Phosphine Catalysis of the Fluorination of Unactivated Tertiary Alkyl Chlorides Under Mild and Convenient Conditions

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Supporting Information

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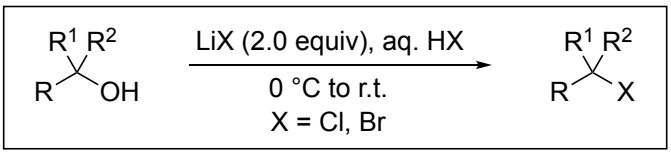
I. General Information

Unless otherwise noted, reagents received from commercial suppliers were used as received. All reactions were performed under an atmosphere of dry nitrogen. Glassware was oven-dried at 150 °C for a minimum of 12 h, or flame-dried utilizing a gas flame under high vacuum. All solvents were either purified by passage through activated aluminum oxide in a solvent-purification system, or they were purchased from commercial suppliers and used as received.

NMR spectra were collected on a Bruker 400 MHz, Varian 500 MHz, or Varian 600 MHz spectrometer at ambient temperature (unless otherwise indicated); chemical shifts (δ) are reported in ppm downfield from tetramethylsilane, using the solvent resonance as an internal standard. FT-IR measurements were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. X-ray crystallographic analyses were carried out in the Caltech X-Ray Crystallography Facility. HRMS were acquired on an Agilent 1260 Infinity II HPLC, Agilent 6230 LC-TOF system in electrospray ionization (ESI+) mode, or by field ionization/field desorption ionization using a JEOL AccuTOF GC-Alpha (JMS-T2000GC) mass spectrometer interfaced with an Agilent 8890 GC system. GC-MS analyses were carried out on an Agilent 6890N GC-MS. SFC analyses were carried out on an Agilent 1260 Infinity II system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm), with samples prepared by dissolving the compound in *i*-PrOH. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 μm, Silicycle). Syringe filters were purchased from VWR (nylon, 13 mm diameter, 0.22 μm pore). Melting points were measured using a Büchi Melting Point B-545 instrument (20 °C – 200 °C; gradient 0.5 °C/s).

II. Preparation of Electrophiles

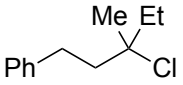
The yields have not been optimized.



General Procedure 1 (GP-1): Chlorination/bromination of tertiary alcohols.

Typical scale: 10 mmol of substrate. A 100-mL round-bottom flask equipped with a PTFE stir bar was charged with LiCl (2 equiv) and aqueous HCl (12 M; 20 mL). The solution was cooled to 0 °C, and then the tertiary alcohol was added dropwise, either neat or dissolved in a minimal amount of CH_2Cl_2, over 5 min. The reaction mixture was allowed to warm to rt, and it was stirred for 12 h. The mixture was then diluted with Et_2O (20 mL) and water (20 mL), and the organic layer was separated. The residual Et_2O in the aqueous layer was recovered by diluting with water (25 mL) and Et_2O (10 mL) (twice) and then saturated aqueous $NaHCO_3$ (25 mL) and Et_2O (10 mL) (twice). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated to provide the crude product.

The bromination of tertiary alcohols utilized the same procedure, with LiBr and aqueous HBr (48 wt%) used in place of LiCl and aqueous HCl.



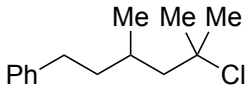
(3-Chloro-3-methylpentyl)benzene (1^{Cl}). Compound $\mathbf{1}^{Cl}$ was synthesized according to **GP-1** and purified by vacuum distillation (250 mbar, 75 °C). Colorless oil. Yield: 4.52 g, 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.29 – 7.23 (m, 3H), 2.92 – 2.77 (m, 2H), 2.21 – 2.01 (m, 2H), 1.99 – 1.83 (m, 2H), 1.64 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 128.52, 128.48, 126.0, 74.8, 45.7, 37.0, 31.3, 29.3, 9.3.

FT-IR (film): 2972, 1497, 1454, 1380, 1031, 806, 743, 607, 628, 553, 505 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{12}H_{17}Cl$: 196.1019, found: 196.1024.



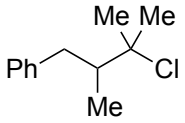
(5-Chloro-3,5-dimethylhexyl)benzene (3). Compound **3** was synthesized according to **GP-1** and purified by flash column chromatography (100% hexanes). Colorless oil. Yield: 1.17 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.17 (m, 3H), 2.76 – 2.56 (m, 2H), 1.90 (dd, *J* = 14.3, 3.6 Hz, 1H), 1.86 – 1.66 (m, 3H), 1.61 (s, 6H), 1.60 – 1.52 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 128.4, 128.3, 125.7, 71.5, 52.8, 40.7, 33.5, 33.2, 32.9, 29.9, 22.0.

FT-IR (film): 2925, 1496, 1453, 1370, 1116, 1031, 745, 697, 570, 509 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{14}H_{21}Cl$: 224.1332, found: 224.1341.



(3-Chloro-2,3-dimethylbutyl)benzene (4). Compound **4** was synthesized according to **GP-1** and purified by vacuum distillation (75 °C, 250 mTorr). Colorless oil. Yield: 2.12 g.

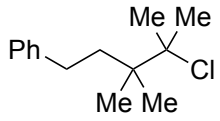
According to ^{1}H NMR spectroscopic analysis, compound **4** contains ~3% of a rearranged isomer, (2-chloro-2,3-dimethylbutyl)benzene, which cannot be separated from compound **4**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 3.24 (dd, *J* = 13.1, 2.7 Hz, 1H), 2.24 (dd, *J* = 13.1, 11.0 Hz, 1H), 2.00 (dqd, *J* = 11.0, 6.7, 2.6 Hz, 1H), 1.65 (dd, *J* = 22.9, 1.5 Hz, 6H), 0.90 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 129.2, 128.3, 125.9, 75.2, 48.1, 38.8, 31.2, 29.5, 14.5.

FT-IR (film): 2975, 1495, 1454, 1370, 1125, 1077, 776, 737, 698, 632, 573, 499, 466 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{12}H_{17}Cl$: 196.1019, found: 196.1024.



(4-Chloro-3,3,4-trimethylpentyl)benzene (5). Compound **5** was synthesized according to **GP-1** and purified by recrystallization from acetone and water. White waxy solid. Yield: 1.86 g, 46%.

According to ^{1}H NMR spectroscopic analysis, compound **5** contains ~11% of a rearranged isomer, (3-chloro-3,4,4-trimethylpentyl)benzene, which cannot be separated from compound **5**.

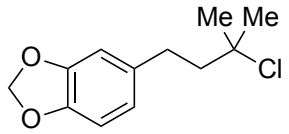
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 2.66 – 2.58 (m, 2H), 1.80 – 1.72 (m, 2H), 1.60 (s, 6H), 1.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 128.4 (2), 125.8, 80.1, 41.8, 39.6, 31.6, 28.5, 22.1.

FT-IR (film): 2973, 1601, 1491, 1453, 1378, 1145, 1125, 1097, 1030, 921, 819, 749, 696, 614, 568, 520, 463, 424 cm^{-1}.

HRMS (FI^{+}-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{14}H_{21}Cl$: 224.1332, found: 224.1340.

m.p.: 46.0 °C.



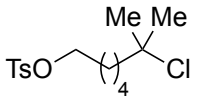
5-(3-Chloro-3-methylbutyl)benzo[d][1,3]dioxole (6). Compound **6** was synthesized according to **GP-1** and purified by flash column chromatography (2% EtOAc in hexanes). Colorless oil. Yield: 2.82 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.67 – 6.63 (m, 1H), 5.92 (s, 2H), 2.80 – 2.63 (m, 2H), 2.09 – 1.87 (m, 2H), 1.63 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.7, 135.6, 121.1, 108.9, 108.2, 100.8, 70.5, 48.2, 32.5, 31.4.

FT-IR (film): 2972, 1502, 1488, 1441, 1370, 1244, 1189, 1159, 1094, 1038, 927, 861, 804, 771, 636, 563, 532, 421 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{12}H_{15}O_2Cl$: 226.0761, found: 226.0772.



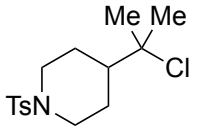
6-Hydroxy-6-methylheptyl 4-methylbenzenesulfonate (7). Compound **7** was synthesized according to **GP-1** and purified by flash column chromatography (10% EtOAc in hexanes). Colorless oil. Yield: 1.53 g, 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 1.73 – 1.62 (m, 4H), 1.53 (s, 6H), 1.48 – 1.38 (m, 2H), 1.38 – 1.27 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 133.2, 129.9, 127.9, 70.9, 70.4, 45.7, 32.4, 28.7, 25.4, 24.4, 21.7.

FT-IR (film): 2940, 1598, 1454, 1356, 1174, 1097, 953, 813, 755, 727, 662, 553 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{15}H_{23}O_3ClS$: 318.1056, found: 318.1056.



4-(2-Chloropropan-2-yl)-1-tosylpiperidine (8). Compound **8** was synthesized according to **GP-1** and purified by recrystallization from EtOAc and hexanes. White solid. Yield: 1.80 g, 62%.

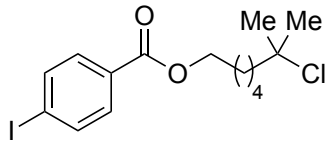
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.92 – 3.84 (m, 2H), 2.43 (s, 3H), 2.27 – 2.12 (m, 2H), 1.95 – 1.90 (m, 2H), 1.59 – 1.39 (m, 3H), 1.50 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.0, 129.6, 127.8, 72.9, 48.2, 46.5, 29.9, 26.9, 21.5.

FT-IR (film): 2980, 1597, 1461, 1372, 1333, 1302, 1250, 1161, 1113, 1089, 1055, 926, 870, 808, 728, 653, 638, 584, 548, 517, 494, 411 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{22}NO_2ClS$: 316.1133, found: 316.1133.

m.p.: 127.0 °C.



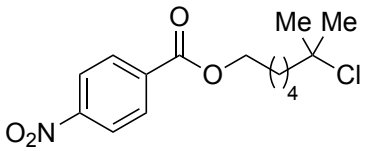
6-Chloro-6-methylheptyl 4-iodobenzoate (9). Compound **9** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (3% EtOAc in hexanes). Colorless oil. Yield: 1.74 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.76 – 7.72 (m, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.85 – 1.73 (m, 4H), 1.60 – 1.52 (m, 2H), 1.57 (s, 6H), 1.50 – 1.40 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 137.7, 131.0, 129.9, 100.6, 71.0, 65.2, 45.9, 32.5, 28.6, 26.2, 24.8.

FT-IR (film): 2939, 1717, 1586, 1466, 1392, 1369, 1265, 1176, 1101, 1007, 845, 752, 682, 627, 571, 462 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{15}H_{20}O_2ClI$: 394.0197, found: 394.0201.



6-Chloro-6-methylheptyl 4-nitrobenzoate (10). Compound **10** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (5% → 10% EtOAc in hexanes). White solid. Yield: 1.47 g.

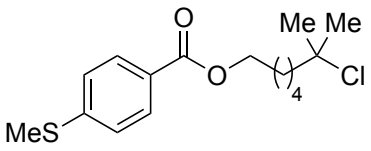
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.26 (m, 2H), 8.23 – 8.18 (m, 2H), 4.38 (t, *J* = 6.6 Hz, 2H), 1.89 – 1.73 (m, 4H), 1.63 – 1.53 (m, 2H), 1.57 (s, 6H), 1.52 – 1.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 150.5, 135.8, 130.7, 123.6, 71.0, 66.0, 45.9, 32.5, 28.6, 26.1, 24.8.

FT-IR (film): 2949, 1715, 1598, 1521, 1468, 1347, 1319, 1278, 1126, 1104, 1059, 1012, 974, 871, 813, 787, 713, 570, 504 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{15}H_{20}NO_4Cl$: 313.1081, found: 313.1056.

m.p.: 42.5 °C.



6-Chloro-6-methylheptyl 4-(methylthio)benzoate (11). Compound **11** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (5% → 10% EtOAc in hexanes). White solid. Yield: 1.45 g.

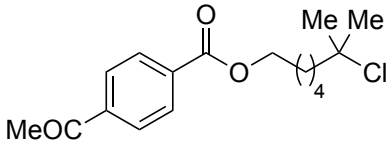
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.27 – 7.23 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.52 (s, 3H), 1.87 – 1.71 (m, 4H), 1.61 – 1.52 (m, 2H), 1.57 (s, 6H), 1.50 – 1.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 145.3, 129.9, 126.6, 124.9, 71.1, 64.9, 45.9, 32.4, 28.7, 26.2, 24.9, 14.9.

FT-IR (film): 2983, 2939, 1698, 1593, 1470, 1403, 1368, 1272, 1185, 1126, 1110, 1058, 1013, 953, 841, 822, 759, 688, 559, 524, 478 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{16}H_{23}O_2ClS$: 314.1107, found: 314.1098.

m.p.: 37.5 °C.



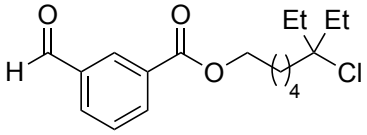
6-Chloro-6-methylheptyl 4-acetylbenzoate (12). Compound **12** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (12% EtOAc/hexanes). Colorless oil. Yield: 1.36 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.1 Hz, 2H), 4.35 (t, *J* = 6.7 Hz, 2H), 2.64 (s, 3H), 1.87 – 1.72 (m, 4H), 1.61 – 1.53 (m, 2H), 1.57 (s, 6H), 1.52 – 1.41 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 165.8, 140.2, 134.2, 129.8, 128.2, 71.0, 65.5, 45.9, 32.5, 28.6, 26.9, 26.2, 24.8.

FT-IR (film): 2940, 1719, 1688, 1406, 1357, 1258, 1108, 1016, 957, 859, 768, 741, 696, 611, 589, 572 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{17}H_{23}O_3Cl$: 310.1336, found: 310.1322.



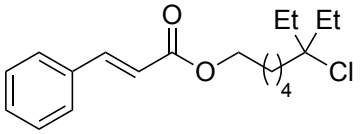
6-Chloro-6-ethyloctyl 3-formylbenzoate (13). Compound **13** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (6% EtOAc in hexanes). Colorless oil. Yield: 2.01 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.62 – 8.51 (m, 1H), 8.33 (dt, *J* = 7.7, 1.5 Hz, 1H), 8.11 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.73 – 7.62 (m, 1H), 4.40 (t, *J* = 6.7 Hz, 2H), 1.91 – 1.73 (m, 8H), 1.54 – 1.46 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 165.5, 136.5, 135.2, 133.1, 131.5, 131.2, 129.3, 79.4, 65.6, 40.2, 33.3, 28.6, 26.3, 23.9, 8.8.

FT-IR (film): 2941, 1721, 1702, 1603, 1459, 1381, 1283, 1185, 1162, 1101, 1074, 964, 819, 747, 700, 677, 647, 609 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M-H]^{+\bullet}$ calcd for $C_{18}H_{25}O_3Cl$: 323.1414, found: 323.1417.



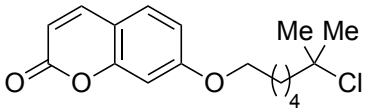
6-Chloro-6-ethyloctyl cinnamate (14). Compound **14** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (5% EtOAc in hexanes). Colorless oil. Yield: 1.90 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.42 – 7.36 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.86 – 1.69 (m, 8H), 1.52 – 1.38 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 144.7, 134.5, 130.3, 128.9, 128.1, 118.2, 79.5, 64.6, 40.2, 33.4, 28.7, 26.3, 23.9, 8.8.

FT-IR (film): 2941, 1710, 1637, 1450, 1381, 1308, 1269, 1201, 1164, 978, 863, 835, 766, 710, 683, 610, 573, 485 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{19}H_{27}O_2Cl$: 322.1700, found: 322.1696.



7-((6-Chloro-6-methylheptyl)oxy)-2*H*-chromen-2-one (15). Compound **15** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (15% EtOAc in hexanes). Yield: 1.84 g, 80%.

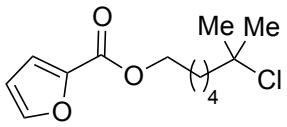
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.5 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.79 – 1.72 (m, 2H), 1.60 – 1.46 (m, 4H), 1.56 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 161.3, 155.9, 143.5, 128.8, 112.94, 112.92, 112.4, 101.4, 71.1, 68.5, 45.9, 32.5, 28.9, 26.1, 24.9.

FT-IR (film): 2951, 1713, 1606, 1505, 1472, 1395, 1373, 1349, 1281, 1234, 1199, 1158, 1123, 1044, 1004, 988, 889, 855, 826, 759, 731, 629, 617, 522, 456, 428 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{21}O_3Cl$: 309.1252, found: 309.1246.

m.p.: 65.0 °C.



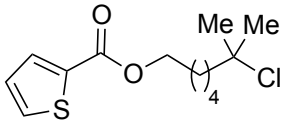
6-Chloro-6-methylheptyl furan-2-carboxylate (16). Compound **16** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (3% EtOAc in hexanes). Colorless oil. Yield: 1.75 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.17 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.83 – 1.71 (m, 4H), 1.58 – 1.51 (m, 2H), 1.56 (s, 6H), 1.49 – 1.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 146.2, 144.8, 117.8, 111.8, 71.0, 64.9, 45.9, 32.4, 28.6, 26.1, 24.8.

FT-IR (film): 2940, 1715, 1581, 1473, 1399, 1370, 1292, 1230, 1179, 1115, 1076, 1012, 960, 885, 761, 616, 596, 571 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{13}H_{19}O_3Cl$: 258.1023, found: 258.1031.



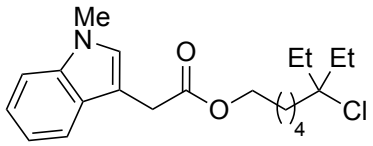
6-Chloro-6-methylheptyl thiophene-2-carboxylate (17). Compound **17** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (3% EtOAc in hexanes). Colorless oil. Yield: 1.10 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.72 (m, 4H), 1.60 – 1.52 (m, 2H), 1.57 (s, 6H), 1.49 – 1.33 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 134.0, 133.3, 132.2, 127.7, 71.0, 65.1, 45.9, 32.4, 28.7, 26.1, 24.8.

FT-IR (film): 2940, 1705, 1525, 1419, 1358, 1256, 1224, 1093, 1073, 1038, 860, 750, 718, 630, 571 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{13}H_{19}O_2ClS$: 274.0794, found: 274.0802.



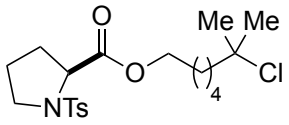
6-Chloro-6-ethyloctyl 2-(1-methyl-1*H*-indol-3-yl)acetate (18). Compound **18** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (5% → 8% EtOAc in hexanes). Pale yellow oil. Yield: 2.58 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 1H), 7.33 – 7.28 (m, 1H), 7.26 – 7.21 (m, 1H), 7.16 – 7.10 (m, 1H), 7.05 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 5H), 1.77 (q, *J* = 7.4 Hz, 4H), 1.72 – 1.60 (m, 4H), 1.44 – 1.26 (m, 4H), 0.95 (d, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 136.9, 127.7 (2), 121.8, 119.1, 119.0, 109.3, 106.9, 79.5, 64.8, 40.1, 33.3, 32.7, 31.3, 28.6, 26.2, 23.9, 8.8.

FT-IR (film): 2941, 1731, 1461, 1375, 1330, 1247, 1148, 1064, 1013, 834, 730, 609, 427 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{21}H_{30}NO_2Cl$: 363.1965, found: 363.1975.



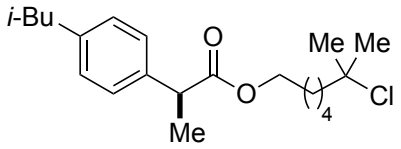
6-Chloro-6-methylheptyl tosyl-L-prolinate (19). Compound **19** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (10% → 20% EtOAc in hexanes). Colorless oil. Yield: 1.79 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (dd, *J* = 8.6, 0.8 Hz, 2H), 4.29 (dd, *J* = 8.1, 4.0 Hz, 1H), 4.19 – 4.05 (m, 2H), 3.53 – 3.44 (m, 1H), 3.36 – 3.26 (m, 1H), 2.42 (s, 3H), 2.08 – 1.89 (m, 3H), 1.80 – 1.71 (m, 3H), 1.70 – 1.62 (m, 2H), 1.56 (s, 6H), 1.55 – 1.46 (m, 2H), 1.43 – 1.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 143.5, 135.4, 129.6, 127.5, 71.1, 65.3, 60.5, 48.4, 45.9, 32.4, 31.0, 28.4, 25.9, 24.8, 24.7, 21.6.

FT-IR (film): 2981, 1747, 1598, 1452, 1347, 1282, 1156, 1093, 1012, 815, 708, 662, 591, 547 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{30}NO_4ClS$: 416.1657, found: 416.4658.



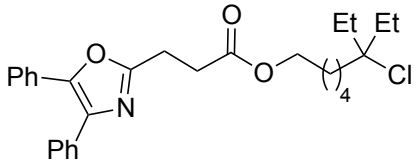
6-Chloro-6-methylheptyl (S)-2-(4-isobutylphenyl)propanoate (20). Compound **20** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (3% EtOAc in hexanes). Colorless oil. Yield: 2.79 g.

^1H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 7.11 – 7.07 (m, 2H), 4.07 (td, *J* = 6.6, 1.8 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.72 – 1.56 (m, 4H), 1.55 (s, 6H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.47 – 1.38 (m, 2H), 1.32 – 1.21 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 140.5, 137.9, 129.3, 127.2, 71.0, 64.6, 45.9, 45.2, 45.0, 32.4, 30.2, 28.5, 25.9, 24.7, 22.4, 18.5.

FT-IR (film): 2951, 1732, 1512, 1464, 1369, 1331, 1200, 1162, 1070, 1022, 848, 729, 572 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{21}H_{33}O_2Cl$: 352.2169, found: 352.2157.



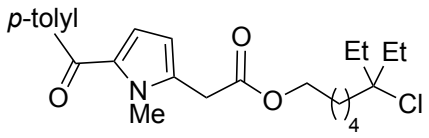
6-Chloro-6-ethyloctyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (21). Compound **21** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (10% EtOAc in hexanes). Viscous colorless oil. Yield: 1.92 g.

^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.39 – 7.29 (m, 6H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.19 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.91 (dd, *J* = 8.2, 6.9 Hz, 2H), 1.75 (q, *J* = 7.3 Hz, 4H), 1.72 – 1.61 (m, 4H), 1.47 – 1.30 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 161.8, 145.4, 135.1, 132.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 126.5, 79.5, 64.8, 40.1, 33.3, 31.2, 28.6, 26.1, 23.9, 23.6, 8.8.

FT-IR (film): 2941, 1734, 1571, 1502, 1445, 1166, 1057, 1025, 962, 834, 762, 693, 674, 607, 522 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{28}H_{34}NO_3Cl$: 468.2300, found: 468.2296.



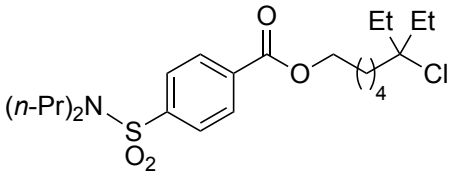
6-Chloro-6-ethyloctyl 2-(1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl)acetate (22). Compound **22** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (10% EtOAc in hexanes). Viscous yellow oil. Yield: 1.64 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 4.0 Hz, 1H), 6.11 (d, *J* = 4.1 Hz, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 3.71 (s, 2H), 2.42 (s, 3H), 1.77 (q, *J* = 7.4 Hz, 4H), 1.73 – 1.64 (m, 4H), 1.47 – 1.29 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9, 169.5, 141.9, 137.3, 134.6, 131.4, 129.5, 128.7, 122.3, 109.4, 79.4, 65.4, 40.1, 33.3, 33.2, 33.0, 28.5, 26.1, 23.8, 21.6, 8.8.

FT-IR (film): 2941, 1736, 1624, 1480, 1455, 1373, 1262, 1172, 1067, 1041, 976, 882, 833, 790, 748, 704, 619, 480 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{34}NO_3Cl$: 432.2300, found: 432.2297.



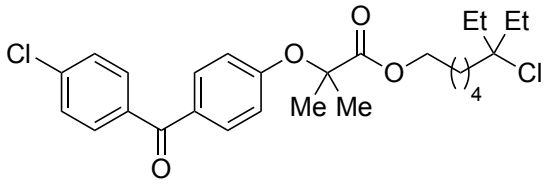
6-Chloro-6-ethyloctyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (23). Compound **23** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (7% EtOAc in hexanes). Viscous colorless oil. Yield: 3.09 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.13 – 3.08 (m, 4H), 1.88 – 1.71 (m, 8H), 1.63 – 1.43 (m, 8H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.87 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 144.2, 133.7, 130.2, 127.0, 79.4, 65.7, 49.9, 40.2, 33.3, 28.6, 26.3, 23.9, 22.0, 11.2, 8.8.

FT-IR (film): 2968, 1721, 1460, 1343, 1270, 1158, 1106, 1087, 991, 862, 765, 740, 694, 601, 561, 448 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{38}NO_4ClS$: 460.2283, found: 460.2276.



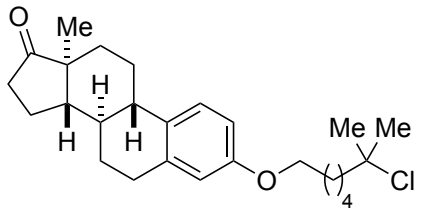
6-Chloro-6-ethyloctyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (24). Compound **24** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (10% EtOAc in hexanes). Viscous colorless oil. Yield: 3.01 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 4H), 7.50 – 7.44 (m, 2H), 6.92 – 6.85 (m, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 1.76 (q, *J* = 7.4 Hz, 4H), 1.70 (s, 6H), 1.68 – 1.62 (m, 4H), 1.44 – 1.32 (m, 2H), 1.31 – 1.20 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 173.8, 159.7, 138.4, 136.4, 132.0, 131.2, 130.3, 128.6, 117.2, 79.4, 79.3, 65.7, 40.1, 33.3, 28.3, 26.0, 25.5, 23.8, 8.8.

FT-IR (film): 2941, 1733, 1654, 1597, 1505, 1461, 1383, 1283, 1248, 1171, 1136, 1089, 1014, 952, 926, 852, 836, 761, 739, 679, 653, 575, 521, 478 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{27}H_{34}O_4Cl$: 492.1834, found: 492.1818.



(8*R*,9*S*,13*S*,14*S*)-3-((6-Chloro-6-methylheptyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (25). Compound **25** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (10% EtOAc in hexanes). White solid. Yield: 1.67 g.

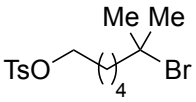
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.7, 1.0 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.65 (d, *J* = 2.7 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.96 – 2.83 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.31 – 2.20 (m, 1H), 2.20 – 2.09 (m, 1H), 2.09 – 1.92 (m, 3H), 1.86 – 1.73 (m, 4H), 1.70 – 1.37 (m, 10H), 1.58 (s, 6H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 157.1, 137.7, 131.9, 126.3, 114.5, 112.1, 71.2, 67.7, 50.4, 48.0, 46.0, 44.0, 38.4, 35.9, 32.5, 31.6, 29.7, 29.3, 26.6, 26.2, 25.9, 24.9, 21.6, 13.9.

FT-IR (film): 2934, 2862, 1737, 1608, 1499, 1453, 1370, 1281, 1234, 1161, 1055, 1006, 819, 749, 697, 615, 570 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{26}H_{37}O_2Cl$: 416.2482, found: 416.2470.

m.p.: 115.5 °C.



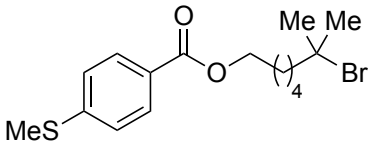
6-Hydroxy-6-methylheptyl 4-methylbenzenesulfonate (26). Compound **26** was synthesized according to **GP-1** and purified by flash column chromatography (10% EtOAc in hexanes). Colorless oil. Yield: 1.80 g, 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 1.80 – 1.60 (m, 4H), 1.72 (s, 6H) 1.52 – 1.41 (m, 2H), 1.40 – 1.29 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 133.2, 129.9, 127.9, 70.4, 68.1, 47.2, 34.2, 28.7, 25.6, 25.3, 21.7.

FT-IR (film): 2939, 2864, 1598, 1452, 1359, 1177, 1120, 1098, 905, 825, 760, 728, 665 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M\text{-}HBr]^{+\bullet}$ calcd for $C_{15}H_{23}O_3S$: 283.1368, found: 283.1365.



6-Bromo-6-methylheptyl 4-(methylthio)benzoate (27). Compound **27** was synthesized according to **GP-1** and purified by flash column chromatography on silica gel (5% → 10% EtOAc in hexanes). Pale yellow liquid. Yield: 1.08 g.

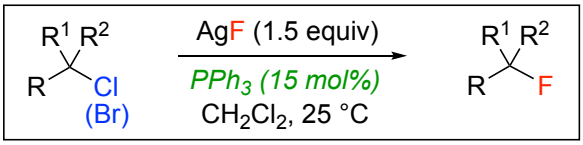
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.52 (s, 3H), 1.85 – 1.77 (m, 4H), 1.76 (s, 6H), 1.65 – 1.55 (m, 2H), 1.53 – 1.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 145.3, 129.9, 126.6, 124.9, 68.3, 64.9, 47.4, 34.3, 28.7, 26.1, 26.1, 14.9.

FT-IR (film): 2919, 2860, 1712, 1594, 1443, 1384, 1264, 1180, 1106, 1015, 960, 842, 759, 688 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M\text{-}H]^{+\bullet}$ calcd for $C_{16}H_{23}O_2BrS$: 358.0602, found: 358.0598.

III. Fluorination of Unactivated Tertiary Alkyl Halides



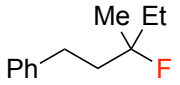
General Procedure 2 (GP-2). Fluorination.

An oven-dried 40-mL vial equipped with a cross-shaped PTFE stir bar (19 mm diameter; 9.5 mm height) and a PTFE-lined cap was evacuated and backfilled with nitrogen once.

If the starting material is a non-viscous liquid: PPh_3 (31 mg, 0.12 mmol) and AgF (152 mg, 1.2 mmol) were added to the vial. The vial was sealed with a PTFE-lined cap, and then evacuated and backfilled with nitrogen (three cycles) to establish an inert atmosphere. Anhydrous CH_2Cl_2 (8 mL) was then added, and the mixture was stirred for 10 min. The alkyl chloride (0.80 mmol) was then introduced into the vial using a microsyringe.

If the starting material is a viscous liquid or a solid: PPh_3 (31.4 mg, 0.12 mmol), AgF (152 mg, 1.2 mmol), and the alkyl chloride (0.80 mmol) were added to the vial. The vial was evacuated and backfilled with nitrogen (three cycles), and then anhydrous CH_2Cl_2 (8 mL) was added to the vial via syringe.

In both cases, the nitrogen line attached to the 40-mL vial was then disconnected, and the puncture site was sealed using vacuum grease. The interface between the cap and the vial was wrapped with electrical tape. The reaction mixture was then stirred vigorously (~1500 rpm) for 24 h, maintained at 25 °C using an oil bath. Next, the reaction mixture was filtered through a pad of silica gel. The vial, cap, and pad of silica gel were rinsed with Et_2O, and the combined organic washings were transferred to a round-bottom flask. The solution was then concentrated, and the crude product was purified using flash column chromatography on silica gel.



(3-Fluoro-3-methylpentyl)benzene (1^{F}). The title compound was synthesized from (3-chloro-3-methylpentyl)benzene $\mathbf{1}^{Cl}$ according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% Et_2O in hexanes). Colorless oil.

Run 1: 110 mg, 76% yield. Run 2: 112 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 2.71 (dd, *J* = 9.5, 7.9 Hz, 2H), 2.01 – 1.81 (m, 2H), 1.79 – 1.60 (m, 2H), 1.37 (d, *J* = 21.8 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 128.5, 128.3, 125.9, 97.4 (d, *J* = 167.7 Hz), 41.1 (d, *J* = 23.0 Hz), 32.3 (d, *J* = 23.7 Hz), 30.0 (d, *J* = 5.5 Hz), 23.7 (d, *J* = 25.0 Hz), 8.1 (d, *J* = 7.0 Hz).

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –146.6 (s).

FT-IR (film): 2975, 1496, 1455, 1379, 1191, 1031, 930, 876, 757, 727, 697, 514 cm^{-1}.

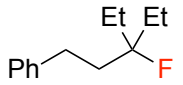
HRMS (FI^{+}-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{12}H_{17}F$: 180.1314, found: 180.1309.

Gram-scale synthesis: A flame-dried 250-mL round-bottom flask equipped with a PTFE stir bar and a rubber septum was evacuated and backfilled with nitrogen once. PPh_3 (315 mg, 1.2 mmol) and AgF (1.27 g, 10.0 mmol) were added to the flask, and then the flask was evacuated and backfilled with nitrogen (three cycles). CH_2Cl_2 (80 mL) was added via a syringe, a nitrogen balloon was attached, and 3-chloro-3-methylpentyl)benzene ($\mathbf{1}^{Cl}$; 1.57 g, 8.0 mmol) was added via a syringe. The mixture was allowed to stir vigorously (>1200 rpm) at r.t. for 24 h. Next, the reaction mixture was filtered through a pad of silica gel. The flask, septum, and pad of silica gel were rinsed with Et_2O, and the combined organic washings were concentrated. The crude product was purified using flash column chromatography on silica gel, employing 2% Et_2O in hexanes as the eluent.

Run 1: 1.05 g, 73% yield. Run 2: 1.05 g, 73% yield.

The reaction was carried out according to **GP-2** with $\mathbf{1}^{Br}$.

Run 1: 102 mg, 71% yield. Run 2: 100 mg, 69% yield.



(3-Ethyl-3-fluoropentyl)benzene (2^F). The title compound was synthesized from (3-ethyl-3-chloropentyl)benzene **2** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% Et_2O in hexanes). Colorless oil.

Run 1: 126 mg, 81% yield. Run 2: 121 mg, 78% yield.

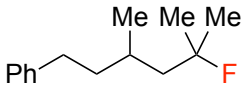
^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 2.73 – 2.62 (m, 2H), 1.99 – 1.83 (m, 2H), 1.80 – 1.62 (m, 4H), 0.94 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 128.5, 128.3, 125.9, 99.3 (d, *J* = 169.9 Hz), 38.3 (d, *J* = 23.1 Hz), 29.7 (d, *J* = 5.8 Hz), 29.0 (d, *J* = 23.8 Hz), 7.8 (d, *J* = 7.3 Hz).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –154.6 (s).

FT-IR (film): 2971, 1496, 1455, 1365, 1031, 971, 907, 752, 716, 696, 512 cm^{-1}.

HRMS (FI^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{13}H_{19}F$: 194.1471, found: 194.1465.



(5-Fluoro-3,5-dimethylhexyl)benzene (3^F). The title compound was synthesized from (5-chloro-3,5-dimethylhexyl)benzene **3** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% Et_2O in hexanes). Colorless oil.

Run 1: 114 mg, 69% yield. Run 2: 114 mg, 69% yield.

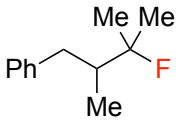
^1H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 2.62 (dddd, *J* = 29.8, 13.5, 10.2, 5.6 Hz, 2H), 1.83 – 1.60 (m, 3H), 1.58 – 1.44 (m, 2H), 1.35 (d, *J* = 21.3 Hz, 6H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 128.4, 128.3, 125.6, 96.1 (d, *J* = 165.3 Hz), 47.9 (d, *J* = 21.5 Hz), 40.1 (d, *J* = 1.3 Hz), 33.3, 28.9 (d, *J* = 1.9 Hz), 27.6 (d, *J* = 24.9 Hz), 27.0 (d, *J* = 25.0 Hz), 21.2 (d, *J* = 2.2 Hz).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –135.8 (s).

FT-IR (film): 2927, 1496, 1454, 1372, 1171, 1031, 863, 745, 697, 512, 476 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{14}H_{21}F$: 208.1627, found: 208.1622.



(3-Fluoro-2,3-dimethylbutyl)benzene (4^F). The title compound was synthesized from (4-chloro-3,4-dimethylpentyl)benzene **4** (1.2-mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% Et_2O in hexanes). Colorless oil. The desired product contained ~4% (according to ^1H and ^{19}F NMR spectroscopy) of an isomer, which originated in alkyl chloride **4** (see Section II).

Run 1: 127 mg, 59%. Run 2: 130 mg, 60%.

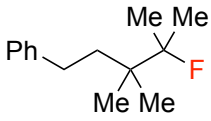
^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 3.06 (dd, *J* = 13.0, 2.9 Hz, 1H), 2.16 (dd, *J* = 13.0, 11.3 Hz, 1H), 1.97 (ddtd, *J* = 18.1, 11.2, 6.9, 3.0 Hz, 1H), 1.38 (dd, *J* = 22.0, 2.9 Hz, 6H), 0.81 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 129.2, 128.3, 125.9, 98.1 (d, *J* = 167.1 Hz), 45.1 (d, *J* = 21.6 Hz), 37.7 (d, *J* = 5.8 Hz), 25.2 (d, *J* = 25.0 Hz), 23.3 (d, *J* = 25.0 Hz), 14.1 (d, *J* = 7.0 Hz).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –137.8 (s). ($^{19}F\{^1H\}$ NMR for the isomer: –148.5 (s).)

FT-IR (film): 2979, 1494, 1454, 1388, 1373, 1256, 1152, 1083, 940, 903, 875, 845, 756, 725, 698, 579, 502, 457 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{12}H_{17}F$: 180.1314, found: 180.1310.



(4-Fluoro-3,3,4-trimethylpentyl)benzene (5^F). The title compound was synthesized from (4-fluoro-3,3,4-trimethylpentyl)benzene **5** (1.2-mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% Et_2O in hexanes). Colorless oil.

The desired product contained ~11% (according to ^{1}H and ^{19}F NMR spectroscopy) of an isomer, which originated in alkyl chloride **5** (see Section II).

Run 1: 121 mg, 58%. Run 2: 124 mg, 59%.

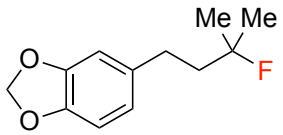
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 2.67 – 2.58 (m, 2H), 1.69 – 1.59 (m, 2H), 1.34 (d, *J* = 22.2 Hz, 6H), 1.04 (d, *J* = 0.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 128.39, 128.38, 125.7, 100.3 (d, *J* = 171.3 Hz), 40.11 (d, *J* = 3.3 Hz), 40.07 (d, *J* = 20.3 Hz), 31.2 (d, *J* = 2.3 Hz), 23.1 (d, *J* = 25.4 Hz), 21.9 (d, *J* = 5.3 Hz).

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –145.8 (s). ($^{19}F\{^{1}H\}$ NMR for the isomer: –160.2 (s).)

FT-IR (film): 2972, 1604, 1495, 1455, 1377, 1241, 1158, 1069, 1030, 935, 862, 803, 747, 698, 588, 516, 487 cm^{-1}.

HRMS (FI^{+}-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{14}H_{21}F$: 208.1627, found: 208.1621.



5-(3-Fluoro-3-methylbutyl)benzo[d][1,3]dioxole (6^{F}). The title compound was synthesized from 5-(3-chloro-3-methylbutyl)benzo[d][1,3]dioxole **6** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% Et_2O in hexanes). Colorless oil.

The title compound coeluted with olefin side products (no other impurities) that were not separable via chromatography. The yield was therefore determined via ^{1}H NMR spectroscopy: the ratio between the multiplet at δ 1.83 – 1.92 (2H, alkyl fluoride) versus at δ 5.91 – 5.92 (2H, alkyl fluoride plus olefins) allowed the determination of the ratio of alkyl fluoride : olefins and the yield**.**

Run 1: 171 mg, with 1.00 : 0.27 ratio of **6^{F}** : olefins (molar ratio). 82% yield.

Run 2: 168 mg, with 1.00 : 0.23 ratio of **6^{F}** : olefins (molar ratio). 82% yield.

Run 3: 170 mg, with 1.00 : 0.25 ratio of **6^{F}** : olefins (molar ratio). 82% yield.

Run 4: 169 mg, with 1.00 : 0.27 ratio of **6^{F}** : olefins (molar ratio). 81% yield. The eluent for this run was 1% Et_2O in pentane.

The spectral data were collected for pure compound obtained by preparative TLC.

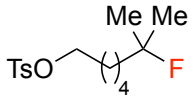
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 6.64 (ddt, *J* = 7.8, 1.6, 0.7 Hz, 1H), 5.92 (s, 2H), 2.69 – 2.61 (m, 2H), 1.97 – 1.80 (m, 2H), 1.40 (d, *J* = 21.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.6, 135.9, 120.9, 108.8, 108.2, 100.8, 95.3 (d, *J* = 165.7 Hz), 43.6 (d, *J* = 22.8 Hz), 30.0 (d, *J* = 5.4 Hz), 26.7 (d, *J* = 24.7 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –138.9 (s).

FT-IR (film): 2980, 1503, 1489, 1441, 1372, 1241, 1187, 1096, 1038, 927, 885, 810, 782, 753, 632, 606, 474, 426 cm^{-1}.

HRMS (FI$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{12}H_{15}O_2F$: 210.1056, found: 210.1049.



6-Fluoro-6-methylheptyl 4-methylbenzenesulfonate (7^{F}). The title compound was synthesized from 6-chloro-6-methylheptyl 4-methylbenzenesulfonate **7** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (9% → 12% Et_2O in pentane). Colorless oil.

Run 1: 189 mg, 78% yield. Run 2: 183 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 1.70 – 1.58 (m, 2H), 1.59 – 1.46 (m, 2H), 1.33 – 1.29 (m, 4H), 1.29 (d, *J* = 21.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 133.2, 129.8, 127.9, 95.5 (d, *J* = 164.7 Hz), 70.5, 41.1 (d, *J* = 22.8 Hz), 28.7, 26.6 (d, *J* = 24.7 Hz), 25.7, 23.3 (d, *J* = 5.2 Hz), 21.6.

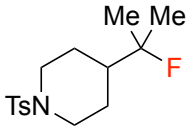
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –137.9 (s).

FT-IR (film): 2941, 1598, 1465, 1356, 1114, 1097, 953, 813, 757, 662, 575, 553 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{23}O_3FSNa$: 325.1245, found: 325.1234.

The reaction was carried out according to **GP-2** with **26**.

Run 1: 157 mg, 65% yield. Run 2: 154 mg, 64% yield.



4-(2-Fluoropropan-2-yl)-1-tosylpiperidine (8^F). The title compound was synthesized from 4-(2-chloropropan-2-yl)-1-tosylpiperidine **8** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (8% → 15% EtOAc in hexanes). White solid.

Run 1: 142 mg, 59% yield. Run 2: 137 mg, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.91 – 3.82 (m, 2H), 2.43 (s, 3H), 2.25 – 2.16 (m, 2H), 1.81 – 1.71 (m, 2H), 1.50 – 1.38 (m, 3H), 1.26 (d, *J* = 22.0 Hz, 6H).

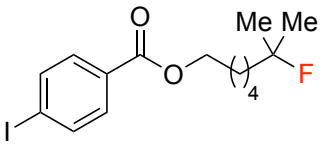
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.0, 129.6, 127.7, 96.6 (d, *J* = 167.0 Hz), 46.5, 45.2 (d, *J* = 22.8 Hz), 26.1 (d, *J* = 6.2 Hz), 24.2 (d, *J* = 25.0 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ –140.2 – –140.8 (m).

FT-IR (film): 2959, 1598, 1469, 1381, 1335, 1308, 1254, 1094, 1058, 1040, 926, 886, 833, 813, 772, 730, 650, 595, 547, 504, 482, 461, 427 cm^{-1}.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{15}H_{22}NO_2FS$: 300.1429, found: 300.1424.

m.p.: 113.5 °C.



6-Fluoro-6-methylheptyl 4-iodobenzoate (9^F). The title compound was synthesized from 6-chloro-6-methylheptyl 4-iodobenzoate **9** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (2% → 5% Et_2O in pentane). Colorless oil.

Run 1: 249 mg, 82% yield. Run 2: 246 mg, 81% yield.

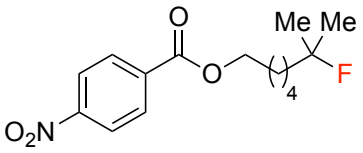
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.76 – 7.71 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 1.78 (pent, *J* = 7.0 Hz, 2H), 1.69 – 1.56 (m, 2H), 1.48 – 1.42 (m, 4H), 1.34 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 137.7, 131.0, 129.9, 100.6, 95.6 (d, *J* = 164.6 Hz), 65.2, 41.3 (d, *J* = 22.8 Hz), 28.6, 26.7 (d, *J* = 24.8 Hz), 26.4, 23.6 (d, *J* = 5.1 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –137.7 (s).

FT-IR (film): 2939, 1717, 1586, 1466, 1392, 1372, 1265, 1176, 1108, 1007, 845, 752, 682, 462 cm^{-1}.

HRMS (FI^{+}-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{15}H_{20}O_2FI$: 378.0492, found: 378.0488.



6-Fluoro-6-methylheptyl 4-nitrobenzoate (10^{F}). The title compound was synthesized from 6-chloro-6-methylheptyl 4-nitrobenzoate **10** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (4% → 8% Et_2O in pentane). Colorless oil.

Run 1: 186 mg, 78% yield. Run 2: 186 mg, 78% yield.

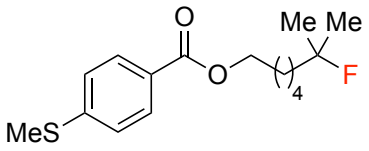
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.26 (m, 2H), 8.23 – 8.17 (m, 2H), 4.38 (t, *J* = 6.7 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.69 – 1.57 (m, 2H), 1.51 – 1.44 (m, 4H), 1.34 (d, *J* = 21.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 150.5, 135.8, 130.7, 123.5, 95.6 (d, *J* = 164.7 Hz), 66.0, 41.2 (d, *J* = 22.8 Hz), 28.6, 26.7 (d, *J* = 24.9 Hz), 26.3, 23.6 (d, *J* = 5.0 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –138.0 (s).

FT-IR (film): 2941, 1722, 1608, 1527, 1467, 1348, 1269, 1102, 958, 873, 785, 758, 716, 502 cm^{-1}.

HRMS (FD^{+}-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{15}H_{20}NO_4F$: 297.1376, found: 297.1371.



6-Fluoro-6-methylheptyl 4-(methylthio)benzoate (11^{F}). The title compound was synthesized from 6-chloro-6-methylheptyl 4-(methylthio)benzoate **11** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (4% → 8% Et_2O in pentane). Colorless oil.

Run 1: 186 mg, 78% yield. Run 2: 182 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.28 – 7.25 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.54 (s, 3H), 1.84 – 1.76 (m, 2H), 1.72 – 1.58 (m, 2H), 1.52 – 1.45 (m, 4H), 1.36 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 145.3, 129.9, 126.6, 124.9, 95.6 (d, *J* = 164.6 Hz), 64.9, 41.3 (d, *J* = 22.9 Hz), 28.7, 26.8 (d, *J* = 25.0 Hz), 26.4, 23.7 (d, *J* = 5.2 Hz), 14.9.

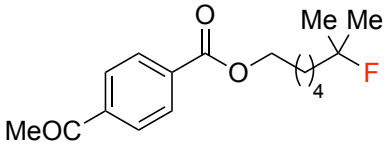
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –137.6 (s).

FT-IR (film): 2939, 1711, 1593, 1437, 1372, 1266, 1180, 1107, 1014, 966, 842, 757, 690, 480 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{16}H_{23}O_2FSNa$: 321.1295, found: 321.1299.

The reaction was carried out according to **GP-2** with **27**.

Run 1: 139 mg, 58% yield. Run 2: 149 mg, 62% yield.



6-Fluoro-6-methylheptyl 4-acetylbenzoate (12^{F}). The title compound was synthesized from 6-chloro-6-methylheptyl 4-acetylbenzoate **12** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (5% → 10% EtOAc in pentane). Colorless oil.

Run 1: 187 mg, 80% yield. Run 2: 195 mg, 83% yield.

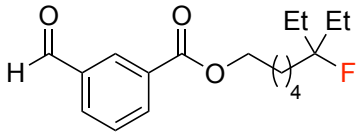
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 8.03 – 7.99 (m, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 2.64 (s, 3H), 1.84 – 1.77 (m, 2H), 1.71 – 1.57 (m, 2H), 1.49 – 1.45 (m, 4H), 1.34 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 165.8, 140.2, 134.2, 129.8, 128.2, 95.6 (d, *J* = 164.6 Hz), 65.5, 41.3 (d, *J* = 22.8 Hz), 28.6, 26.8, 26.7 (d, *J* = 24.8 Hz), 26.4, 23.6 (d, *J* = 5.0 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –137.8 (s).

