162.8944
159.6313
159.5876
155.3034
155.1656
151.8556
151.7126
129.9574
129.9359
129.8530
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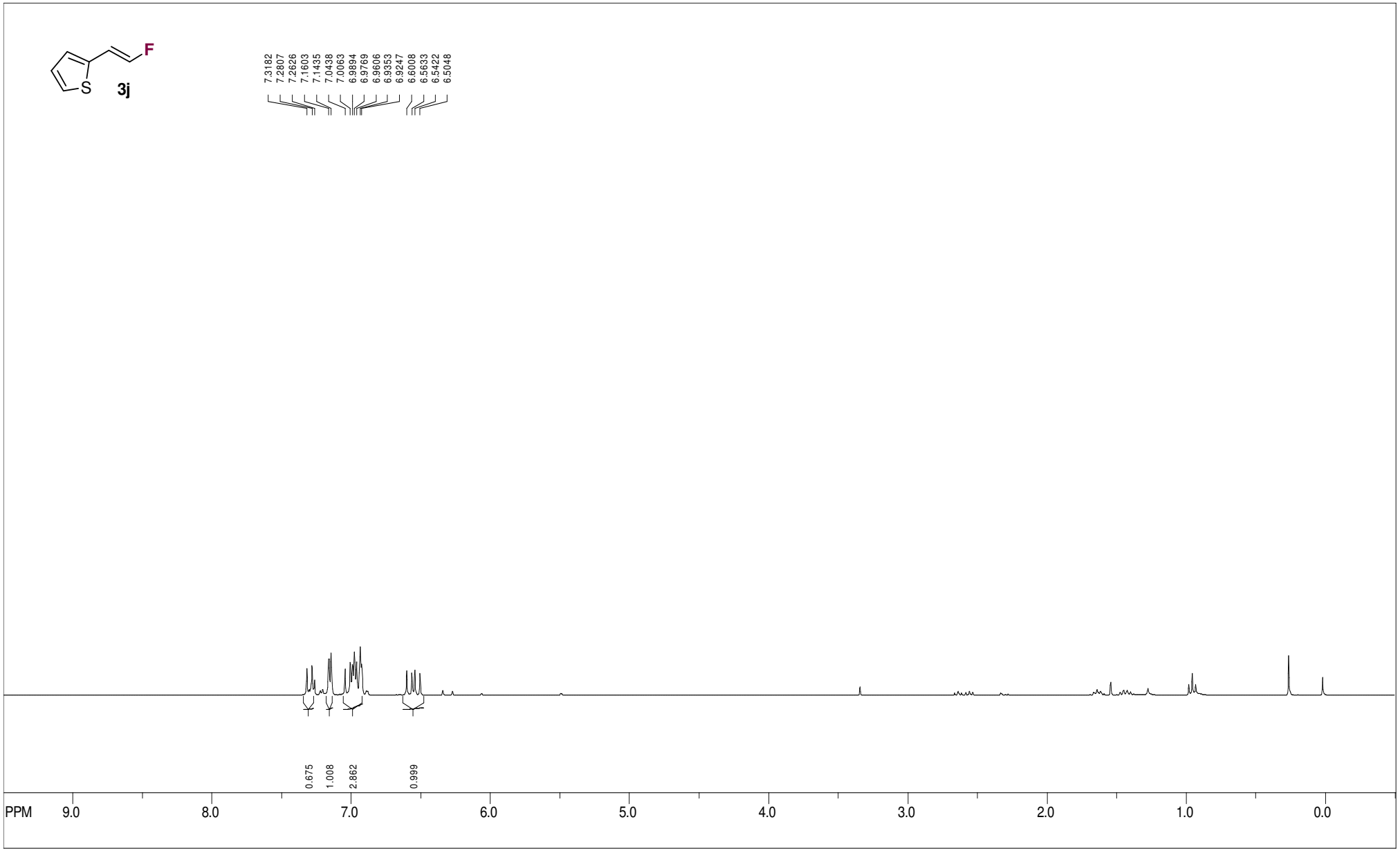
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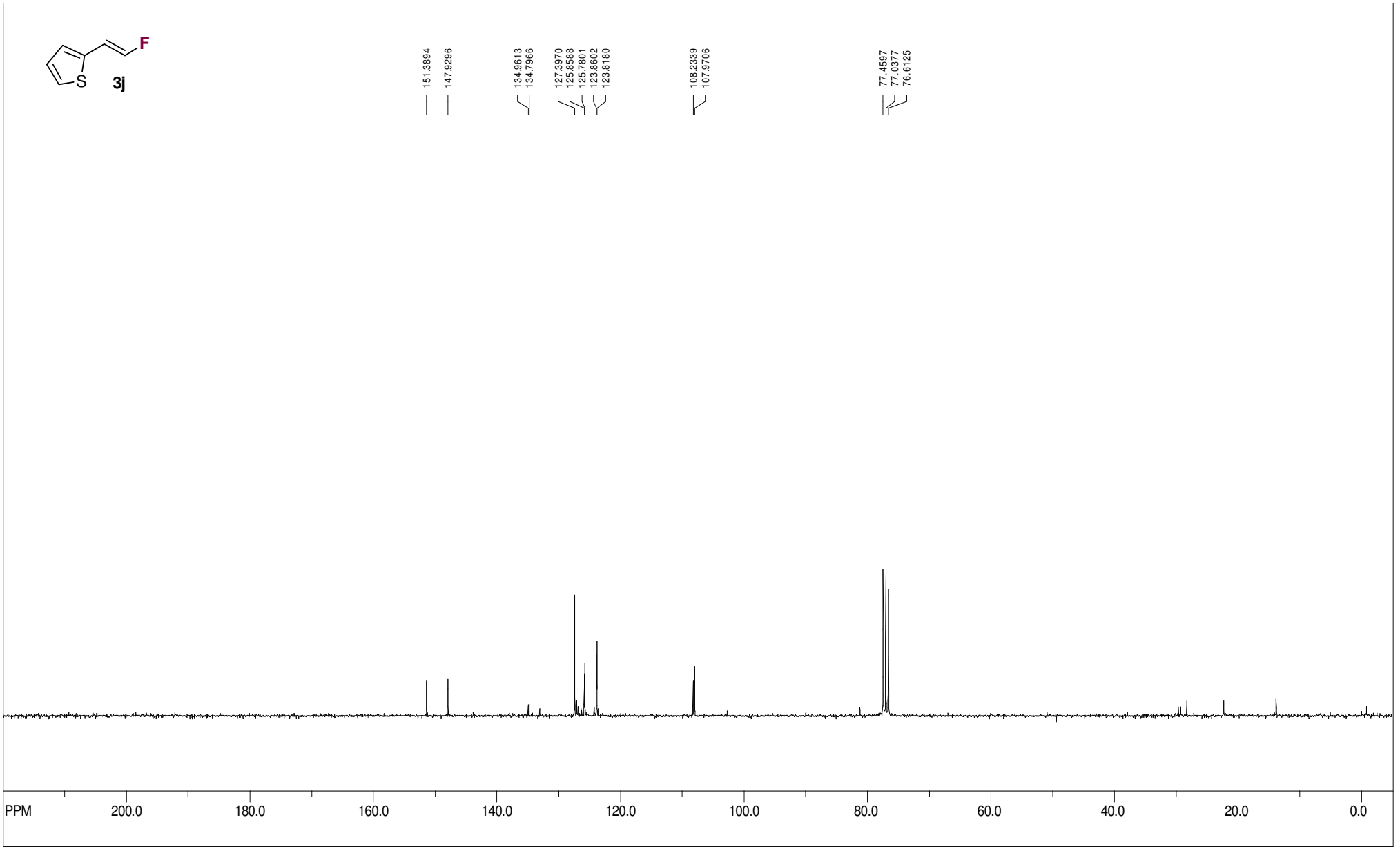
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