FT-IR (film): 2940, 1719, 1688, 1407, 1373, 1259, 1178, 1108, 1016, 958, 860, 768, 696, 611, 589, 499 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M]$^{+\bullet}$ calcd for $C_{17}H_{23}O_3F$: 294.1631, found: 294.1629.



6-Ethyl-6-fluorooctyl 3-formylbenzoate (13^F). The title compound was synthesized from 6-ethyl-6-chlorooctyl 3-formylbenzoate **13** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (7% → 12% Et_2O in pentane). Colorless oil.

Run 1: 188 mg, 76% yield. Run 2: 191 mg, 77% yield.

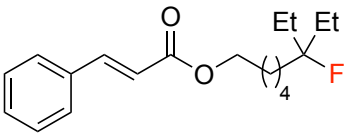
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.52 (td, *J* = 1.7, 0.6 Hz, 1H), 8.30 (dt, *J* = 7.7, 1.5 Hz, 1H), 8.08 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.69 – 1.53 (m, 6H), 1.52 – 1.34 (m, 4H), 0.88 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 165.5, 136.6, 135.2, 133.0, 131.6, 131.2, 129.3, 99.5 (d, *J* = 169.3 Hz), 65.6, 36.0 (d, *J* = 23.1 Hz), 29.1, 28.8 (d, *J* = 17.7 Hz), 26.5, 23.0 (d, *J* = 5.5 Hz), 7.7 (d, *J* = 7.0 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –154.2 (s).

FT-IR (film): 2943, 1720, 1702, 1603, 1461, 1382, 1283, 1185, 1163, 1103, 1075, 961, 911, 818, 748, 701, 678, 647, 475 cm^{-1}.

HRMS (FD$^+$-MS) *m*/*z* [M-H]$^{+\bullet}$ calcd for $C_{18}H_{25}O_3F$: 307.1710, found: 307.1712.



6-Ethyl-6-fluorooctyl cinnamate (14^{F}). The title compound was synthesized from 6-ethyl-6-chlorooctyl cinnamate **14** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (3% → 5% Et_2O in pentane). Pale yellow oil.

Run 1: 190 mg, 78% yield. Run 2: 192 mg, 78% yield.

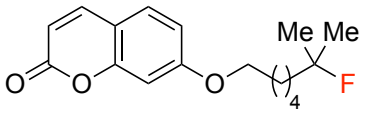
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.41 – 7.37 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.73 (m, 2H), 1.68 – 1.54 (m, 6H), 1.50 – 1.33 (m, 4H), 0.89 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 144.7, 134.5, 130.3, 128.9, 128.1, 118.2, 99.5 (d, *J* = 169.1 Hz), 64.6, 36.0 (d, *J* = 23.0 Hz), 29.1, 28.8 (d, *J* = 16.0 Hz), 26.5, 23.0 (d, *J* = 5.6 Hz), 7.7 (d, *J* = 7.0 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –154.1 (s).

FT-IR (film): 2942, 1711, 1637, 1450, 1309, 1269, 1201, 1165, 979, 911, 864, 766, 710, 684, 574, 484 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{27}O_2FNa$: 306.1995, found: 306.1992.



7-((6-Fluoro-6-methylheptyl)oxy)-2*H*-chromen-2-one (15^{F}). The title compound was synthesized from 7-((6-chloro-6-methylheptyl)oxy)-2*H*-chromen-2-one **15** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (10% → 20% EtOAc in pentane). White solid.

Run 1: 186 mg, 80% yield. Run 2: 183 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 9.4 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 9.5 Hz, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.71 – 1.57 (m, 2H), 1.54 – 1.43 (m, 4H), 1.35 (d, *J* = 21.4 Hz, 6H).

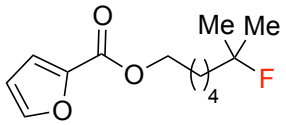
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 161.3, 155.9, 143.5, 128.7, 112.98, 112.95, 112.4, 101.3, 95.6 (d, *J* = 164.6 Hz), 68.5, 41.3 (d, *J* = 22.9 Hz), 28.9, 26.7 (d, *J* = 24.7 Hz), 26.3, 23.7 (d, *J* = 5.1 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –137.8 (s).

FT-IR (film): 2939, 2864, 1710, 1606, 1558, 1506, 1473, 1408, 1395, 1372, 1348, 1278, 1231, 1201, 1158, 1119, 1089, 1042, 1007, 988, 892, 865, 846, 831, 760, 735, 711, 632, 616, 551, 486, 458, 417 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{17}H_{21}O_3FNa$: 315.1267, found: 315.1263.

m.p.: 58.0 °C.



6-Fluoro-6-methylheptyl furan-2-carboxylate (16^{F}). The title compound was synthesized from 6-chloro-6-methylheptyl furan-2-carboxylate **16** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (3% → 4% EtOAc in hexanes). Colorless oil.

Run 1: 158 mg, 82% yield. Run 2: 159 mg, 82% yield.

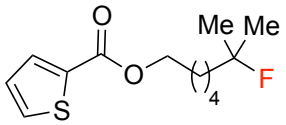
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, *J* = 1.5, 0.6 Hz, 1H), 7.17 (dt, *J* = 3.5, 0.6 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.30 (t, *J* = 6.7 Hz, 2H), 1.82 – 1.70 (m, 2H), 1.67 – 1.54 (m, 2H), 1.44 (dq, *J* = 7.5, 3.8 Hz, 4H), 1.33 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 146.2, 144.9, 117.8, 111.8, 95.6 (d, *J* = 164.6 Hz), 64.9, 41.3 (d, *J* = 22.8 Hz), 28.7, 26.6 (d, *J* = 24.8 Hz), 26.3, 23.6 (d, *J* = 5.2 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –137.6 (s).

FT-IR (film): 2941, 1716, 1581, 1474, 1373, 1293, 1230, 1178, 1116, 1076, 1012, 961, 884, 760, 616, 597 cm^{-1}.

HRMS (FI^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{13}H_{19}O_3F$: 242.1318, found: 242.1313.



6-Fluoro-6-methylheptyl thiophene-2-carboxylate (17^F). The title compound was synthesized from 6-chloro-6-methylheptyl thiophene-2-carboxylate **17** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (4% → 6% Et_2O in pentane). Colorless oil.

Run 1: 173 mg, 84% yield. Run 2: 173 mg, 84% yield.

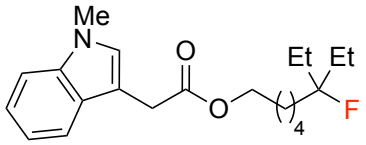
^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.67 – 1.58 (m, 2H), 1.47 – 1.40 (m, 4H), 1.34 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 134.0, 133.3, 132.2, 127.7, 95.7 (d, *J* = 164.6 Hz), 65.1, 41.3 (d, *J* = 22.8 Hz), 28.7, 26.7 (d, *J* = 24.9 Hz), 26.4, 23.7 (d, *J* = 5.2 Hz).

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –137.6.

FT-IR (film): 2940, 1706, 1526, 1419, 1373, 1358, 1257, 1224, 1093, 1074, 860, 750, 718 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{13}H_{19}O_2FSNa$: 281.0982, found: 281.0987.



6-Ethyl-6-fluorooctyl 2-(1-methyl-1H-indol-3-yl)acetate (18^F). The title compound was synthesized from 6-ethyl-6-chlorooctyl 2-(1-methyl-1H-indol-3-yl)acetate **18** according to **GP-2**.

The compound was purified by flash column chromatography on silica gel (5% → 12% EtOAc in pentane). Yellow oil.

Run 1: 199 mg, 72% yield. Run 2: 198 mg, 71% yield.

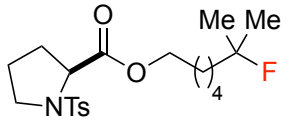
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.16 – 7.11 (m, 1H), 7.05 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 5H), 1.72 – 1.48 (m, 8H), 1.33 (pent, *J* = 3.6 Hz, 4H), 0.89 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 136.9, 127.7 (2), 121.7, 119.1, 119.0, 109.3, 107.0, 99.5 (d, *J* = 169.1 Hz), 64.8, 35.9 (d, *J* = 23.1 Hz), 32.7, 31.3, 29.0 (d, *J* = 23.8 Hz), 28.6, 26.4, 22.9 (d, *J* = 5.6 Hz), 7.7 (d, *J* = 7.0 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –154.1 (s).

FT-IR (film): 2941, 1731, 1462, 1375, 1330, 1246, 1139, 1013, 970, 911, 737, 427 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{30}NO_2F$: 348.2334, found: 348.2332.



6-Fluoro-6-methylheptyl tosyl-L-prolinate (19^{F}). The title compound was synthesized from 6-chloro-6-methylheptyl tosyl-L-prolinate **19** (0.60-mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (15% → 25% EtOAc in pentane). Colorless oil.

Run 1: 180 mg, 75% yield. Run 2: 178 mg, 74% yield.

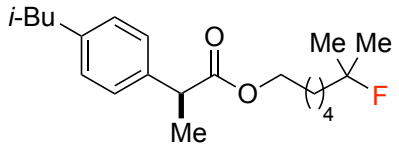
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.35 – 4.28 (m, 1H), 4.20 – 4.06 (m, 2H), 3.58 – 3.44 (m, 1H), 3.40 – 3.28 (m, 1H), 2.45 (s, 3H), 2.17 – 1.91 (m, 3H), 1.83 – 1.73 (m, 1H), 1.72 – 1.57 (m, 4H), 1.54 – 1.30 (m, 4H), 1.35 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 143.5, 135.4, 129.6, 127.5, 95.7 (d, *J* = 164.4 Hz), 65.3, 60.5, 48.4, 41.3 (d, *J* = 22.9 Hz), 31.0, 28.5, 26.7 (d, *J* = 24.9 Hz), 26.1, 24.7, 23.6 (d, *J* = 5.1 Hz), 21.6.

^{19}F NMR (376 MHz, $CDCl_3$): –137.4 – –137.9 (m).

FT-IR (film): 2977, 2863, 1750, 1460, 1352, 1159, 1066, 907, 816, 709, 633, 592, 548 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{30}NO_4FS$: 400.1953, found: 400.1953.



6-Fluoro-6-methylheptyl (*S*)-2-(4-isobutylphenyl)propanoate (20^F). The title compound was synthesized from 6-chloro-6-methylheptyl (*S*)-2-(4-isobutylphenyl)propanoate **20** according to **GP-2**. The compound was purified by flash column chromatography on silica gel (3% → 6% Et_2O in pentane). Colorless oil.

Run 1: 212 mg, 79% yield. Run 2: 210 mg, 78%.

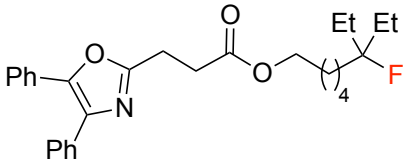
^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.06 (td, *J* = 6.6, 1.1 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.65 – 1.50 (m, 4H), 1.48 (d, *J* = 7.1 Hz, 3H), 1.41 – 1.20 (m, 4H), 1.32 (d, *J* = 21.4 Hz, 6H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 140.5, 137.9, 129.3, 127.2, 95.6 (d, *J* = 164.6 Hz), 64.6, 45.2, 45.0, 41.3 (d, *J* = 22.9 Hz), 30.2, 28.5, 26.6 (d, *J* = 24.7 Hz), 26.1, 23.5 (d, *J* = 5.3 Hz), 22.4, 18.5.

$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –137.5 (s).

FT-IR (film): 2950, 1732, 1512, 1464, 1373, 1319, 1201, 1163, 1070, 1022, 848, 759, 550 cm^{-1}.

HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{21}H_{33}O_2F$: 336.2465, found: 336.2465.



6-Ethyl-6-fluorooctyl 3-(4,5-diphenyloxazol-2-yl)propanoate (21^F). The title compound was synthesized from 6-ethyl-6-chlorooctyl 3-(4,5-diphenyloxazol-2-yl)propanoate **21** (0.60-

mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (9% → 15% EtOAc in pentane). Colorless oil.

Run 1: 172 mg, 63% yield. Run 2: 171 mg, 63% yield.

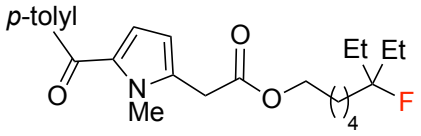
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.40 – 7.28 (m, 6H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.19 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.91 (dd, *J* = 8.2, 6.8 Hz, 2H), 1.70 – 1.48 (m, 8H), 1.41 – 1.29 (m, 4H), 0.87 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 161.8, 145.4, 135.1, 132.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 126.5, 99.5 (d, *J* = 169.1 Hz), 64.8, 35.9 (d, *J* = 23.1 Hz), 31.2, 29.0 (d, *J* = 23.8 Hz), 28.6, 26.4, 23.6, 22.9 (d, *J* = 5.6 Hz), 7.7 (d, *J* = 7.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): –152.5 – –155.8 (m).

FT-IR (film): 2942, 1734, 1571, 1444, 1167, 1058, 1026, 962, 913, 763, 693, 674, 584, 523.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{28}H_{34}NO_3F$: 432.2596, found: 432.2592.



6-Ethyl-6-fluorooctyl 2-(1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl)acetate (22^{F}). The title compound was synthesized from 6-ethyl-6-chlorooctyl 2-(1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl)acetate **22** (0.60-mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (9% → 15% EtOAc in pentane). Colorless oil.

Run 1: 173 mg, 69% yield. Run 2: 172 mg, 69% yield.

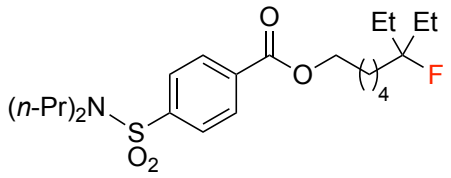
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.25 – 7.22 (m, 2H), 6.67 (d, *J* = 4.0 Hz, 1H), 6.11 (d, *J* = 4.0 Hz, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 3.71 (s, 2H), 2.42 (s, 3H), 1.71 – 1.49 (m, 8H), 1.38 – 1.30 (m, 4H), 0.88 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9, 169.5, 141.9, 137.3, 134.6, 131.4, 129.5, 128.7, 122.3, 109.4, 99.5 (d, *J* = 169.1 Hz), 65.4, 35.9 (d, *J* = 23.1 Hz), 33.2, 33.0, 29.0 (d, *J* = 23.8 Hz), 28.5, 26.3, 22.9 (d, *J* = 5.5 Hz), 21.6, 7.7 (d, *J* = 7.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): –154.0 – –154.4 (m).

FT-IR (film): 2942, 1735, 1624, 1480, 1455, 1373, 1261, 1172, 1041, 975, 912, 882, 833, 790, 747, 705, 620, 480 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{34}NO_3F$: 416.2596, found: 416.2595.



6-Ethyl-6-fluorooctyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (23^F). The title compound was synthesized from 6-ethyl-6-chlorooctyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate **23** (0.60-mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (8% → 12% Et_2O in pentane). Viscous colorless oil.

Run 1: 195 mg, 73% yield. Run 2: 193 mg, 72% yield.

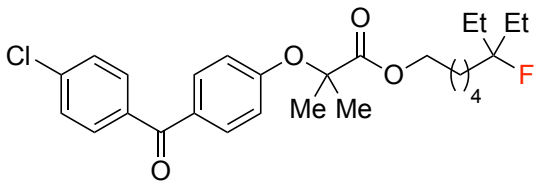
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 3.11 – 3.06 (m, 4H), 1.83 – 1.76 (m, 2H), 1.69 – 1.50 (m, 10H), 1.48 – 1.38 (m, 4H), 0.90 – 0.84 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 144.2, 133.7, 130.2, 127.0, 99.5 (d, *J* = 169.1 Hz), 65.7, 49.9, 36.0 (d, *J* = 23.1 Hz), 29.0 (d, *J* = 23.8 Hz), 28.6, 26.5, 22.9 (d, *J* = 5.5 Hz), 21.9, 11.2, 7.7 (d, *J* = 7.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): –154.0 – –154.4 (m).

FT-IR (film): 2968, 1722, 1461, 1344, 1271, 1107, 1087, 991, 912, 862, 797, 765, 740, 694, 602, 561, 456 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{38}NO_4FS$: 444.2579, found: 444.2569.



6-Ethyl-6-fluorooctyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (24^{F}). The title compound was synthesized from 6-ethyl-6-chlorooctyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate **24** (0.60-mmol scale) according to **GP-2**. The compound was purified by flash column chromatography on silica gel (8% → 12% Et_2O in pentane). Colorless oil.

Run 1: 203 mg, 71% yield. Run 2: 206 mg, 72% yield.

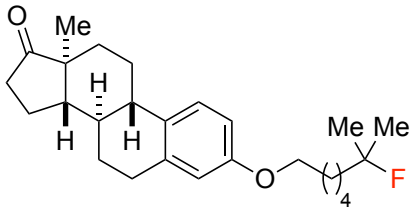
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 13.8, 8.5 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.16 (t, *J* = 6.6 Hz, 2H), 1.67 (s, 6H), 1.64 – 1.42 (m, 8H), 1.33 – 1.18 (m, 4H), 0.85 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 173.8, 159.7, 138.4, 136.4, 132.0, 131.2, 130.3, 128.6, 117.2, 99.4 (d, *J* = 169.3 Hz), 79.4, 65.7, 35.9 (d, *J* = 23.1 Hz), 28.9 (d, *J* = 23.8 Hz), 28.4, 26.2, 25.5, 22.8 (d, *J* = 5.5 Hz), 7.7 (d, *J* = 7.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): –153.6 – –154.9 (m).

FT-IR (film): 2942, 1732, 1654, 1597, 1505, 1462, 1385, 1284, 1249, 1171, 1137, 1089, 1014, 955, 926, 852, 762, 740, 680, 659, 577, 521, 479 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{27}H_{34}O_4ClFNa$: 499.2021, found: 499.2022.



(8*R*,9*S*,13*S*,14*S*)-3-((6-Fluoro-6-methylheptyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (25^{F}). The title compound was synthesized from 8*R*,9*S*,13*S*,14*S*)-3-((6-chloro-6-methylheptyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one **25** (0.60-mmol scale) according to **GP-2**. The

compound was purified by flash column chromatography on silica gel (6% → 15% EtOAc in pentane). White solid.

Run 1: 193 mg, 80% yield. Run 2: 196 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.98 – 2.83 (m, 2H), 2.50 (dd, *J* = 8.6 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.30 – 2.21 (m, 1H), 2.20 – 2.11 (m, 1H), 2.10 – 1.92 (m, 3H), 1.84 – 1.74 (m, 2H), 1.70 – 1.56 (m, 4H), 1.56 – 1.40 (m, 8H), 1.34 (d, *J* = 21.5 Hz, 6H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 157.1, 137.7, 131.9, 126.3, 114.5, 112.1, 95.7 (d, *J* = 164.3 Hz), 67.7, 50.4, 48.0, 44.0, 41.4 (d, *J* = 22.9 Hz), 38.4, 35.9, 31.6, 29.7, 29.3, 26.8, 26.6 (d, *J* = 4.1 Hz), 26.4, 25.9, 23.7 (d, *J* = 5.2 Hz), 21.6, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): –135.7 – –139.5 (m).

FT-IR (film): 2935, 1733, 1607, 1498, 1471, 1373, 1310, 1281, 1233, 1161, 1053, 1027, 1005, 864, 846, 822, 787, 761, 647, 579, 461 cm^{-1}.

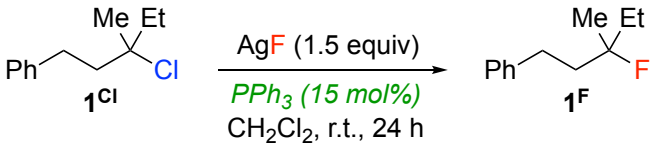
HRMS (FD^+-MS) *m*/*z* $[M]^{+\bullet}$ calcd for $C_{26}H_{37}O_2F$: 400.2778, found: 400.2771.

m.p.: 95.0 °C.

The data are consistent with those reported in the literature.[1]

IV. Effect of Reaction Parameters

General Procedure 3 (GP-3): In a nitrogen-filled glovebox, an oven-dried 4-mL vial that contained a PTFE stir bar was charged with PPh_3 (3.9 mg, 0.015 mmol) and AgF (19.0 mg, 0.15 mmol). Next, CH_2Cl_2 (0.7 mL) was added, and the vial was capped with a PTFE-septum cap. The mixture was stirred at r.t. for 10 min, and then a solution of 3-chloro-3-methylpentyl)benzene (**1**^{Cl}; 19.7 mg, 0.10 mmol), in CH_2Cl_2 (0.3 mL) was added. The vial was removed from the glovebox, the joint was wrapped with electrical tape, and the reaction mixture was allowed to stir at r.t. for 24 h, after which it was a dark gray slurry, which typically indicates the completion of the reaction. A solution of 4-fluorobiphenyl (17.2 mg, 0.10 mmol), an internal standard, in acetone (0.2 mL) was added. The mixture was then filtered through a plug of silica gel. The reaction flask and the plug of silica gel were washed with Et_2O, the combined organic solution was concentrated, and the yield was determined by single-pulse ^{19}F NMR spectroscopy.



"standard conditions"

entry	variation from the "standard conditions"	yield (%)
1	none	79
2	no PPh_3	<3
3	5.0 mol%, instead of 15 mol%, PPh_3	73
4	1.1, instead of 1.5, equiv AgF	73
5	6, instead of 24, h	78
6	1.0 equiv H_2O added	72
7	under air in a closed vial[a]	70
8	KF instead of AgF	<3
9	AgF (0.5 equiv) and KF (1.5 equiv)	<3
10	CsF instead of AgF	<3
11	TBAF trihydrate instead of AgF	<3
12	1.5 equiv CsF and 10 mol% AgF, instead of AgF	<3
13	MeCN instead of CH_2Cl_2	23
14	THF instead of CH_2Cl_2	<3
15	toluene instead of CH_2Cl_2	<3
16	$P(C_6F_5)_3$ instead of PPh_3	<3
17	P(*p*-anisyl)$_3$ instead of PPh_3	68
18	PCy_3 instead of PPh_3	17
19	tol-BINAP instead of PPh_3 (48 h)	67
20	1,10-phenanthroline instead of PPh_3	<3

Table S1. Effect of reaction parameters. Each entry represents the average of two runs. [a]After the addition of the alkyl chloride, the vial was opened to the air for 5 min. The vial was then capped and allowed to stir for 24 h.

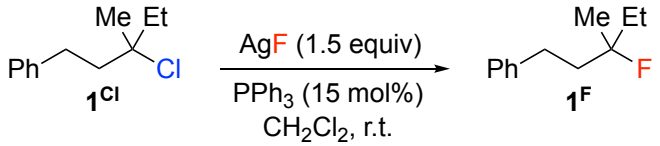
V. Studies of Functional-Group Compatibility

GP-3 was followed, using electrophile **1**^{Cl} and the additives (0.10 mmol, 1.0 equiv) shown in Figure 2A (text). The additive was added immediately before the solution of the electrophile was added; with polar additives, the reaction mixture was passed through a syringe filter rather than a plug of silica gel.

The yield of the fluorination product was determined through analysis via ^{19}F NMR spectroscopy, and the recovery of the additive was determined through analysis via GCMS, both using 4-fluorobiphenyl as the internal standard. Each entry represents an average of two experiments.

VI. Mechanistic Studies

A. ^{31}P NMR Spectroscopy



In a nitrogen-filled glovebox, an oven-dried 4-mL vial that contained a PTFE stir bar was charged in turn with PPh_3 (3.9 mg, 0.015 mmol), AgF (19.0 mg, 0.15 mmol), dry CH_2Cl_2 (1.0 mL), and electrophile **1**^{Cl} (19.0 μL, 19.7 mg, 0.10 mmol). At specified time points, the reaction mixture was filtered by passage through a syringe filter in the glovebox, and the aliquots were analyzed via ^{31}P NMR spectroscopy.

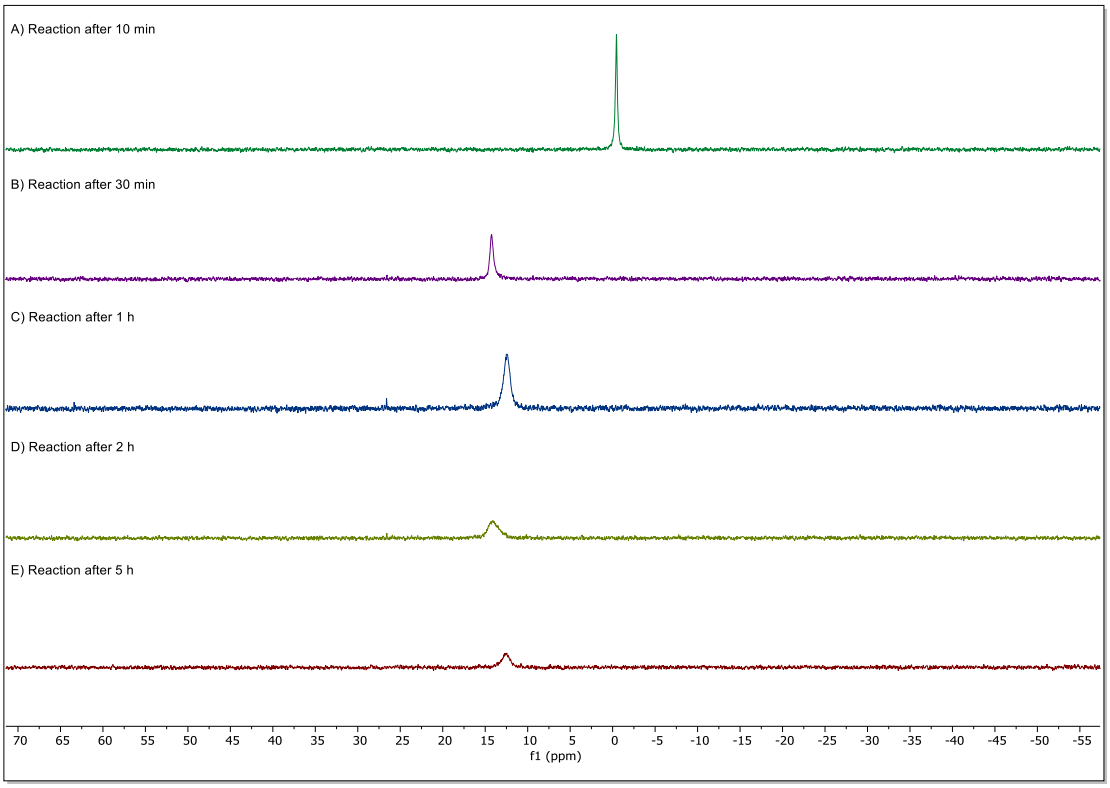


Figure S1. Study via ^{31}P NMR spectroscopy (162 MHz, CH_2Cl_2) of the time course of a fluorination at r.t. ^{31}P chemical shift of free PPh_3: δ –7.9.

A) δ –0.4 (s).

B) δ 14.3 (s, br).

C) δ 12.4 (s, br).

D) δ 14.1 (s, br).

E) δ 12.5 (s, br).

In order to examine whether the broad resonances are due to exchange processes, NMR spectra were obtained at –80 °C.

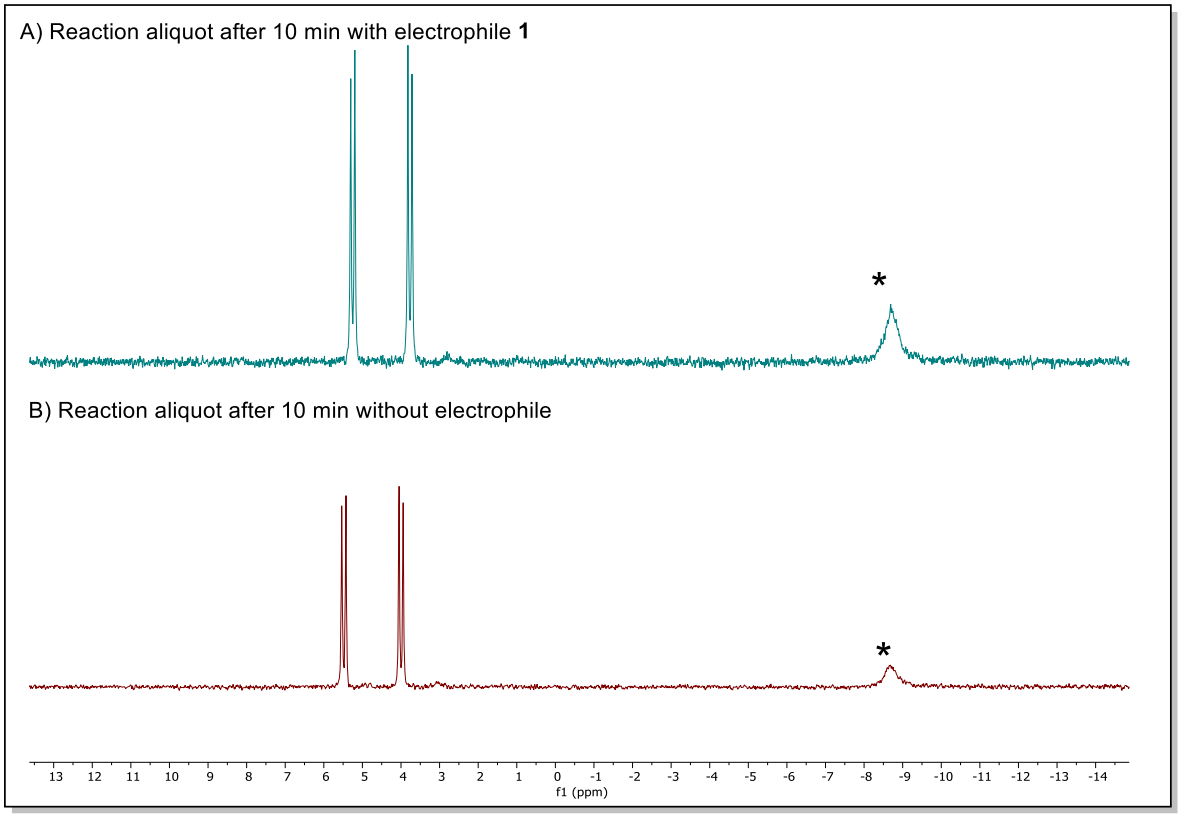


Figure S2. Low-temperature (–80 °C) ^{31}P NMR (162 MHz, CH_2Cl_2) study of reaction aliquots after 10 min. A) Reaction aliquot with tertiary alkyl chloride $\mathbf{1}^{Cl}$. B) Reaction aliquot without tertiary alkyl chloride $\mathbf{1}^{Cl}$. *: free PPh_3.

In order to directly compare these data with literature data,[2] a corresponding study was carried out with P(*p*-tolyl)$_3$.

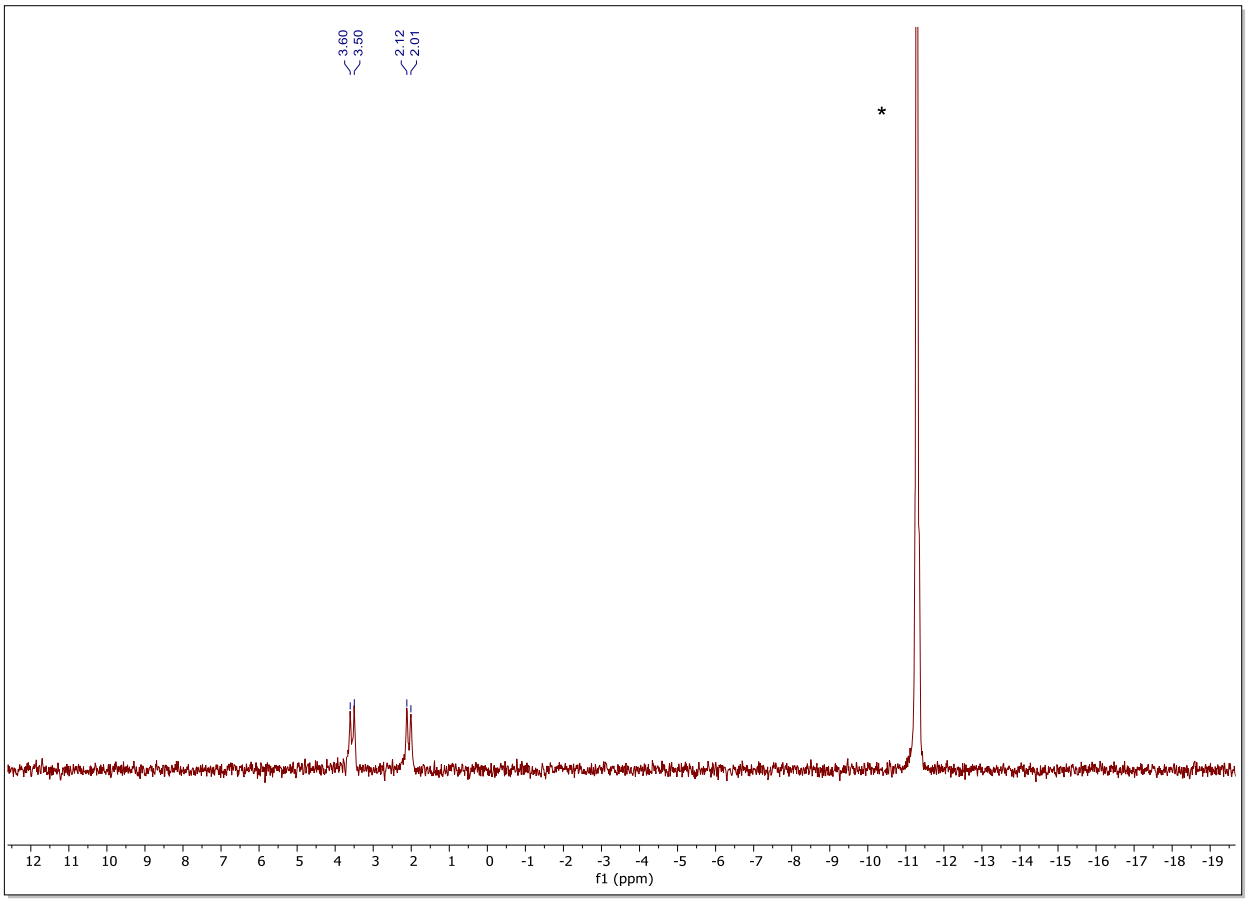


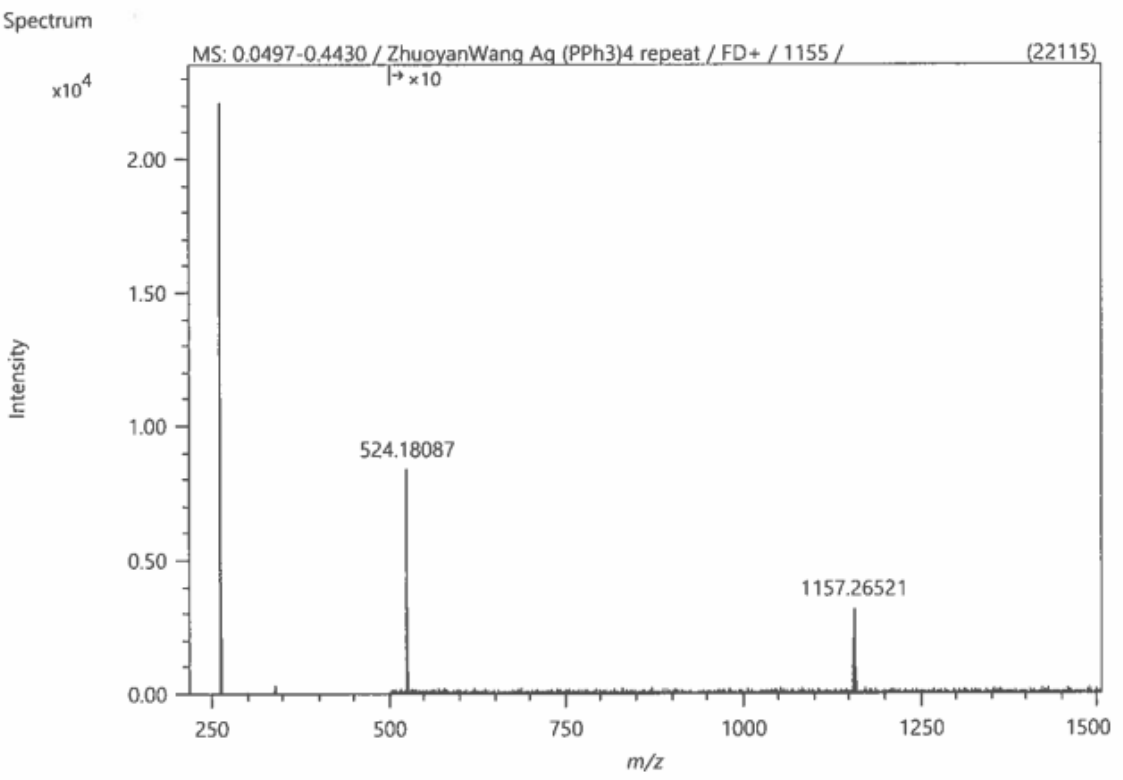
Figure S3. Low-temperature (–80 °C) ^{31}P NMR (162 MHz, CH_2Cl_2) study of a reaction aliquot without tertiary alkyl chloride **1**^{Cl} after 5 min, with P(*p*-tolyl)$_3$ as the ligand. *: free P(*p*-tolyl)$_3$.

δ 3.1 (dd, $^1J(^{107}Ag\text{-}^{31}P)$ = 224 Hz, $^1J(^{109}Ag\text{-}^{31}P)$ = 260 Hz). Both the chemical shift and the J-coupling match a report for [Ag(P(*p*-tolyl)$_3$)$_4$]$^+$.[2]

A) ^{31}P NMR (162 MHz, CH_2Cl_2) δ 4.5 (dd, $^1J(^{107}Ag\text{-}^{31}P)$ = 223 Hz, $^1J(^{109}Ag\text{-}^{31}P)$ = 258 Hz).

B) ^{31}P NMR (162 MHz, CH_2Cl_2) δ 4.7 (dd, $^1J(^{107}Ag\text{-}^{31}P)$ = 223 Hz, $^1J(^{109}Ag\text{-}^{31}P)$ = 258 Hz).

B. Mass Spectrometry



Elemental Composition

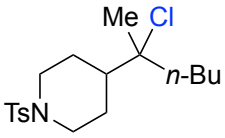
Parameters		Elements Set 3:				
Tolerance:	±3.00 mDa	Symbol	C	H	P	Ag
Electron:	Odd/Even	Min	0	0	0	0
Charge:	0	Max	100	100	5	1
DBE:	-3.5 - 100.0					

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
262.09085	22115.26	C18 H15 P	262.09114	-0.29	-1.11	12.0
524.18087	842.36	C36 H30 P2	524.18227	-1.41	-2.69	23.0
1155.26744	206.76	C72 H60 P4 Ag	1155.26964	-2.20	-1.91	44.5

Figure S4. Mass spectrometric study of a reaction aliquot after 10 min in CH_2Cl_2 with electrophile $\mathbf{1}^{Cl}$ and PPh_3 as the ligand. $[Ag(PPh_3)_4]^+$ (MW=1155.2696) is observed, along with PPh_3 (MW=262.0911).

C. Stereochemistry



4-(2-Chlorohexan-2-yl)-1-tosylpiperidine (A). The title compound was synthesized according to **GP-1** and purified by flash column chromatography on silica gel using 10% EtOAc in hexanes. White solid. Yield: 1.72 g, 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 3.93 – 3.83 (m, 2H), 2.43 (s, 3H), 2.23 – 2.11 (m, 2H), 1.95 (dt, *J* = 12.7, 2.6 Hz, 1H), 1.79 (dt, *J* = 12.1, 2.6 Hz, 1H), 1.74 – 1.65 (m, 2H), 1.64 – 1.46 (m, 3H), 1.43 (s, 3H), 1.40 – 1.21 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.0, 129.6, 127.8, 76.9, 46.6 (d, *J* = 10.7 Hz), 46.2, 41.6, 26.9, 26.6 (d, *J* = 4.4 Hz), 26.4, 22.9, 21.5, 14.0.

FT-IR (film): 2956, 1598, 1467, 1448, 1338, 1253, 1164, 1094, 933, 816, 728, 652 cm^{-1}.

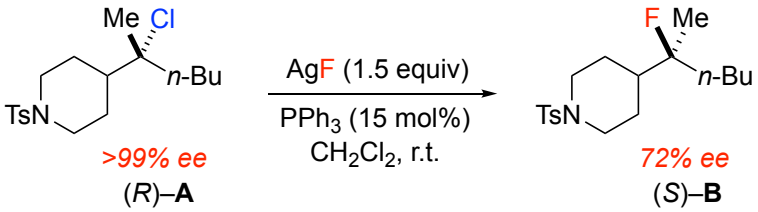
HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{28}NO_2ClS$: 358.1602, found: 358.1611.

m.p.: 93.5 °C.

Enantioenriched **A** was obtained using preparative SFC on a CHIRALPAK AD-H column with 12% EtOH in CO_2 as the eluent.

Fraction 1 (*R*)-**A**: retention time: 7.01 min; >99% ee. $[\alpha]^{24}_D$ = +1.5 (c 1.0, $CHCl_3$).

Fraction 2 (*S*)-**A**: retention time: 7.84 min; –90% ee.



In a glovebox, PPh_3 (3.9 mg, 0.015 mmol), AgF (19.0 mg, 0.15 mmol), enantioenriched electrophile **A** (35.8 mg; 0.10 mmol), and CH_2Cl_2 (1.0 mL) were added in turn to a 4-mL vial

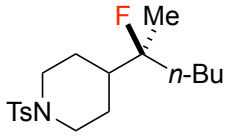
equipped with a PTFE stir bar. The reaction mixture was stirred vigorously for 24 h, and then an internal standard (4-fluorobiphenyl; 17.2 mg, 0.10 mmol; in 0.2 mL of acetone) was added. The mixture was filtered through a pad of silica gel, using Et_2O as the eluent. The filtrate was concentrated, the residue was dissolved in $CDCl_3$, and the yield was determined via ^{19}F NMR spectroscopy. Pure alkyl fluoride **B** was obtained by preparative TLC on silica gel, using 16% EtOAc in hexanes as the eluent.

Crystals suitable for X-ray crystallography were obtained by diffusion of pentane into an a solution of **B** in EtOAc.

The ee was determined via SFC analysis on a CHIRALPAK AD-3 column (10% EtOH in supercritical CO_2, 2.5 mL/min); retention time for (*R*)-**B**: 5.73 min; for (*S*)-**B**: 7.13 min.

From (*R*)-**A** (>99% ee): 43% yield, 72% ee.

[A second experiment was carried out with (*S*)-**A** (90% ee): 51% yield, 64% ee.]



(*S*)-4-(2-Fluorohexan-2-yl)-1-tosylpiperidine (B).

^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.96 – 3.80 (m, 2H), 2.43 (s, 3H), 2.25 – 2.06 (m, 2H), 1.78 (dt, *J* = 12.5, 2.4 Hz, 1H), 1.70 – 1.64 (m, 1H), 1.57 – 1.40 (m, 5H), 1.34 – 1.24 (m, 4H), 1.20 (d, *J* = 22.1 Hz, 3H), 0.92 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.1, 129.6, 127.8, 98.2 (d, *J* = 169.8 Hz), 46.6 (d, *J* = 4.3 Hz), 40.4 (dd, *J* = 647.4, 23.1 Hz), 26.2 (d, *J* = 7.0 Hz), 25.6 (d, *J* = 5.4 Hz), 25.1 (d, *J* = 4.3 Hz), 23.1, 21.5, 21.2 (d, *J* = 25.2 Hz), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –150.0 – –150.6 (m).

FT-IR (film): 2956, 1599, 1465, 1339, 1252, 1164, 1093, 934, 726, 651 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{28}NO_2FS$: 342.1898, found: 342.1907.

$[\alpha]^{24}_D$ = +2.5 (c 1.0, $CHCl_3$).

VII. Determination of Absolute Configuration via X-ray Crystallography

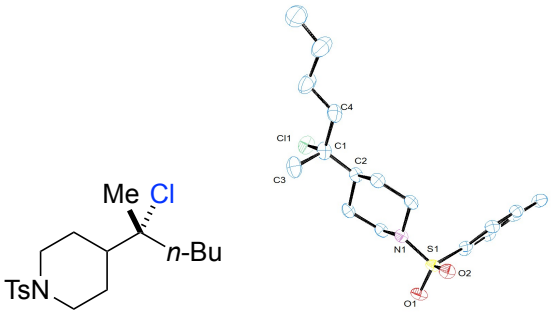


Figure S5. Thermal ellipsoid plot at 50% probability. For clarity, the hydrogen atoms and a second molecule in the asymmetric unit have been omitted.

CCDC 2294879

A colorless needle-like specimen of $C_{18}H_{28}ClNO_2S$, approximate dimensions 0.100 mm x 0.300 mm x 0.500 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 1.54178 Å).

The total exposure time was 8.46 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 55642 reflections to a maximum θ angle of 70.08° (0.82 Å resolution), of which 7073 were independent (average redundancy 7.867, completeness = 99.9%, R_{int} = 8.43%, R_{sig} = 4.51%) and 6492 (91.79%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 10.0070(4) Å, $\underline{b}$ = 6.2510(2) Å, $\underline{c}$ = 29.7769(12) Å, β = 90.585(4)°, volume = 1862.56(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9874 reflections above 20 σ(I) with 5.935° < 2θ < 144.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.671. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3220 and 0.7580.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21 1, with Z = 4 for the formula unit, $C_{18}H_{28}ClNO_2S$. The final anisotropic full-matrix least-squares refinement on F^2 with 421 variables converged at R1 = 4.50% for the observed data and wR2 = 11.84% for all data. The goodness-of-fit was 1.011. The largest peak in the final difference electron density synthesis was 0.830 $e^-/Å^3$, and the largest hole was -0.454 $e^-/Å^3$ with an RMS deviation of 0.063 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.276 g/cm^3 and F(000), 768 e^-.

Sample and crystal data for (*R*)-4-(2-chlorohexan-2-yl)-1-tosylpiperidine

Identification code	V23273	
Chemical formula	$C_{18}H_{28}ClNO_2S$	
Formula weight	357.92 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.100 x 0.300 x 0.500 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.0070(4) Å	α = 90°
	b = 6.2510(2) Å	β = 90.585(4)°
	c = 29.7769(12) Å	γ = 90°
Volume	1862.56(12) $Å^3$	
Z	4	
Density (calculated)	1.276 g/cm^3	
Absorption coefficient	2.927 mm^{-1}	
F(000)	768	

Data collection and structure refinement for (*R*)-4-(2-chlorohexan-2-yl)-1-tosylpiperidine

Theta range for data collection	2.97 to 70.08°	
Index ranges	-12<=h<=12, -7<=k<=7, -36<=l<=36	
Reflections collected	55642	
Independent reflections	7073 [R(int) = 0.0843]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7580 and 0.3220	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7073 / 1 / 421	
Goodness-of-fit on F^2	1.011	
Δ/σ_{max}	0.001	
Final R indices	6492 data; $I>2\sigma(I)$	R1 = 0.0450, wR2 = 0.1120
	all data	R1 = 0.0514, wR2 = 0.1184
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0597P)^2+1.8399P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.043(9)	
Largest diff. peak and hole	0.830 and -0.454 eÅ^{-3}	
R.M.S. deviation from mean	0.063 eÅ^{-3}	

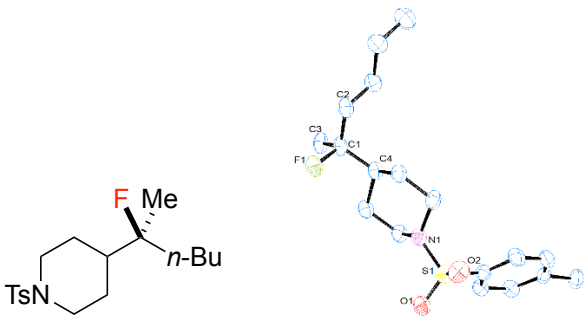


Figure S6. Thermal ellipsoid plot at 50% probability. For clarity, the hydrogen atoms and a second molecule in the asymmetric unit have been omitted.

CCDC 2294881

A colorless needle-like specimen of $C_{18}H_{28}FNO_2S$, approximate dimensions 0.050 mm x 0.050 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 1.54178 Å).

The total exposure time was 11.47 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 31569 reflections to a maximum θ angle of 68.24° (0.83 Å resolution), of which 6445 were independent (average redundancy 4.898, completeness = 99.8%, R_{int} = 10.93%, R_{sig} = 8.22%) and 5303 (82.28%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.9158(11) Å, b = 6.1478(7) Å, c = 29.507(4) Å, β = 93.497(12)°, volume = 1795.4(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 5783 reflections above 20 σ(I) with 6.001° < 2θ < 144.4°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.643. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6210 and 0.9170.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21 1, with Z = 4 for the formula unit, $C_{18}H_{28}FNO_2S$. The final anisotropic full-matrix least-squares refinement on F^2 with 421 variables converged at R1 = 8.04% for the

observed data and wR2 = 21.27% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.428 $e^-/Å^3$, and the largest hole was -0.522 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.263 g/cm^3 and F(000), 736 e^-.

Sample and crystal data for (*S*)-4-(2-fluorohexan-2-yl)-1-tosylpiperidine

Identification code	V23276	
Chemical formula	$C_{18}H_{28}FNO_2S$	
Formula weight	341.47 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.050 x 0.050 x 0.300 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.9158(11) Å	α = 90°
	b = 6.1478(7) Å	β = 93.497(12)°
	c = 29.507(4) Å	γ = 90°
Volume	1795.4(4) $Å^3$	
Z	4	
Density (calculated)	1.263 g/cm^3	
Absorption coefficient	1.757 mm^{-1}	
F(000)	736	

Data collection and structure refinement for (*S*)-4-(2-fluorohexan-2-yl)-1-tosylpiperidine

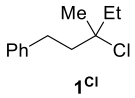
Theta range for data collection	3.00 to 68.24°
Index ranges	-11<=h<=11, -7<=k<=7, -35<=l<=35
Reflections collected	31569
Independent reflections	6445 [R(int) = 0.1093]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9170 and 0.6210
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6445 / 1 / 421
Goodness-of-fit on F^2	1.039
Final R indices	5303 data; $I>2\sigma(I)$ R1 = 0.0804, wR2 = 0.1869
	all data R1 = 0.1165, wR2 = 0.2127
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0866P)^2+4.9502P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.05(4)
Largest diff. peak and hole	0.428 and -0.522 eÅ^{-3}
R.M.S. deviation from mean	0.073 eÅ^{-3}

VIII. References

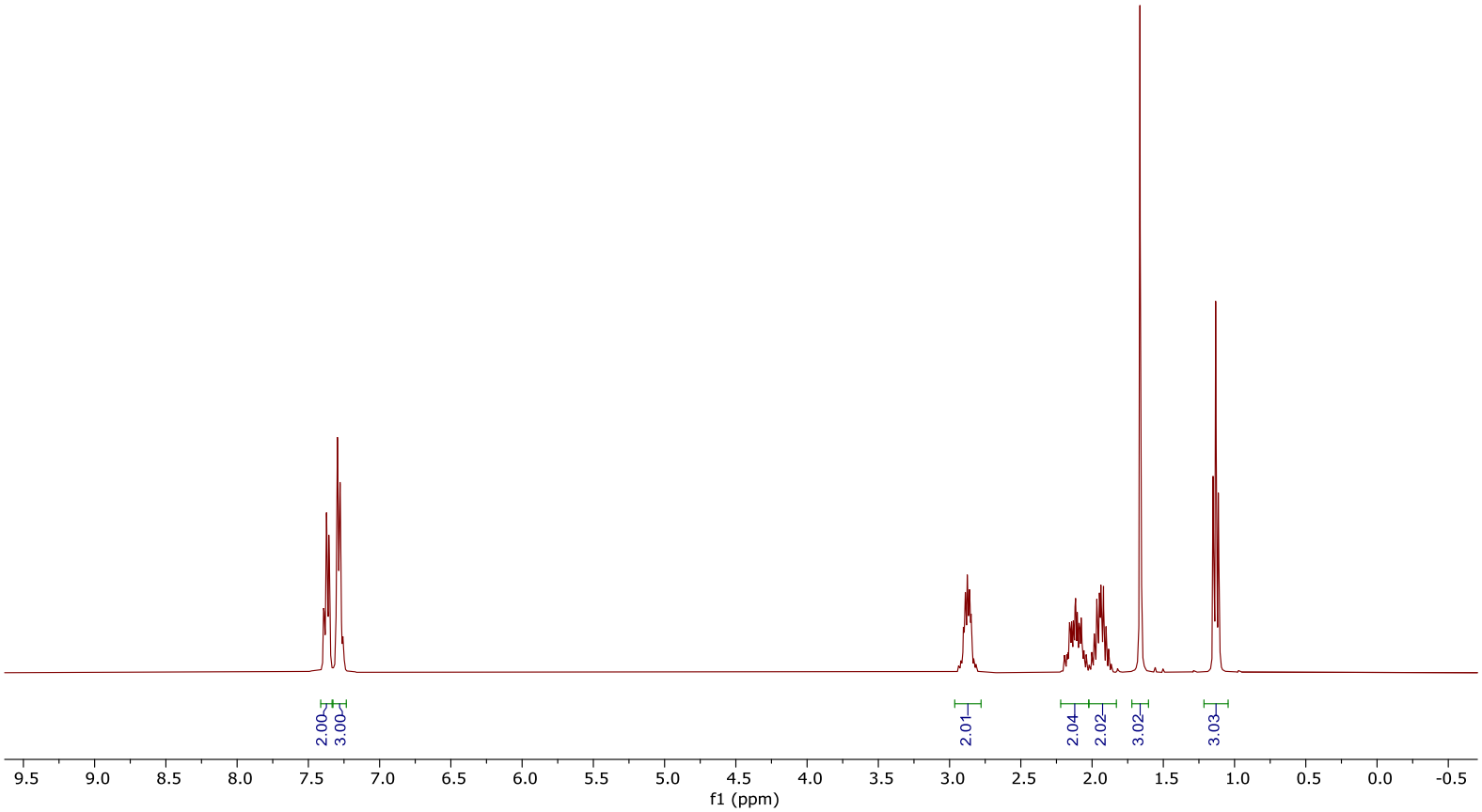
(1) Zhang, W.; Gu, Y.-C.; Lin, J.-H.; Xiao, J.-C. Dehydroxylative Fluorination of Tertiary Alcohols. *Org. Lett.* **2020**, 22, 6642–6646.

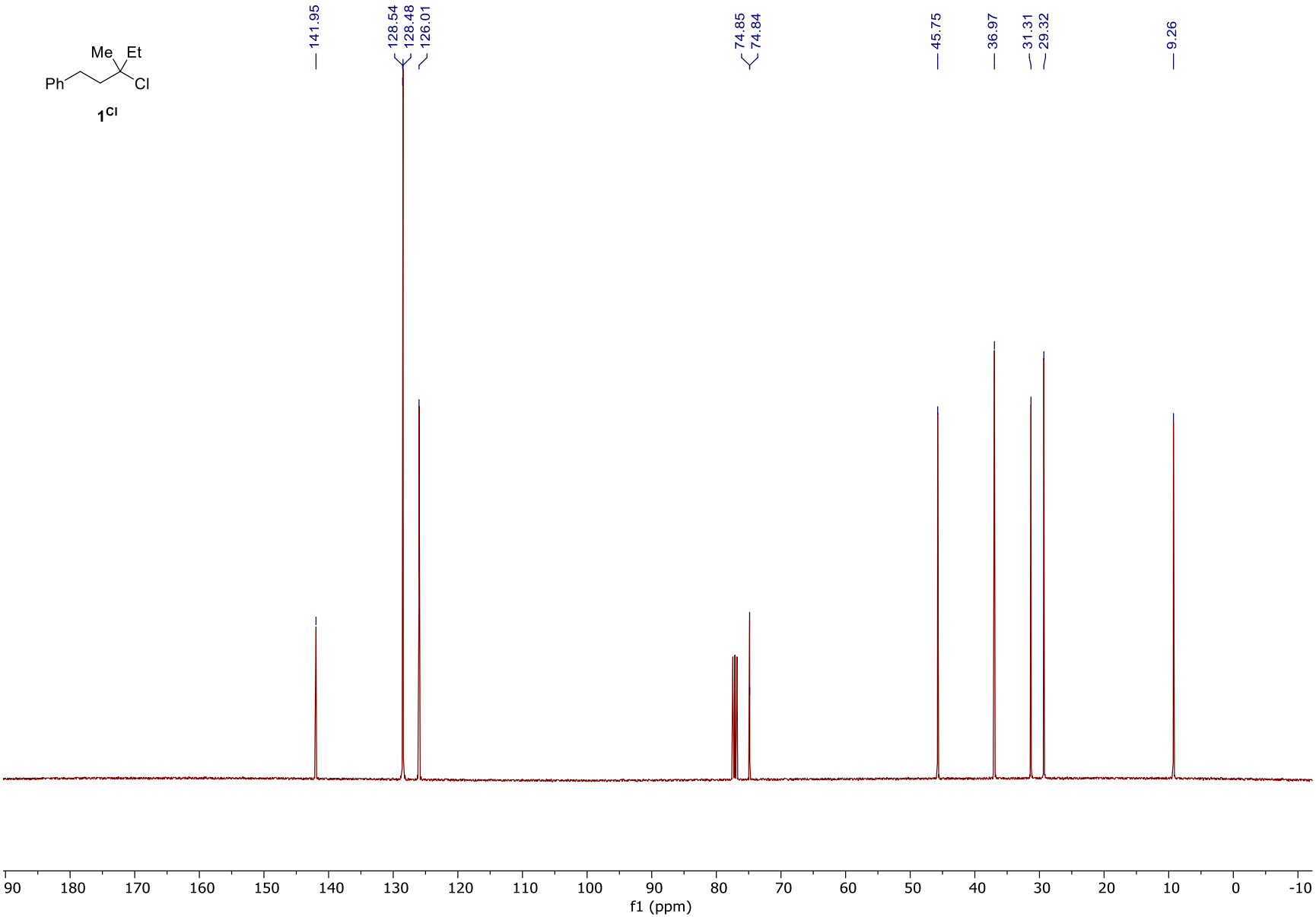
(2) Muetterties, E. L.; Alegranti, C. W. Solution Structure and Kinetic Study of Metal–Phosphine and –Phosphite Complexes. I. The Silver (I) System. *J. Am. Chem. Soc.* **1972**, *94*, 6386–6391.

IX. ^{1}H, ^{13}C and ^{19}F NMR Spectra; ee Analyses



1^{Cl}

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Ph
Cl
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9.26
90
180
170
160
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140
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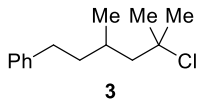
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me Me Me
Ph
Cl

3

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1.00
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
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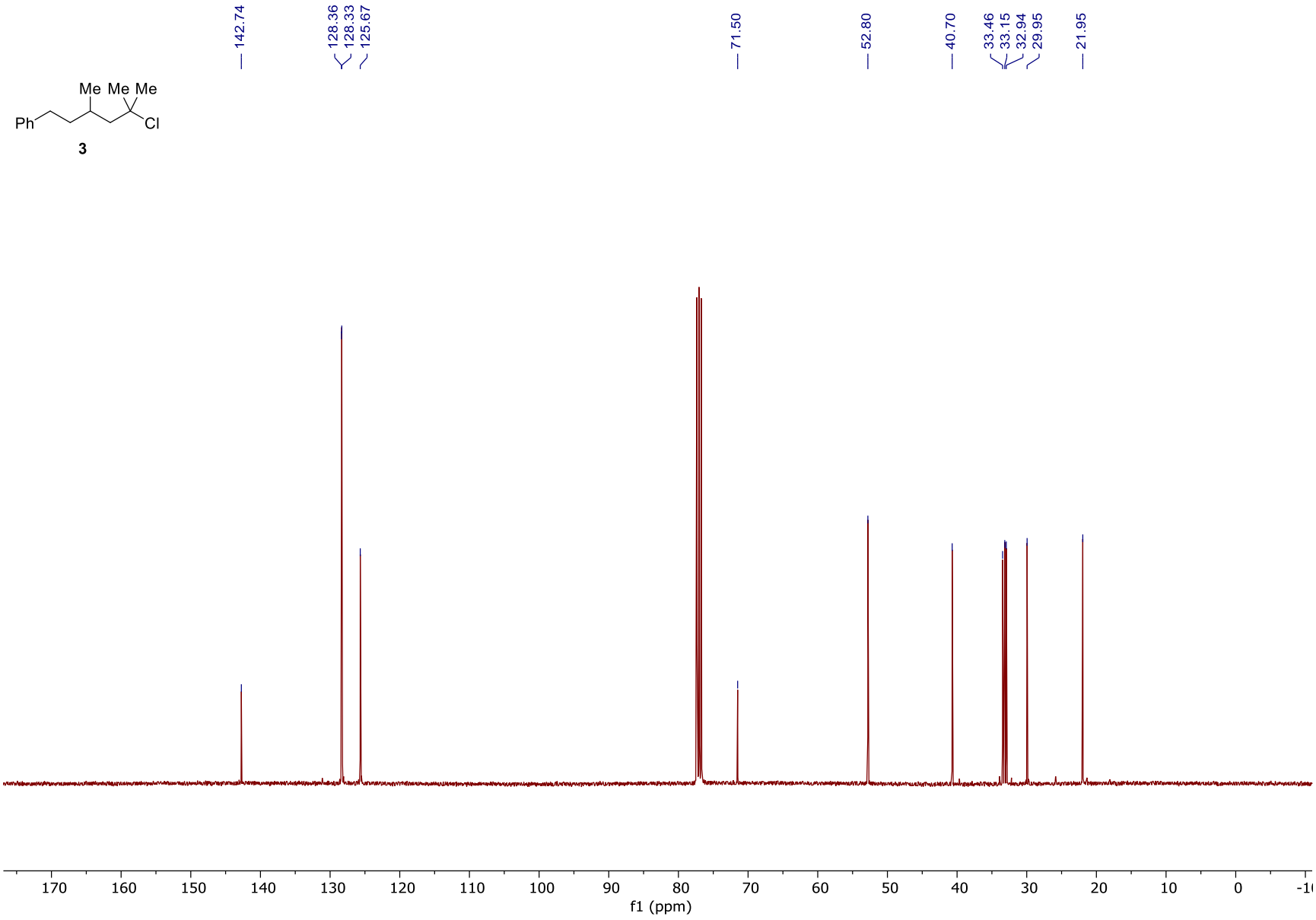
0.5
0.0
-0.
f1 (ppm)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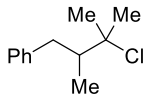
52.80
40.70
33.46
33.15
32.94
29.95
21.95
Me Me Me
Ph
Cl
3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
Ph
Cl
Me

4

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0.20
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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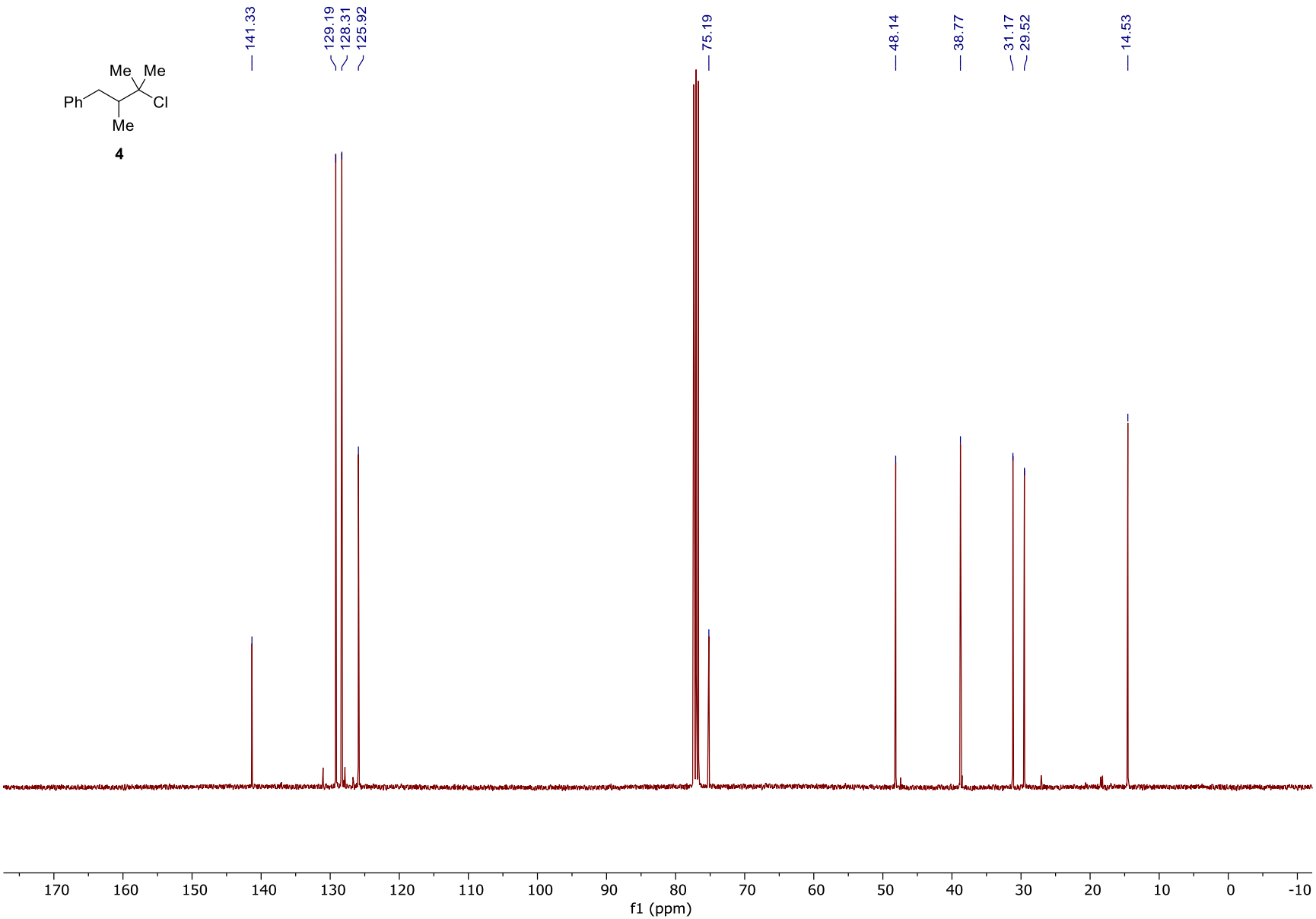
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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75.19
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38.77
31.17
29.52
14.53
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Me
Ph
Cl
Me
4
170
160
150
140
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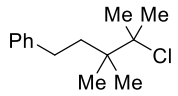
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me Me
Ph
Cl
Me Me

5

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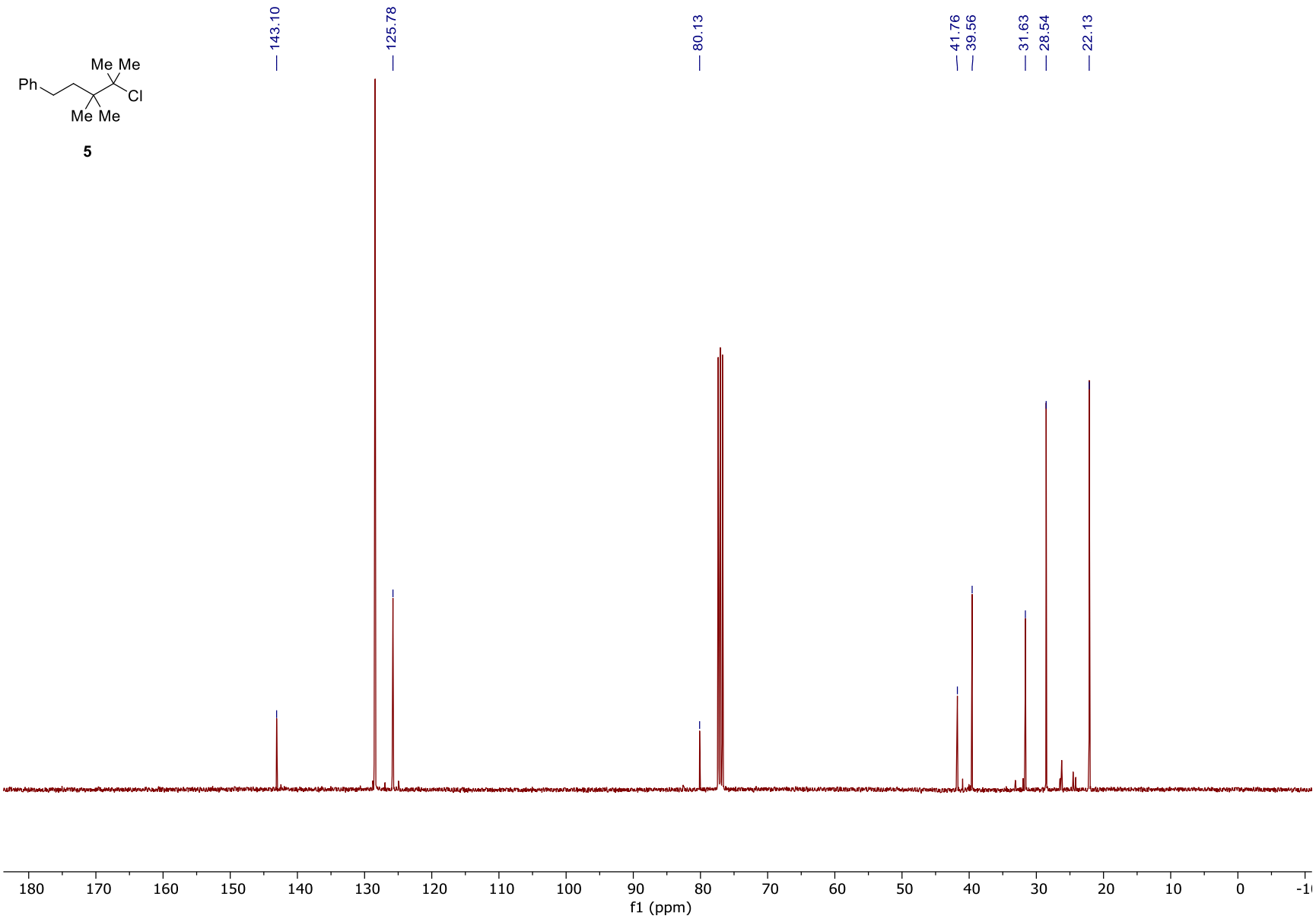
2.01
6.30
6.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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22.13
Ph
Me Me
Cl
Me Me
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180
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110
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90
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70
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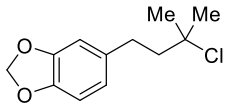
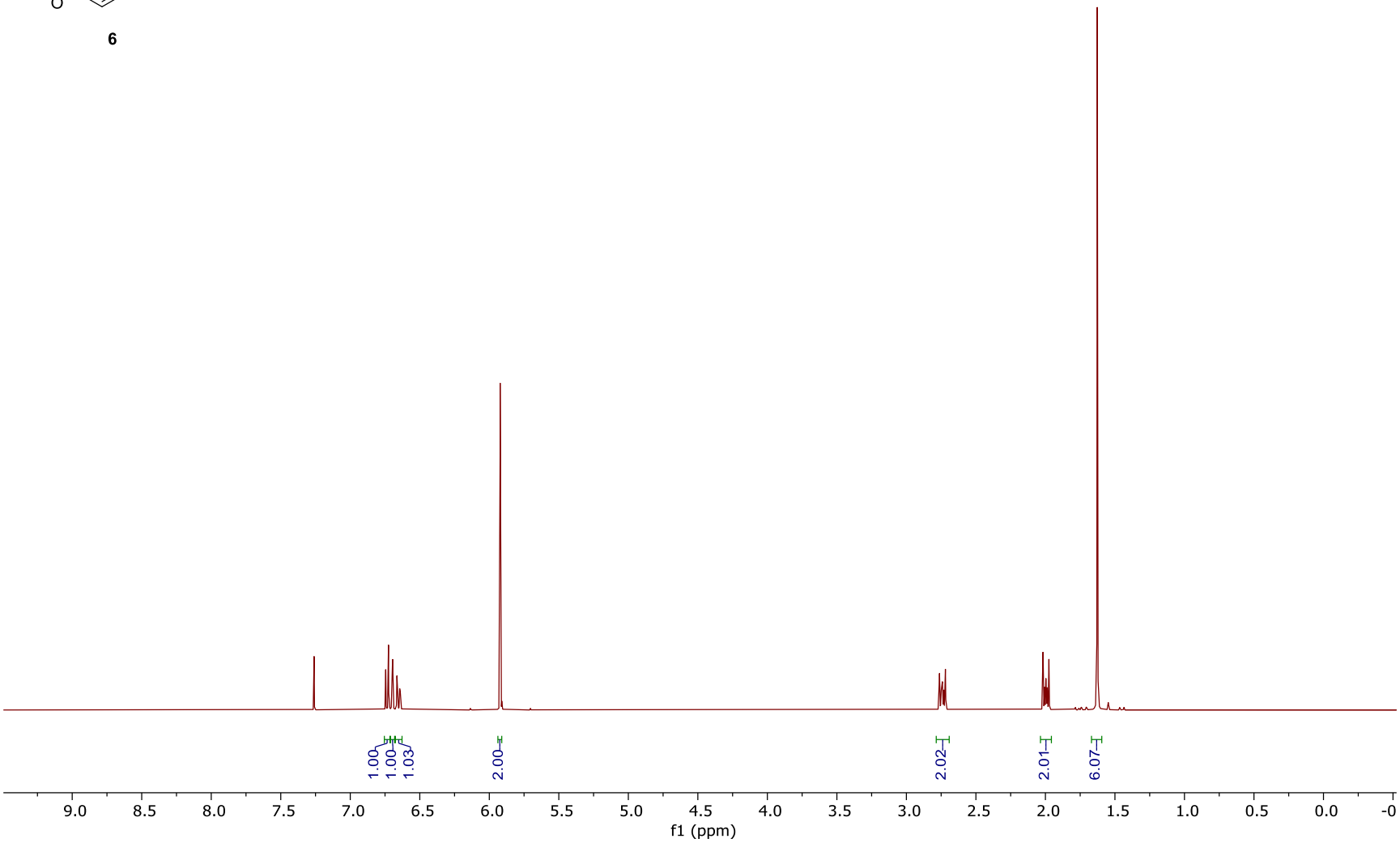
50
40
30
20
10
0
f1 (ppm)


Me
Me
O
O
Cl

6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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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1.0
0.5
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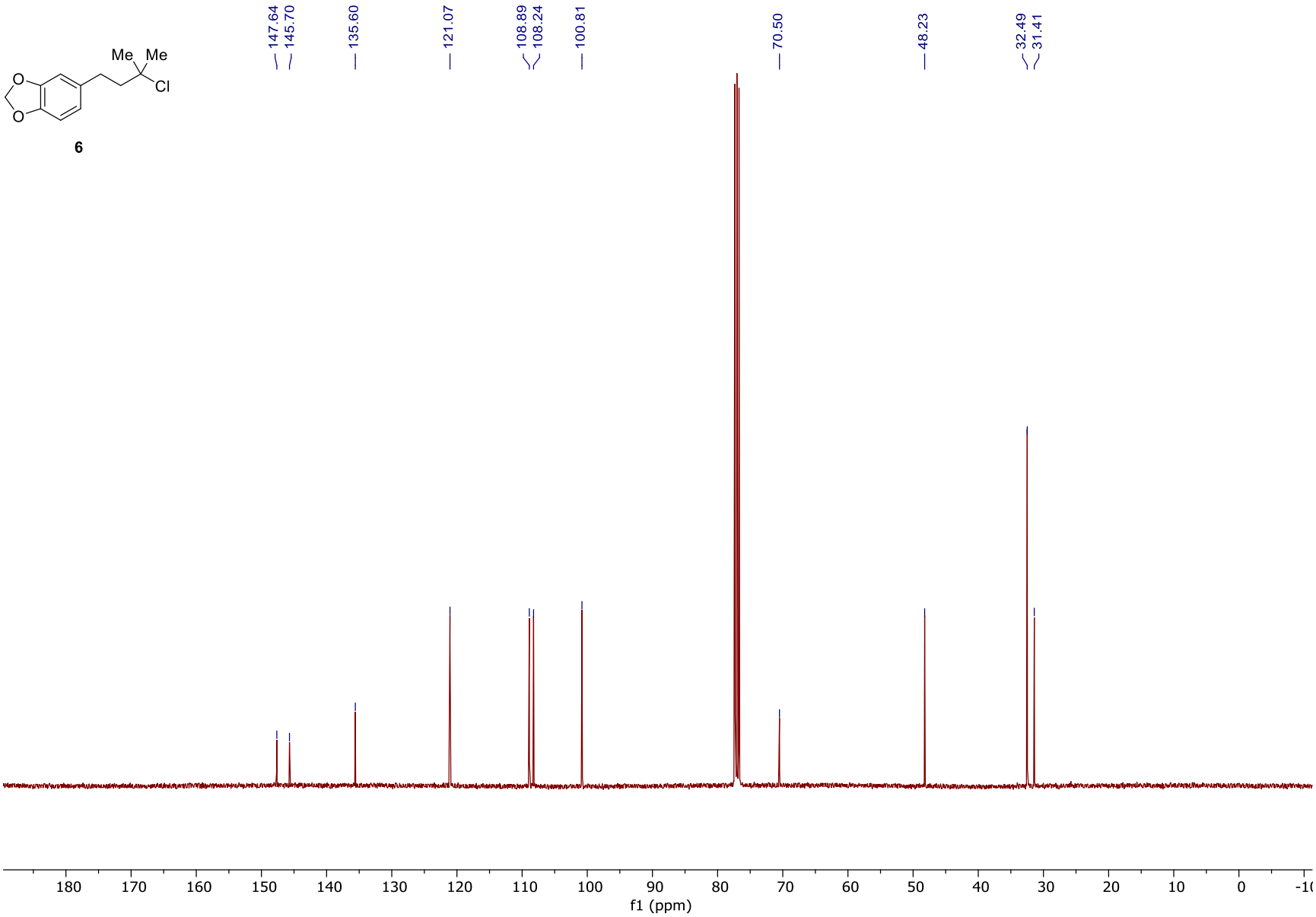
-0
f1 (ppm)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Me
Cl
O
O
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180
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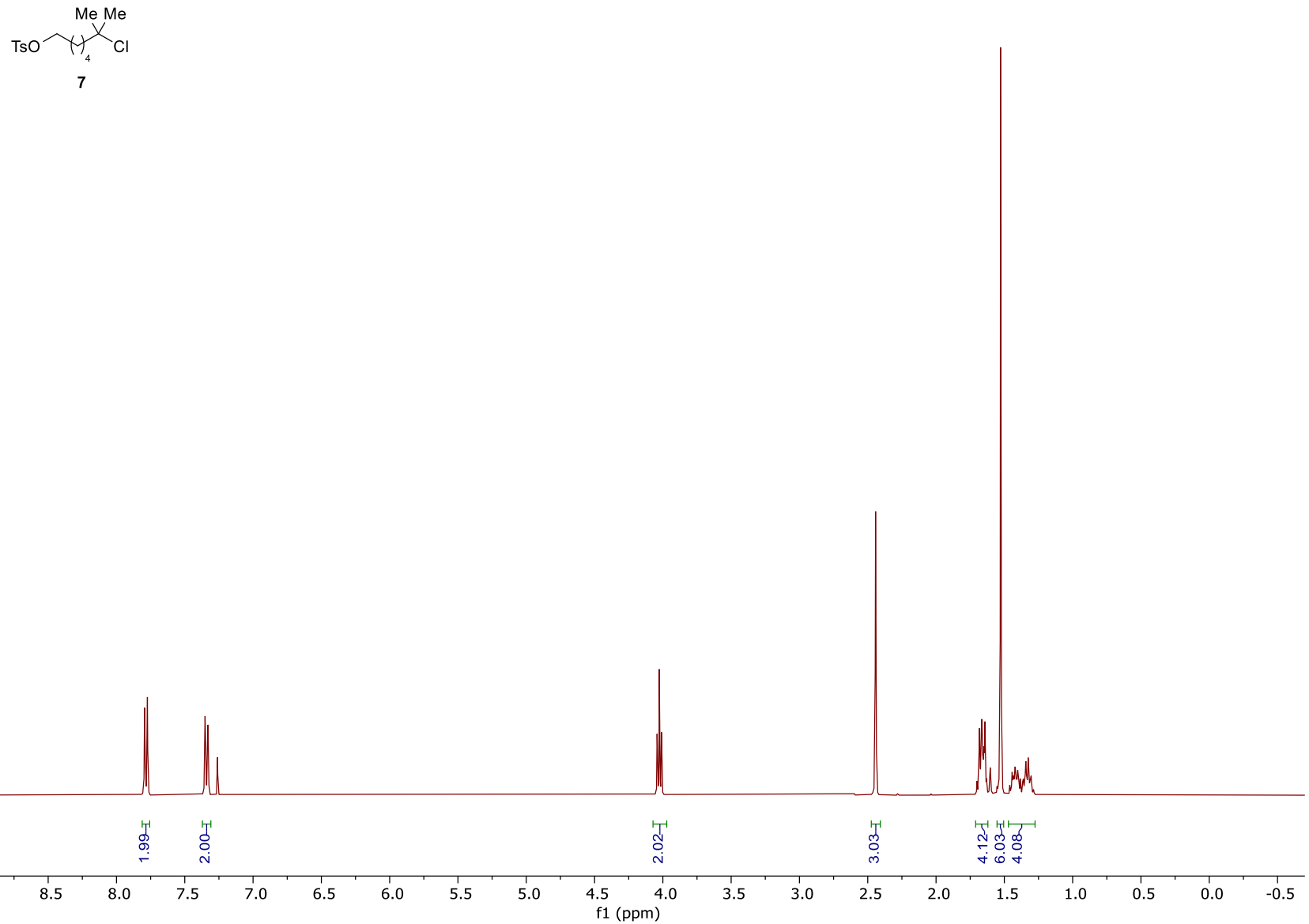
Me Me
TsO
Cl
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8.0
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7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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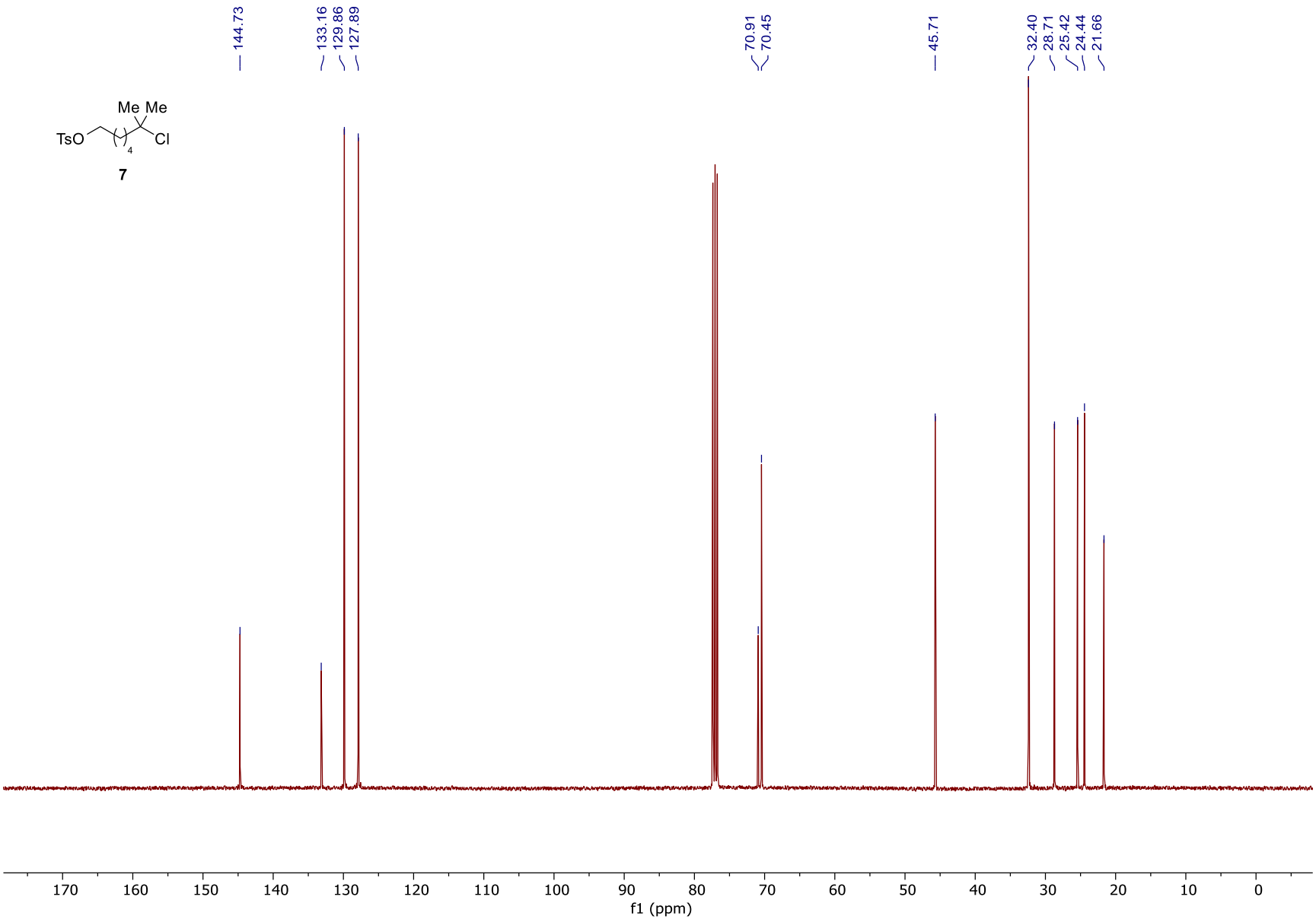
0.5
0.0
-0.5
f1 (ppm)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TsO
Cl
4
7
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10
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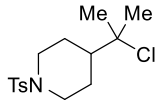
f1 (ppm)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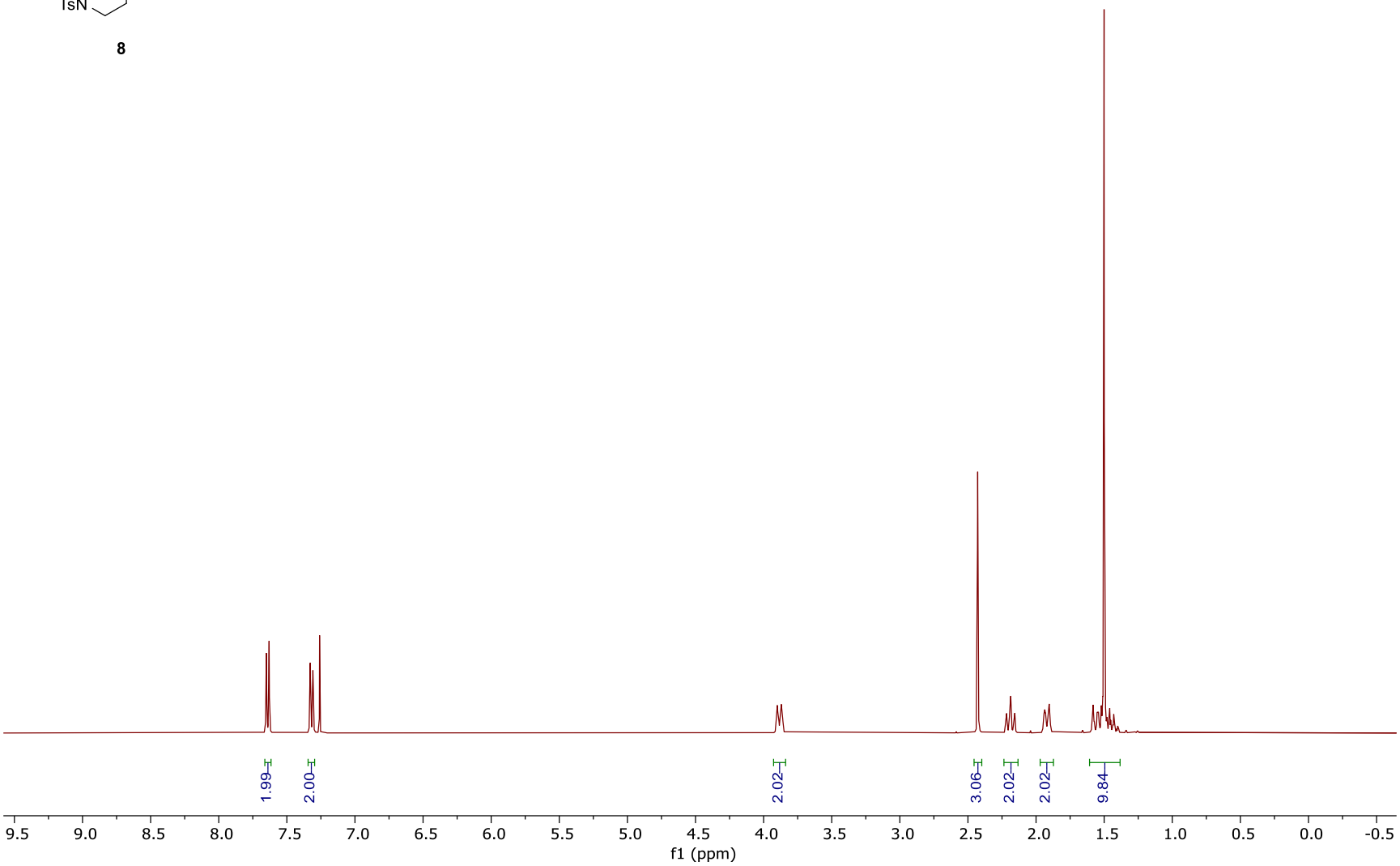
Me
Cl
TsN

8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6.5
6.0
5.5
5.0
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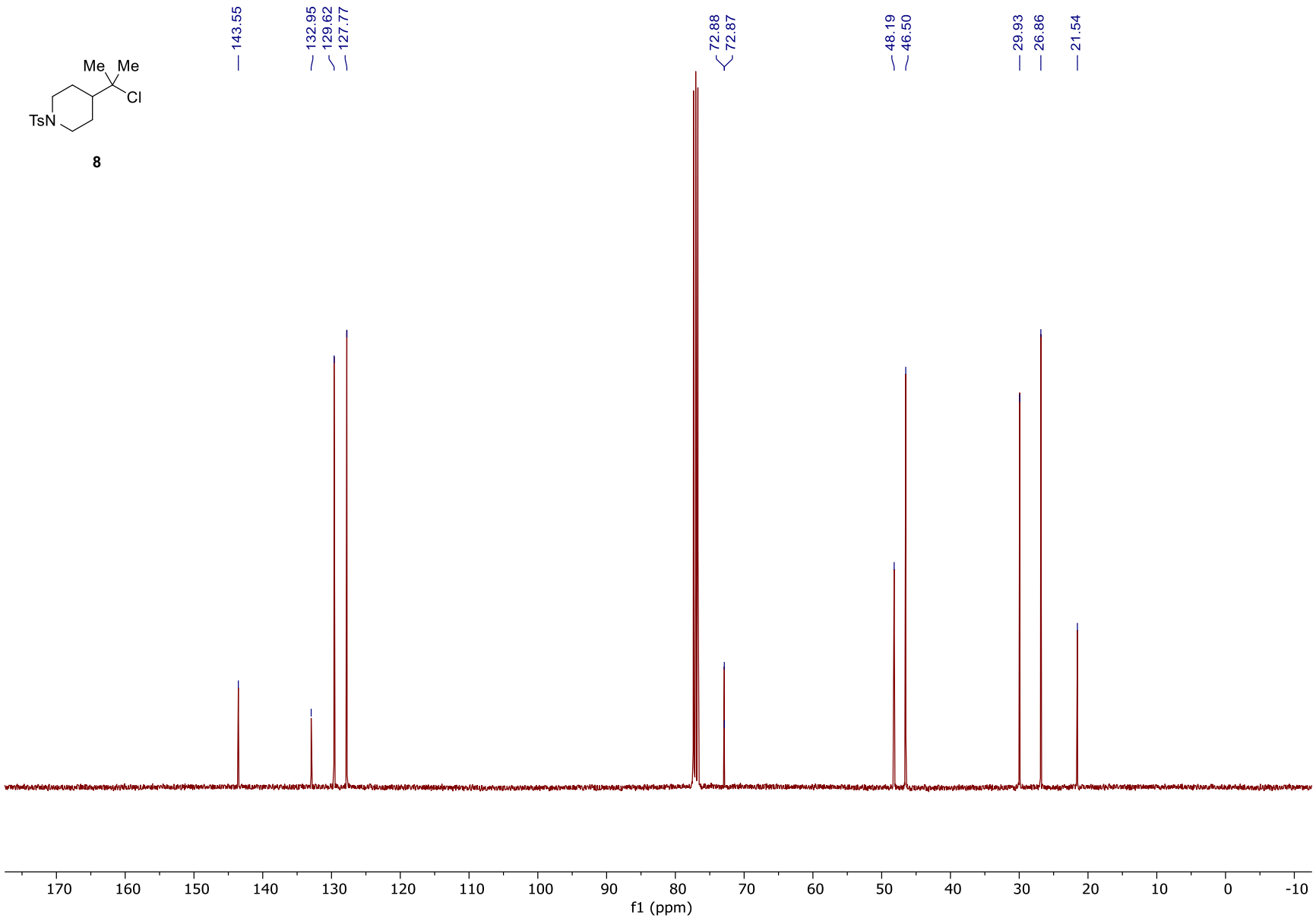
f1 (ppm)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Me
Cl
TsN
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21.54
170
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110
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80
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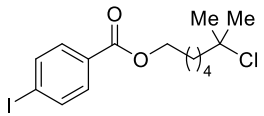
50
40
30
20
10
0
-10
f1 (ppm)