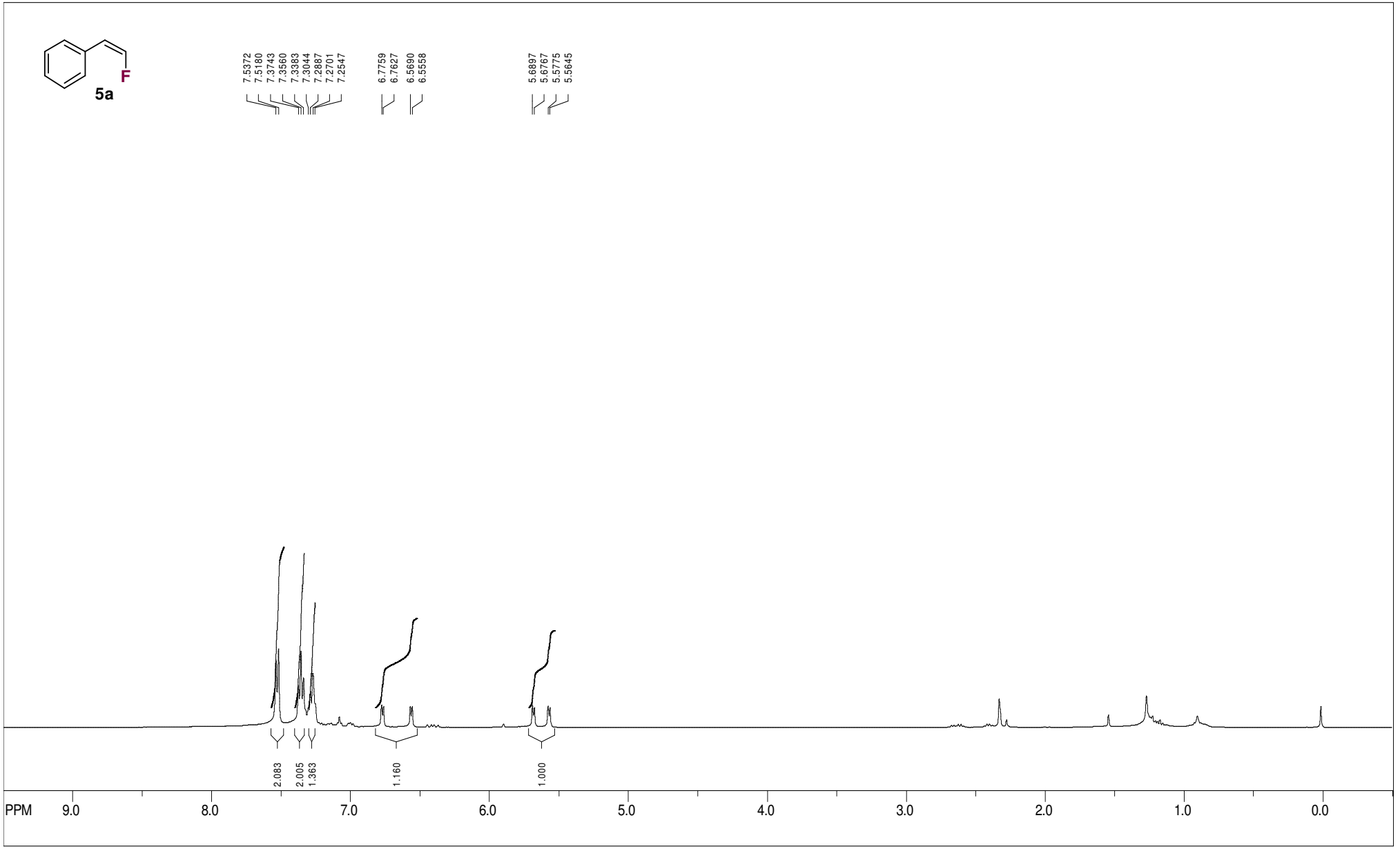
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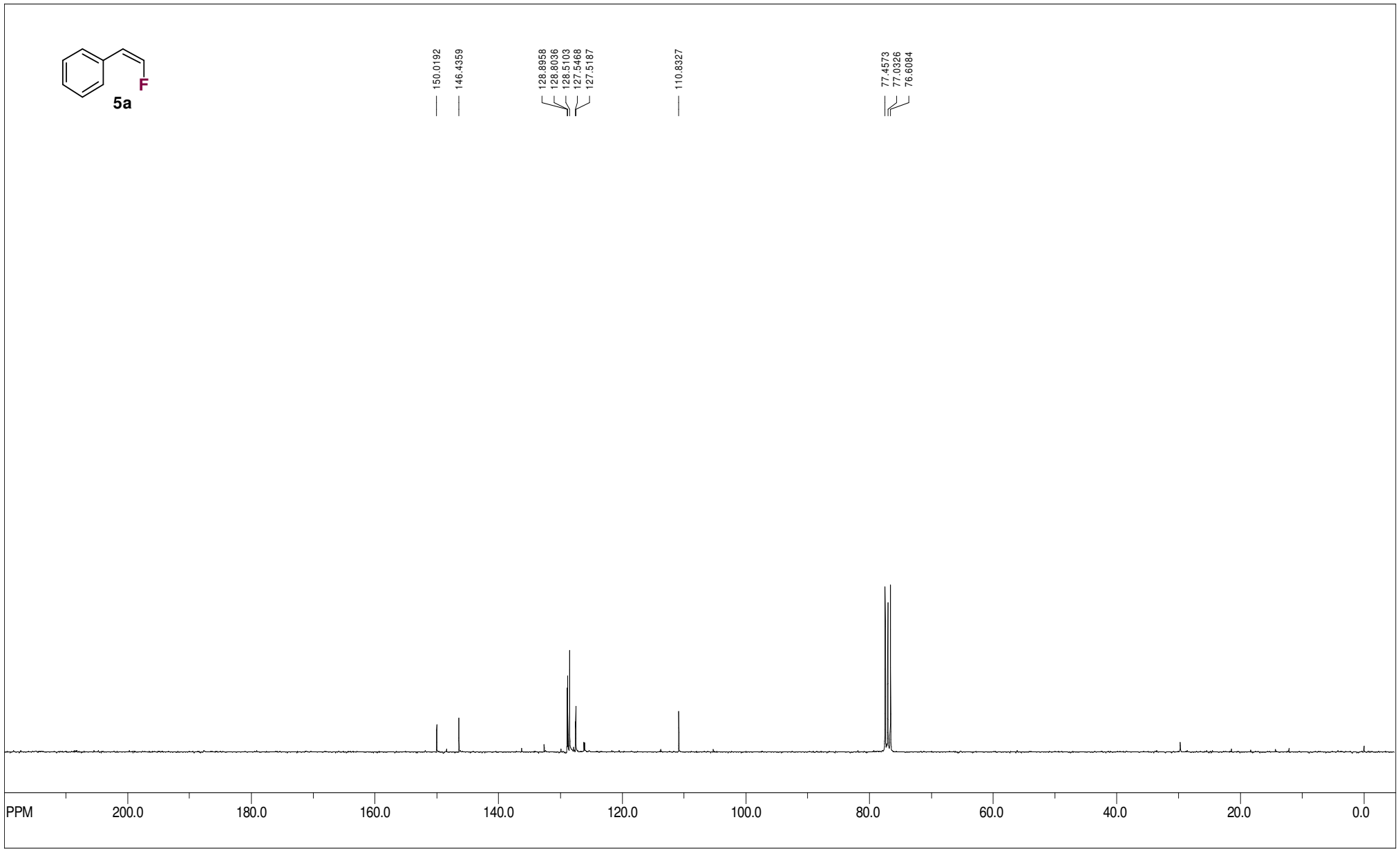