O
Me Me
O
4
Cl
I

9

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2.00
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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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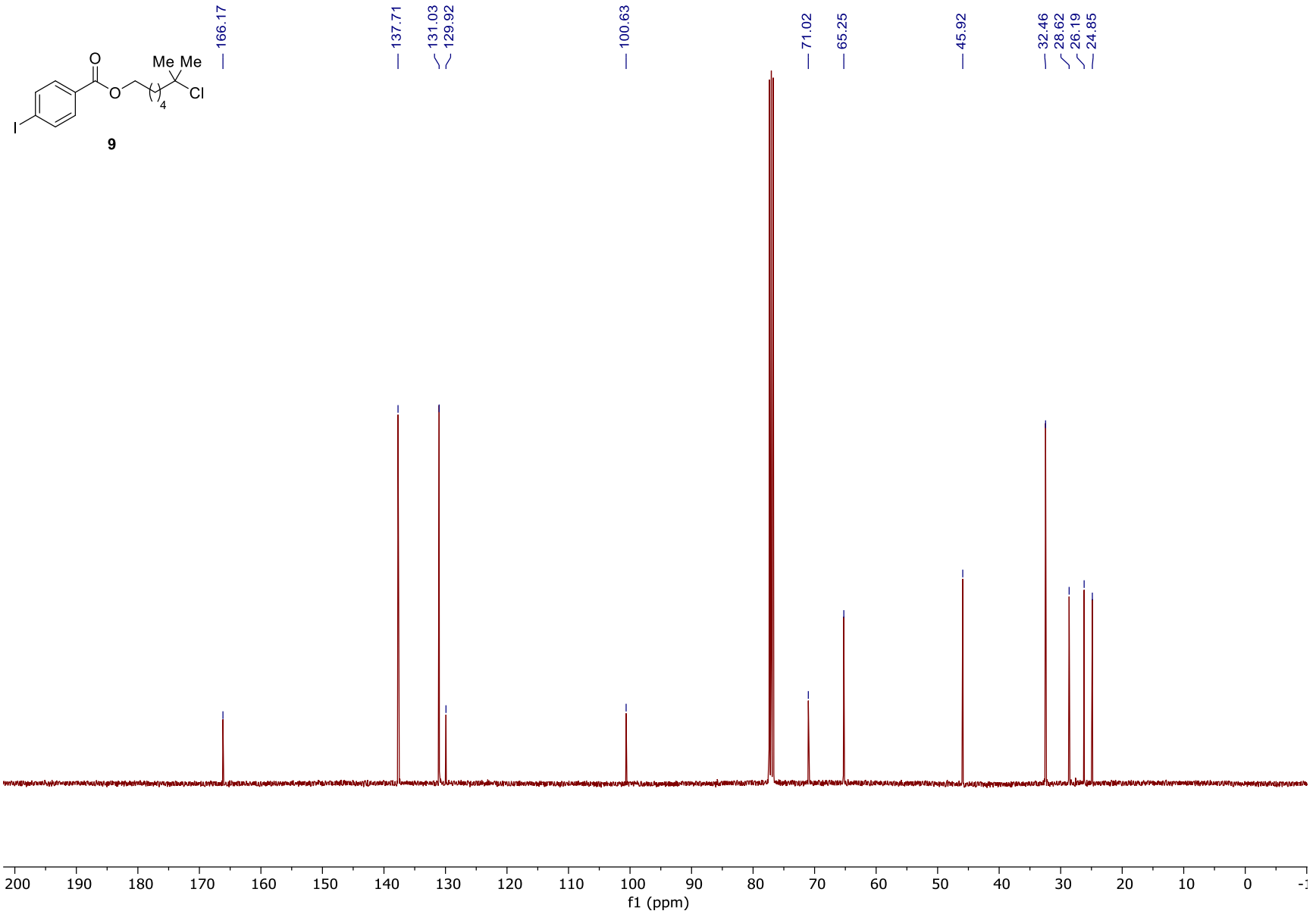
f1 (ppm)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129.92
100.63
71.02
65.25
45.92
32.46
28.62
26.19
24.85
O
Me Me
O
Cl
4
I
9
200
190
180
170
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150
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50
40
30
20
10
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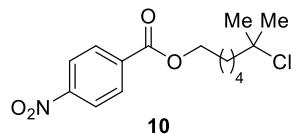
f1 (ppm)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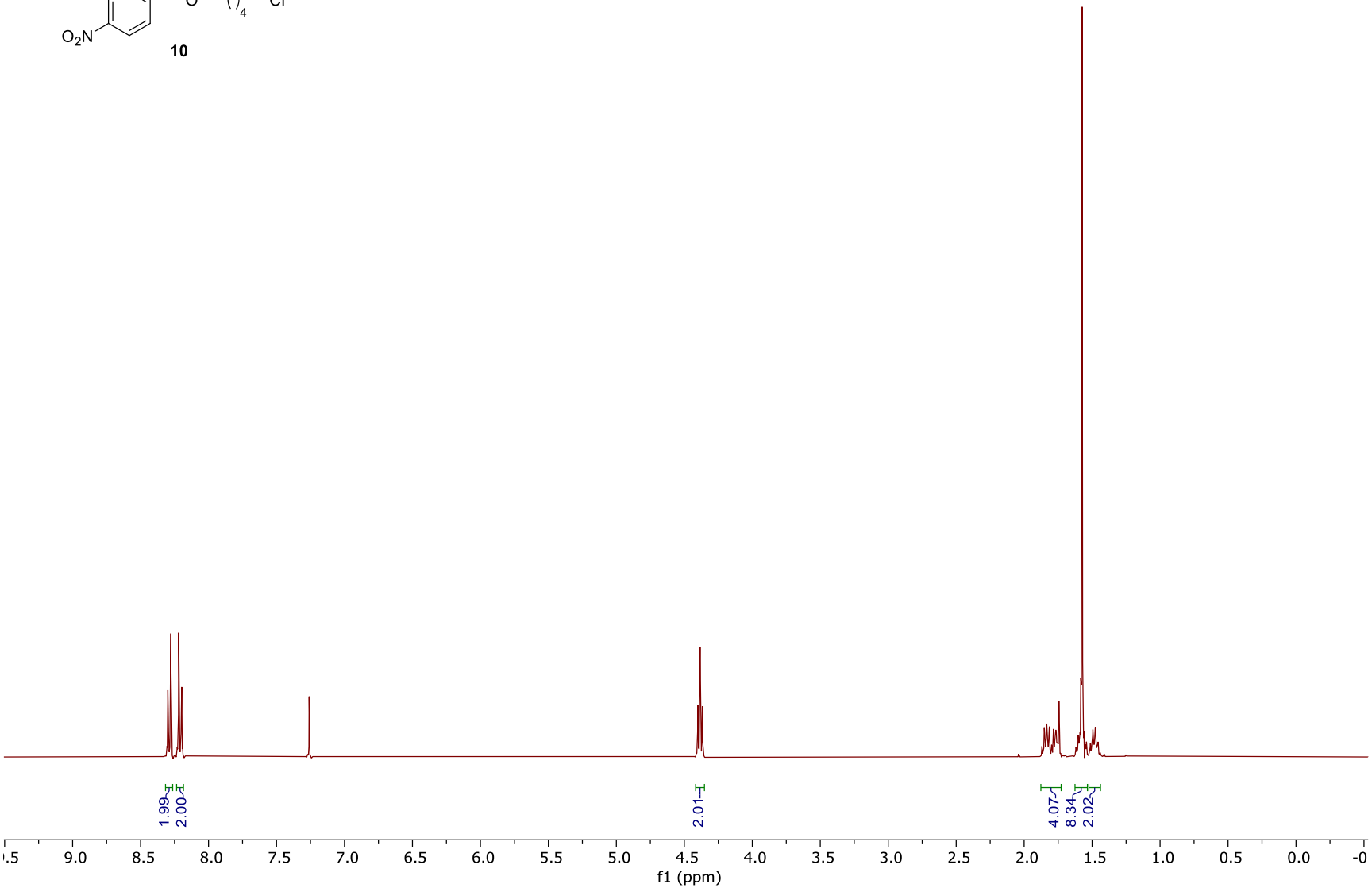
Me Me
O
Cl
4
O_2N

10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7.5
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6.0
5.5
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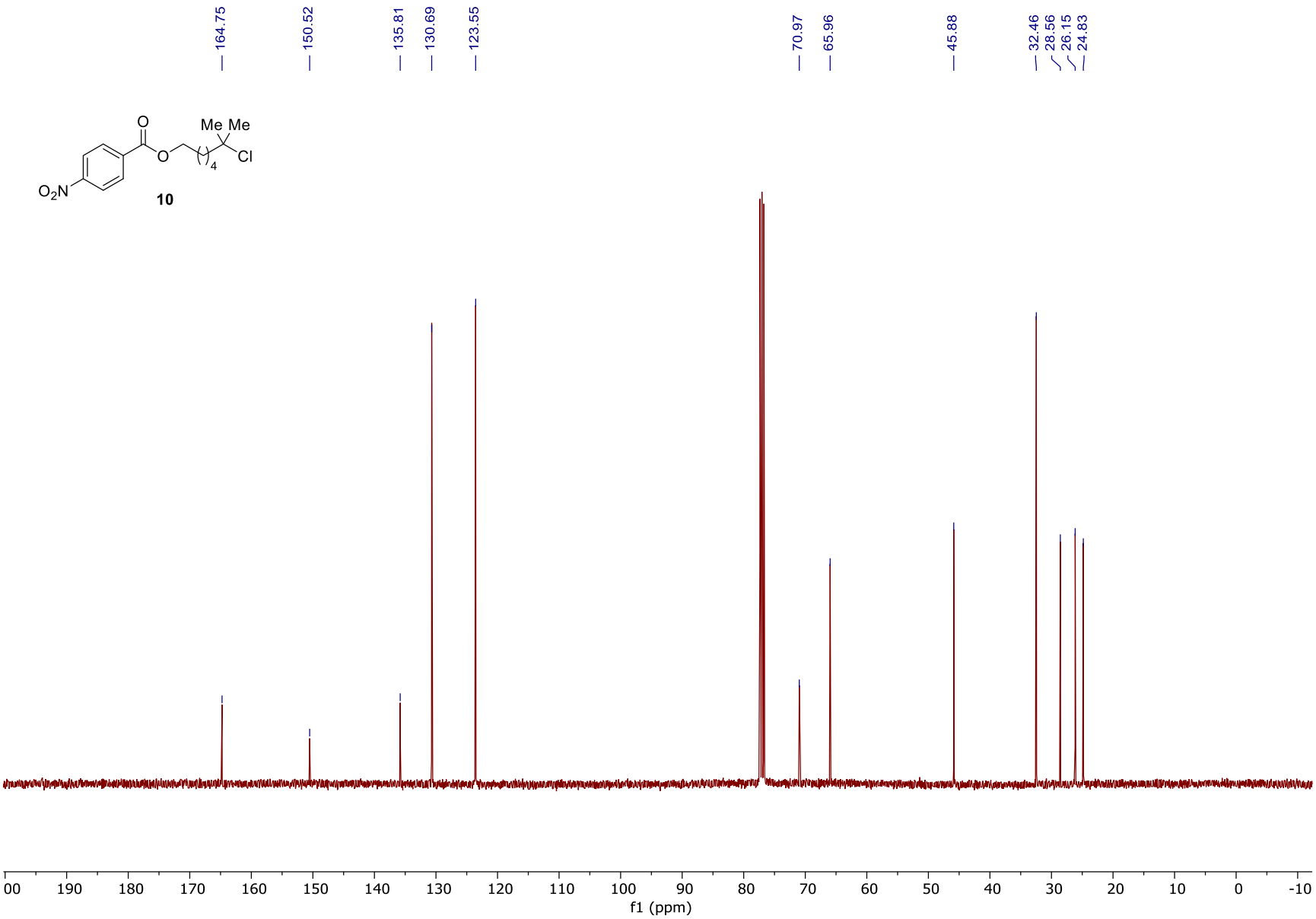
f1 (ppm)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Me Me
O
Cl
4
O2N
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00
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180
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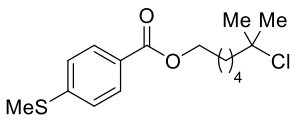
f1 (ppm)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O
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4
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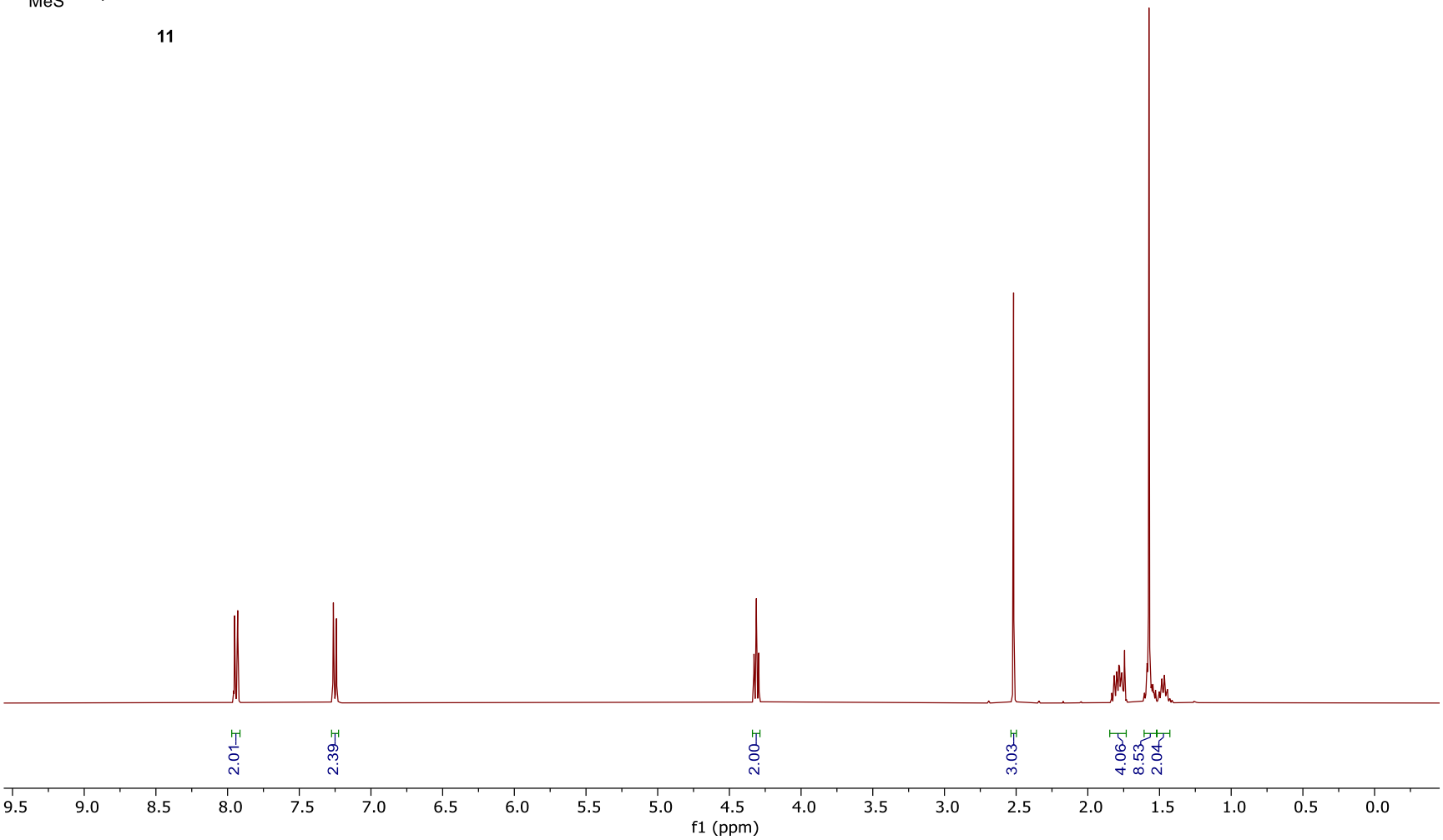
11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6.5
6.0
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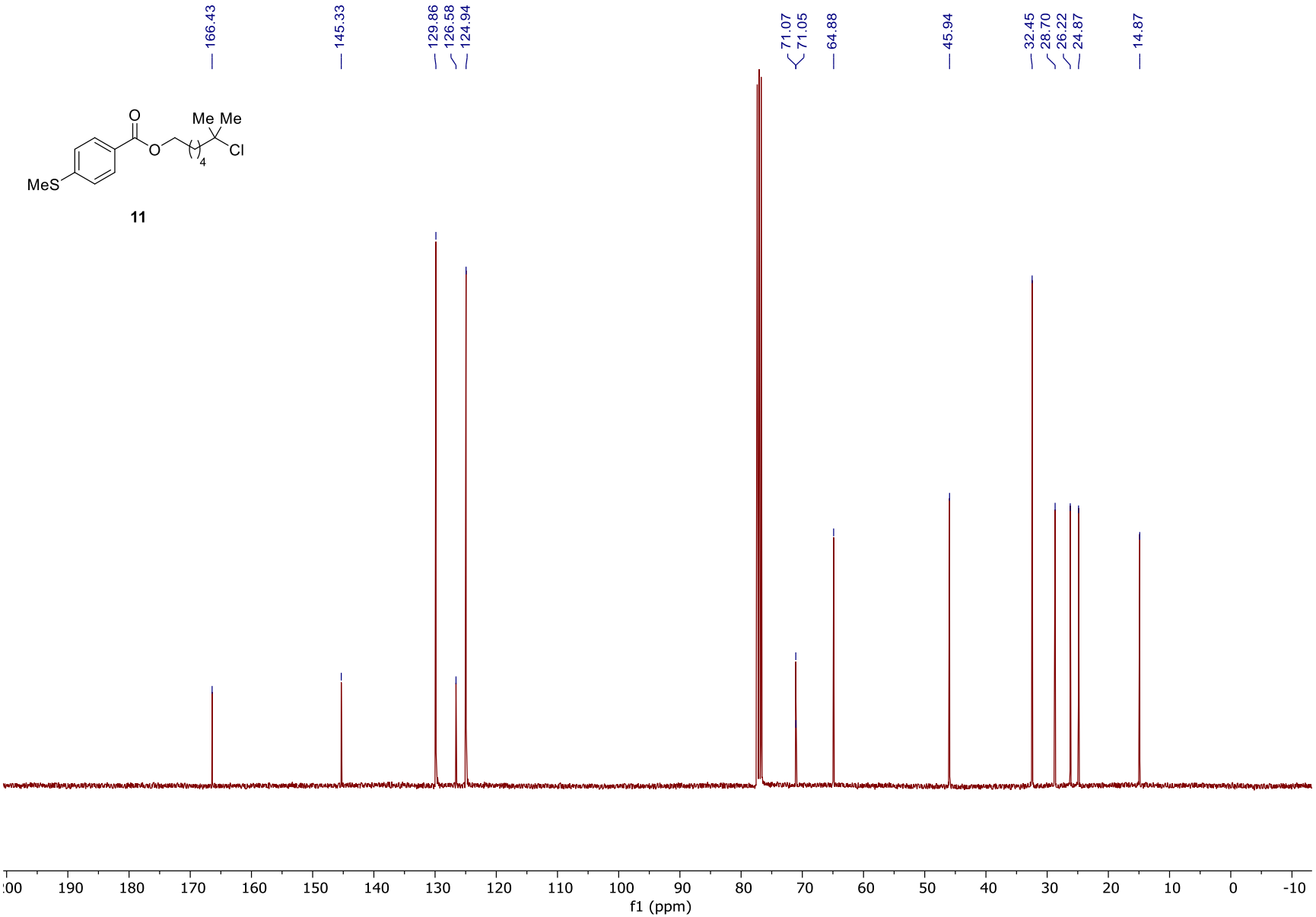
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O
Cl
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MeS
11
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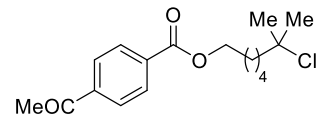
O
Me Me
O
Cl
4
MeOC

12

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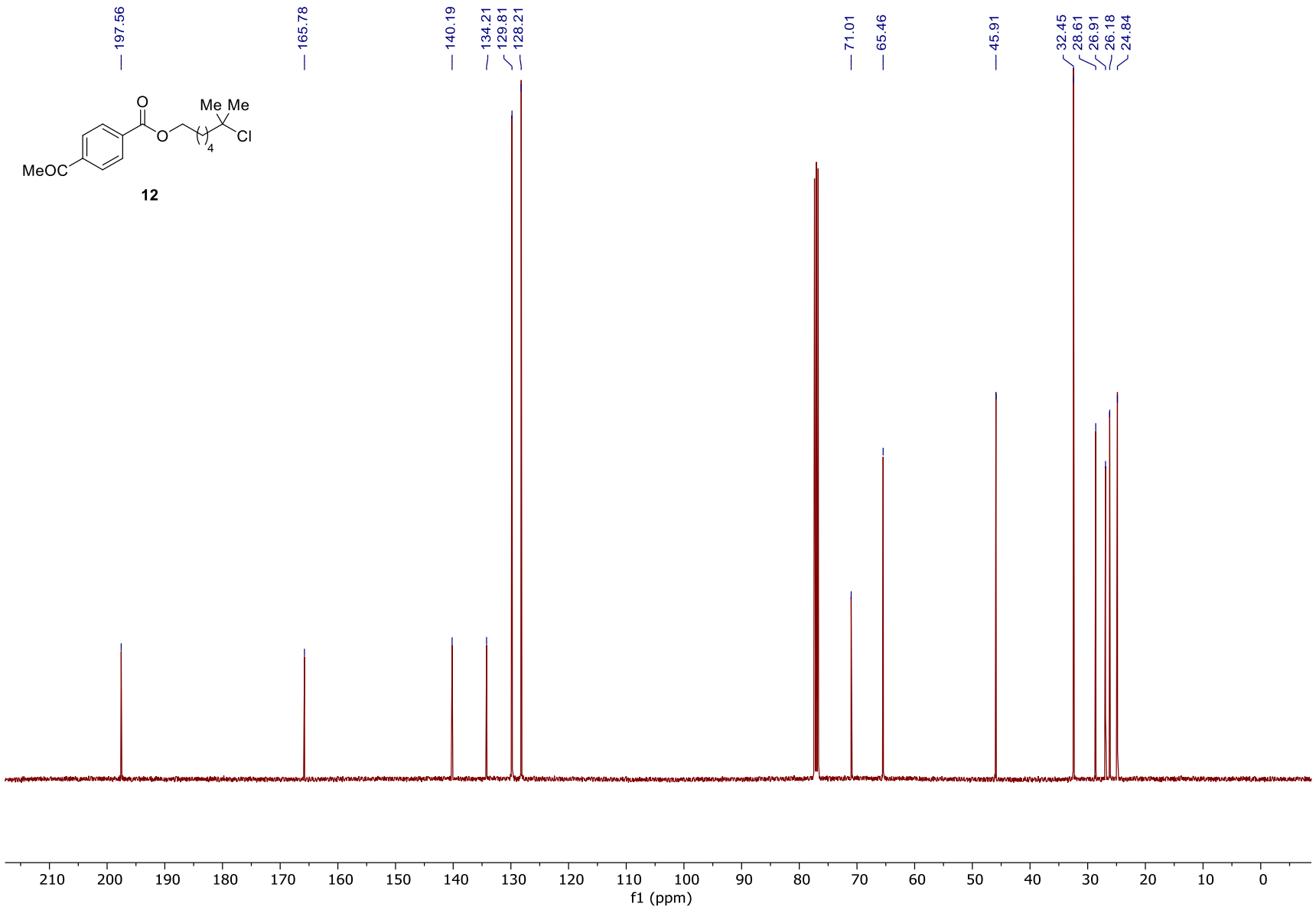
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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26.18
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Me Me
O
Cl
4
MeOC
12
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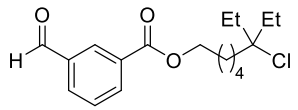
f1 (ppm)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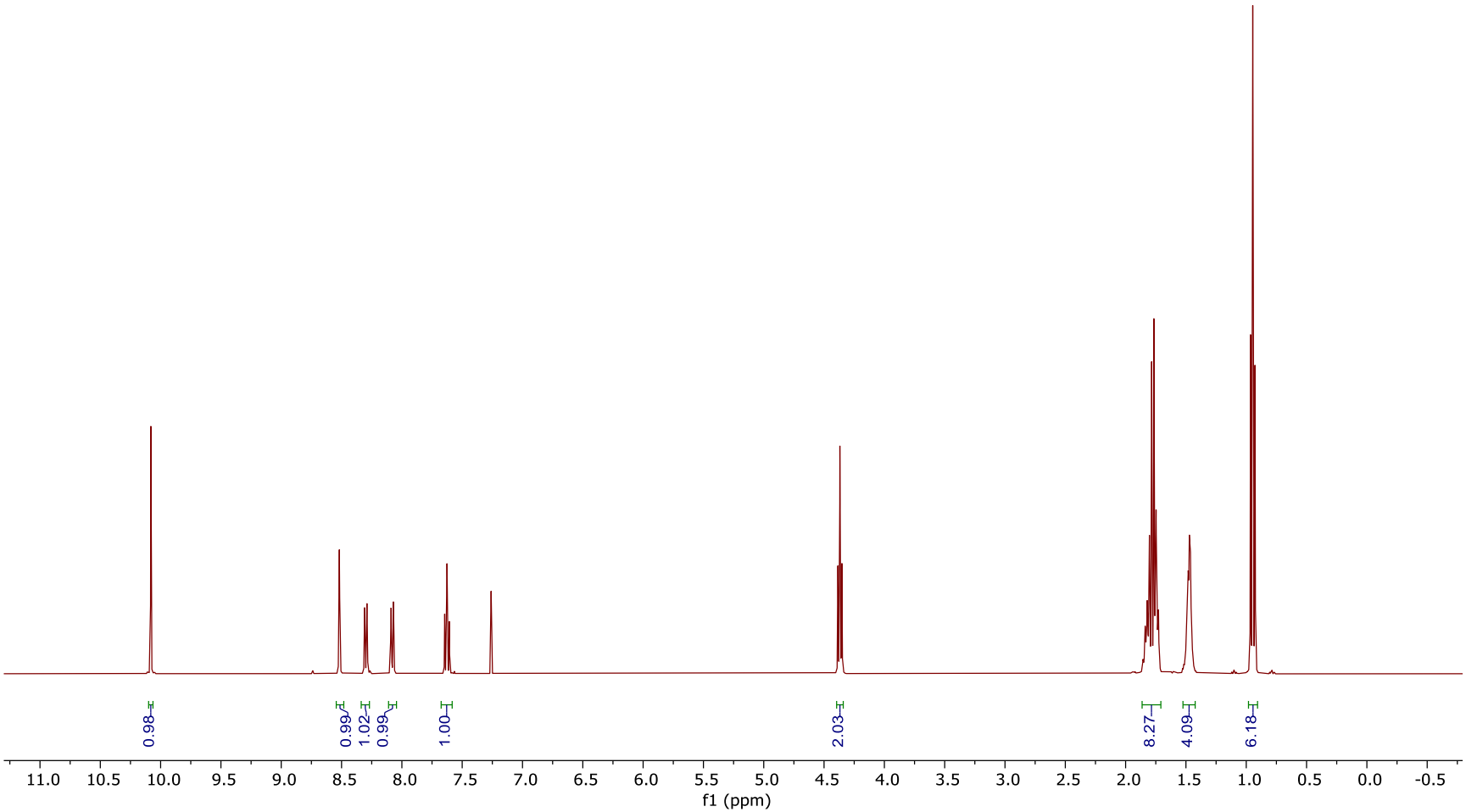
O
Et
Et
H
O
4
Cl

13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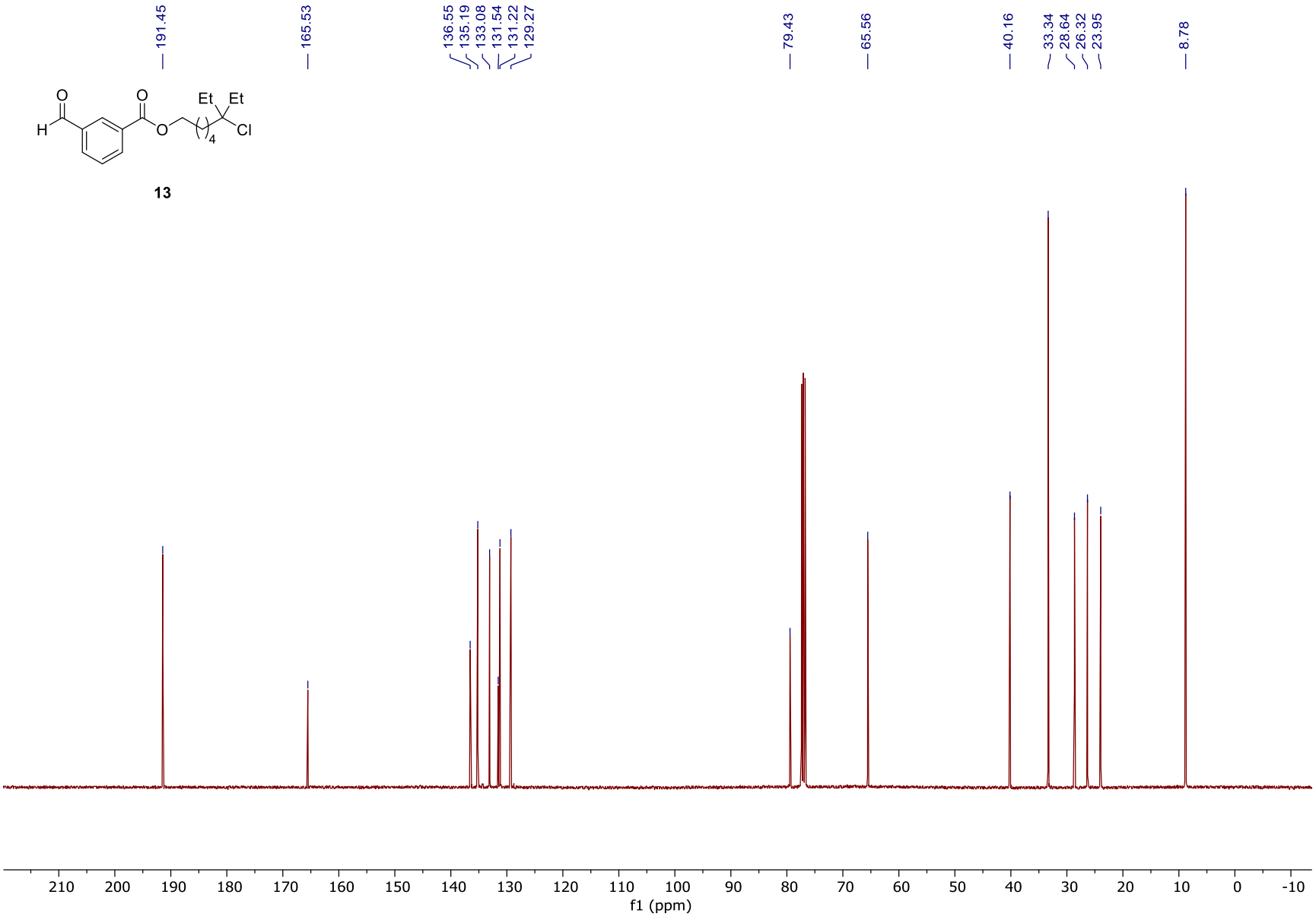
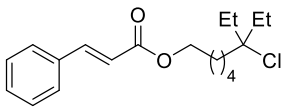
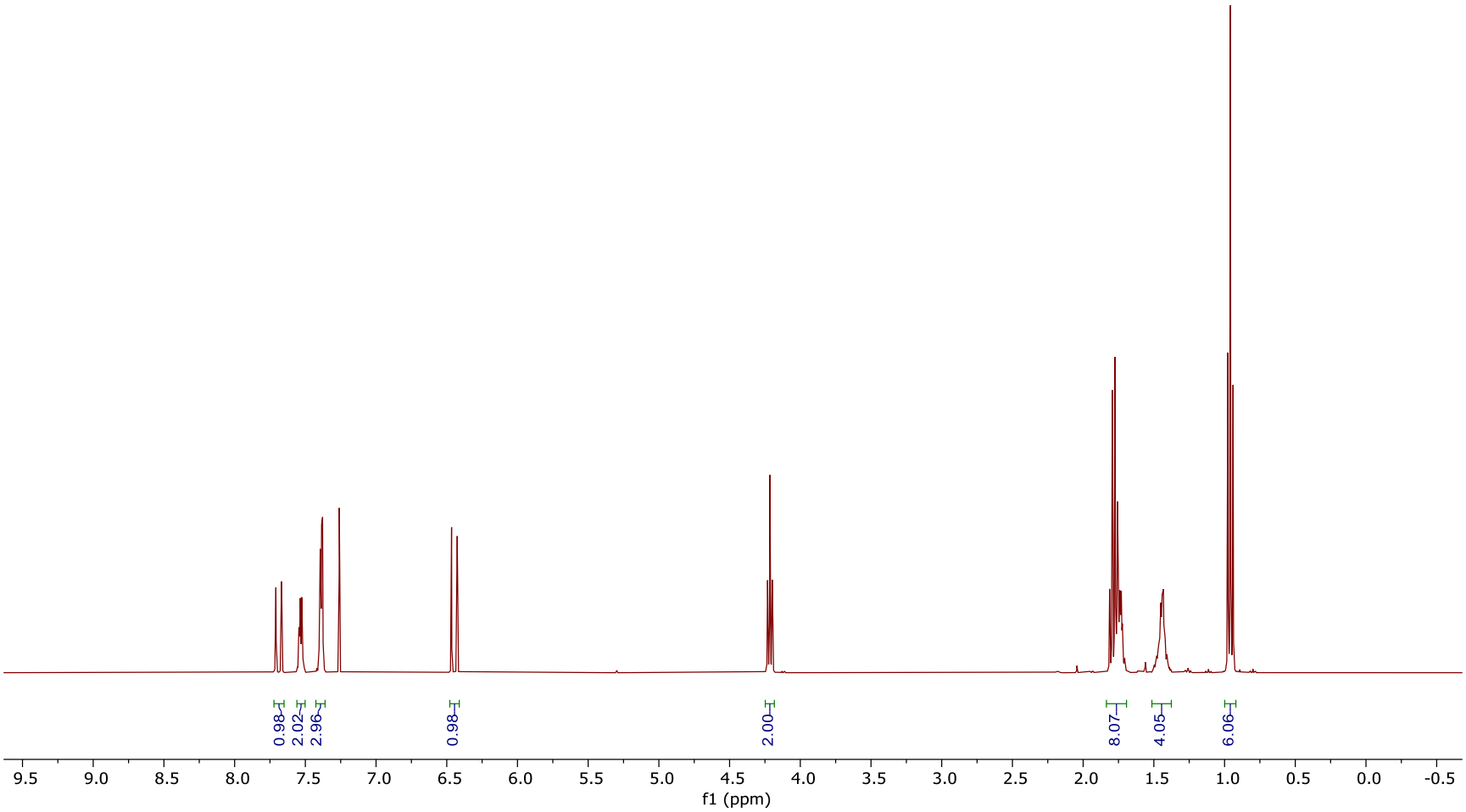
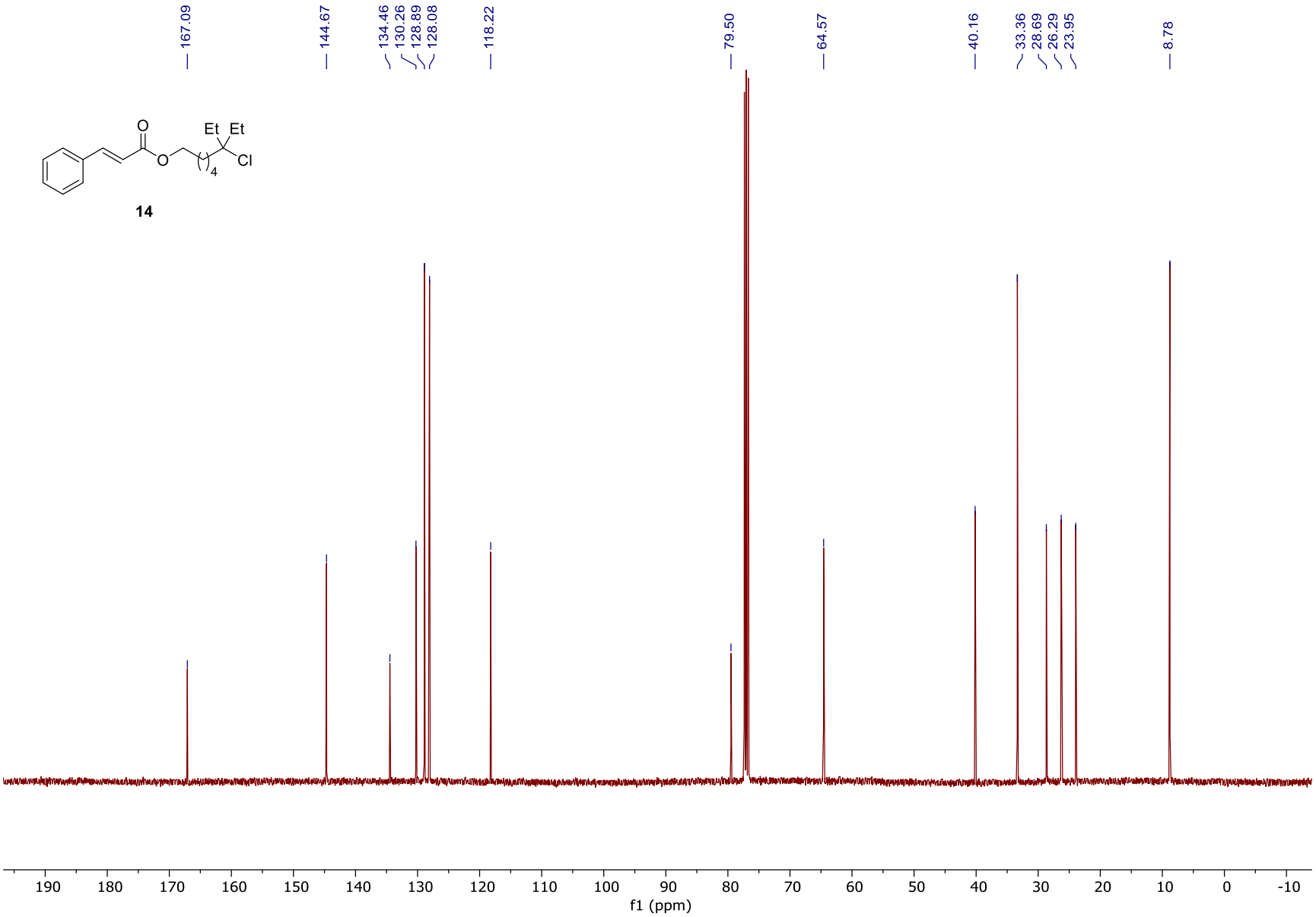
0.99
1.02
0.99
1.00
2.03
8.27
4.09
6.18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

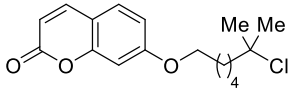

191.45
165.53
136.55
135.19
133.08
131.54
131.22
129.27
79.43
65.56
40.16
33.34
28.64
26.32
23.95
8.78
O
O
H
O
Et
Et
Cl
4
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Et Et
O
Cl
4

14

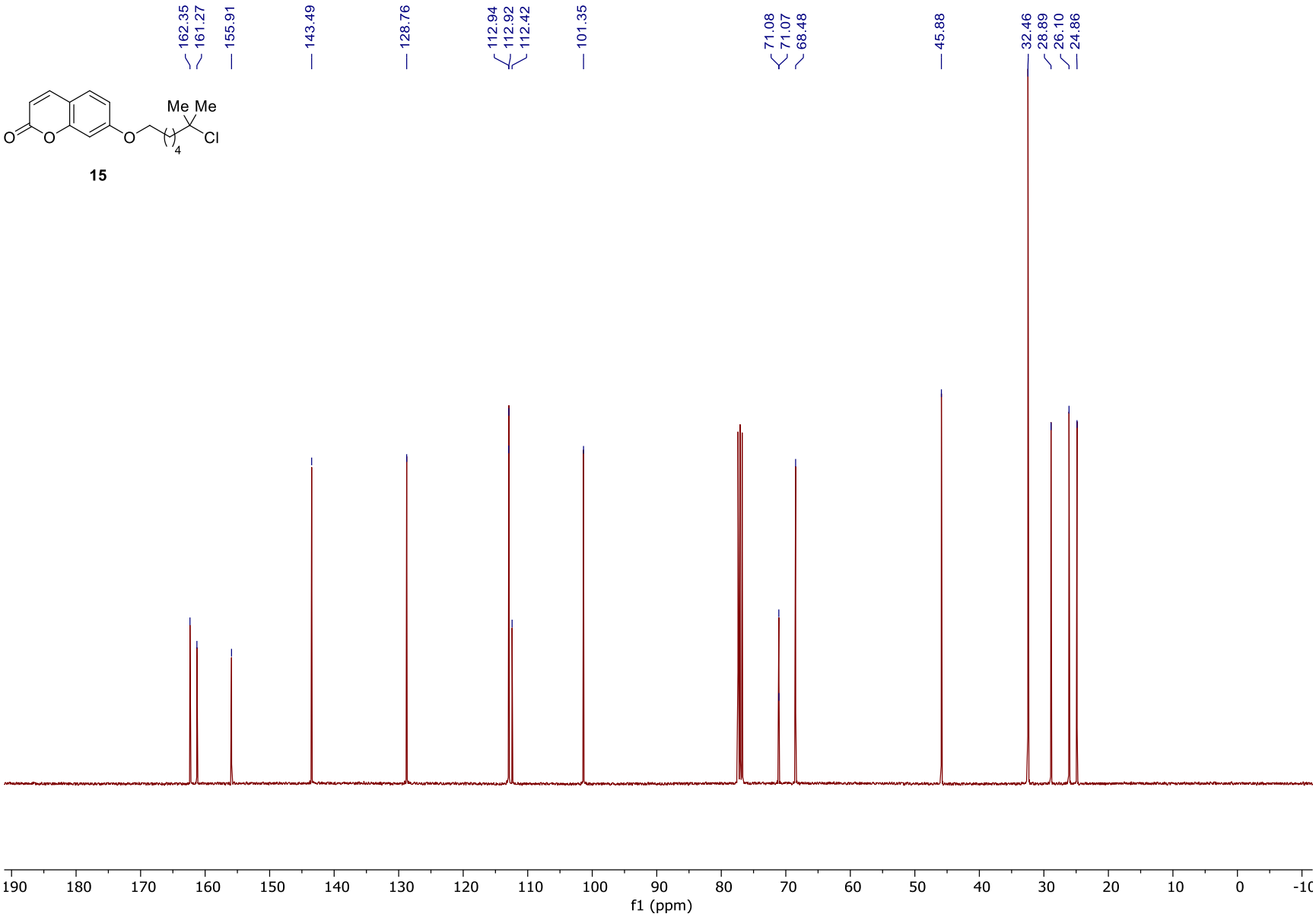

0.98
2.02
2.96
0.98
2.00
8.07
4.05
6.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

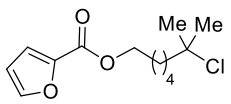

167.09
144.67
134.46
130.26
128.89
128.08
118.22
79.50
64.57
40.16
33.36
28.69
26.29
23.95
8.78
O
O
Et
Et
Cl
4
14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me Me
O
O
O
4
Cl

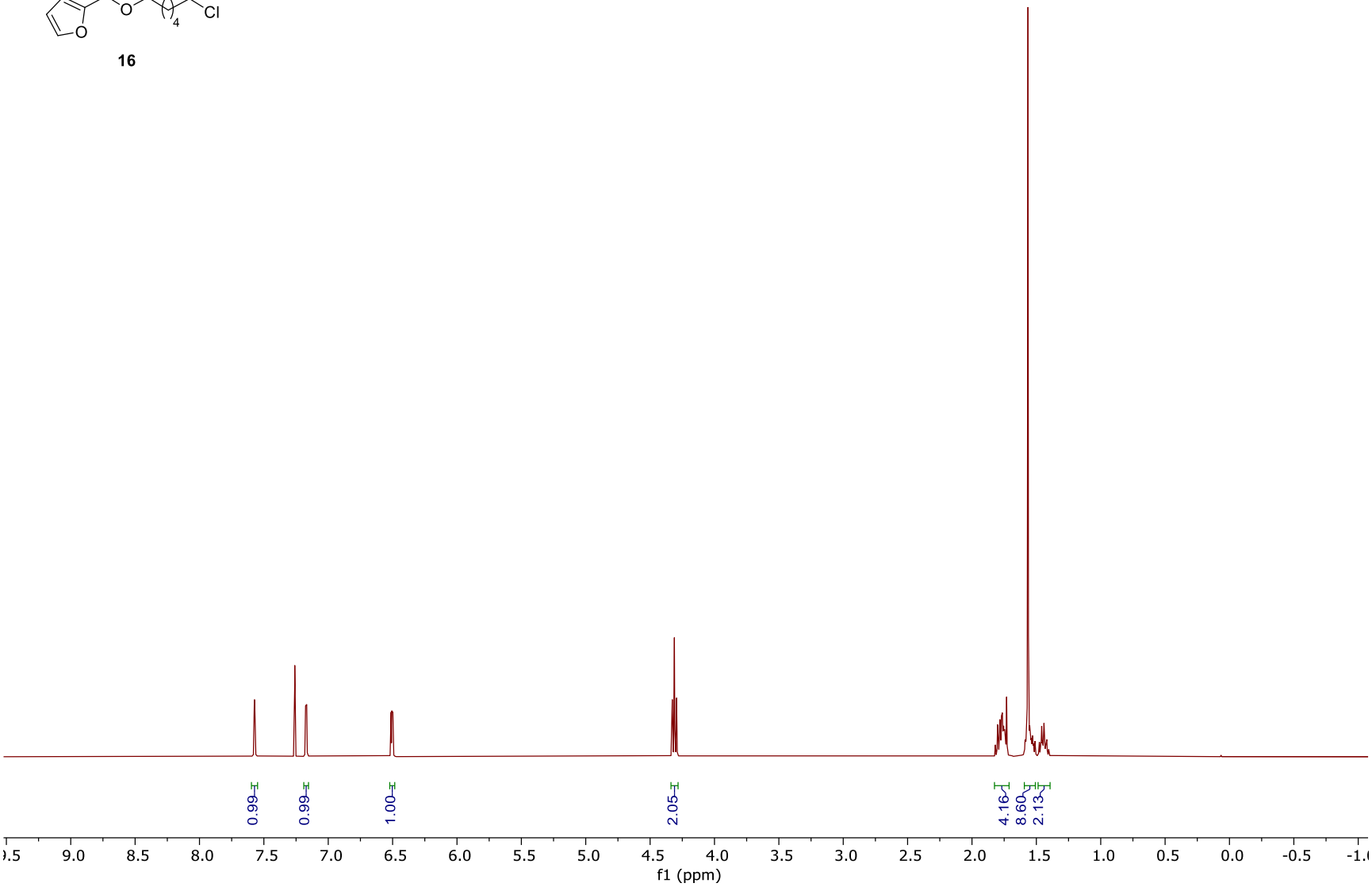
15

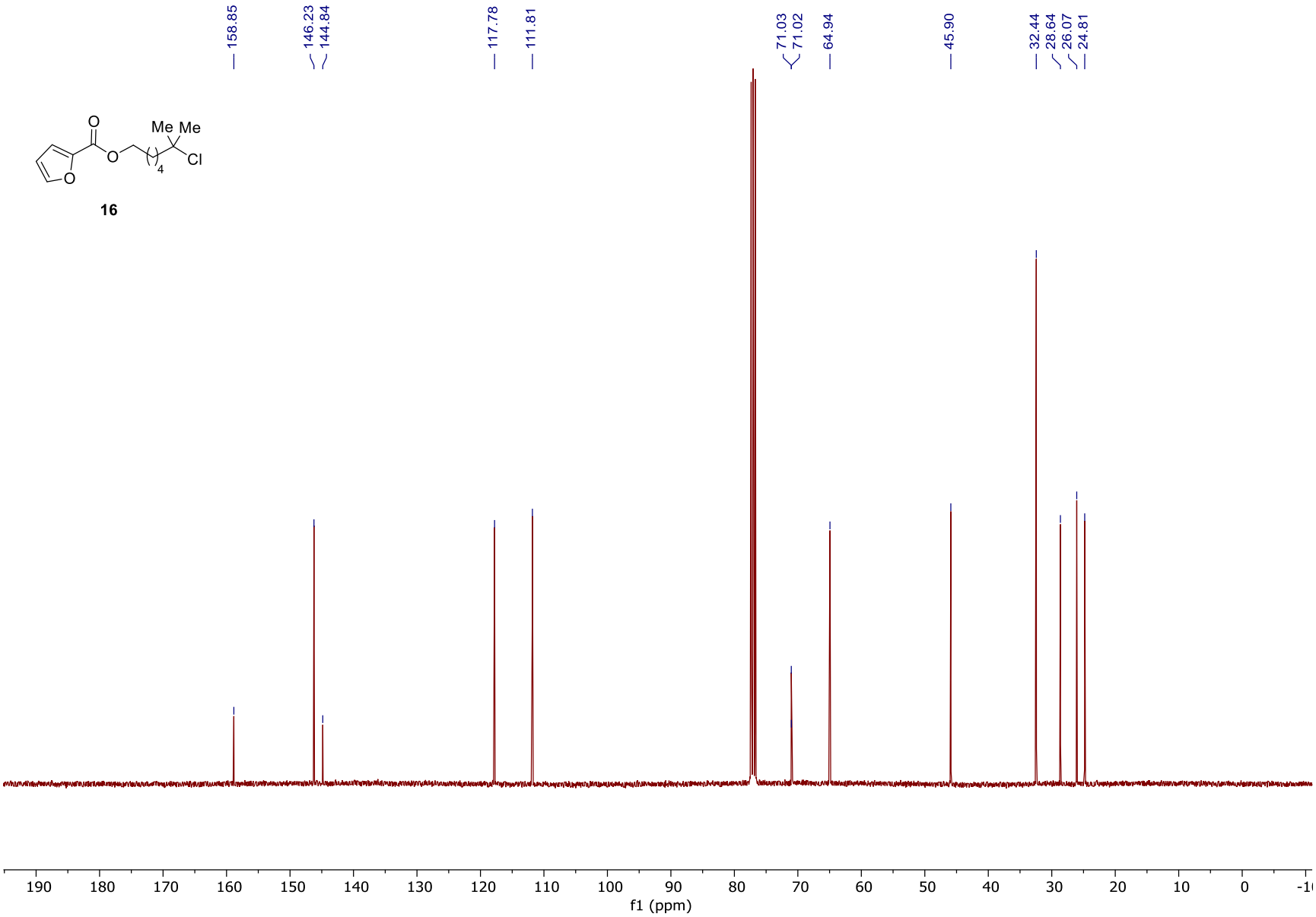
1.01
1.01
1.02
0.99
0.99
2.00
2.05
2.06
10.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

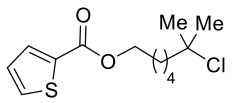

162.35
161.27
155.91
143.49
128.76
112.94
112.92
112.42
101.35
71.08
71.07
68.48
45.88
32.46
28.89
26.10
24.86
Me Me
Cl
O
O
O
4
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Me Me
O
4
Cl
O

16

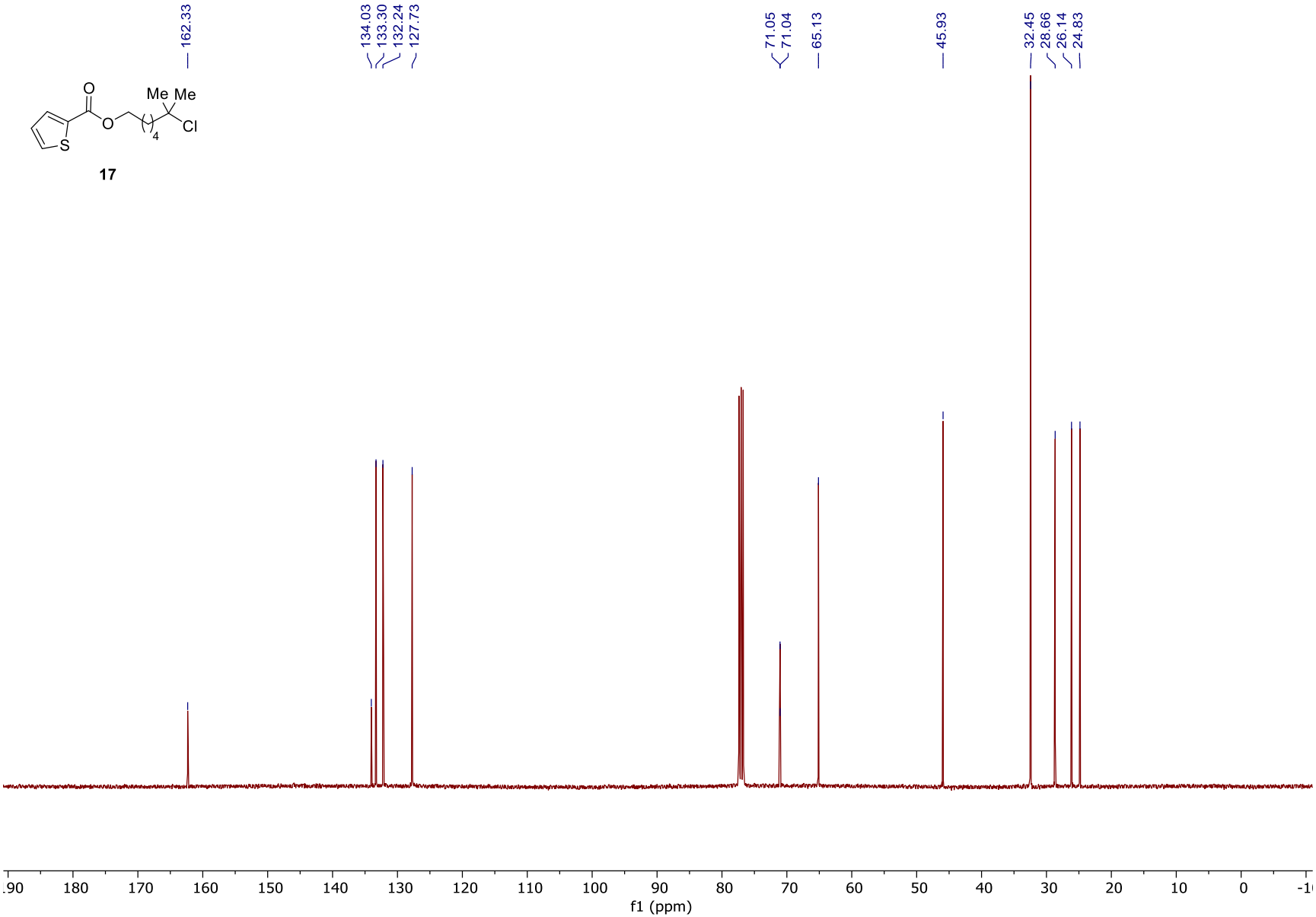

0.99
0.99
1.00
2.05
4.16
8.60
2.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

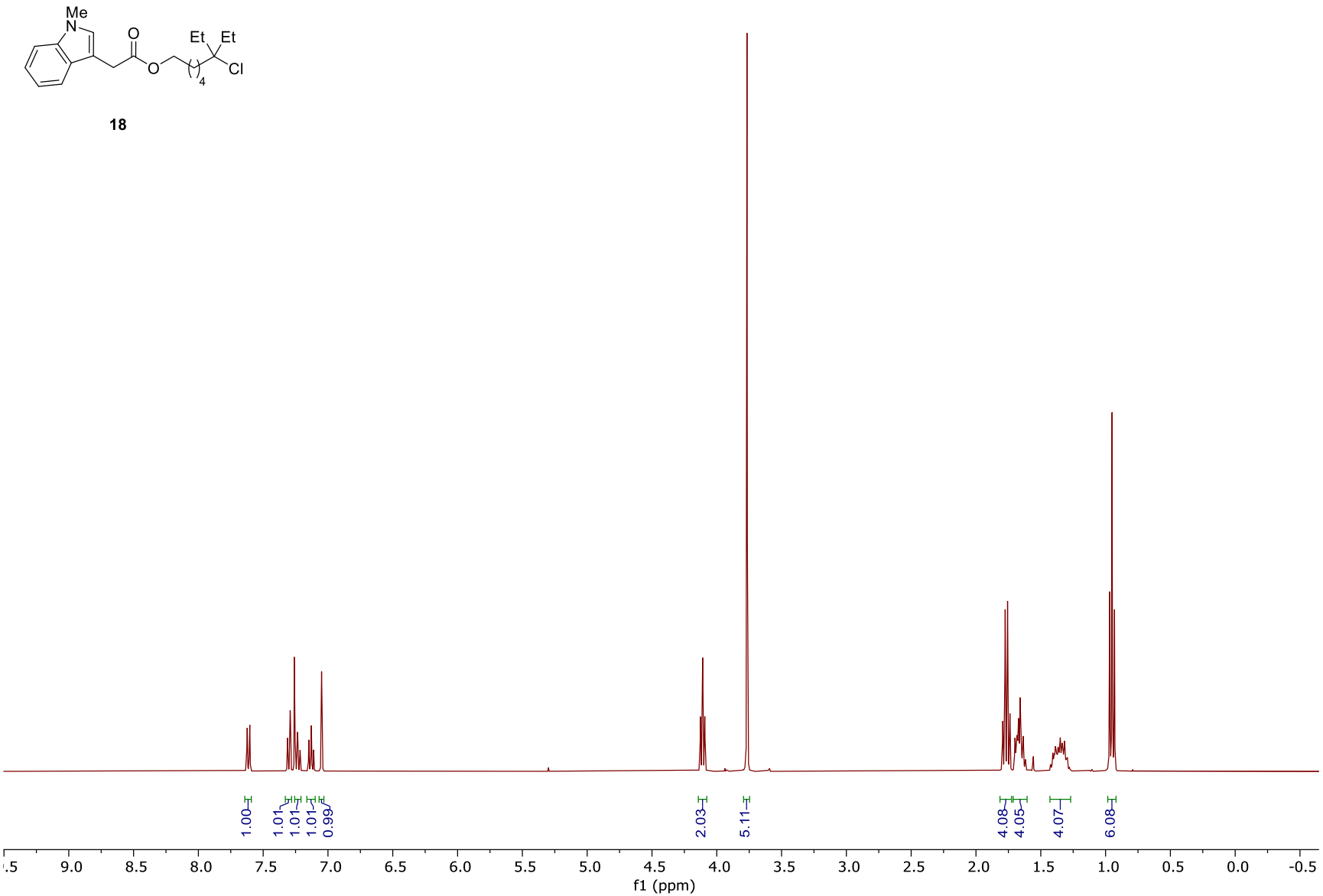

158.85
146.23
144.84
117.78
111.81
71.03
71.02
64.94
45.90
32.44
28.64
26.07
24.81
O
O
O
Me Me
Cl
4
16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

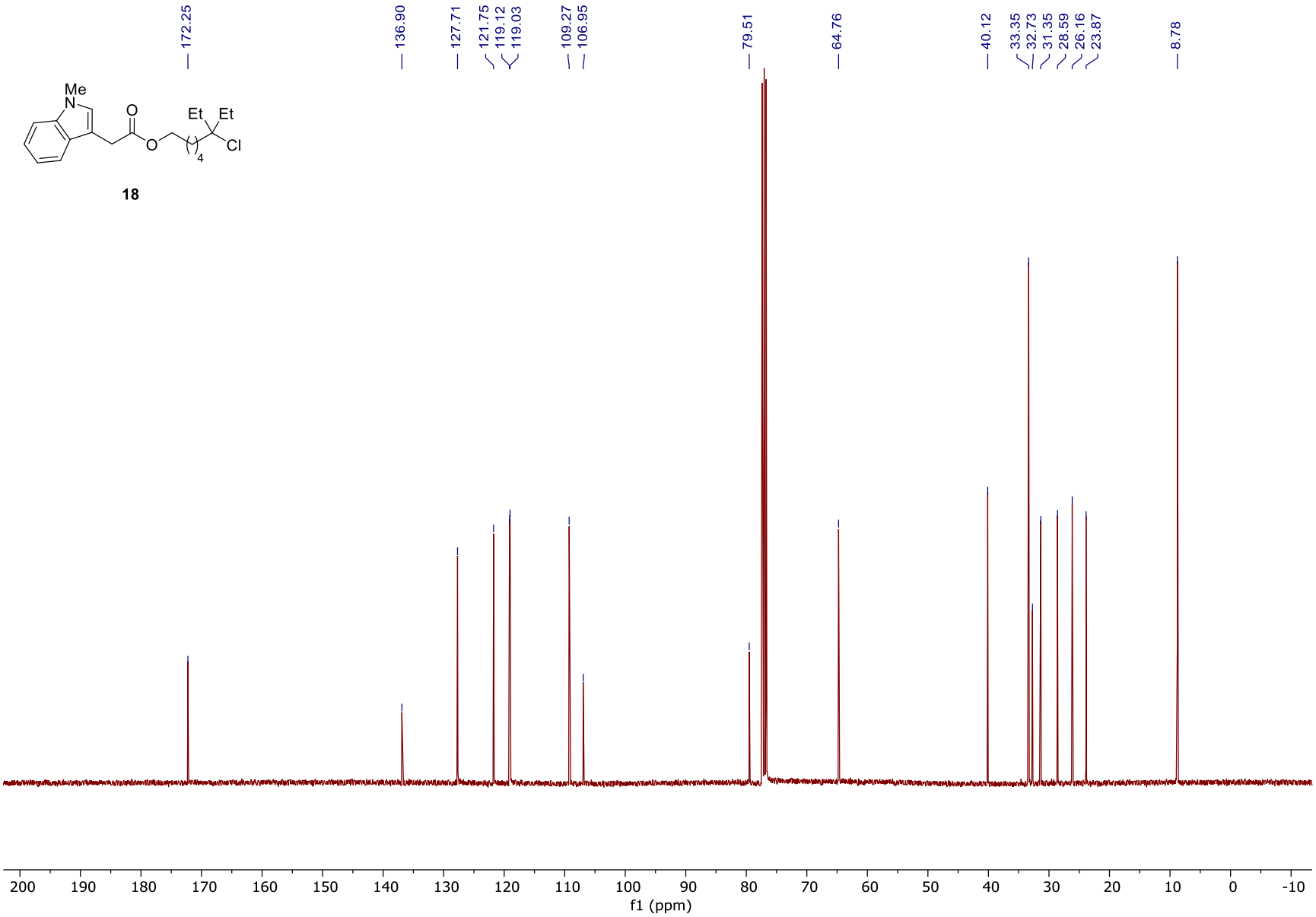

O
Me Me
O
4
Cl
S

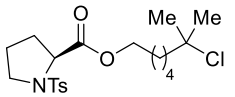
17

1.00
0.99
1.00
2.04
4.15
8.27
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


162.33
134.03
133.30
132.24
127.73
71.05
71.04
65.13
45.93
32.45
28.66
26.14
24.83
O
O
S
Me Me
Cl
4
17
f1 (ppm)

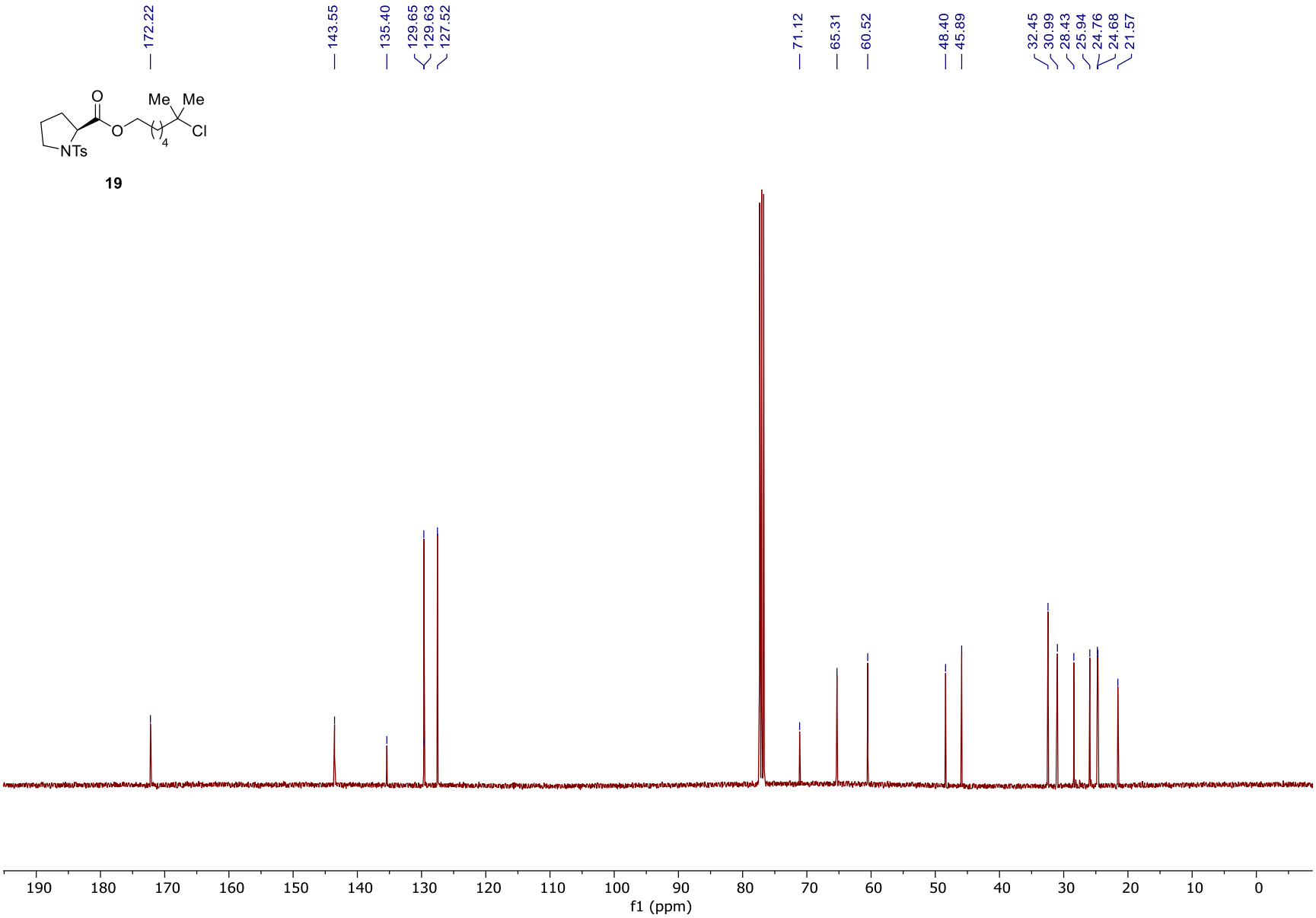

Me
N
O
O
Et
Et
Cl
4
18
1.00
1.01
1.01
1.01
0.99
2.03
5.11
4.08
4.05
4.07
6.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

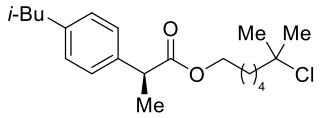

172.25
136.90
127.71
121.75
119.12
119.03
109.27
106.95
79.51
64.76
40.12
33.35
32.73
31.35
28.59
26.16
23.87
8.78
Me
N
O
O
Et
Et
Cl
4
18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Me
Me
O
4
Cl
NTs

19

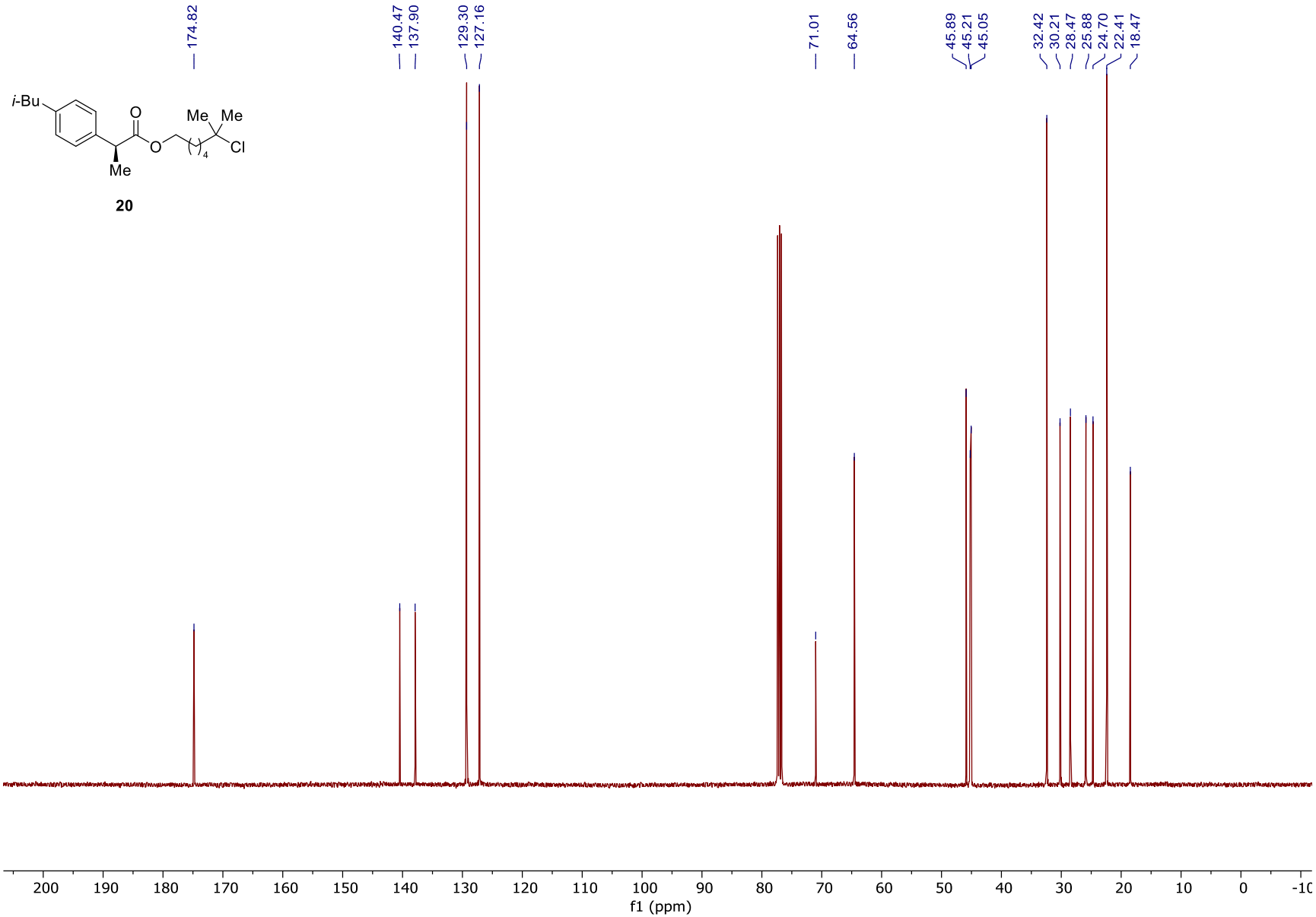
2.00
2.01
1.00
2.01
1.01
0.99
3.02
3.13
3.09
2.03
8.14
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

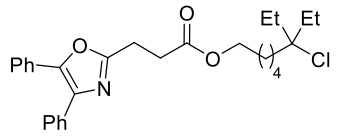

172.22
143.55
135.40
129.65
129.63
127.52
71.12
65.31
60.52
48.40
45.89
32.45
30.99
28.43
25.94
24.76
24.68
21.57
O
Me
Me
O
Cl
4
NTs
19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


i-Bu
O
Me
Me
O
4
Cl
Me

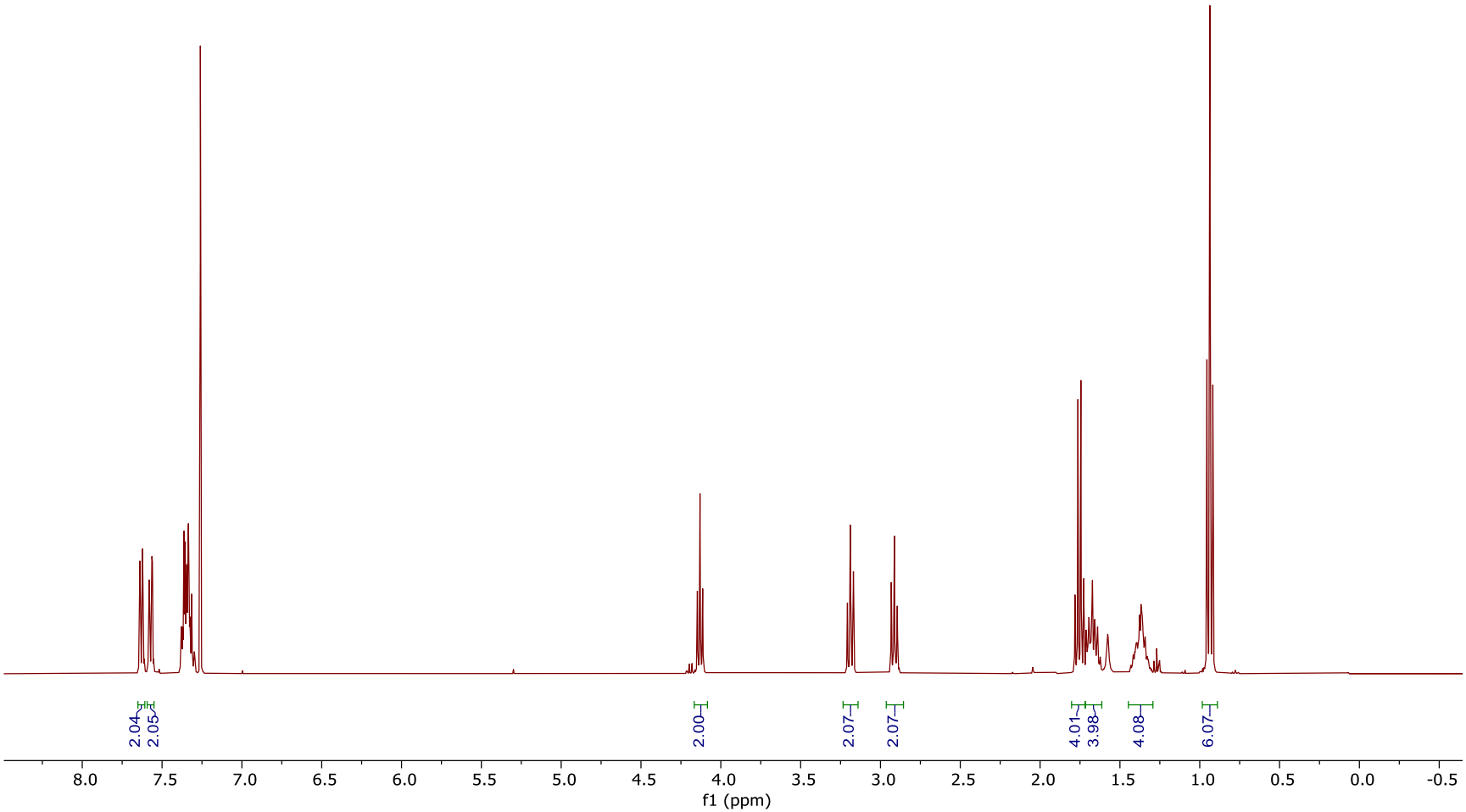
20

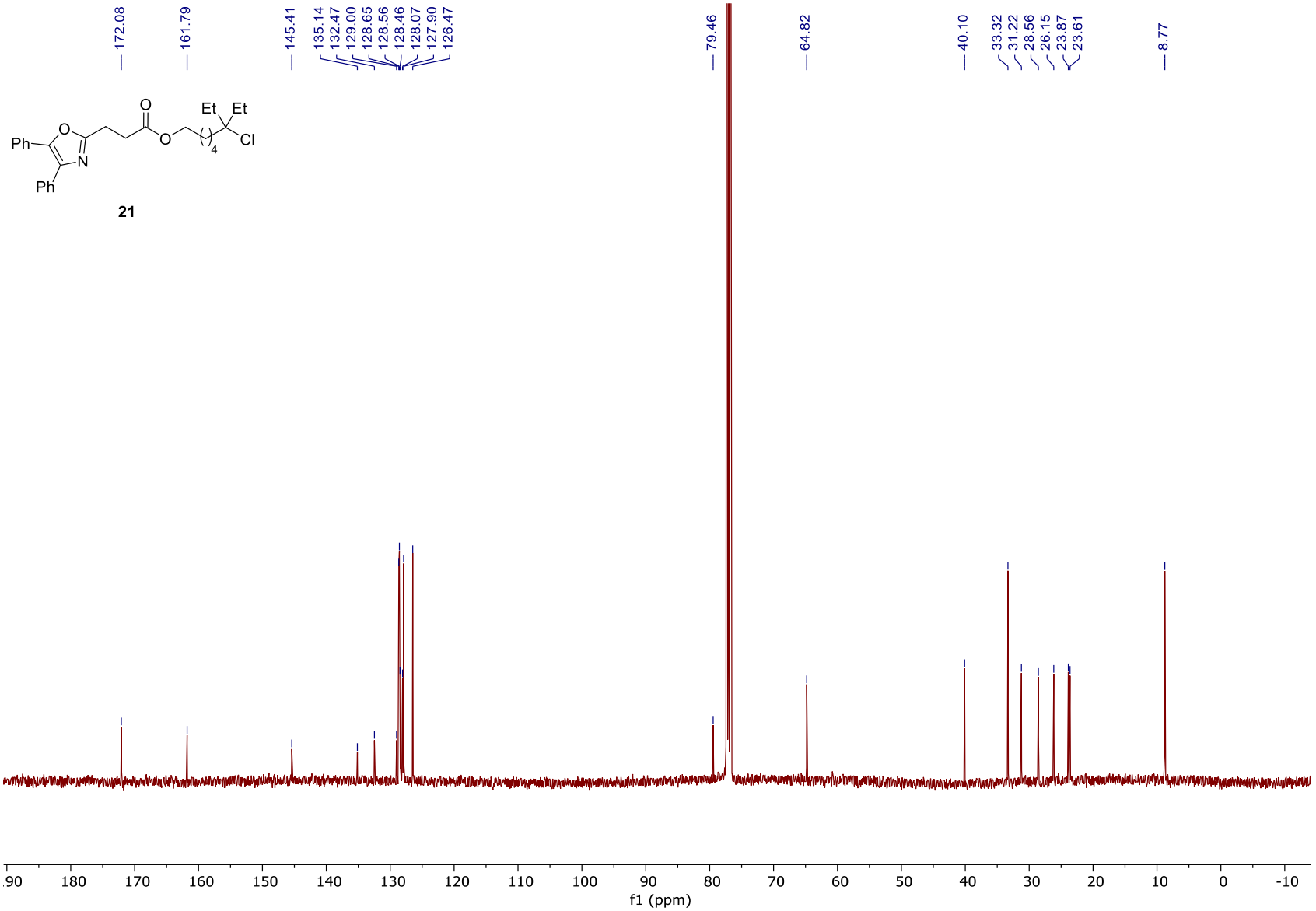
2.02
2.03
2.00
1.00
2.04
1.01
2.09
2.21
6.03
5.14
2.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

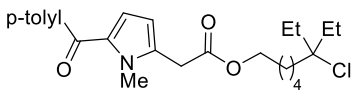

174.82
140.47
137.90
129.30
127.16
71.01
64.56
45.89
45.21
45.05
32.42
30.21
28.47
25.88
24.70
22.41
18.47
i-Bu
O
O
Me
Me
Me
Cl
4
Me
20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Et
Et
Ph
O
O
4
Cl
N
Ph

21

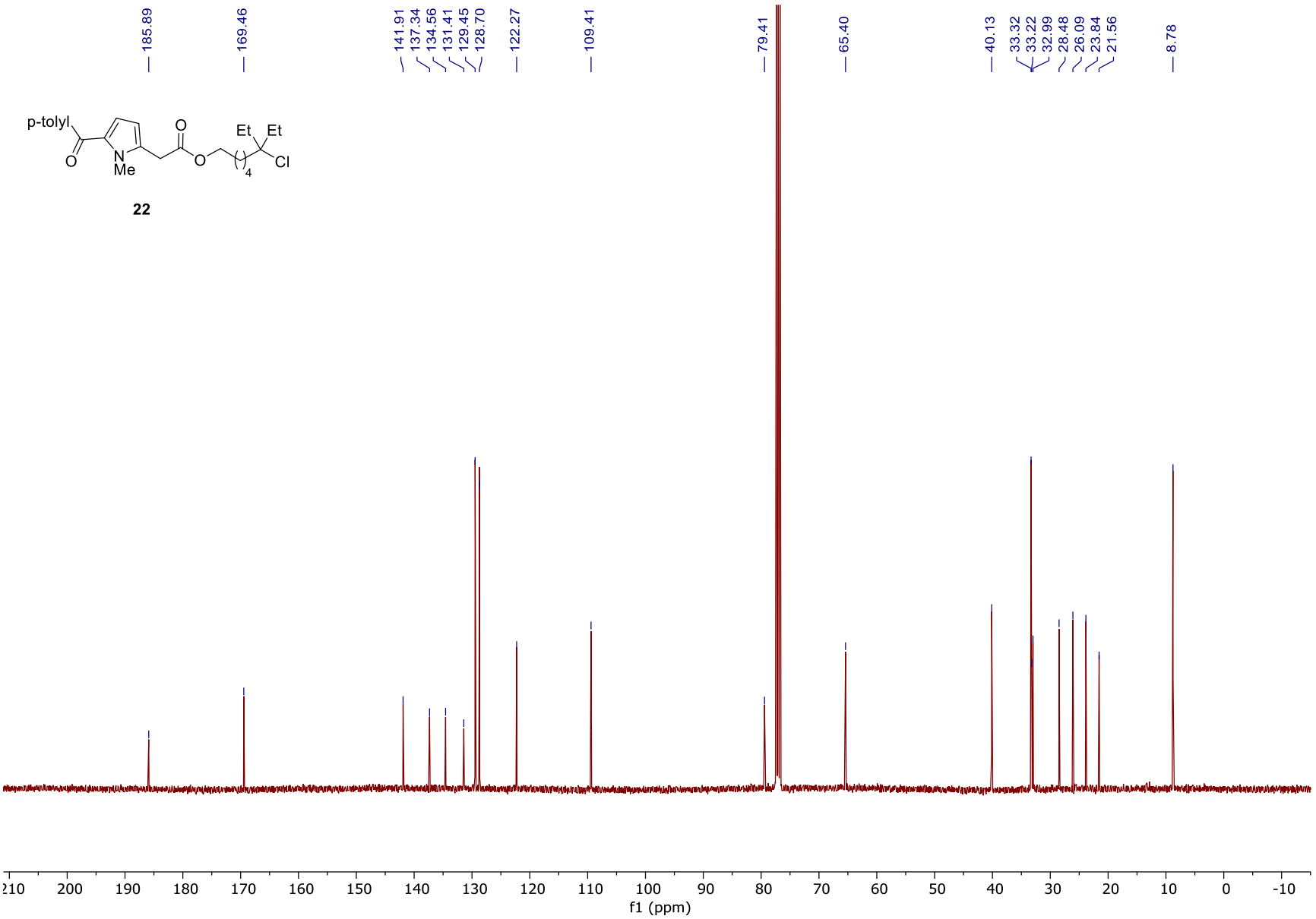

2.04
2.05
2.00
2.07
2.07
4.01
3.98
4.08
6.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

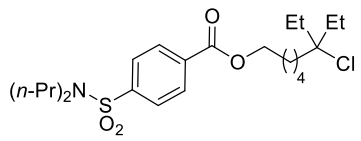

172.08
161.79
145.41
135.14
132.47
129.00
128.65
128.56
128.46
128.07
127.90
126.47
79.46
64.82
40.10
33.32
31.22
28.56
26.15
23.87
23.61
8.77
Ph
O
N
Ph
O
O
Et
Et
Cl
4
21
f1 (ppm)


p-tolyl
O
N
Me
O
O
Et
Et
Cl
4

22

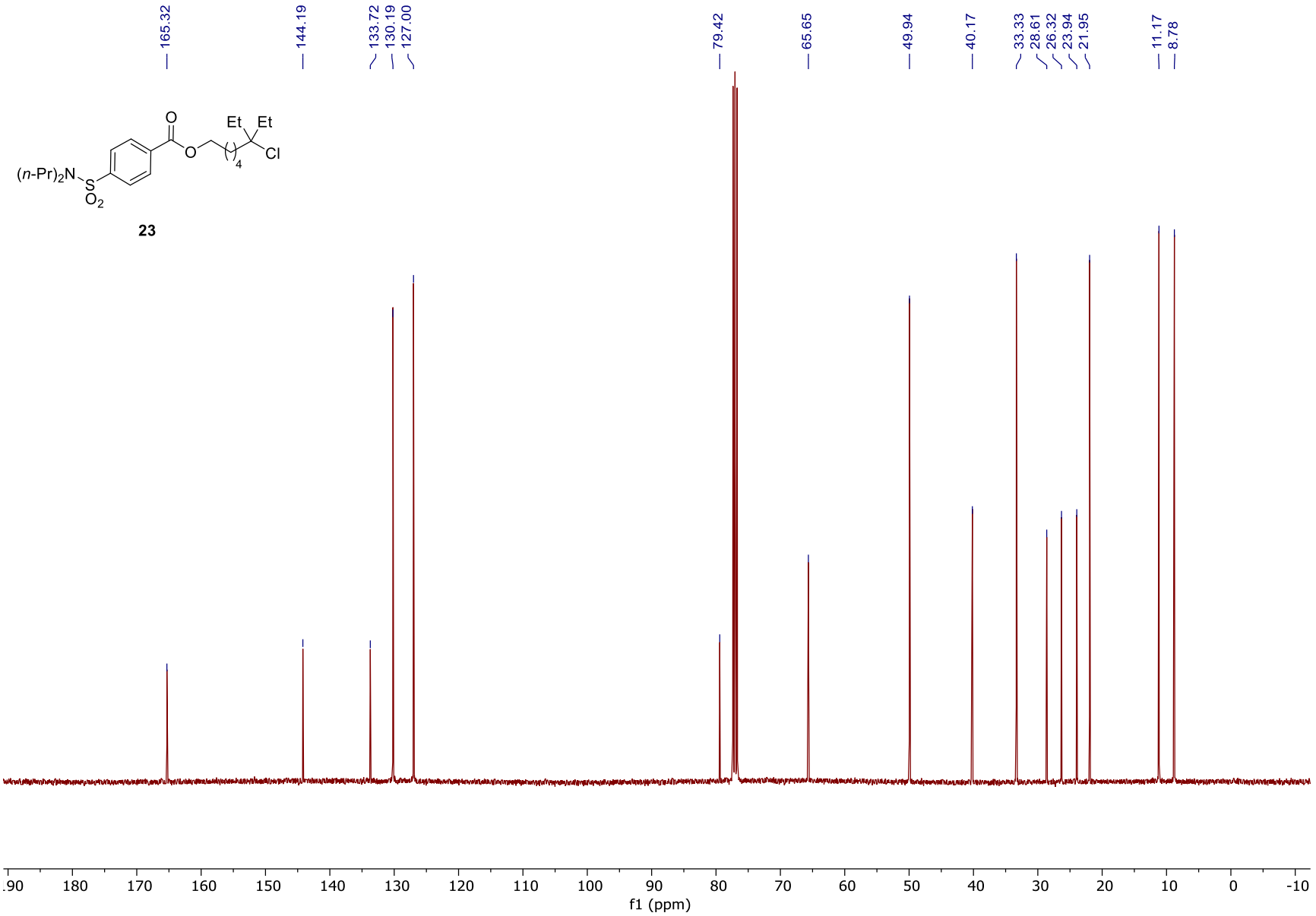
2.01
2.01
1.00
0.99
2.06
3.02
1.99
3.04
3.95
4.01
4.21
6.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

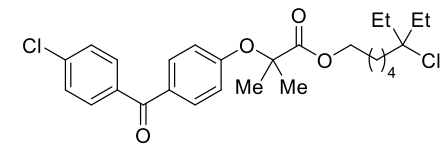

185.89
169.46
141.91
137.34
134.56
131.41
129.45
128.70
122.27
109.41
79.41
65.40
40.13
33.32
33.22
32.99
28.48
26.09
23.84
21.56
8.78
p-tolyl
O
N
Me
O
O
Et
Et
Cl
4
22
f1 (ppm)


O
Et
Et
O
4
Cl
(n-Pr)2N
S
O2

23

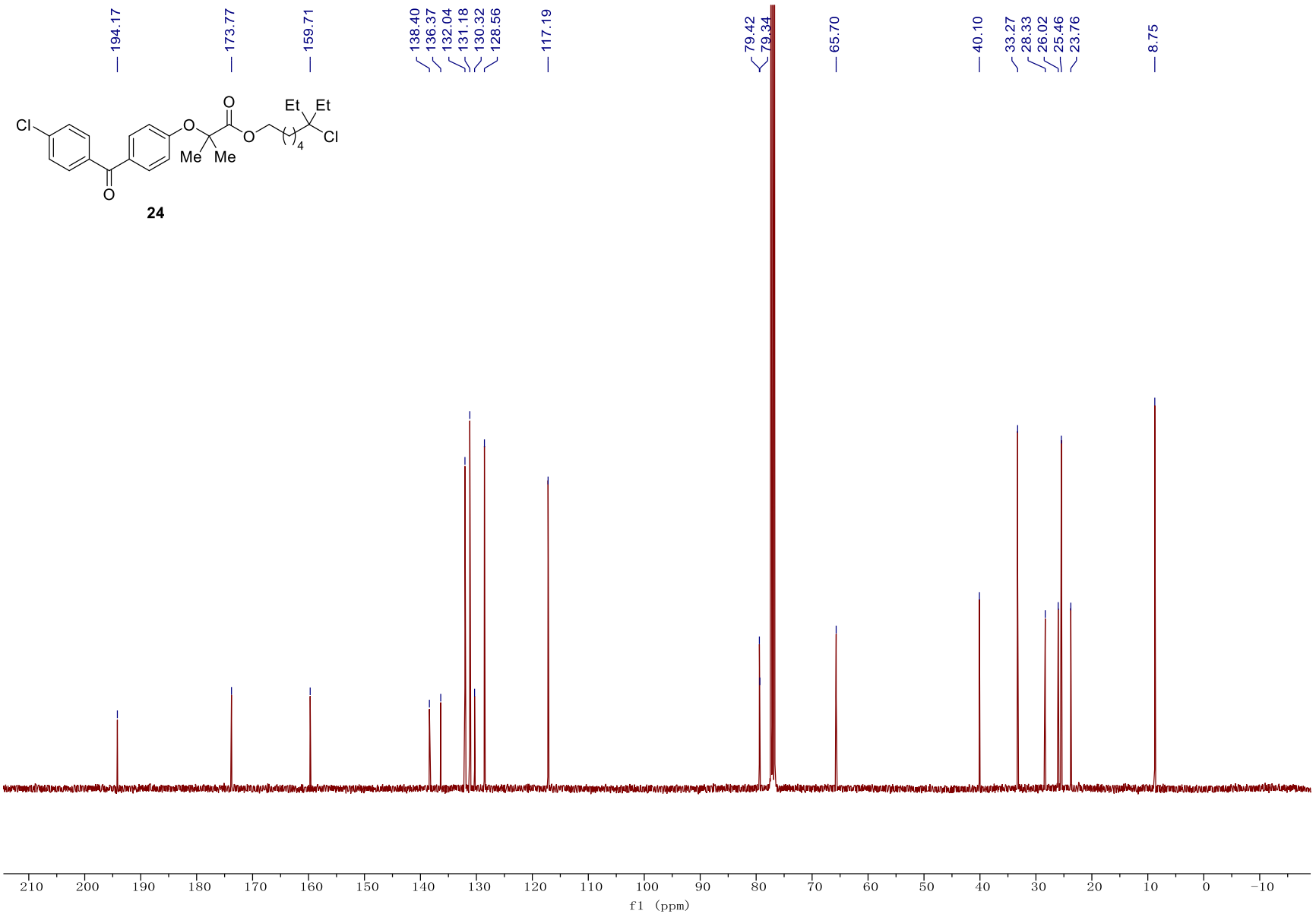
1.99
2.00
1.99
4.02
8.06
8.81
6.05
6.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

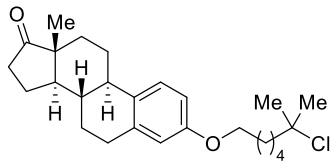

165.32
144.19
133.72
130.19
127.00
79.42
65.65
49.94
40.17
33.33
28.61
26.32
23.94
21.95
11.17
8.78
O
Et
Et
O
Cl
4
(n-Pr)2N
S
O2
23
f1 (ppm)


Cl
O
O
Me
Me
O
O
Et
Et
Cl
4
O

24

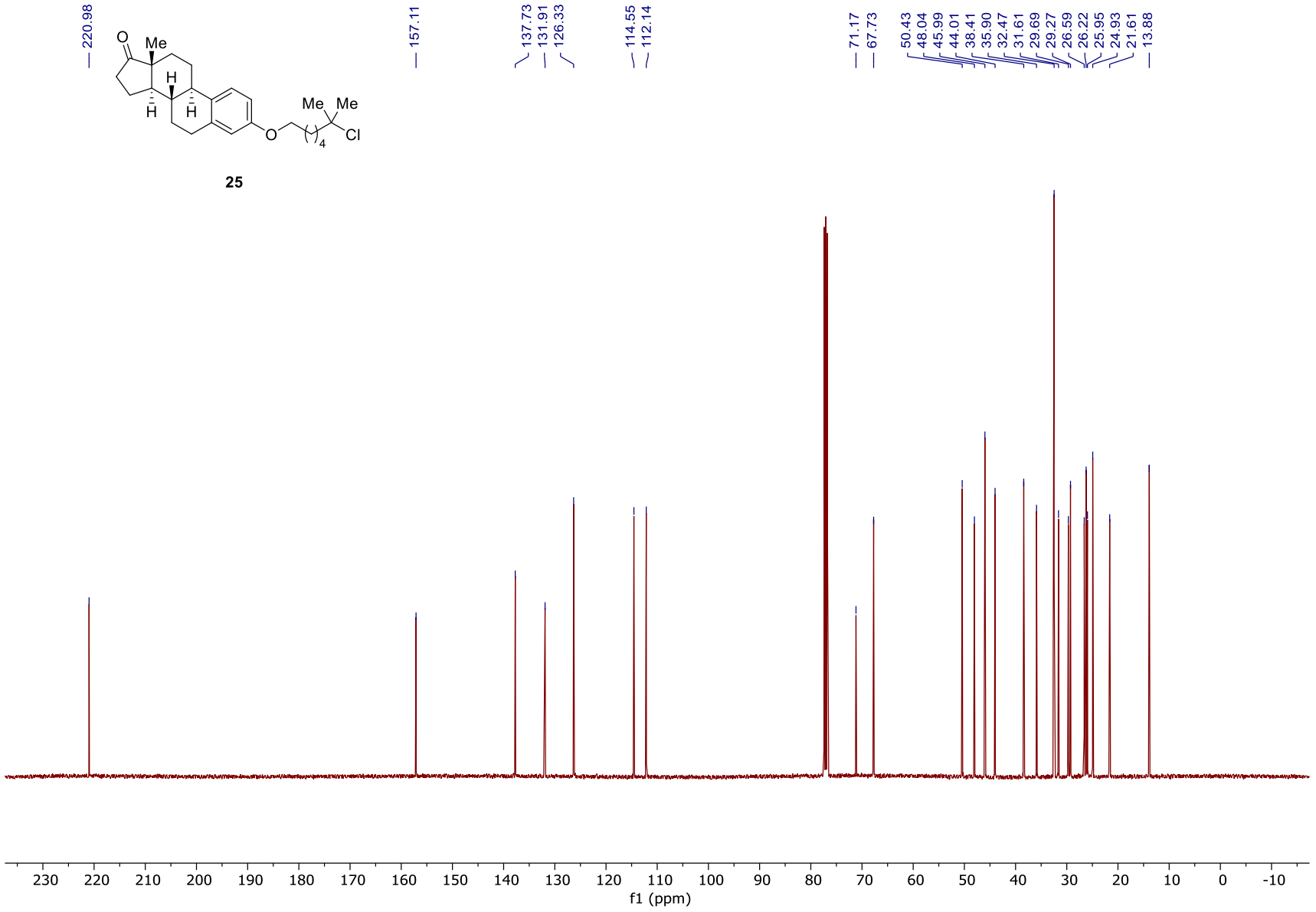
4.04
2.00
1.99
2.01
4.12
5.91
4.01
2.05
2.12
6.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

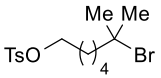

194.17
173.77
159.71
138.40
136.37
132.04
131.18
130.32
128.56
117.19
79.42
79.34
65.70
40.10
33.27
28.33
26.02
25.46
23.76
8.75
Cl
O
O
Et
Et
Cl
Me
Me
4
O
24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
Me
H
H
H
Me
Me
O
4
Cl