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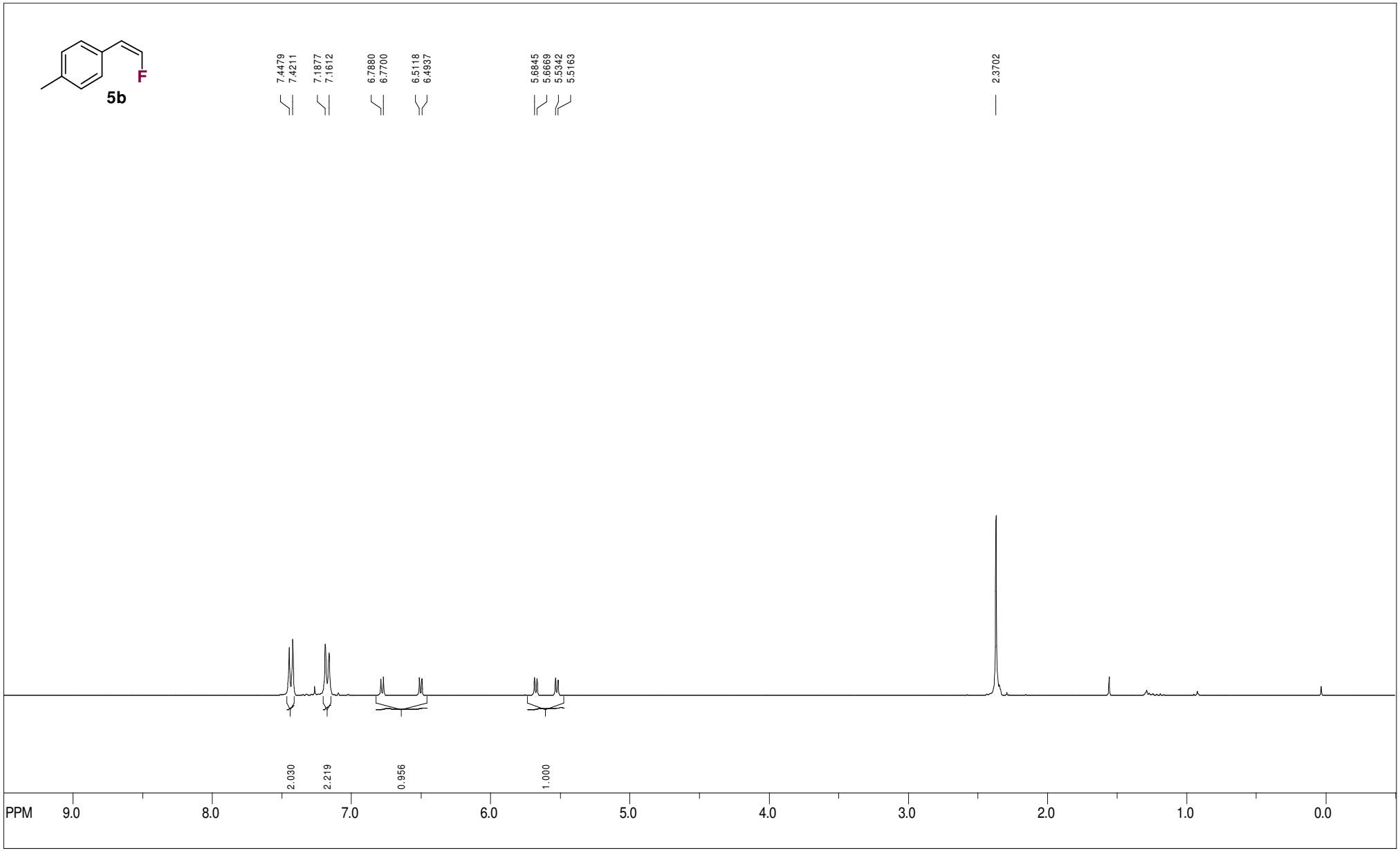
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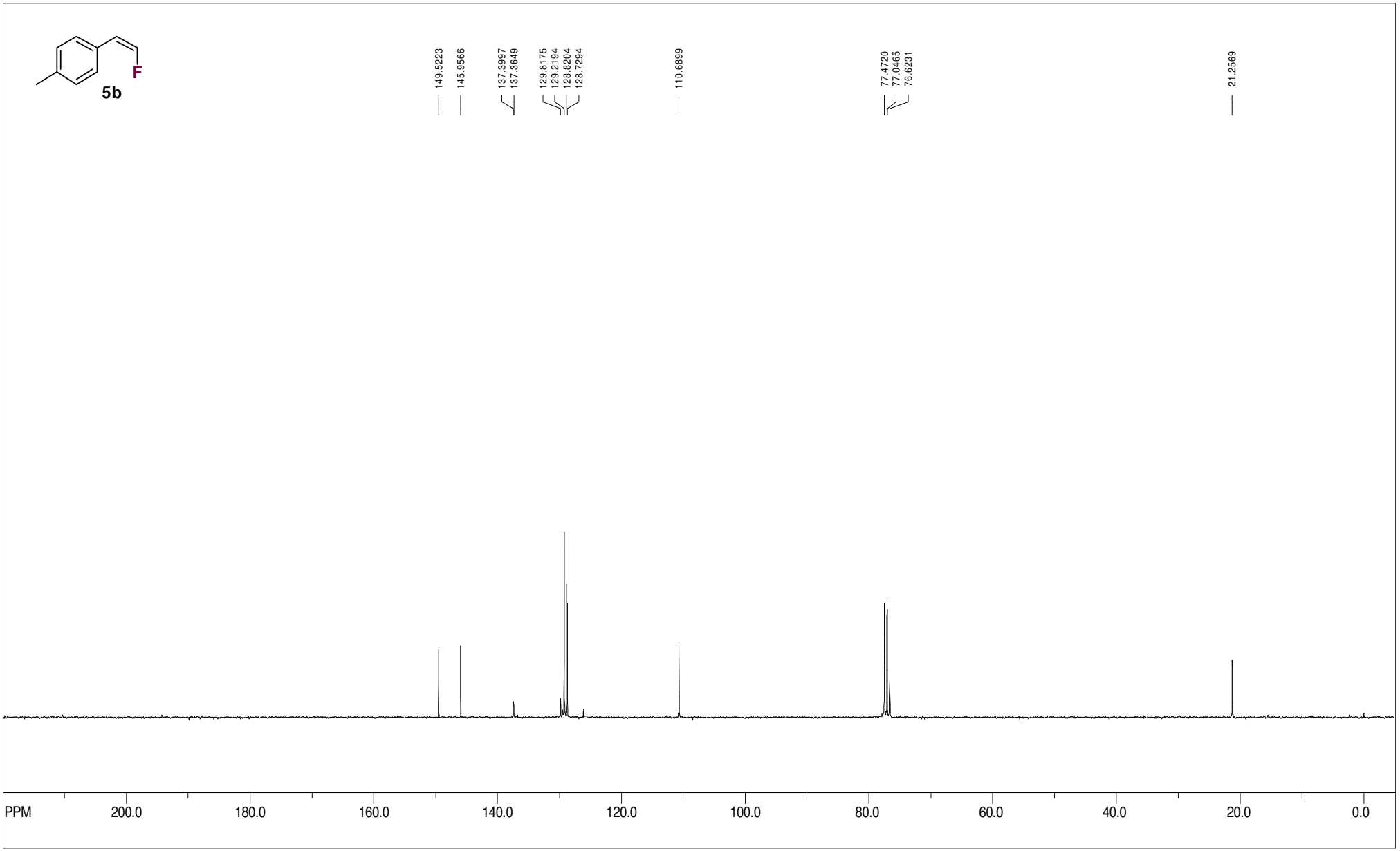