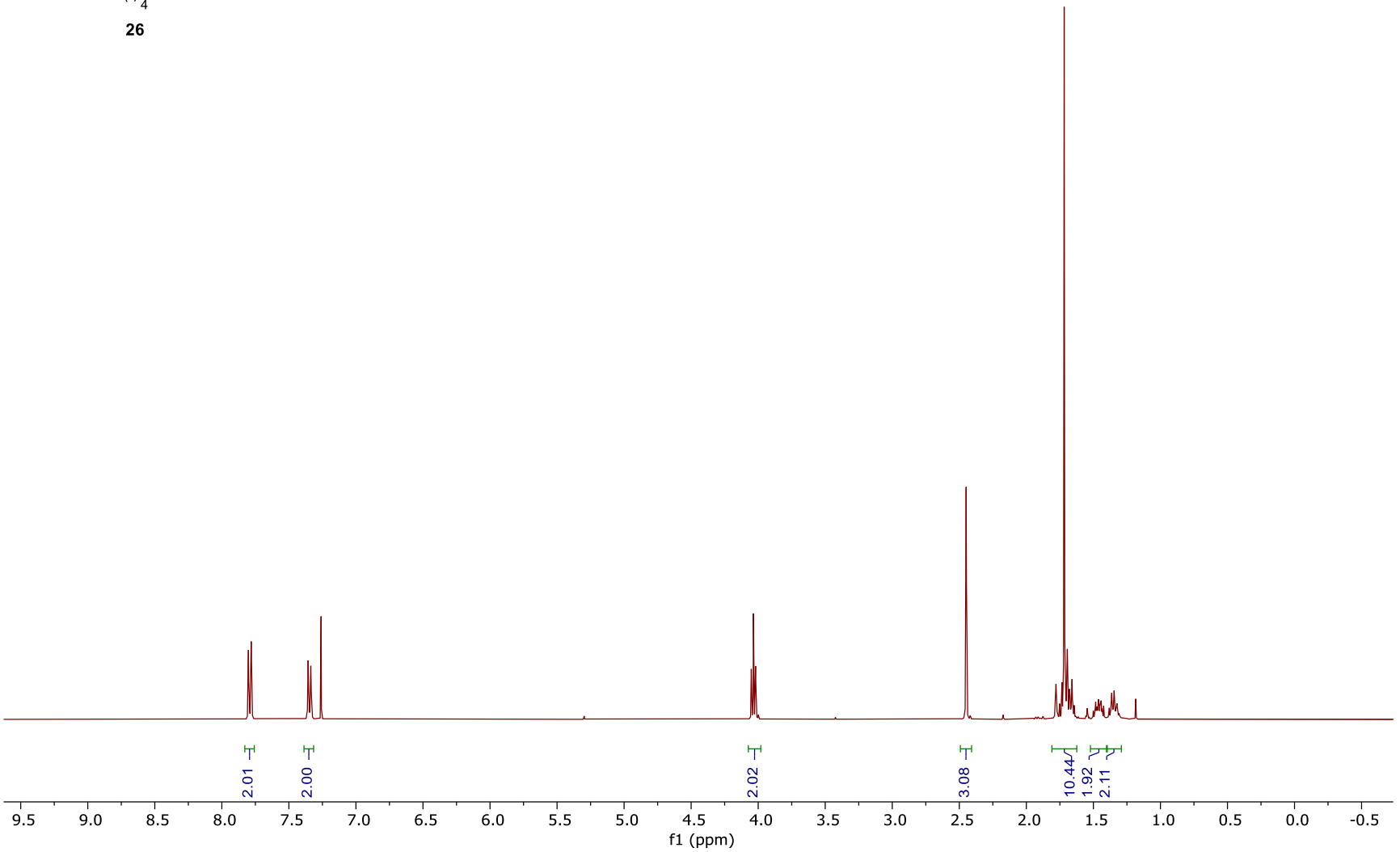
25

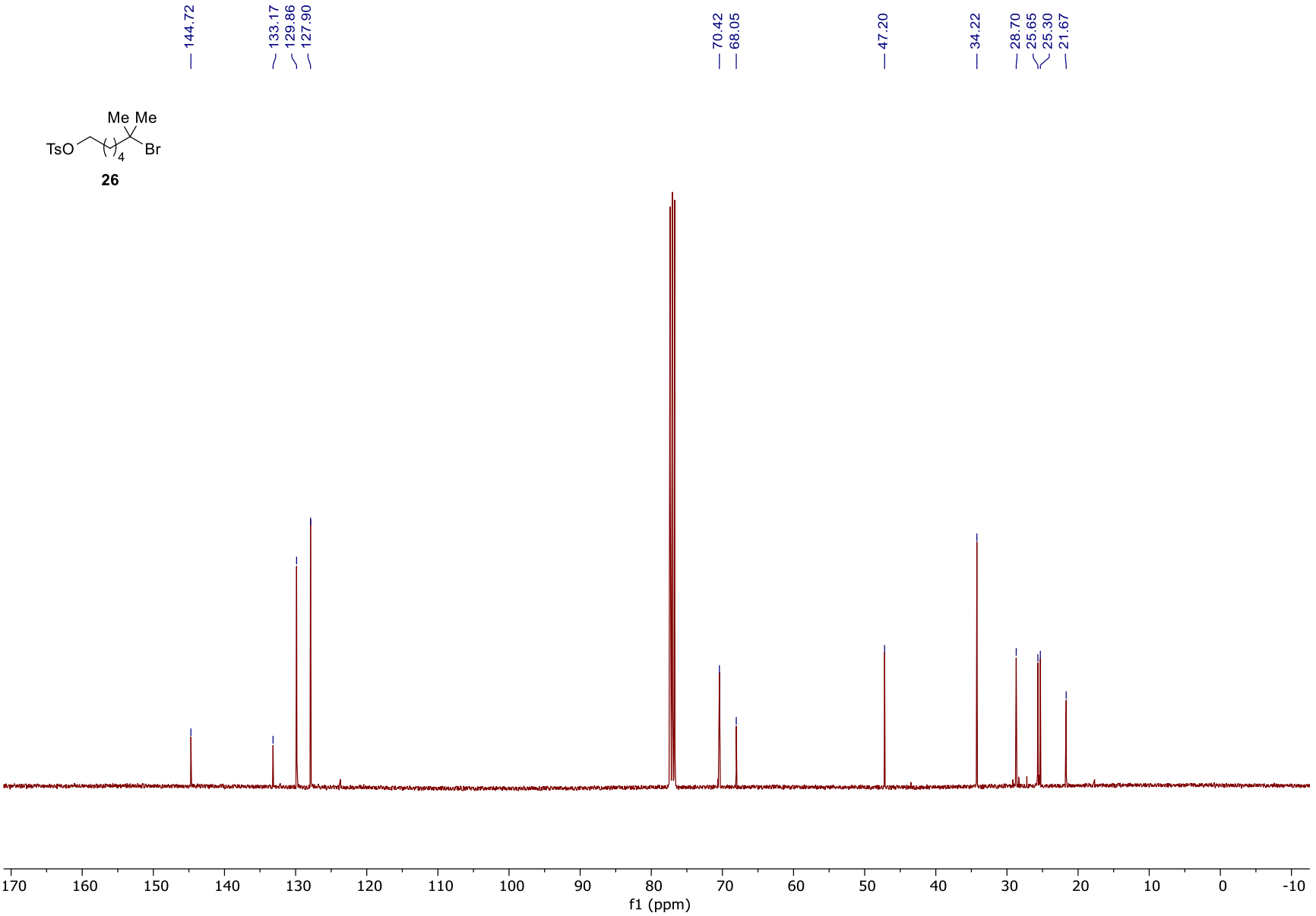
1.00
1.01
1.01
2.04
1.97
1.00
0.98
1.01
1.03
3.10
4.16
16.75
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

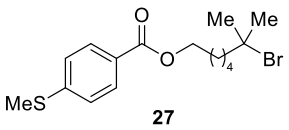

220.98
157.11
137.73
131.91
126.33
114.55
112.14
71.17
67.73
50.43
48.04
45.99
44.01
38.41
35.90
32.47
31.61
29.69
29.27
26.59
26.22
25.95
24.93
21.61
13.88
O
Me
H
H
H
Me
Me
O
4
Cl
25
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me Me
TsO
4
Br

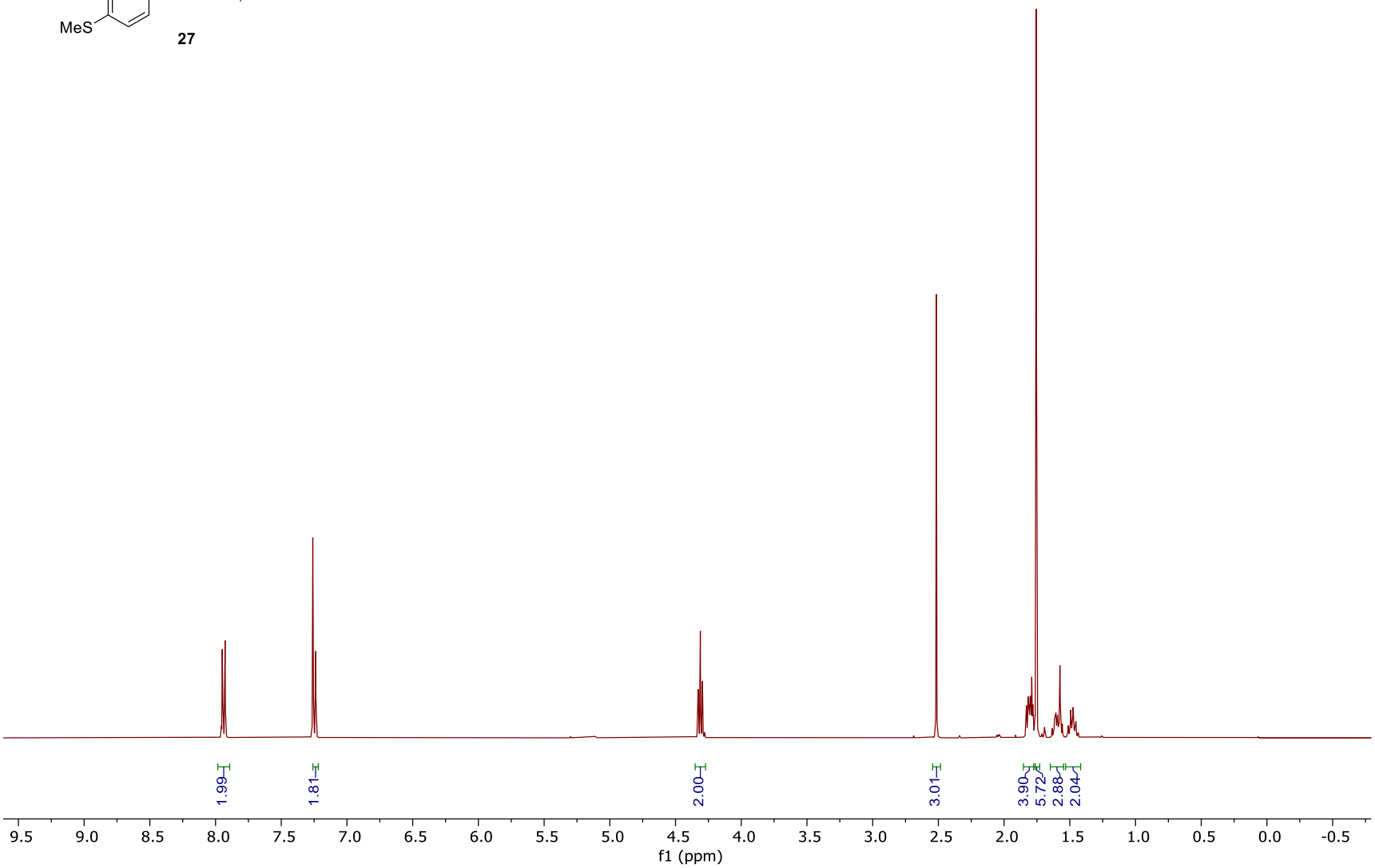
26

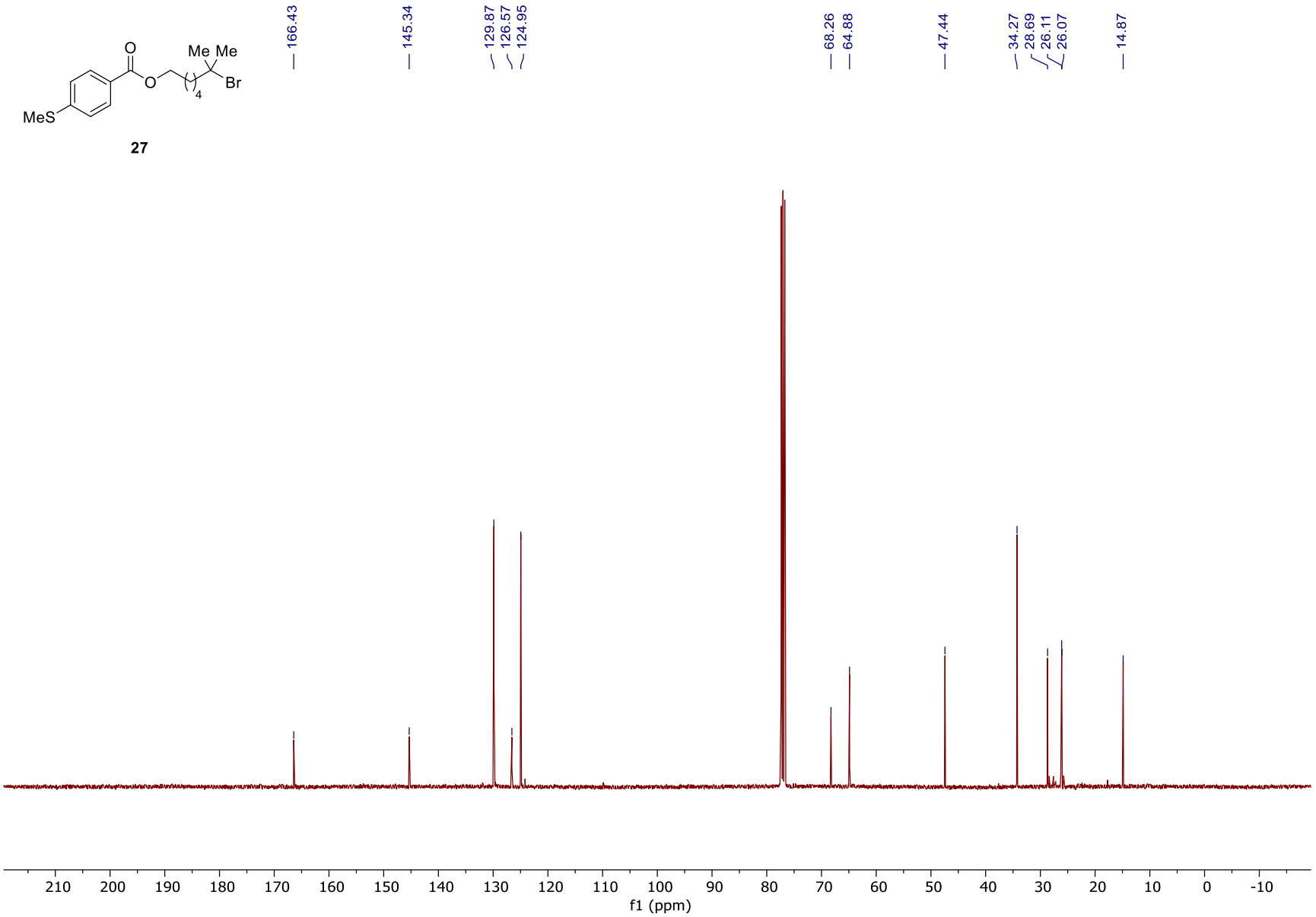

2.01
2.00
2.02
3.08
10.44
1.92
2.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

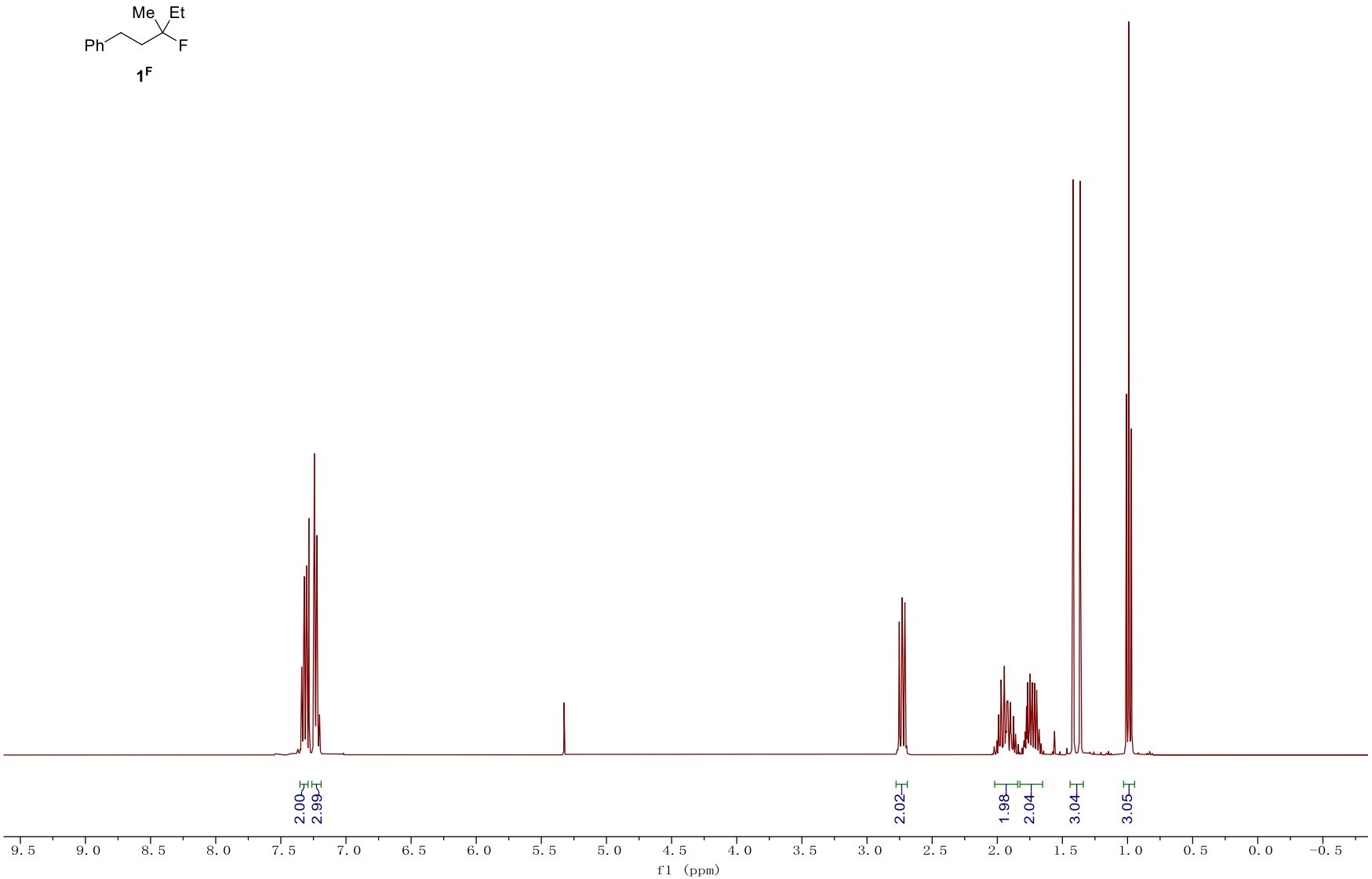

144.72
133.17
129.86
127.90
70.42
68.05
47.20
34.22
28.70
25.65
25.30
21.67
Me Me
TsO
Br
4
26
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

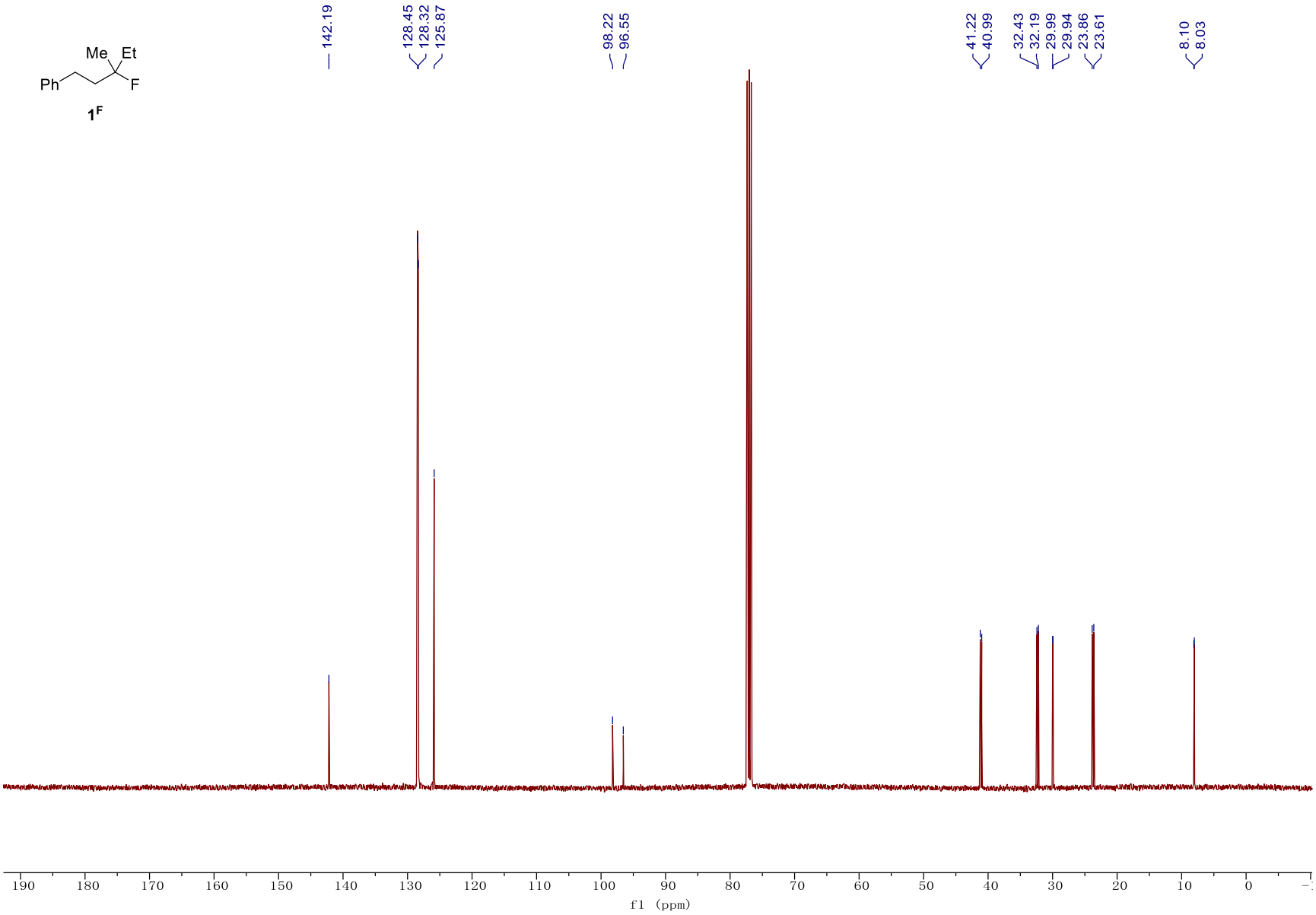

O
Me
Me
O
4
Br
MeS

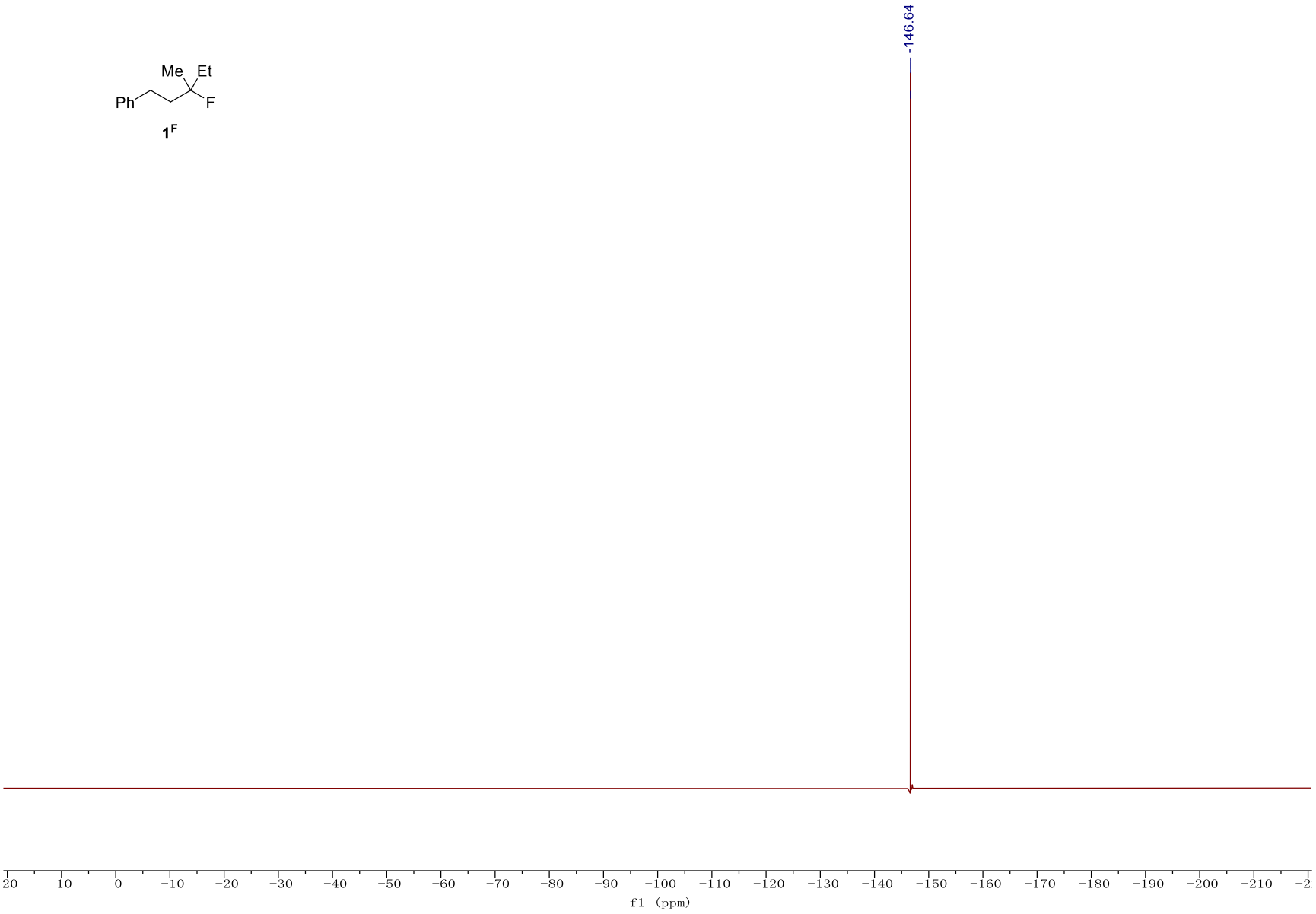
27

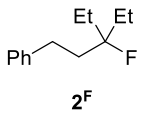

1.99
1.81
2.00
3.01
3.90
5.72
2.88
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.43
145.34
129.87
126.57
124.95
68.26
64.88
47.44
34.27
28.69
26.11
26.07
14.87
O
Me Me
O
Br
4
MeS
27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Et
Ph
F
1F
2.00
2.99
2.02
1.98
2.04
3.04
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

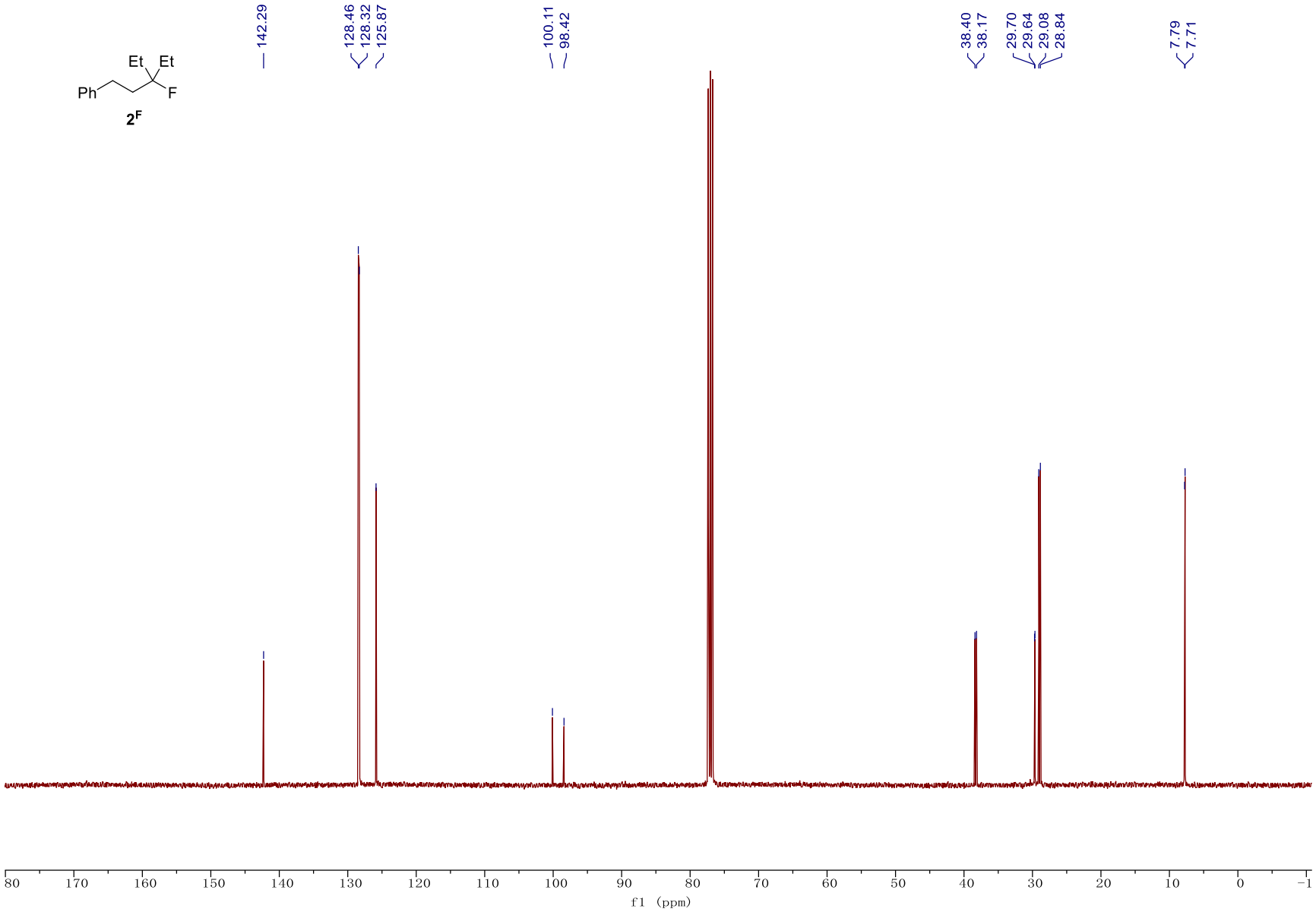

Me
Et
Ph
F
1F
142.19
128.45
128.32
125.87
98.22
96.55
41.22
40.99
32.43
32.19
29.99
29.94
23.86
23.61
8.10
8.03
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

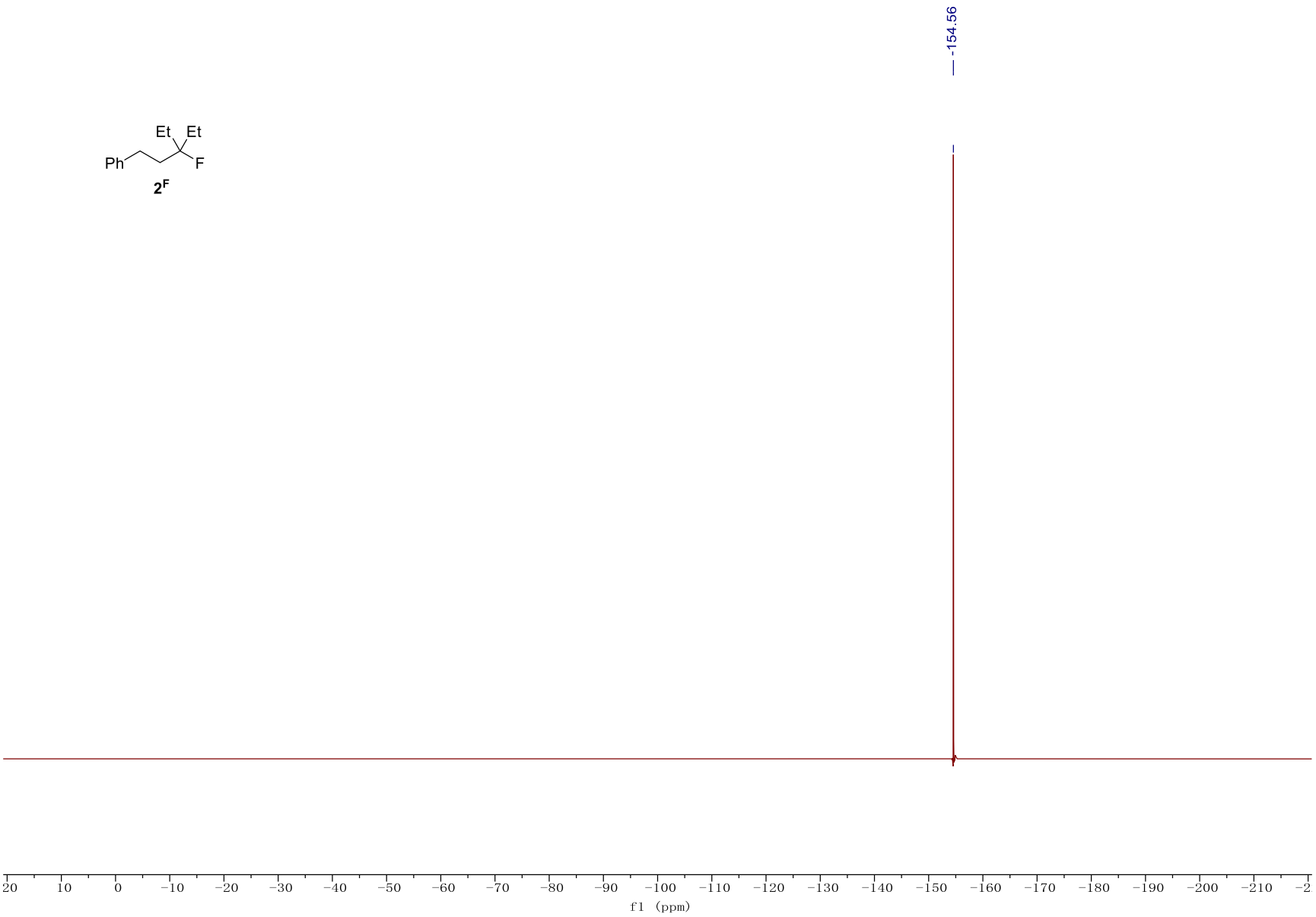

Me
Et
Ph
F
1F
-146.64
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)

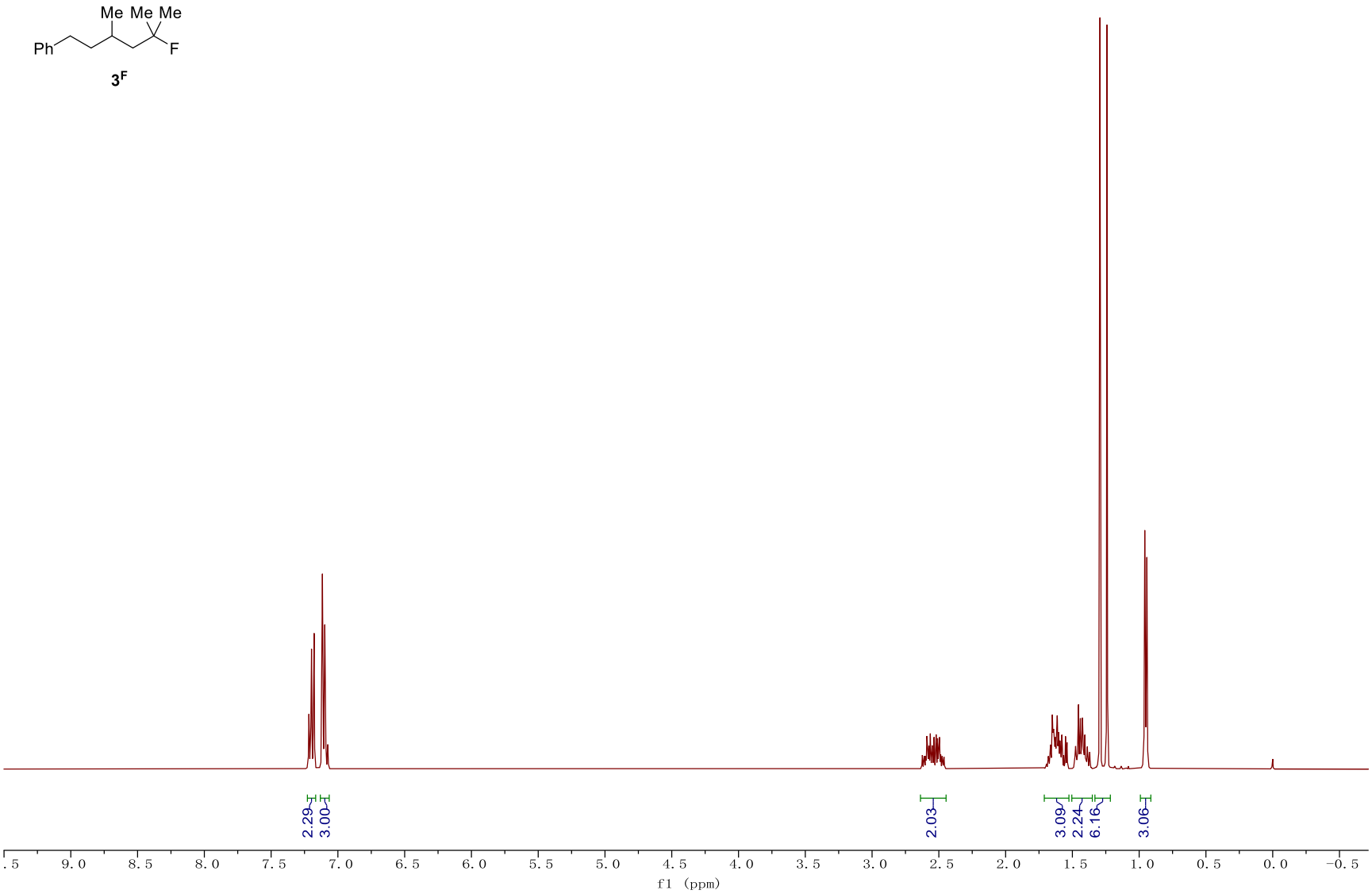

Et
Et
Ph
F

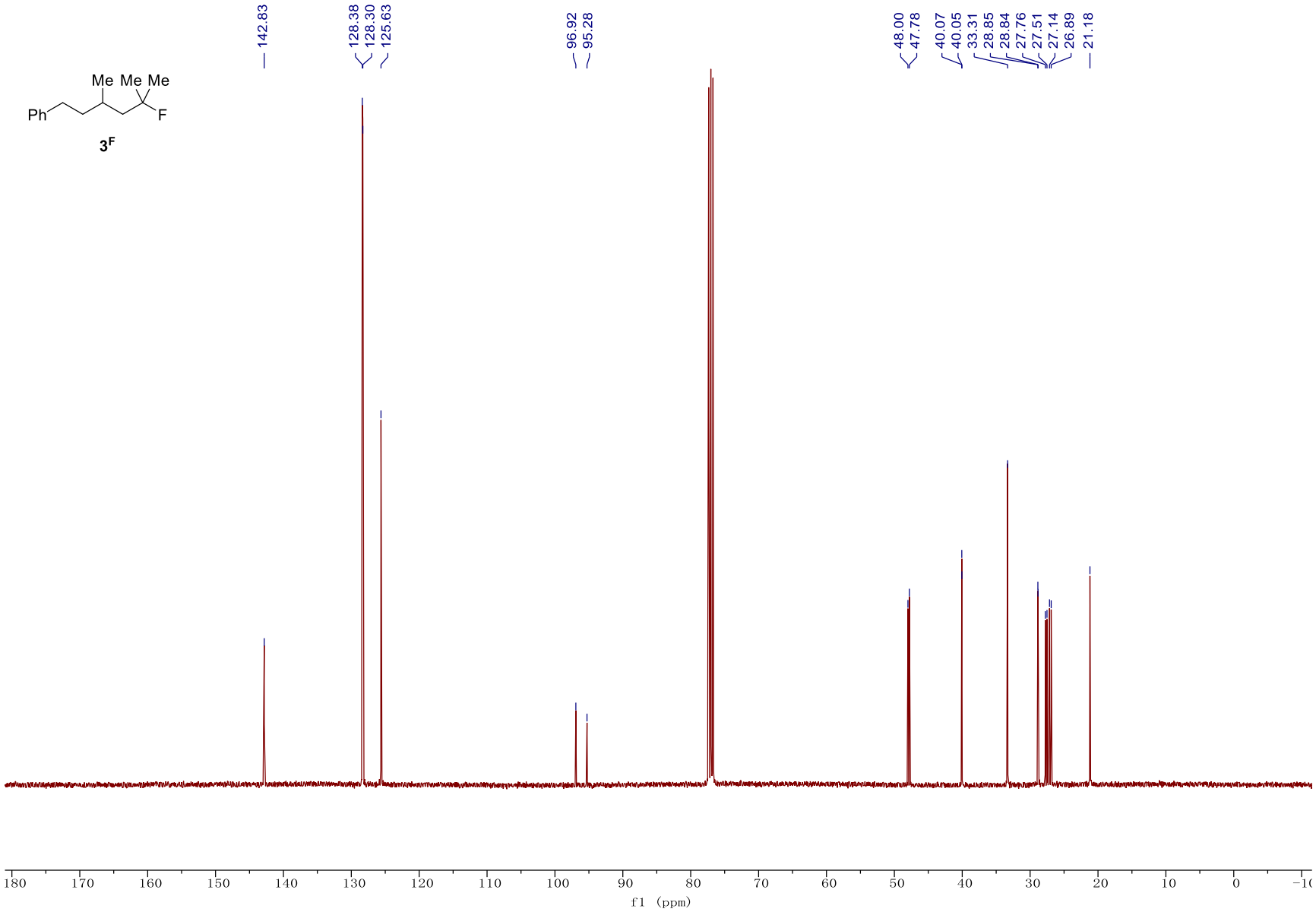
2^{F}

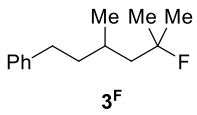
2.00
2.97
2.00
2.04
4.03
6.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.29
128.46
128.32
125.87
100.11
98.42
38.40
38.17
29.70
29.64
29.08
28.84
7.79
7.71
Et
Et
Ph
F
2F
f1 (ppm)


-154.56
Et
Et
Ph
F
2F
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

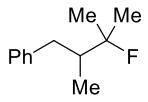

Me Me Me
Ph
F
3F
2.29
3.00
2.03
3.09
2.24
6.16
3.06
f1 (ppm)


142.83
128.38
128.30
125.63
96.92
95.28
48.00
47.78
40.07
40.05
33.31
28.85
28.84
27.76
27.51
27.14
26.89
21.18
Me Me Me
Ph
F
3F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

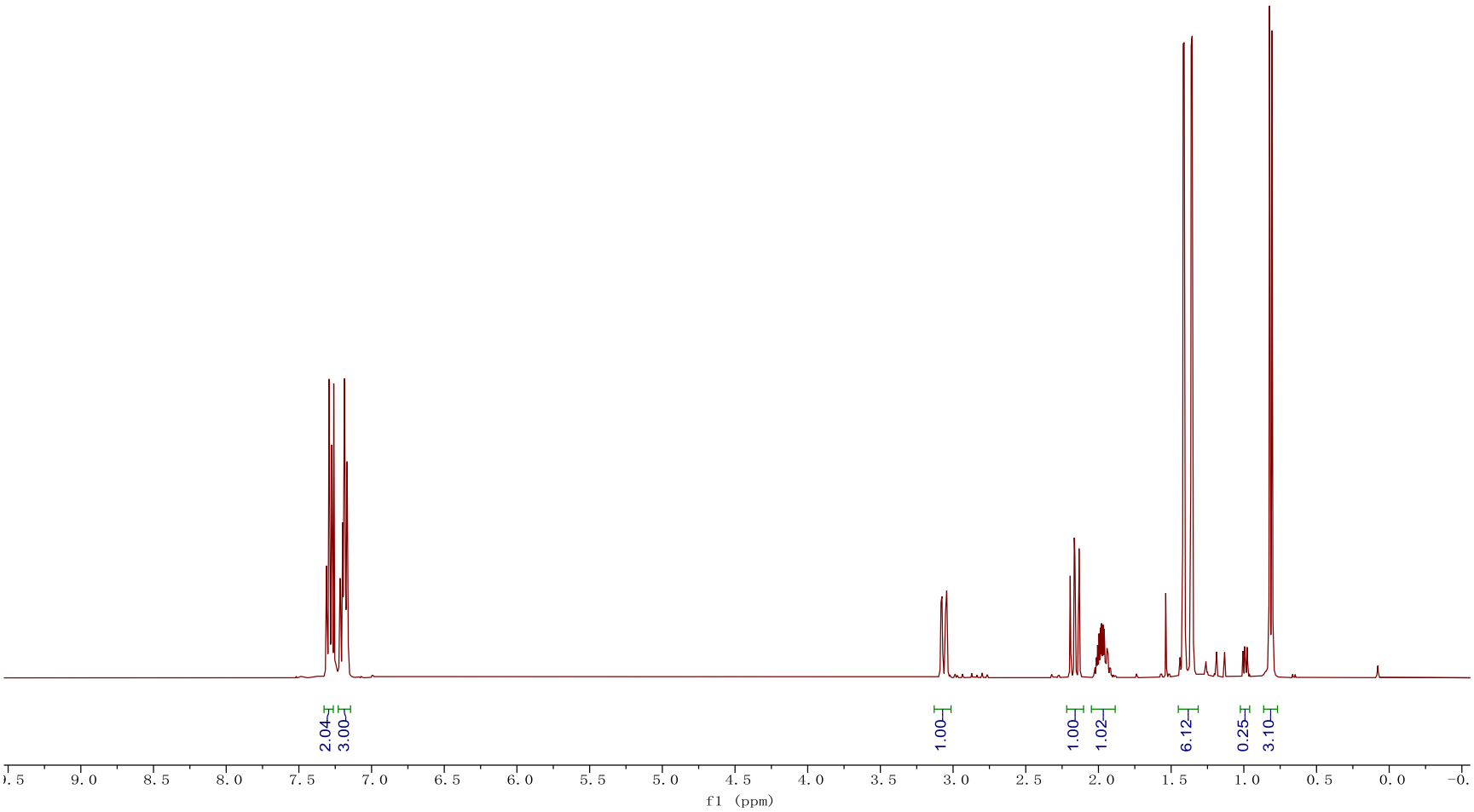

Me Me Me
Ph
F

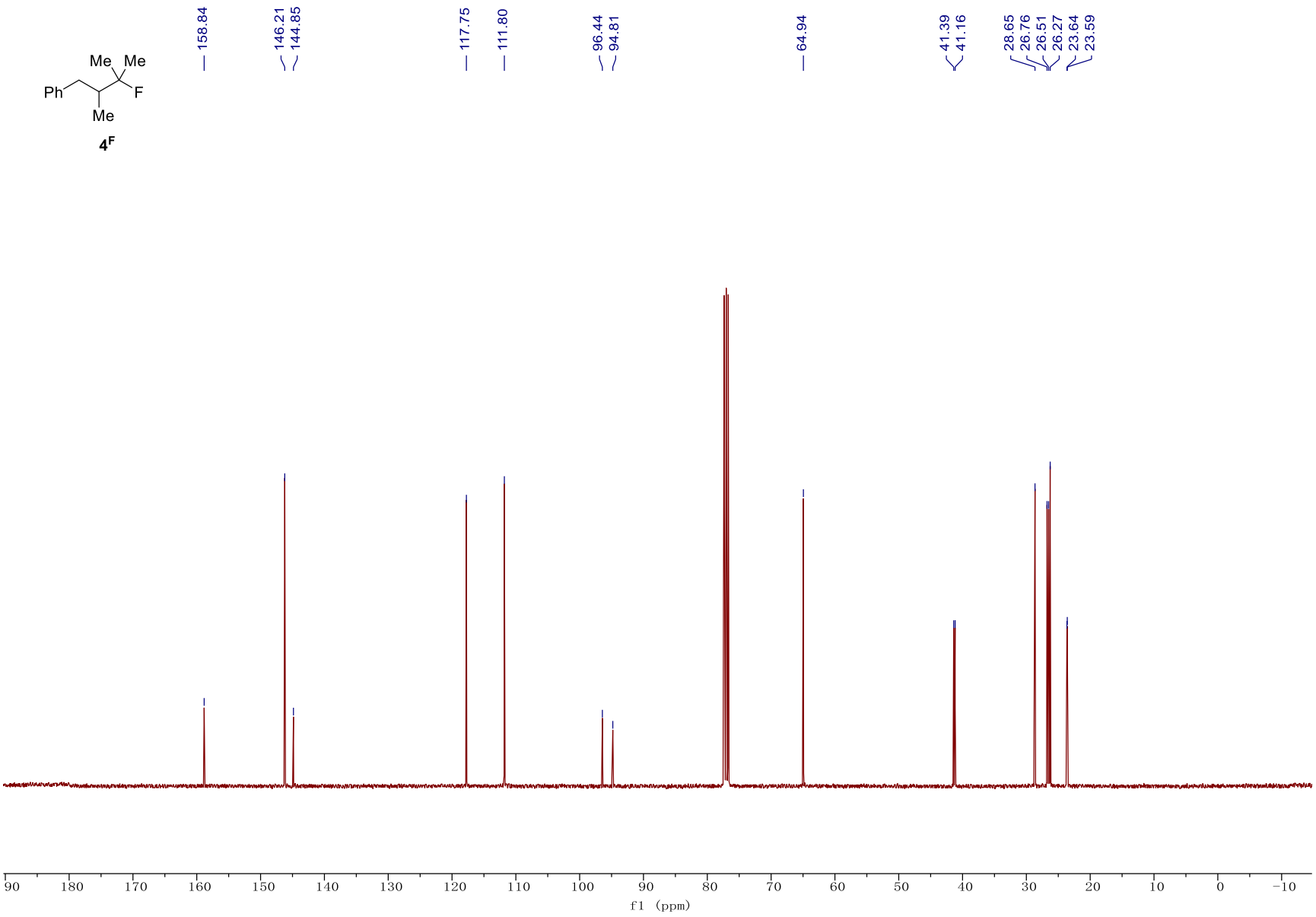
3^{F}

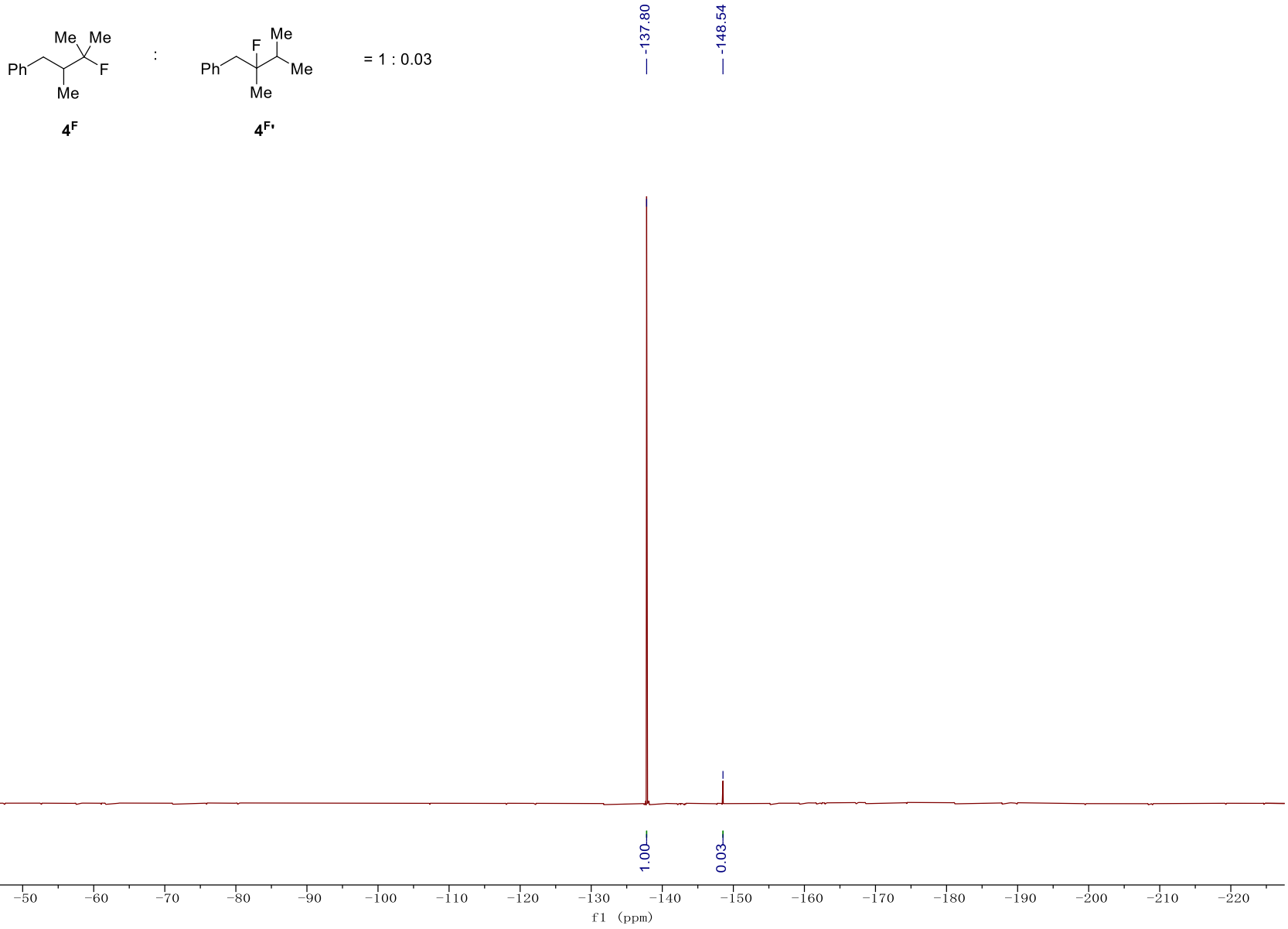
-135.77
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

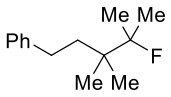

Me
Me
Ph
F
Me

4^{F}

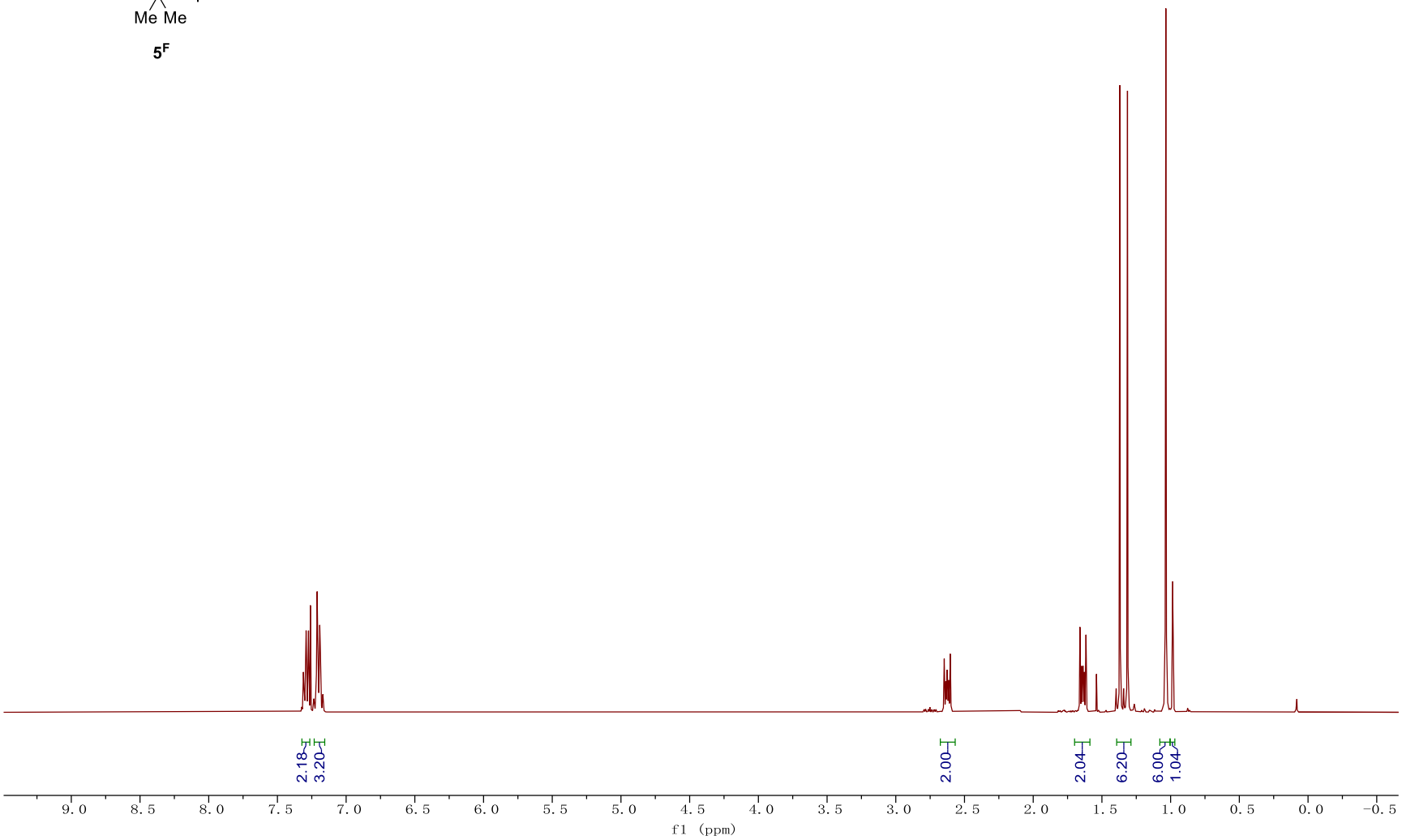

2.04
3.00
1.00
1.00
1.02
6.12
0.25
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

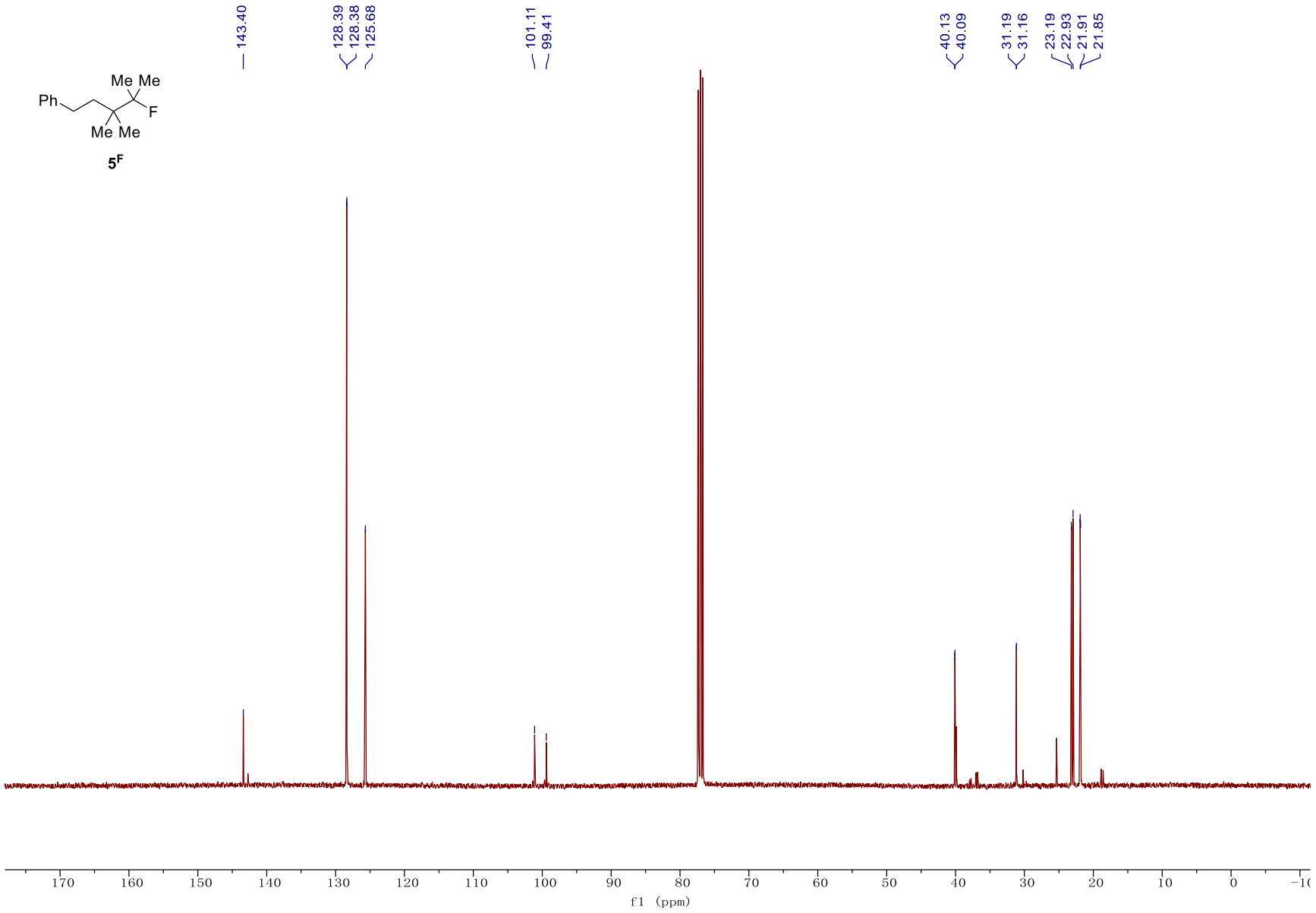

Me
Me
Ph
F
Me
4F
158.84
146.21
144.85
117.75
111.80
96.44
94.81
64.94
41.39
41.16
28.65
26.76
26.51
26.27
23.64
23.59
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

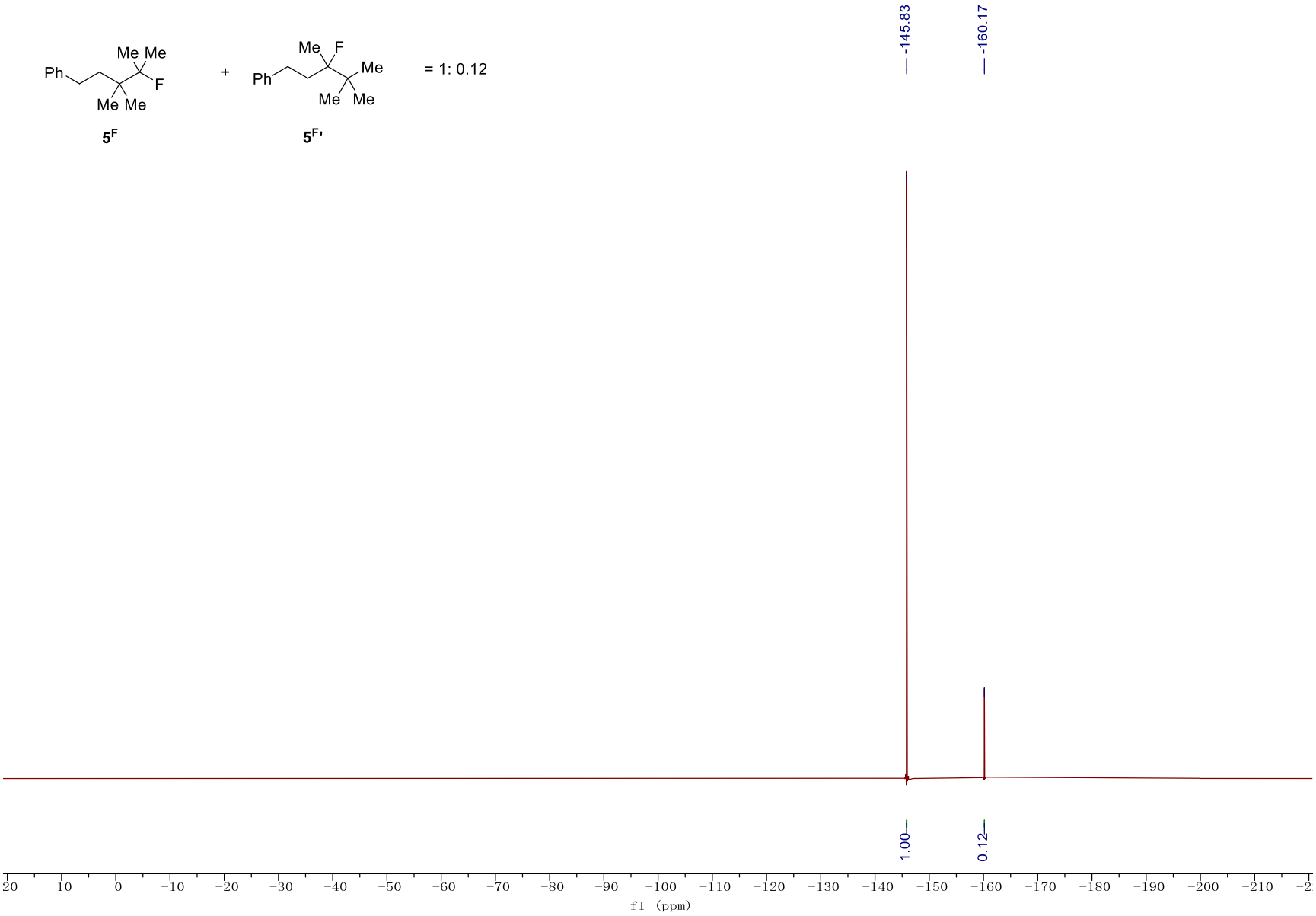

Me
Me
Ph
F
Me
4F
:
F
Me
Ph
Me
Me
4F'
= 1 : 0.03
-137.80
-148.54
1.00
0.03
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

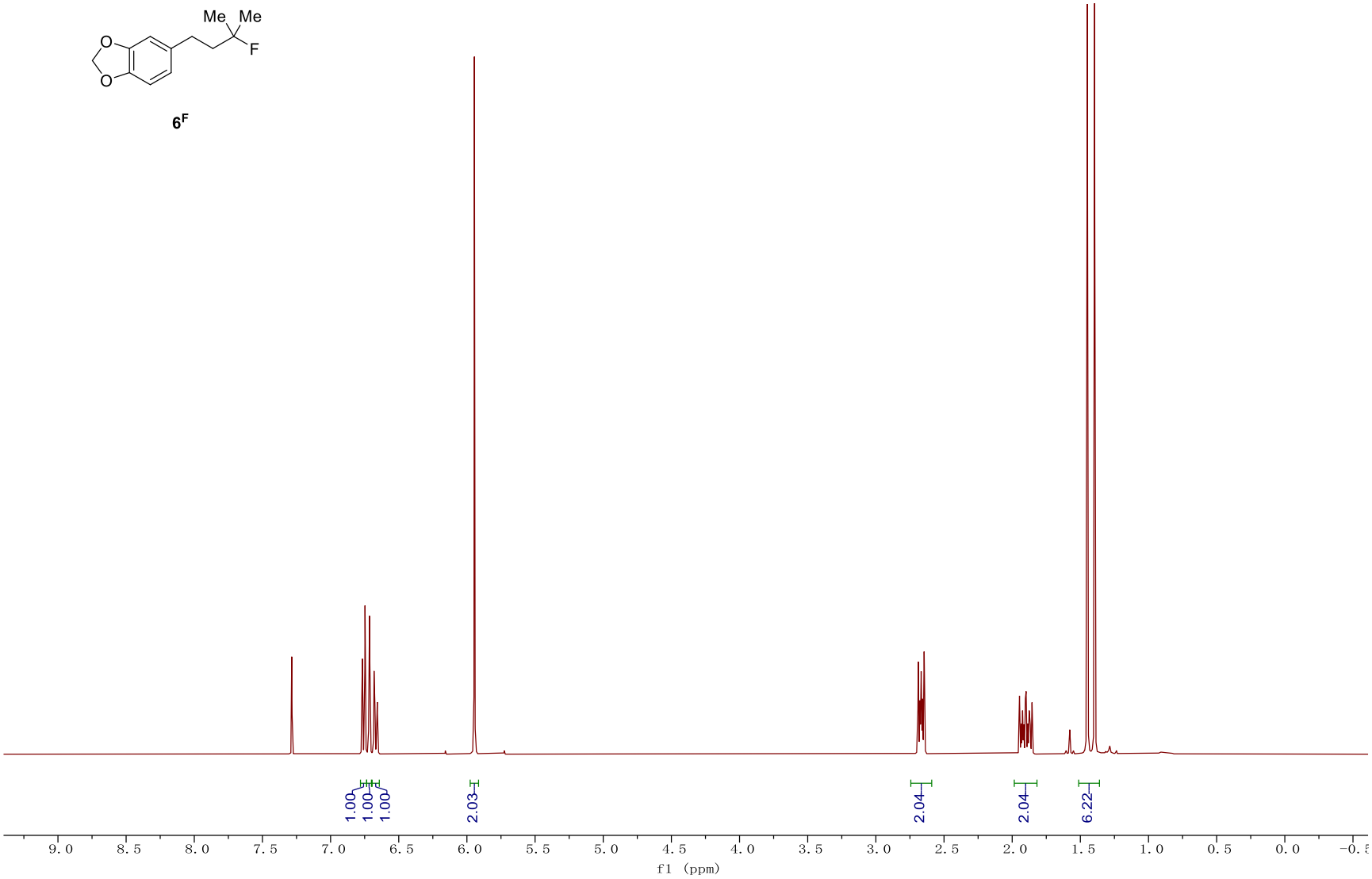

Me Me
Ph
F
Me Me

5^{F}

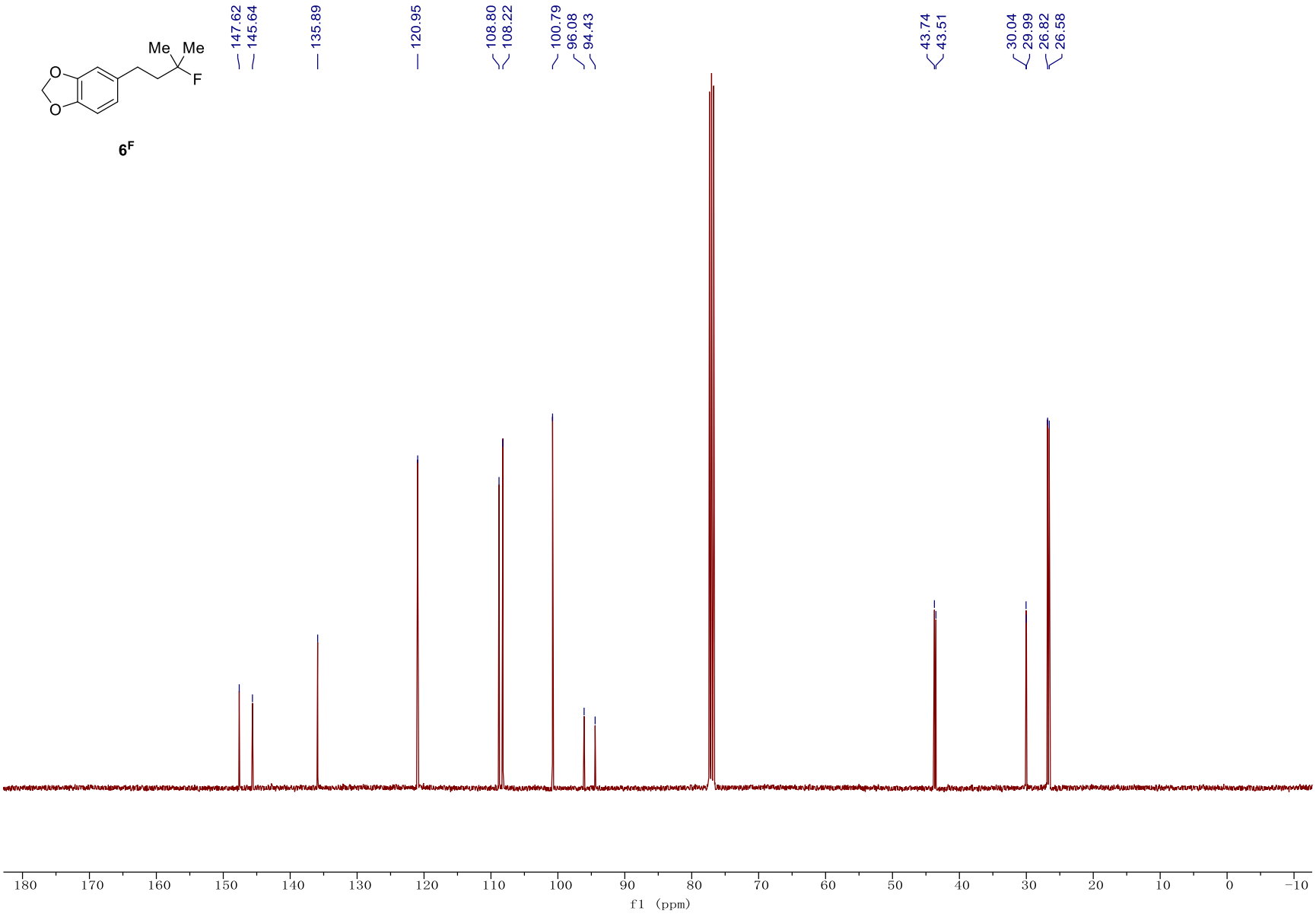

2.18
3.20
2.00
2.04
6.20
6.00
1.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

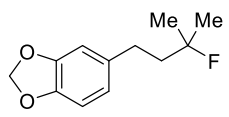

143.40
128.39
128.38
125.68
101.11
99.41
40.13
40.09
31.19
31.16
23.19
22.93
21.91
21.85
Ph
Me Me
Me Me
F
5F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Me Me
F
Me Me
5F
+
Ph
Me F
Me
Me Me
5F'
= 1: 0.12
-145.83
-160.17
1.00
0.12
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)


Me
Me
F
O
O
1.00
1.00
1.00
2.03
2.04
2.04
6.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

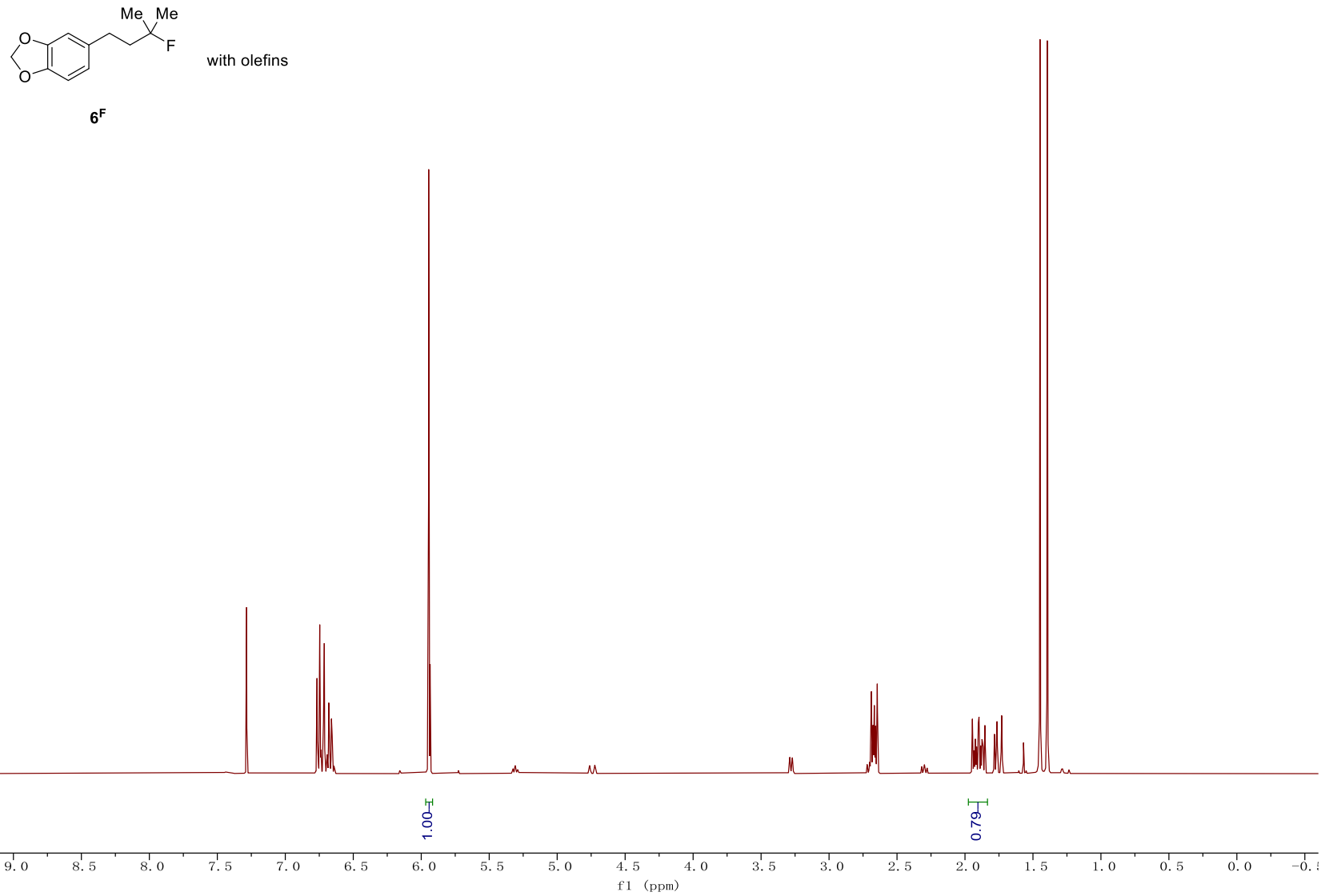
6^{F}


147.62
145.64
135.89
120.95
108.80
108.22
100.79
96.08
94.43
43.74
43.51
30.04
29.99
26.82
26.58
Me Me
F
O
O
6F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

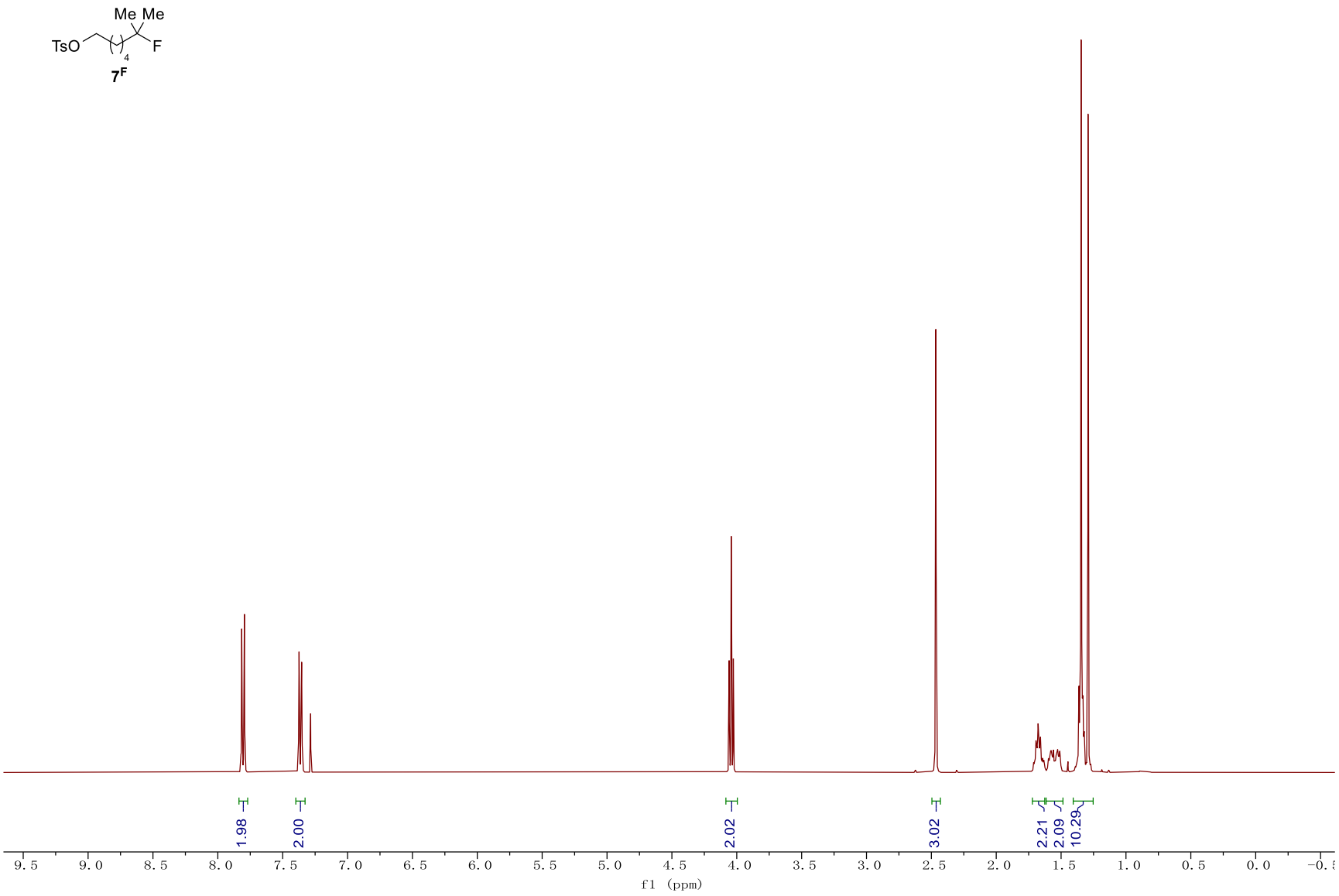

Me
Me
O
O
F

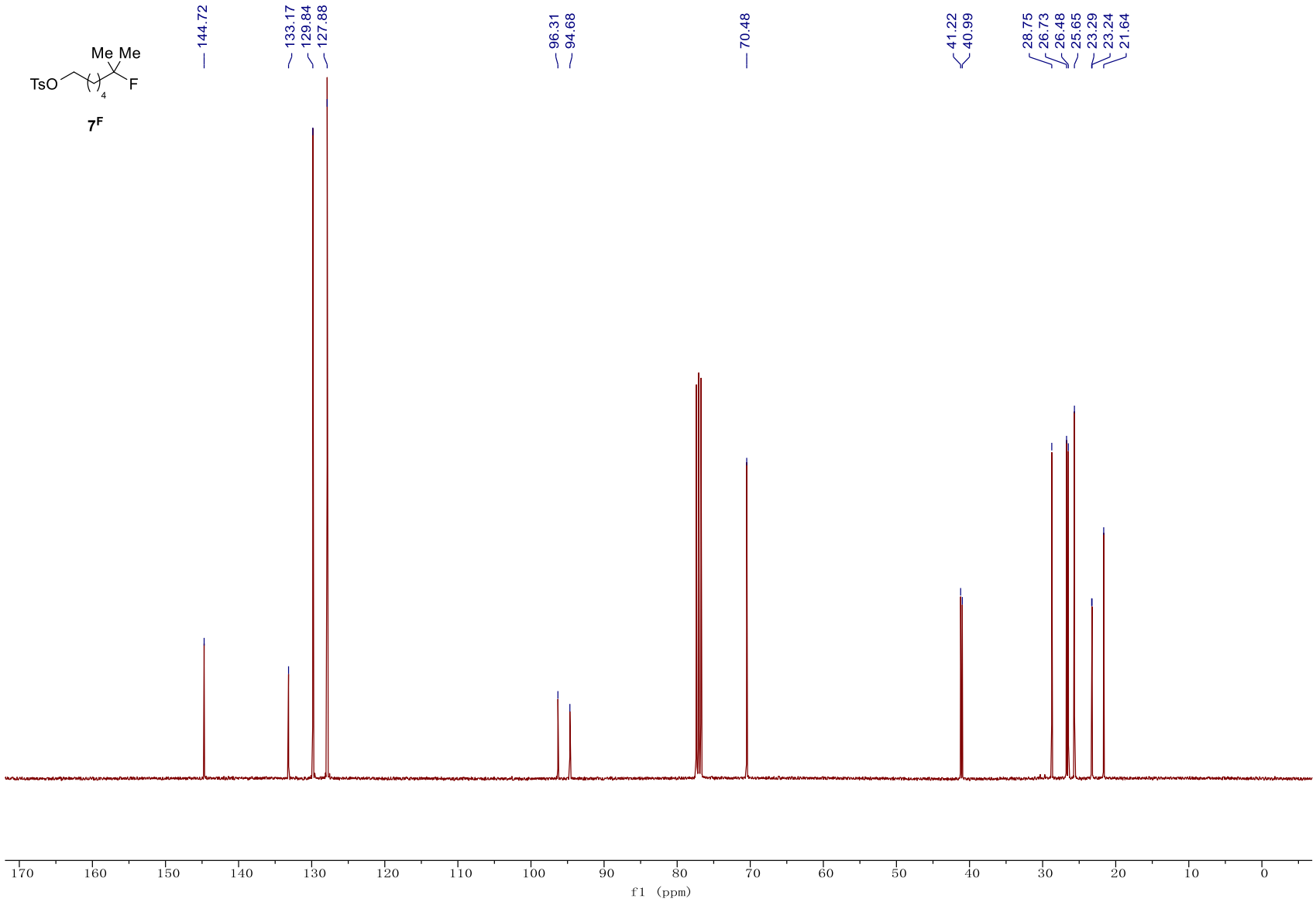
6^{F}

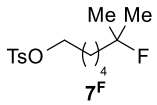
-138.86
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)



A sample spectrum for the determination of yield: 0.79 : 0.21 = 1 : 0.27 alkyl fluoride vs. olefin

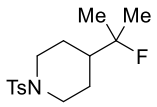

Me Me
TsO
F
4
7F
1.98
2.00
2.02
3.02
2.21
2.09
10.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.72
133.17
129.84
127.88
96.31
94.68
70.48
41.22
40.99
28.75
26.73
26.48
25.65
23.29
23.24
21.64
Me Me
TsO
F
4
7F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

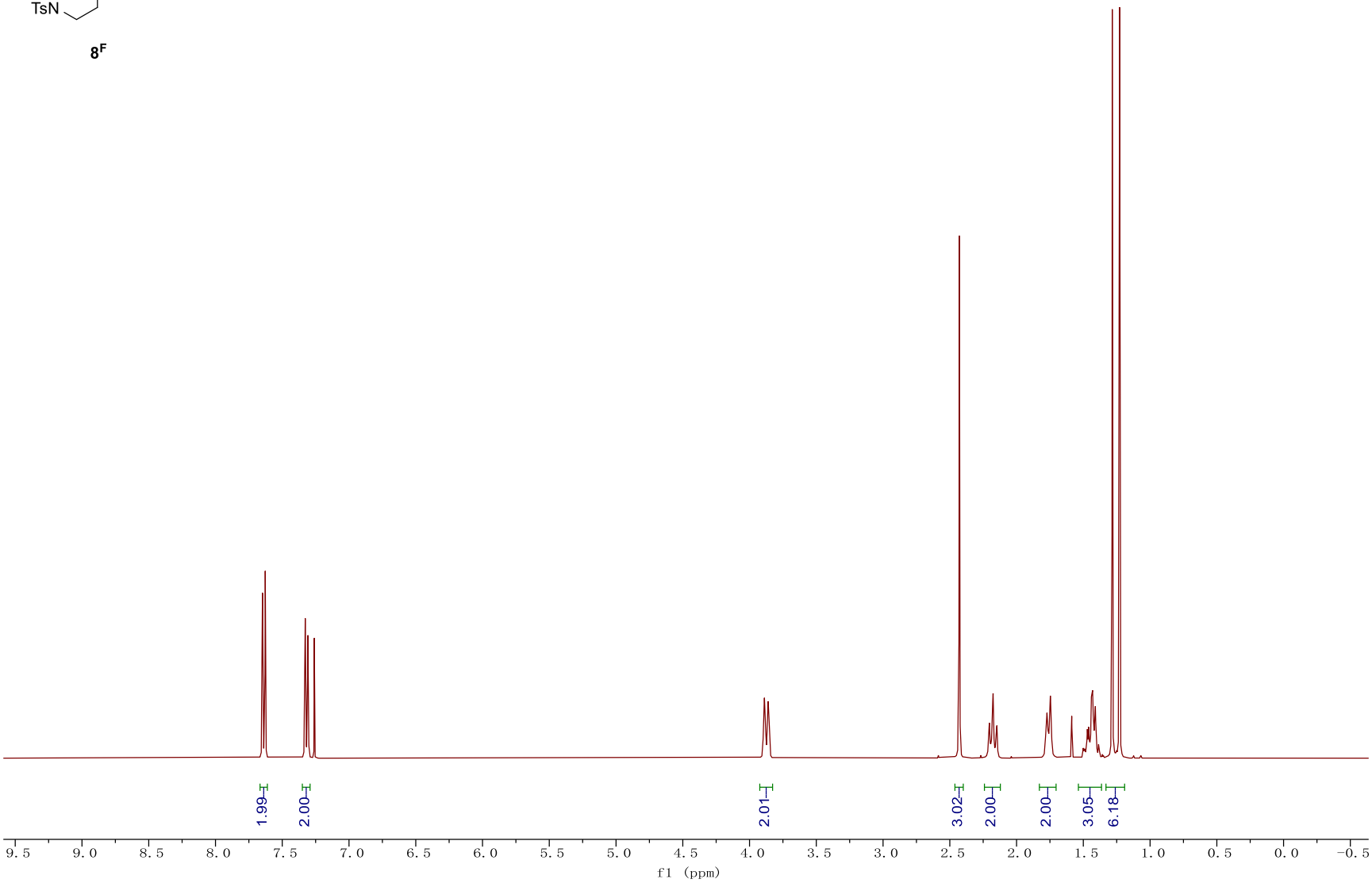

Me Me
TsO
F
4

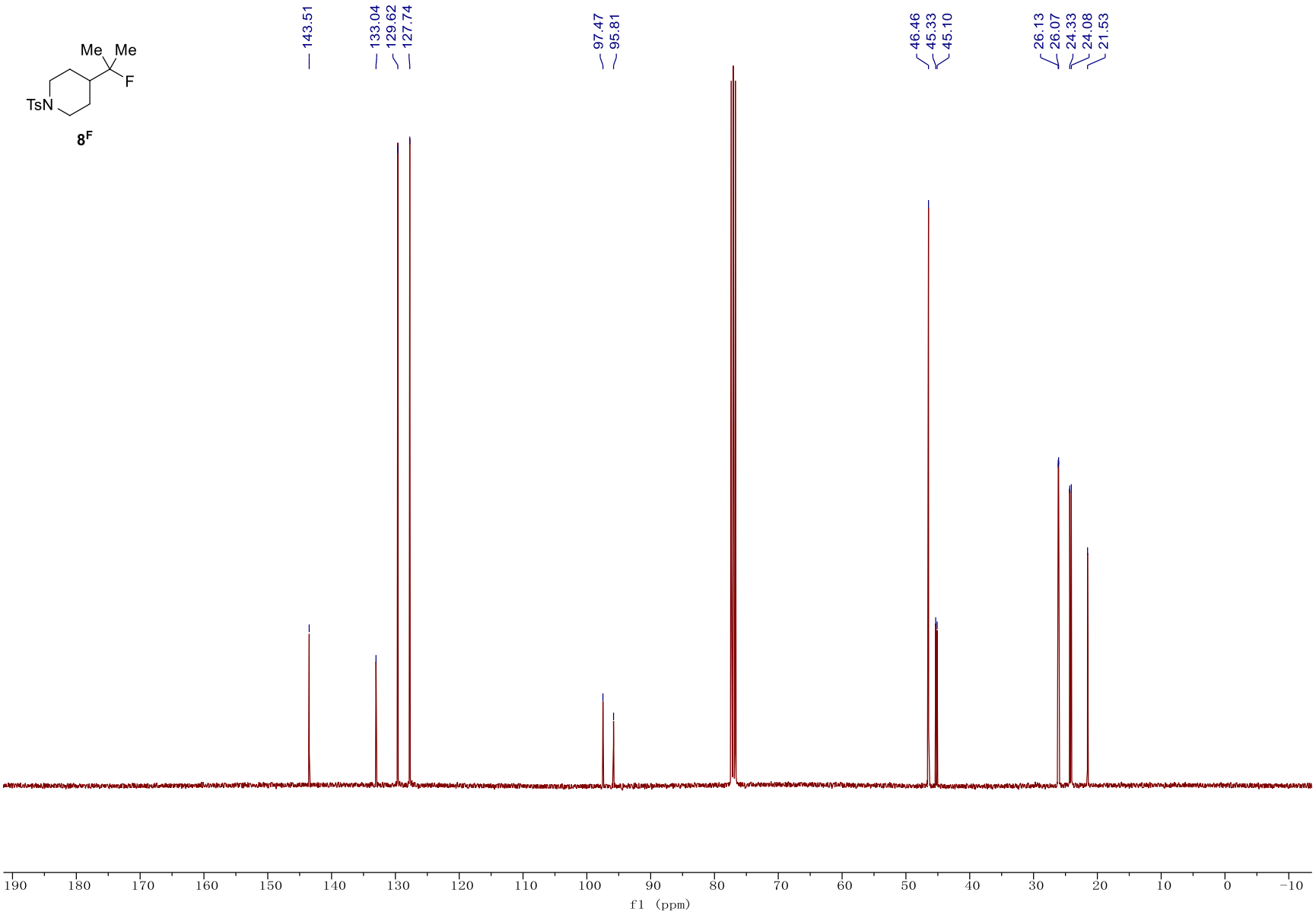
7^{F}

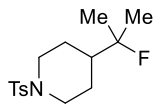
-137.93
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)


Me
Me
F
TsN

8^{F}

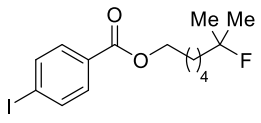

1.99
2.00
2.01
3.02
2.00
2.00
3.05
6.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


Me
Me
F
TsN
8F
143.51
133.04
129.62
127.74
97.47
95.81
46.46
45.33
45.10
26.13
26.07
24.33
24.08
21.53
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
Me
F
TsN

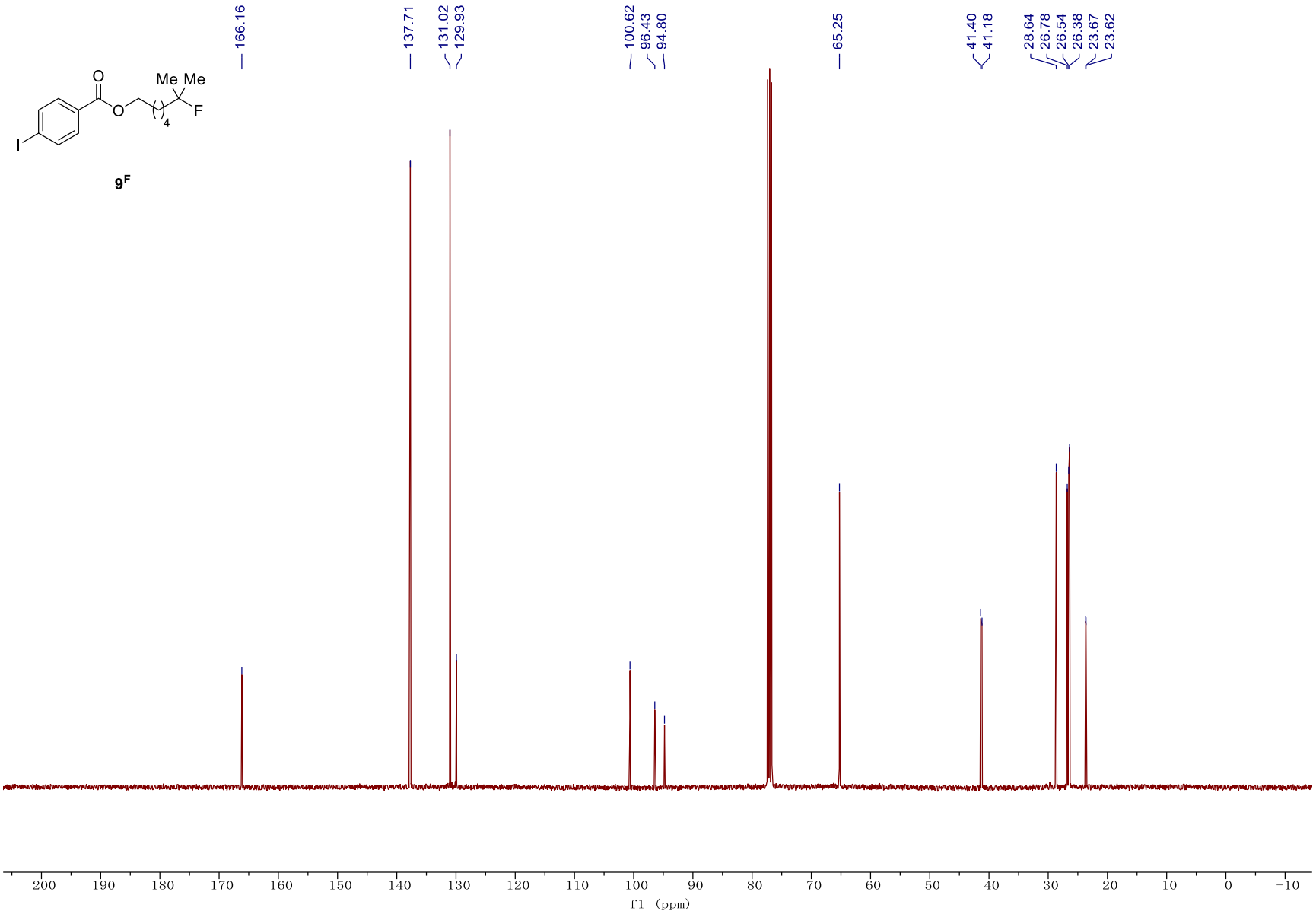
8^{F}

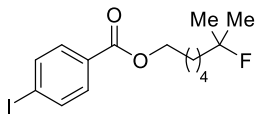
-140.31
-140.33
-140.37
-140.39
-140.43
-140.45
-140.48
-140.51
-140.54
-140.57
-140.60
-140.62
-140.66
-140.68
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)


O
Me Me
O
4
F
I

9^{F}

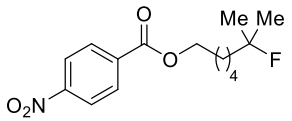
2.01
2.00
2.03
2.02
2.20
4.11
6.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.16
137.71
131.02
129.93
100.62
96.43
94.80
65.25
41.40
41.18
28.64
26.78
26.54
26.38
23.67
23.62
O
Me Me
O
F
4
I
9F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