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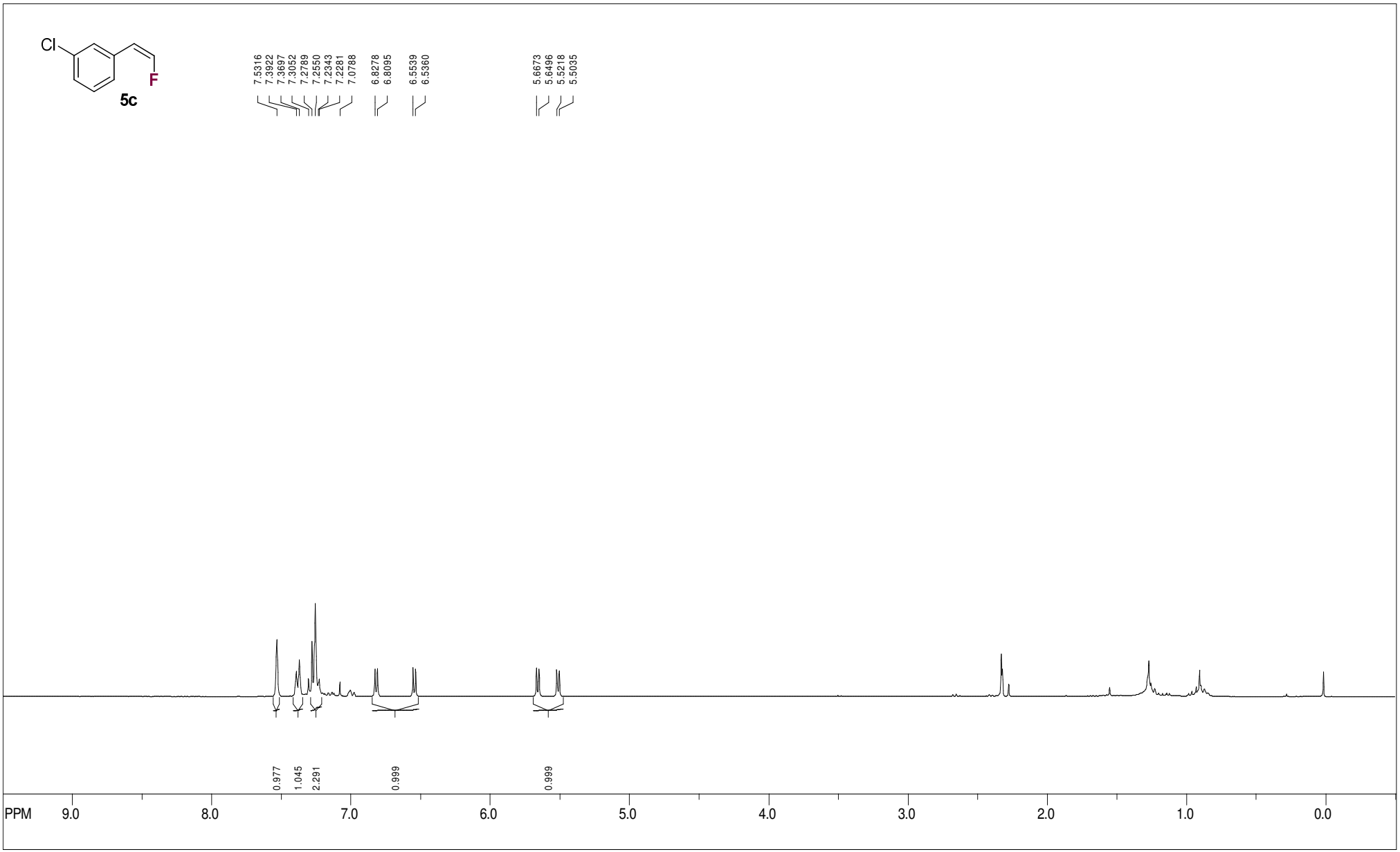
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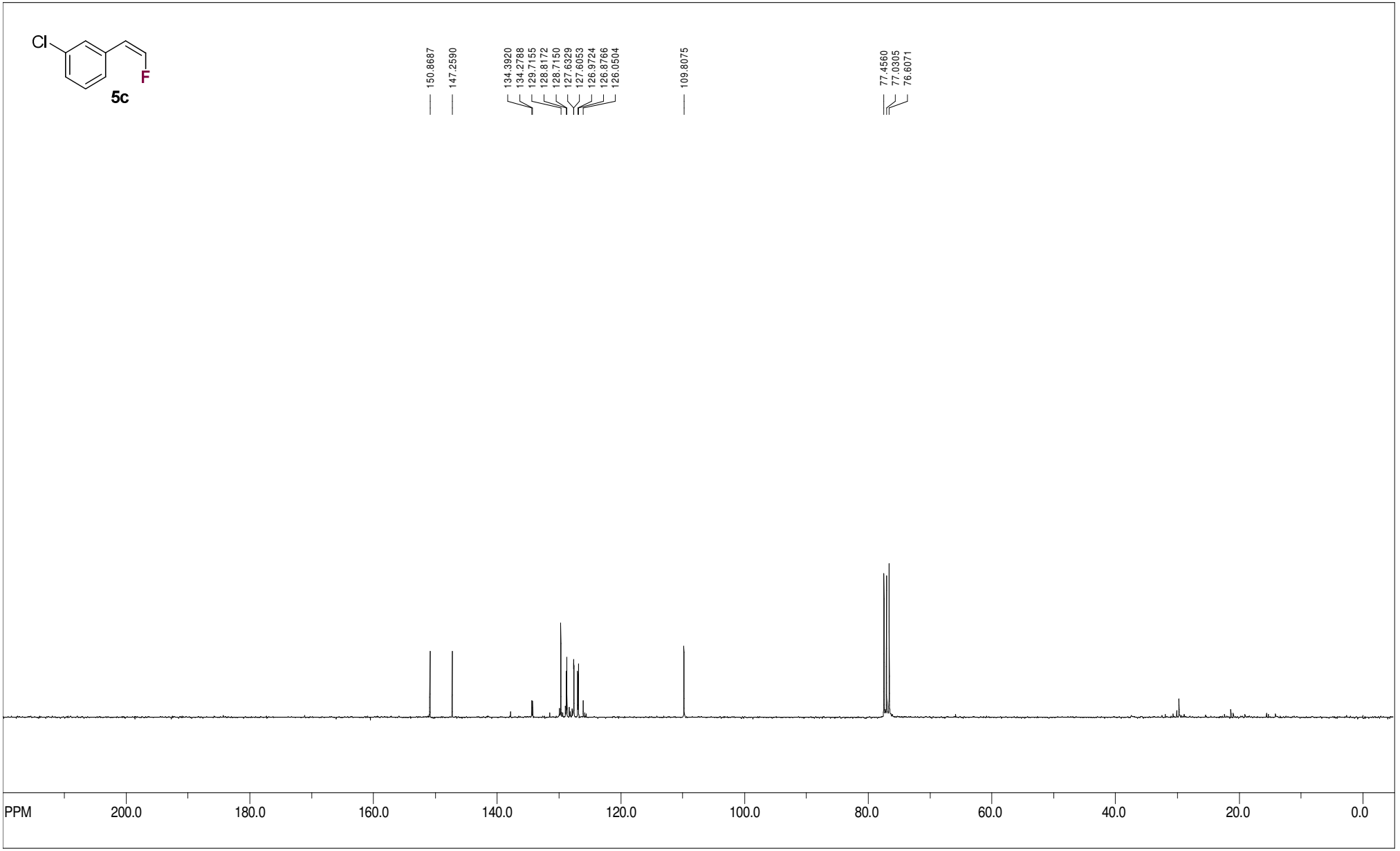
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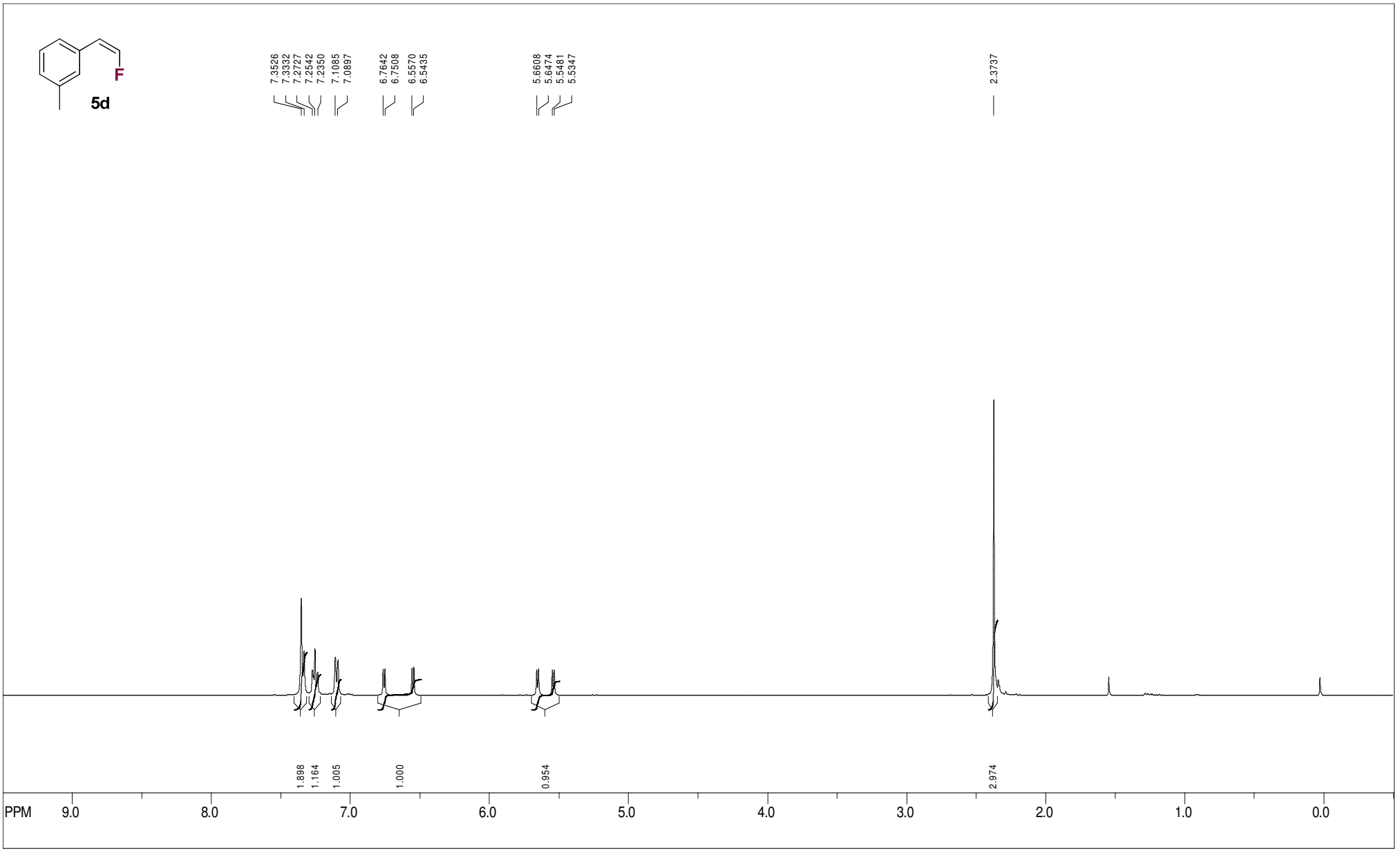
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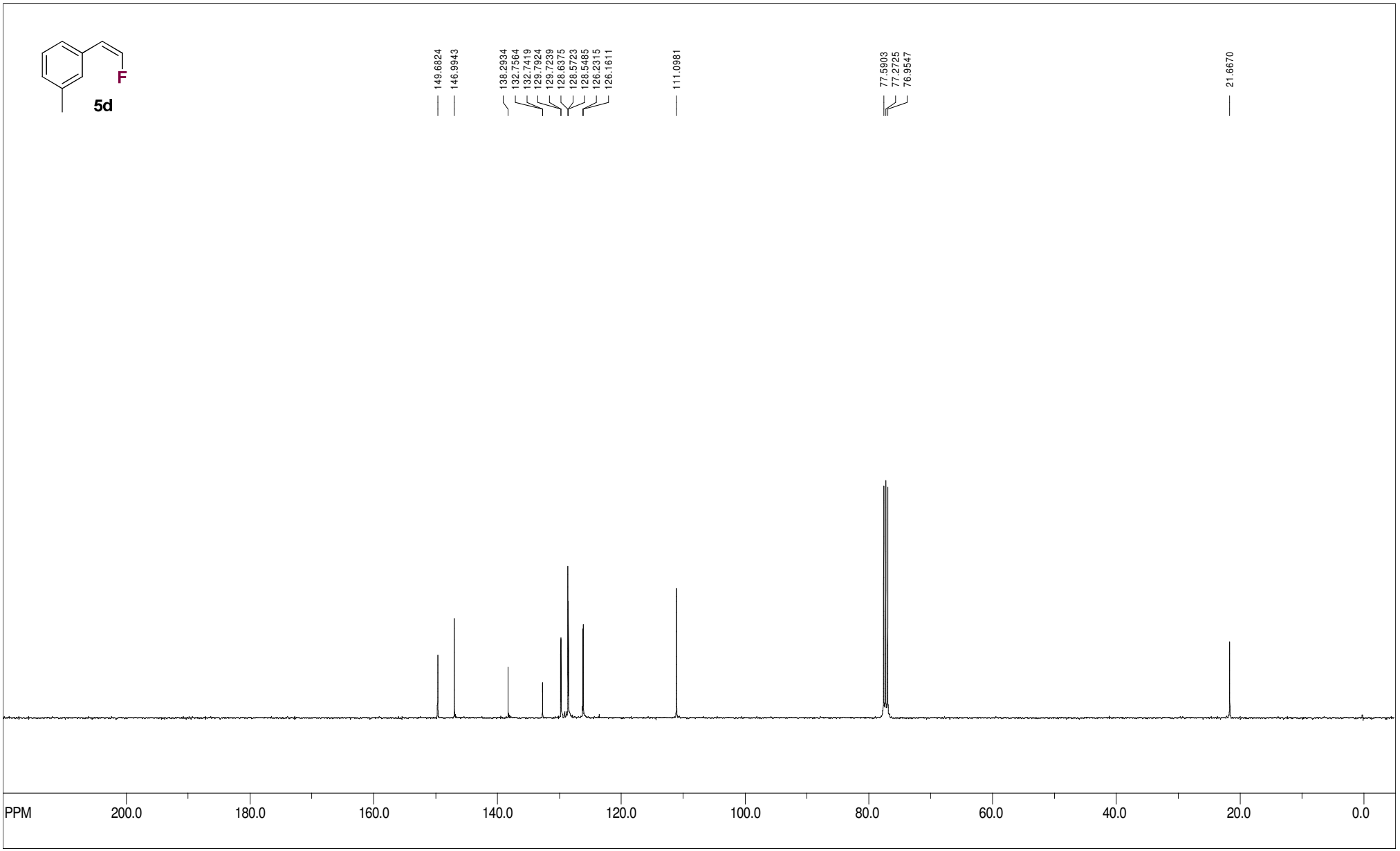
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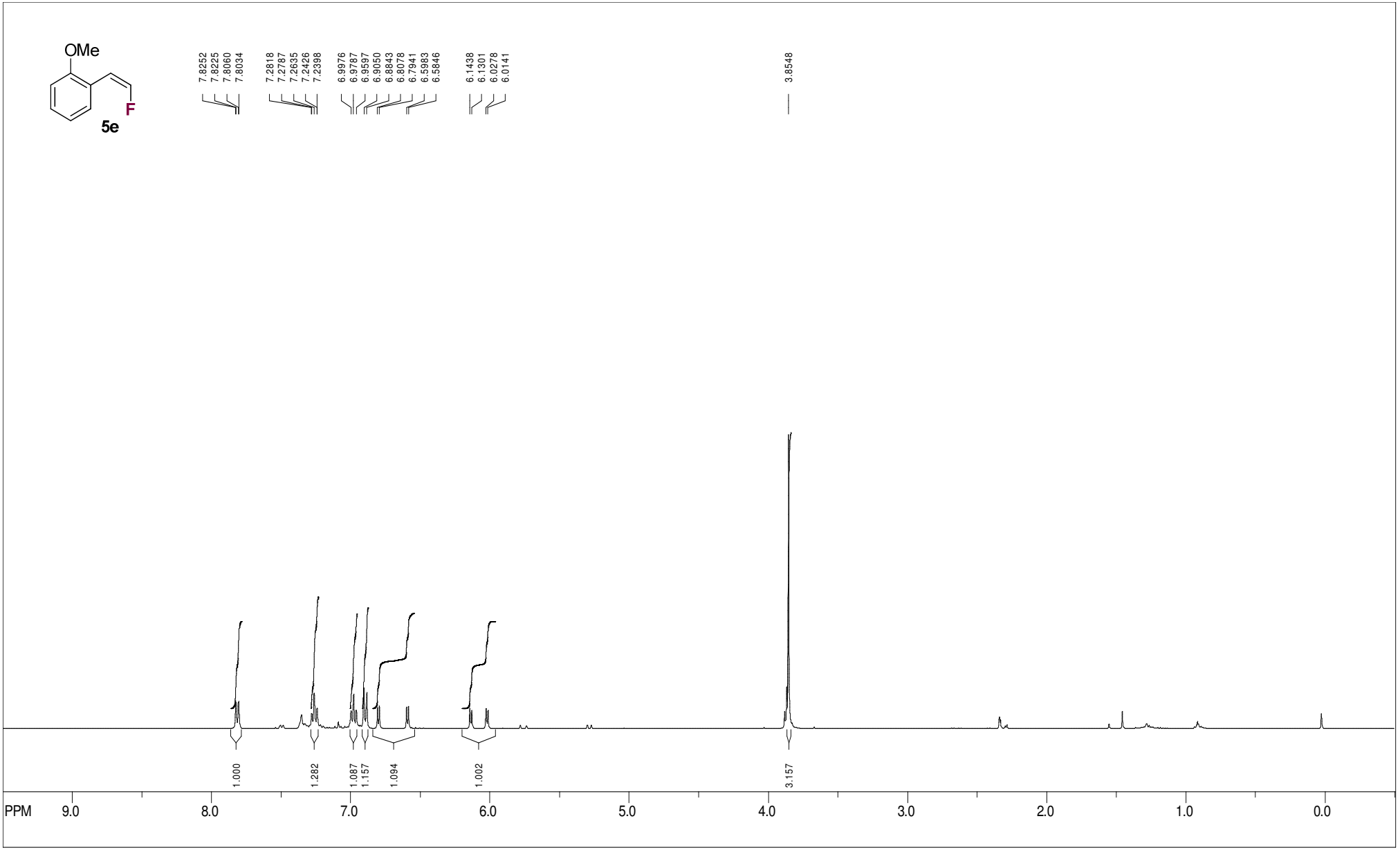
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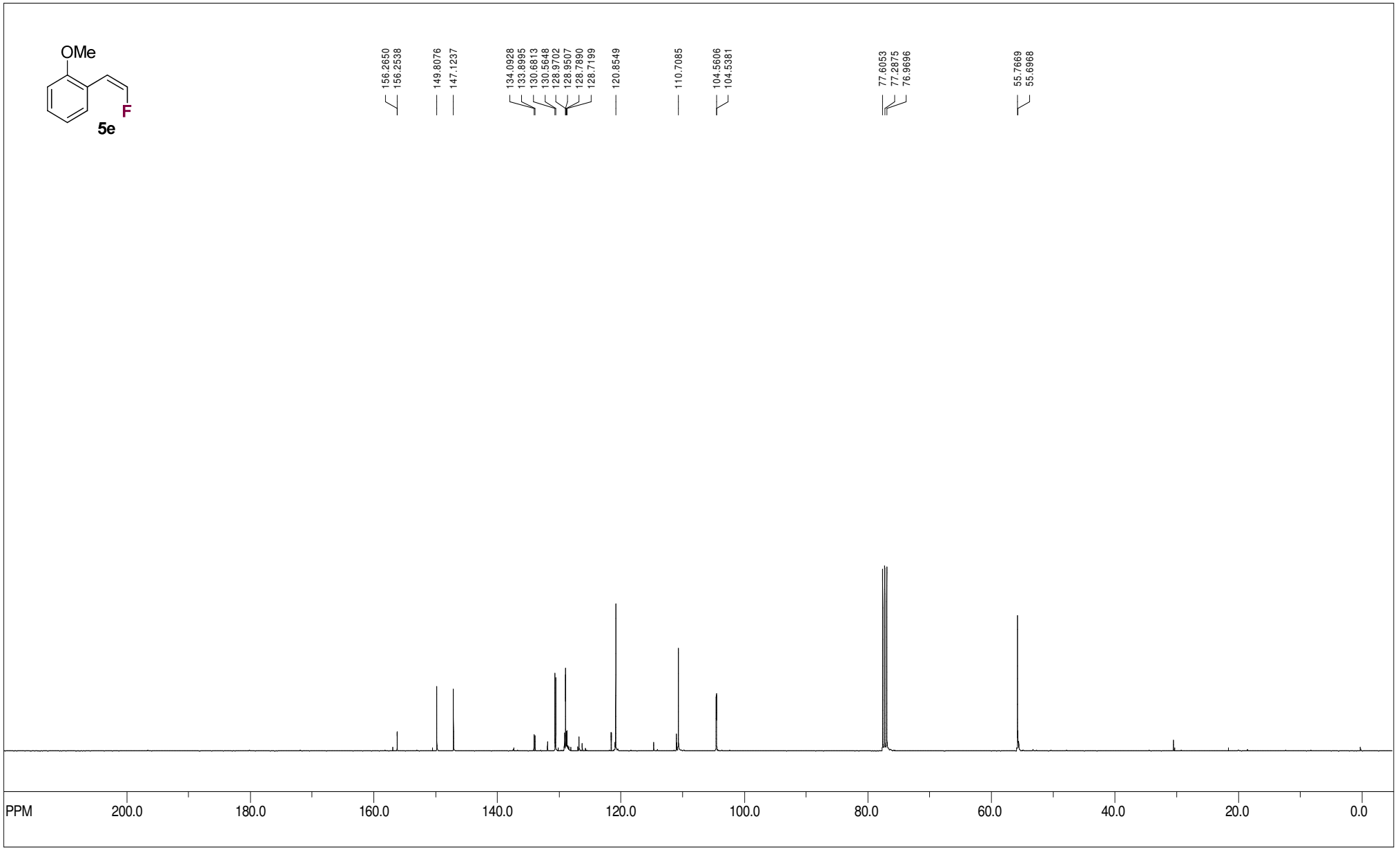
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