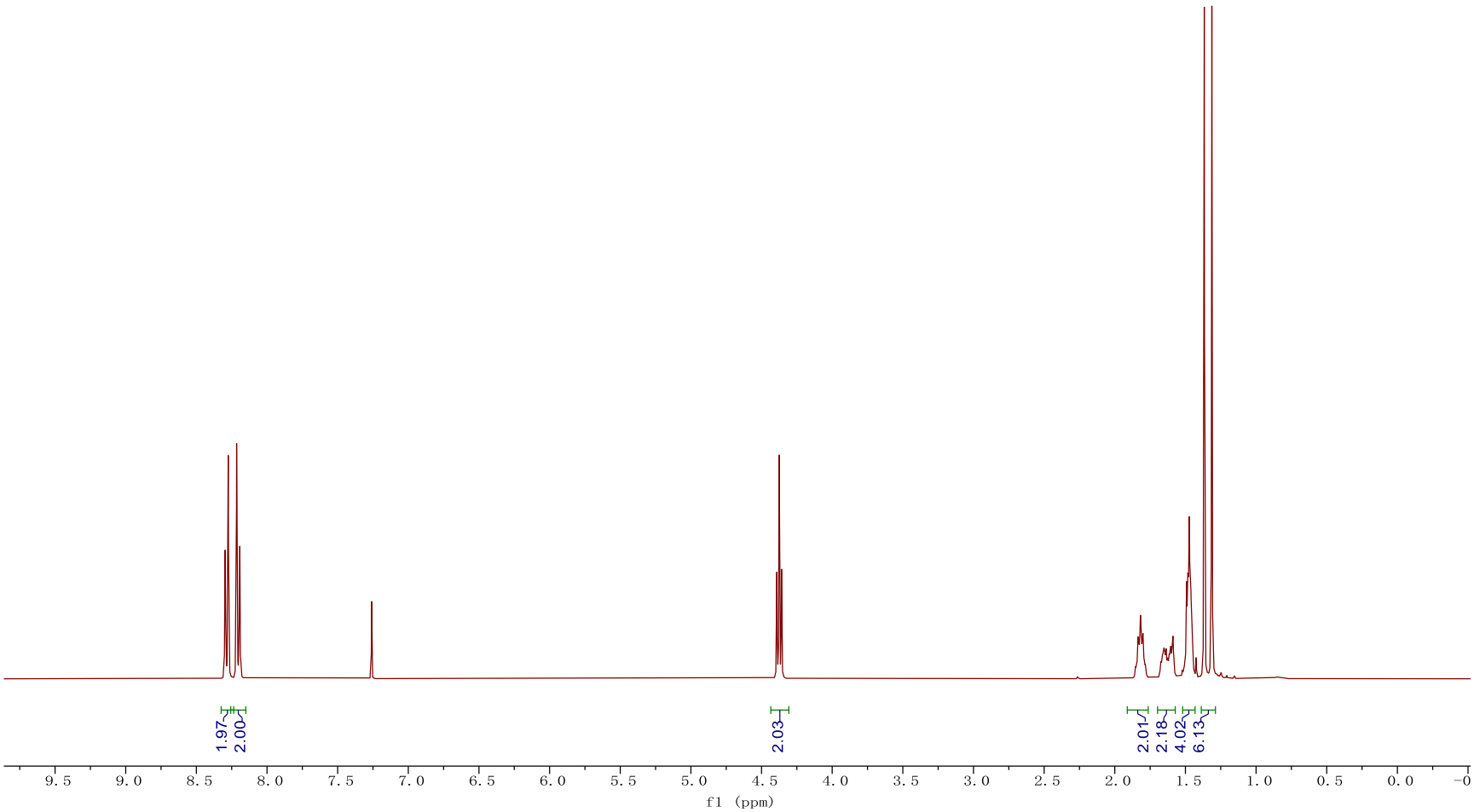

O
Me Me
O
4
F
I

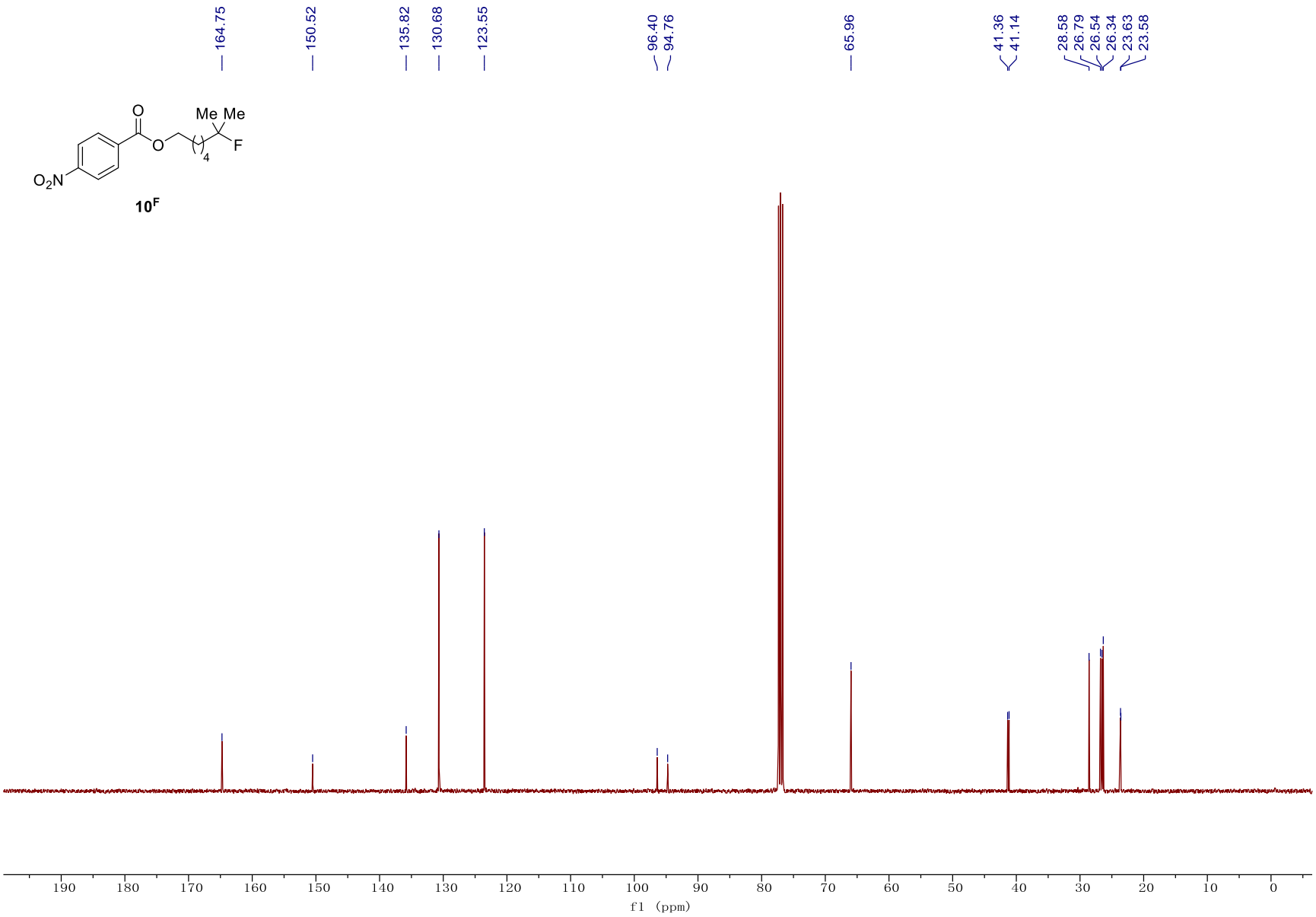
9^{F}

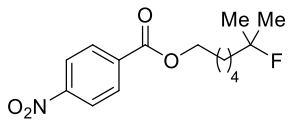
-137.74
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


O
Me Me
O
4
F
O_2N

10^F

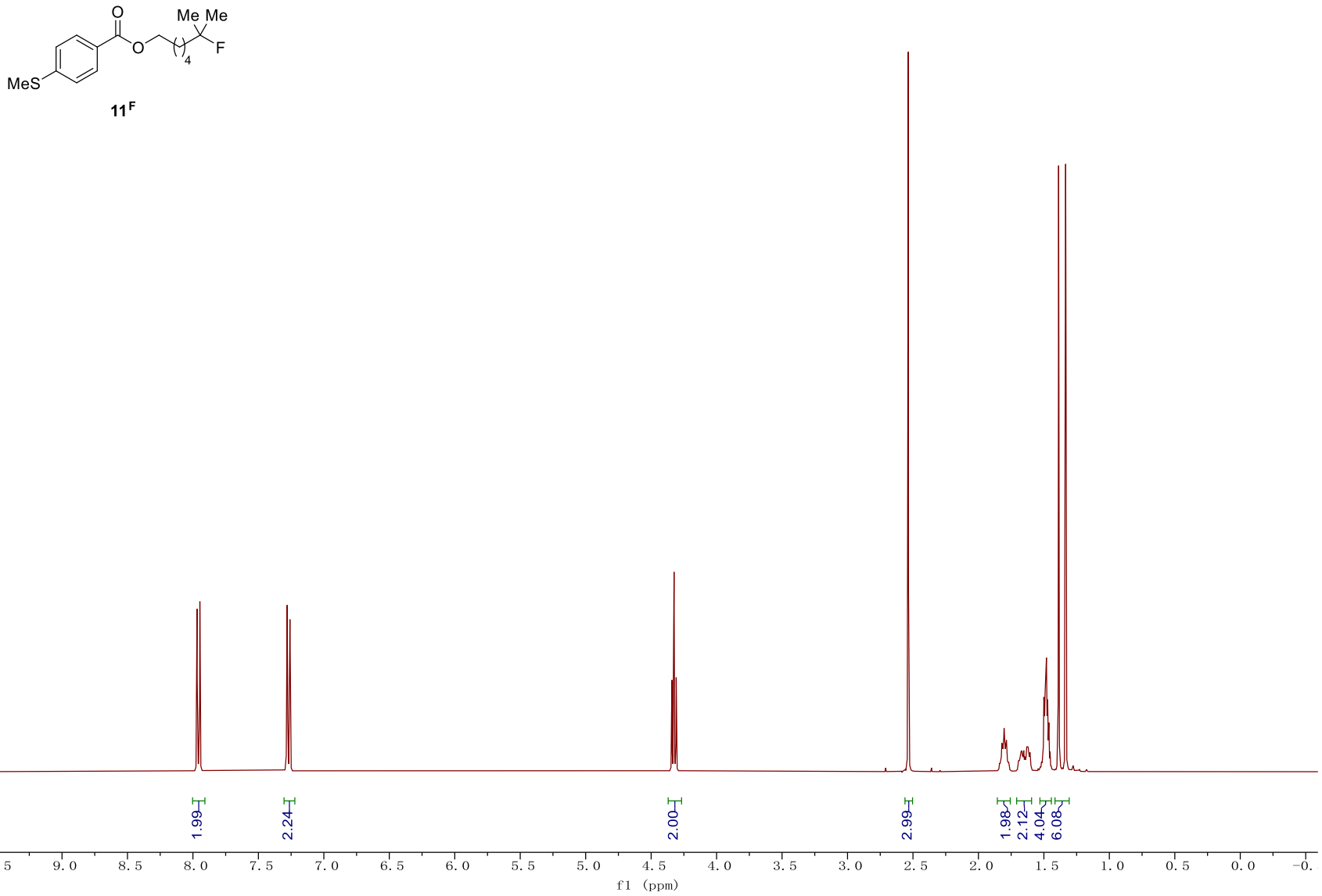

1.97
2.00
2.03
2.01
2.18
4.02
6.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

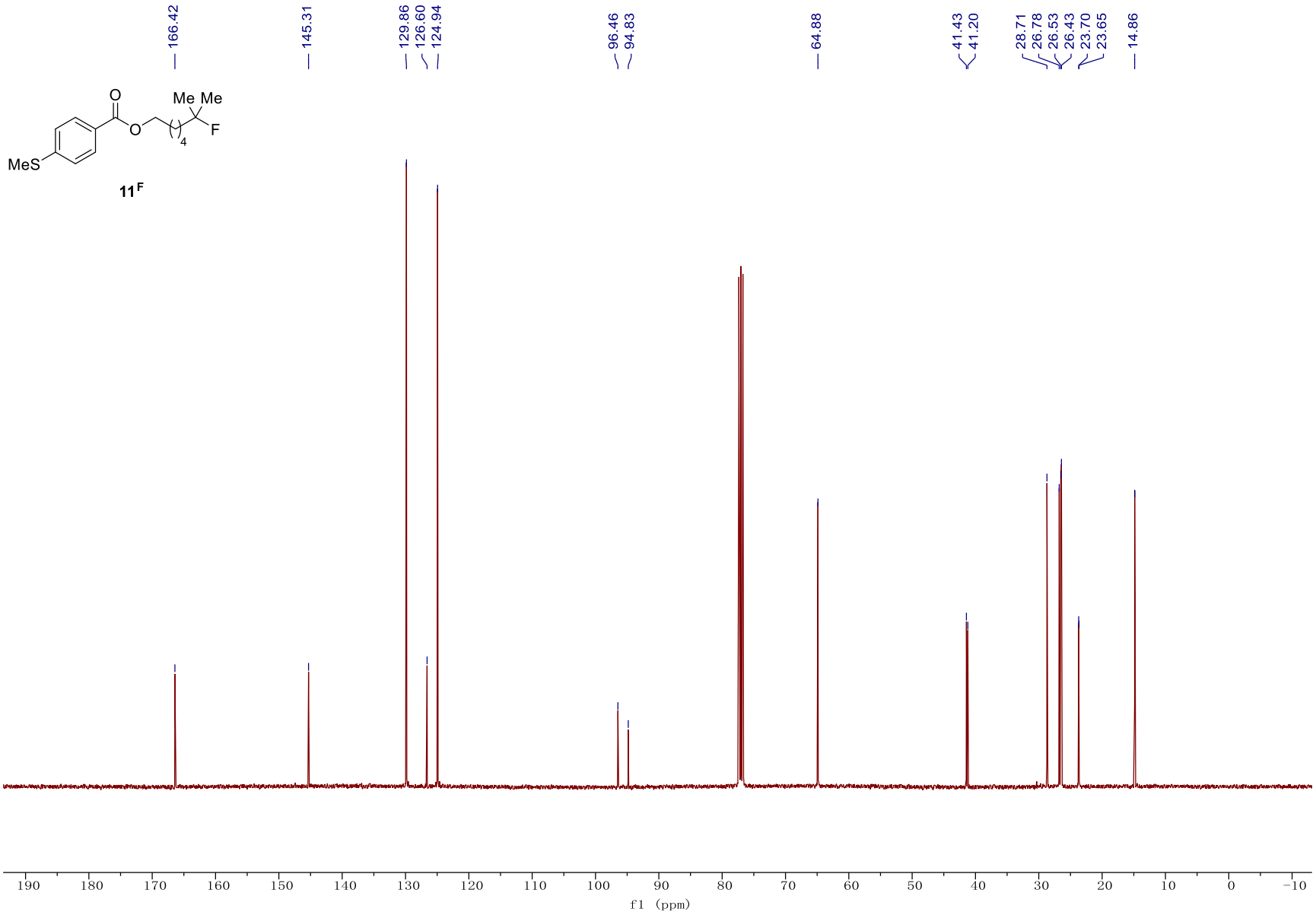

164.75
150.52
135.82
130.68
123.55
96.40
94.76
65.96
41.36
41.14
28.58
26.79
26.54
26.34
23.63
23.58
O
Me Me
O
F
4
O2N
10F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

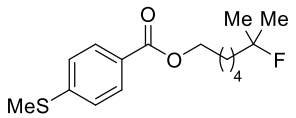

O
Me Me
O
F
4
O_2N

10^F

-137.97
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

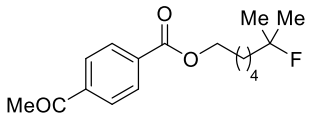

O
Me Me
O
F
4
MeS
11F
1.99
2.24
2.00
2.99
1.98
2.12
4.04
6.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


166.42
145.31
129.86
126.60
124.94
96.46
94.83
64.88
41.43
41.20
28.71
26.78
26.53
26.43
23.70
23.65
14.86
O
Me Me
O
F
4
MeS
11F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

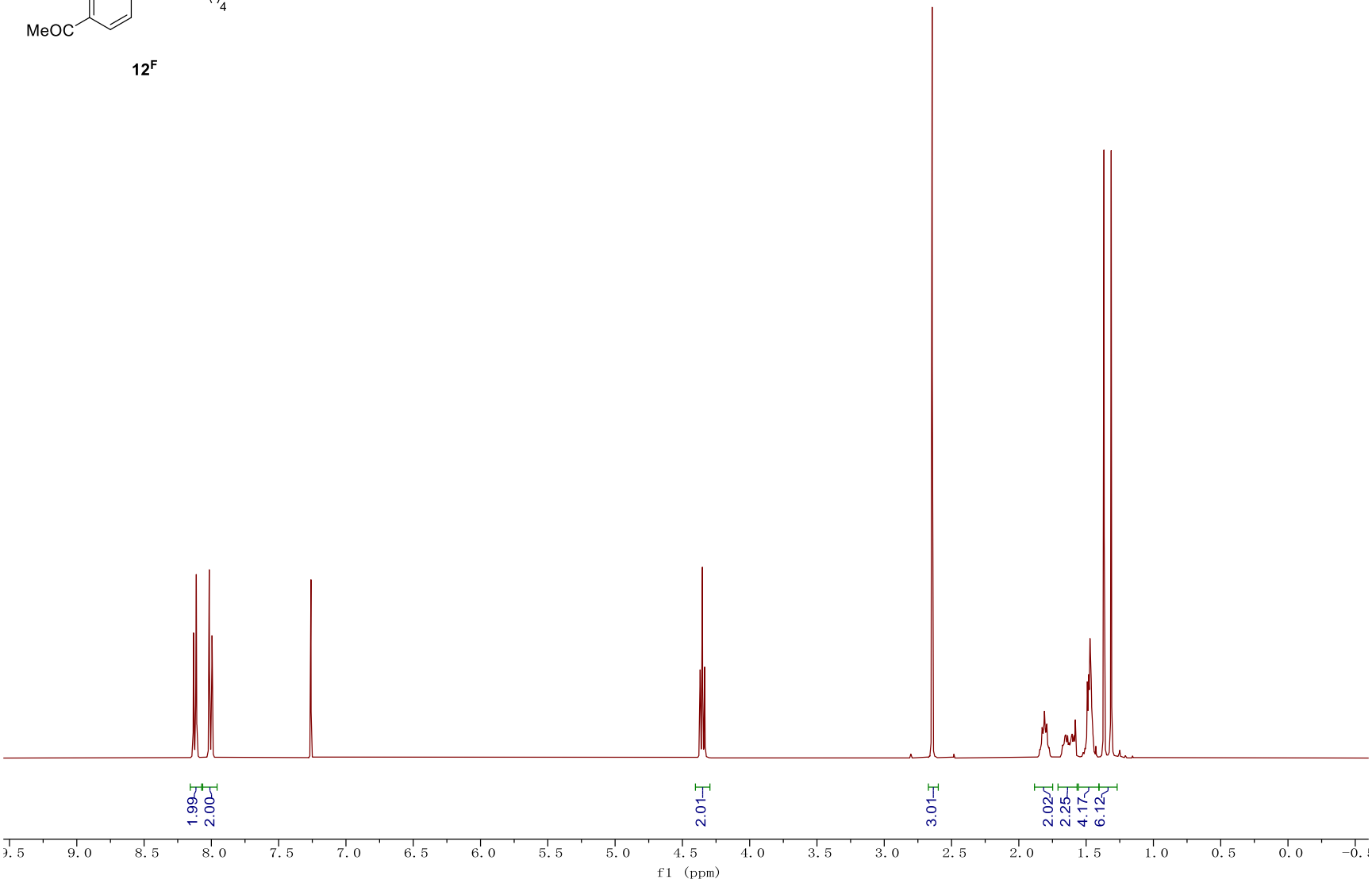

O
Me Me
O
F
4
MeS

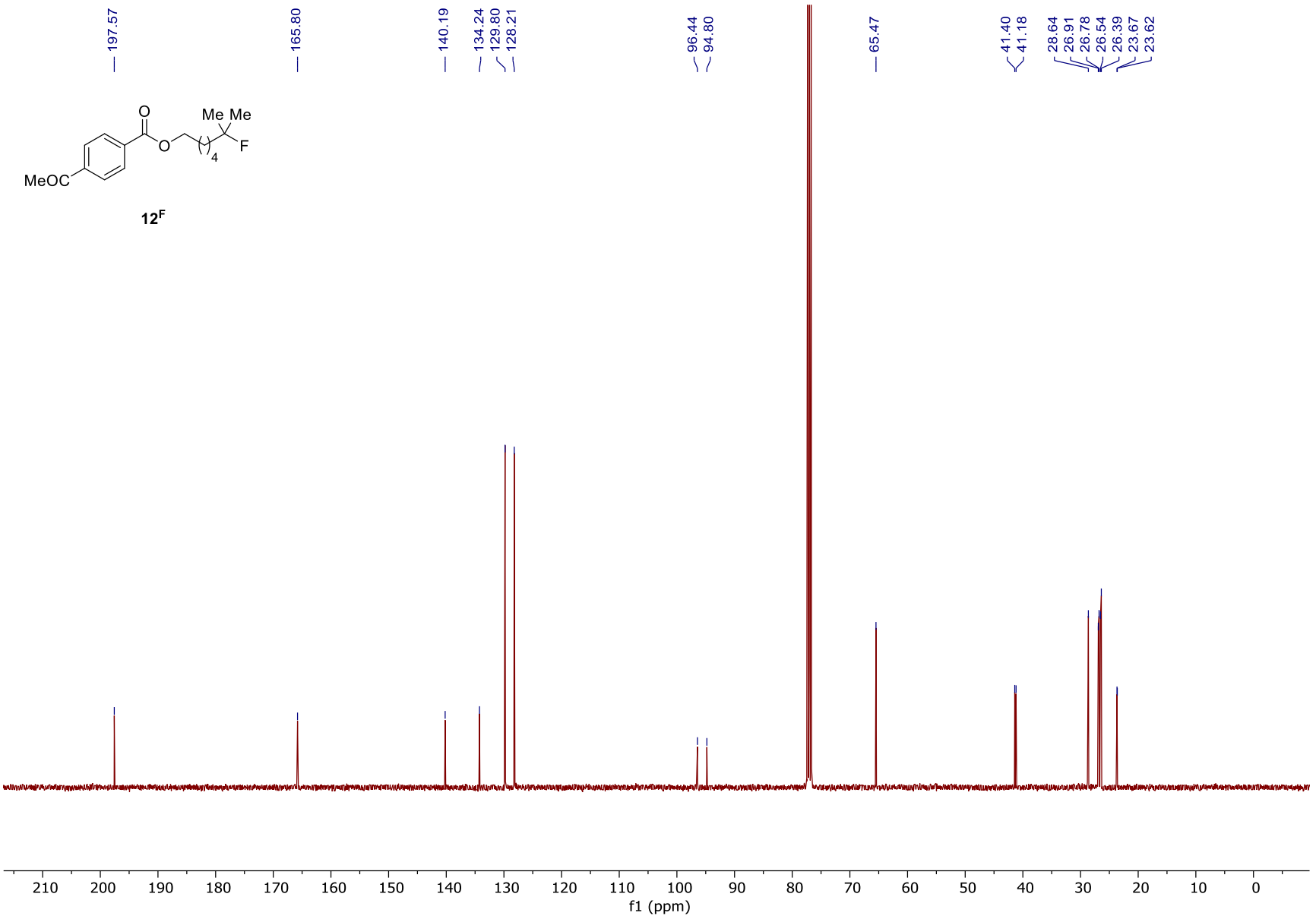
11^{F}

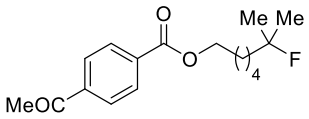
-137.60
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)


O
Me Me
O
F
4
MeOC

12^{F}

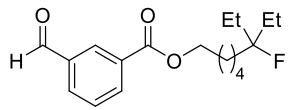

1.99
2.00
2.01
3.01
2.02
2.25
4.17
6.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.57
165.80
140.19
134.24
129.80
128.21
96.44
94.80
65.47
41.40
41.18
28.64
26.91
26.78
26.54
26.39
23.67
23.62
O
Me Me
O
F
4
MeOC
12F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me Me
O
4
F
MeOC

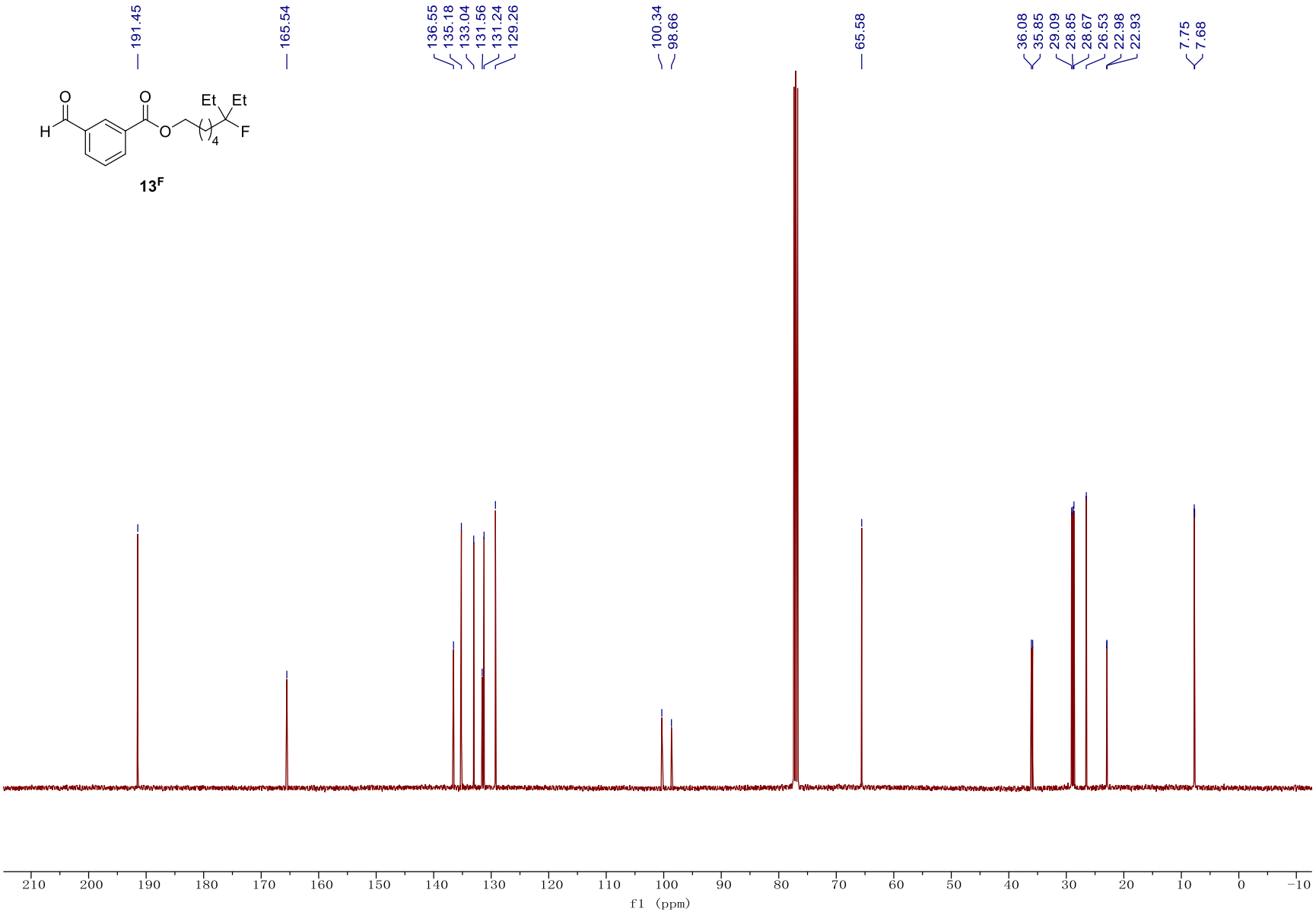
12^{F}

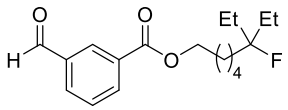
-137.78
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
O
Et
Et
H
O
4
F

13^{F}

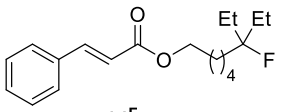
0.97
1.00
1.00
1.00
1.00
2.04
2.03
6.31
4.10
6.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


191.45
165.54
136.55
135.18
133.04
131.56
131.24
129.26
100.34
98.66
65.58
36.08
35.85
29.09
28.85
28.67
26.53
22.98
22.93
7.75
7.68
O
O
Et
Et
H
O
4
F
13F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

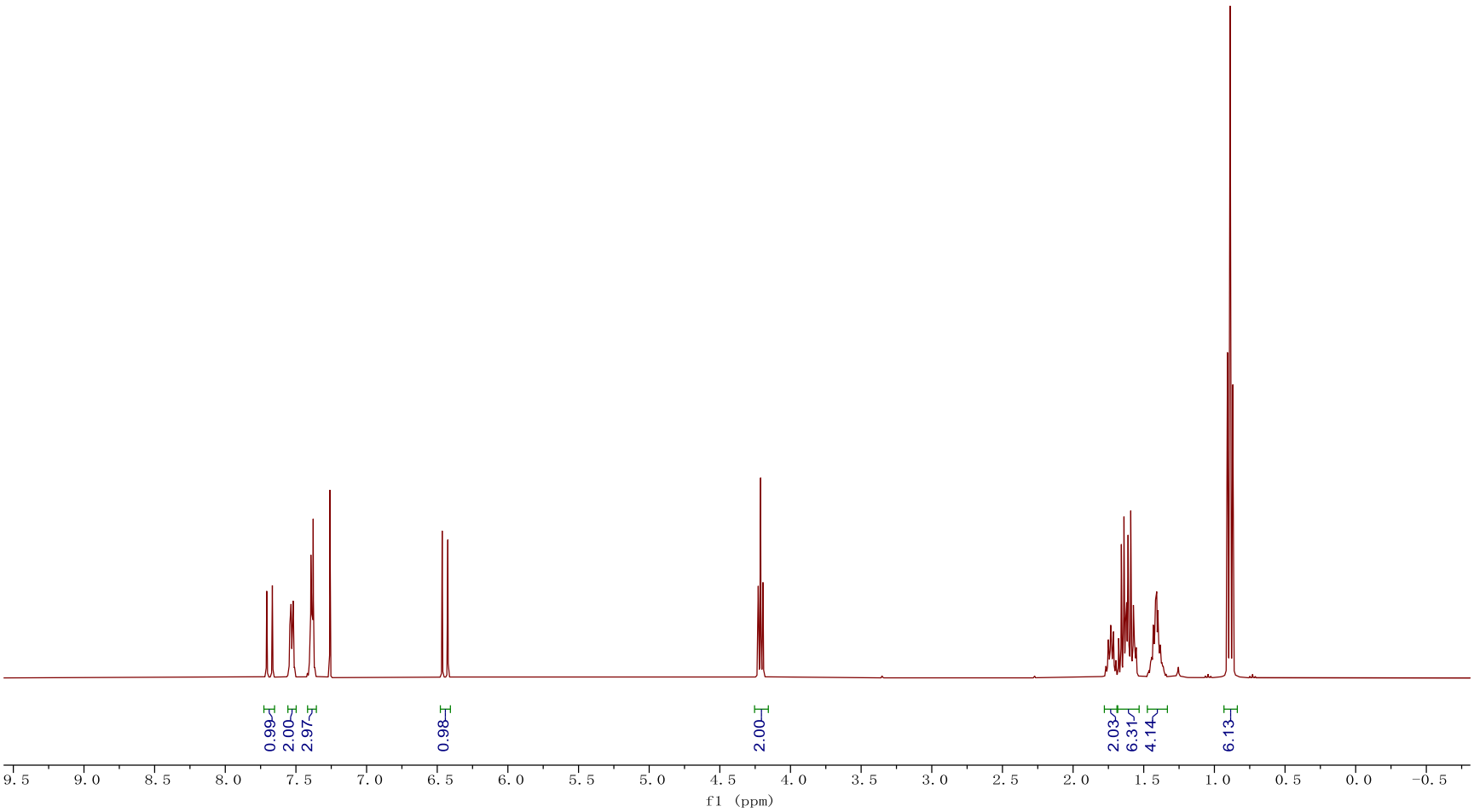

O
O
Et
Et
H
O
4
F

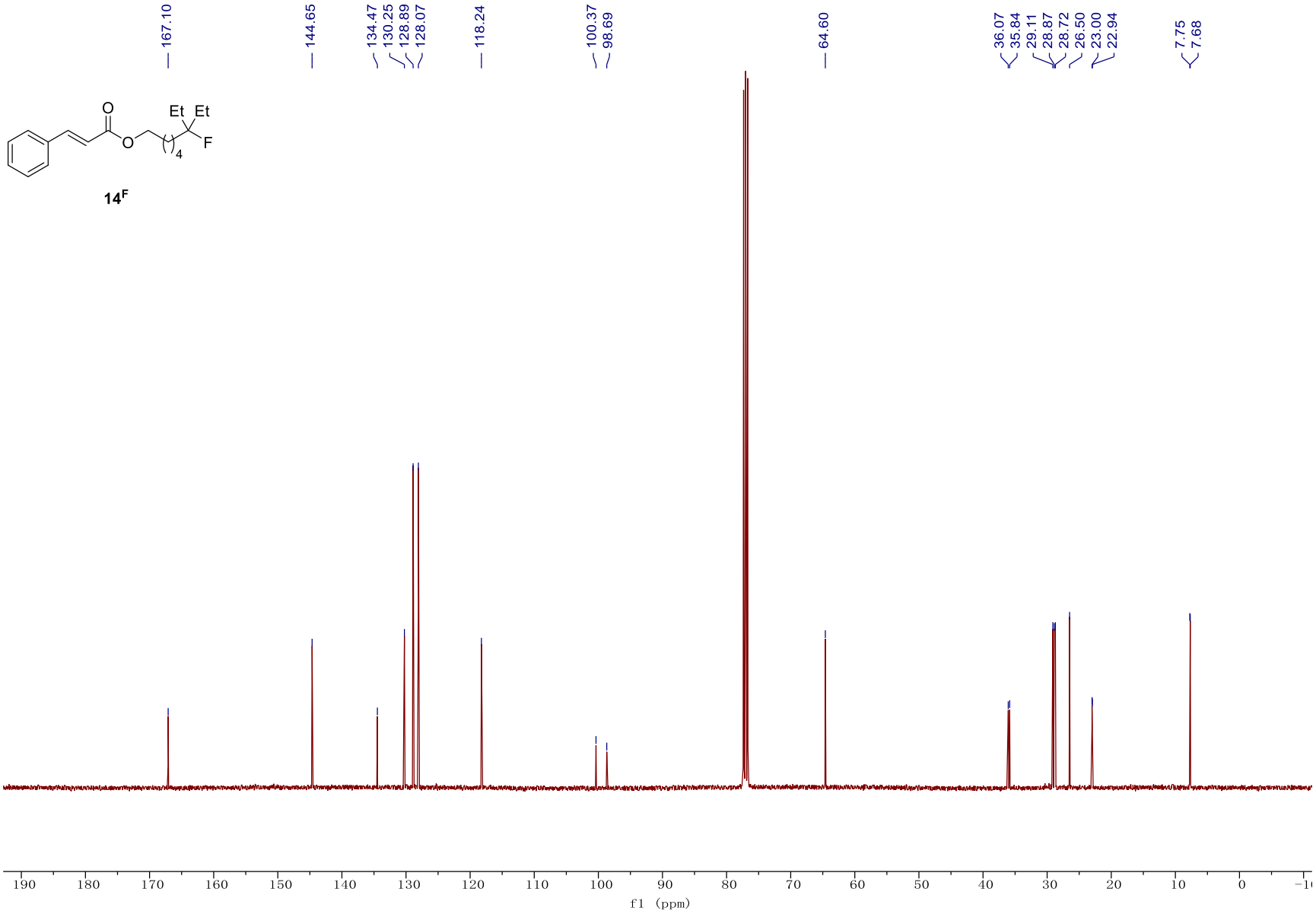
13^{F}

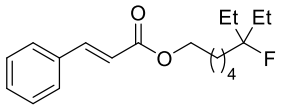
-154.15
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


O
Et Et
O
F
4

14^{F}

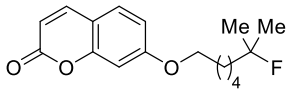

0.99
2.00
2.97
0.98
2.00
2.03
6.31
4.14
6.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


167.10
144.65
134.47
130.25
128.89
128.07
118.24
100.37
98.69
64.60
36.07
35.84
29.11
28.87
28.72
26.50
23.00
22.94
7.75
7.68
O
O
Et
Et
F
4
14F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Et Et
O
4
F

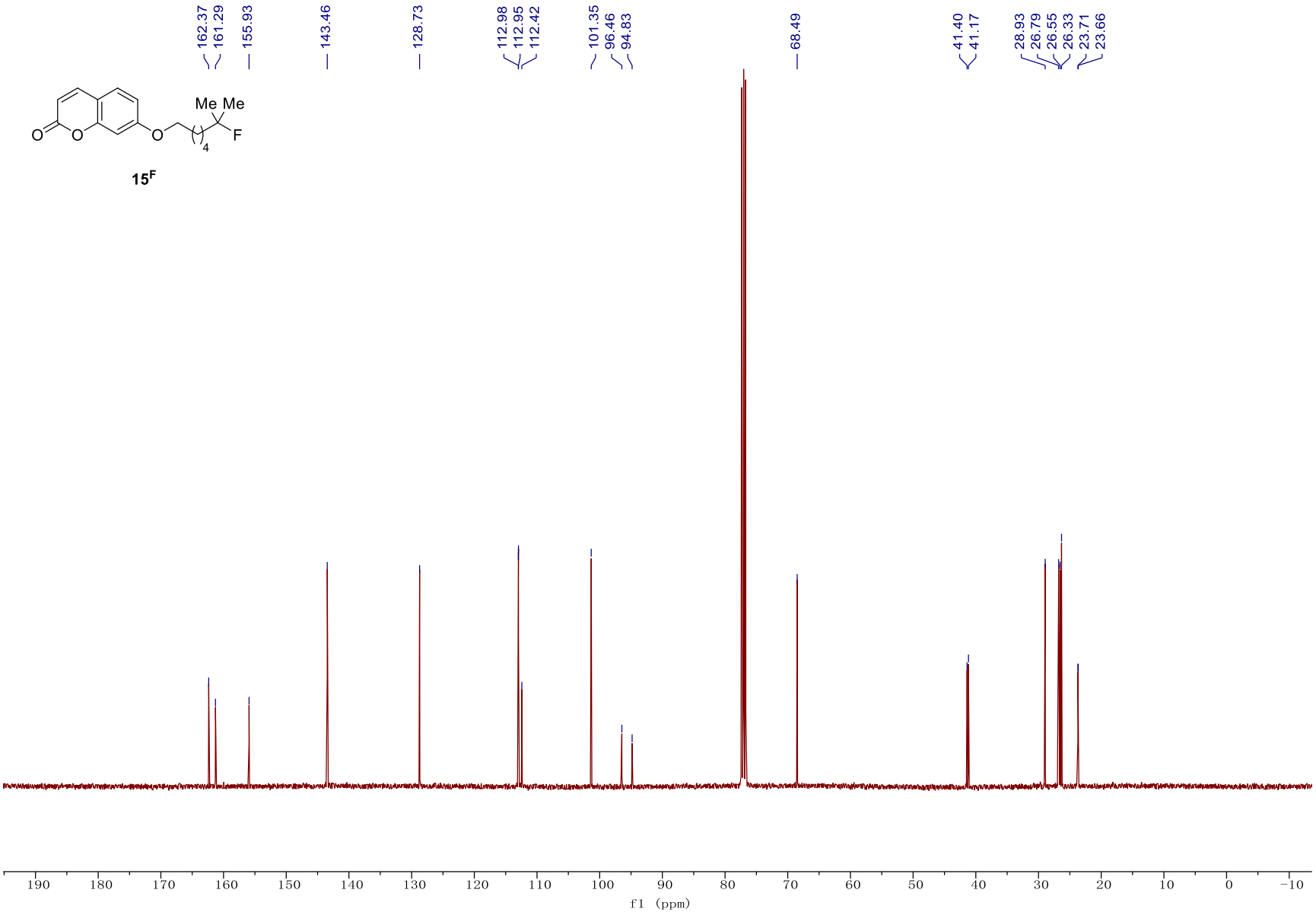
14^{F}

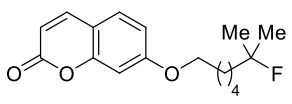
-154.13
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


Me Me
O
O
O
4
F

15^{F}

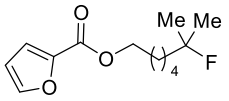
1.01
1.01
1.03
1.00
1.00
2.04
2.02
2.16
4.08
6.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


162.37
161.29
155.93
143.46
128.73
112.98
112.95
112.42
101.35
96.46
94.83
68.49
41.40
41.17
28.93
26.79
26.55
26.33
23.71
23.66
Me Me
F
4
15F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

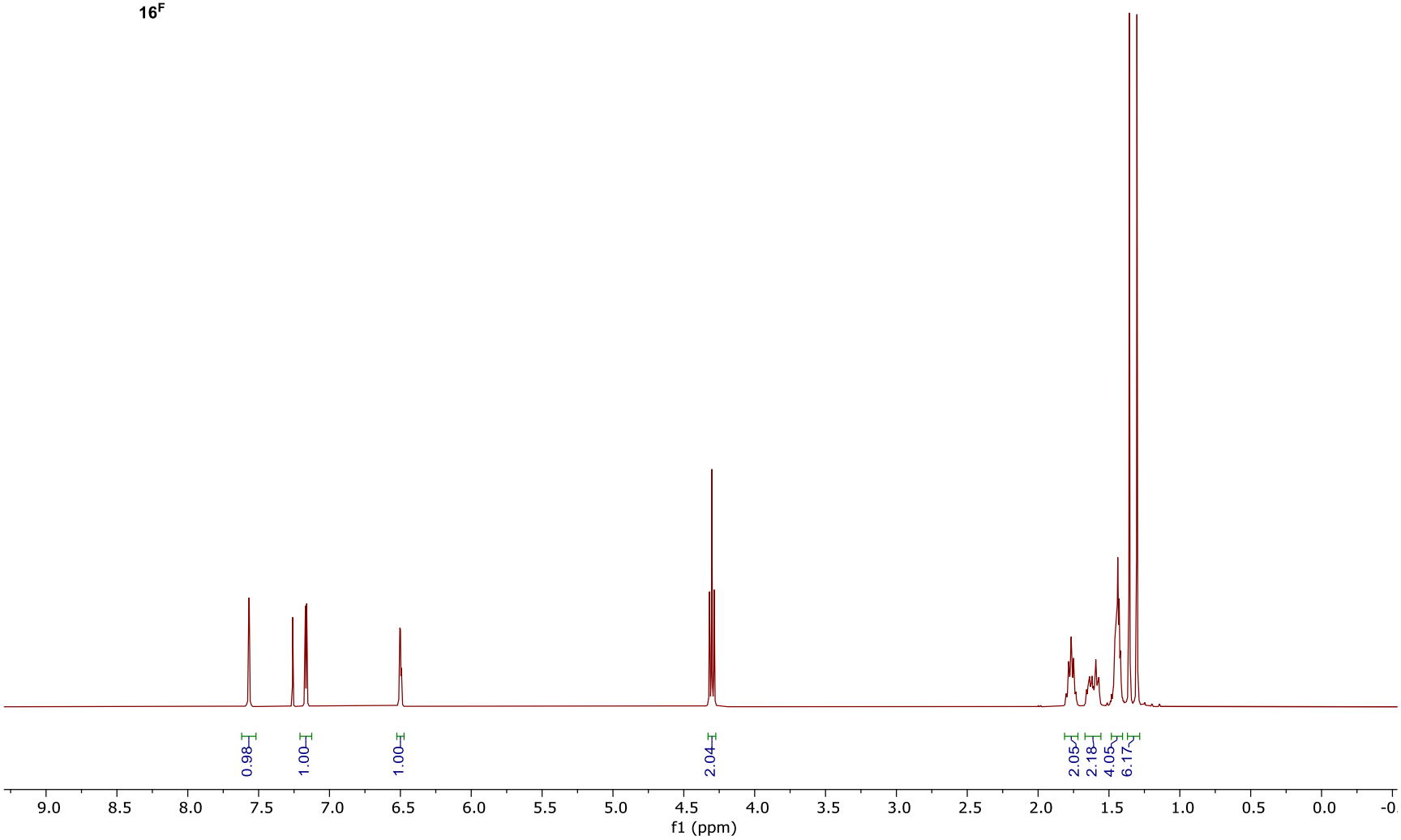

Me Me
O
O
O
4
F

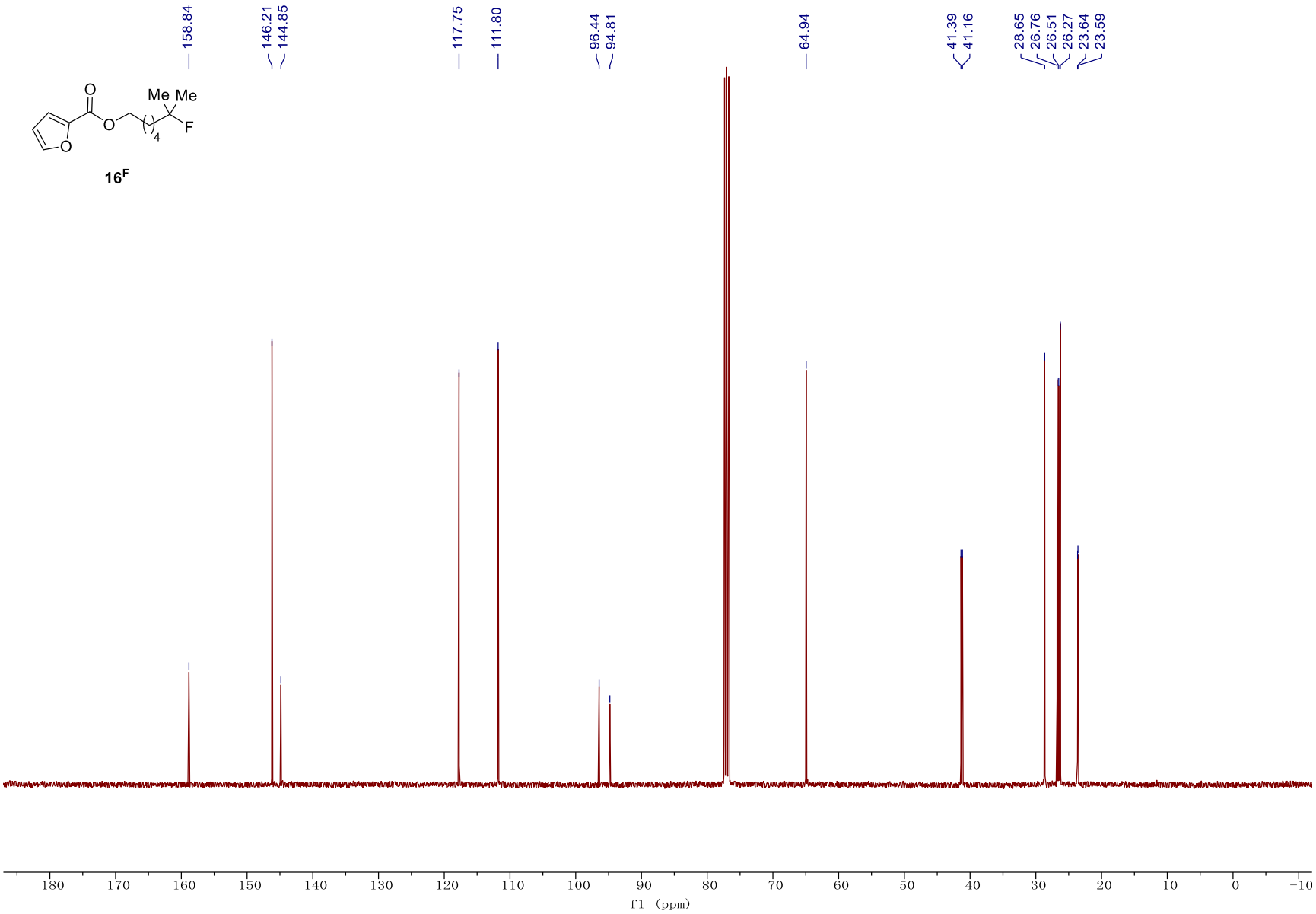
15^{F}

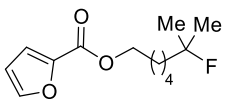
-137.75
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)


O
Me Me
O
4
F
O

16^{F}

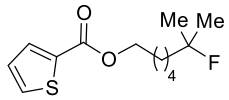

0.98
1.00
1.00
2.04
2.05
2.18
4.05
6.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


158.84
146.21
144.85
117.75
111.80
96.44
94.81
64.94
41.39
41.16
28.65
26.76
26.51
26.27
23.64
23.59
O
O
O
Me Me
F
4
16F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
Me Me
O
4
F
O

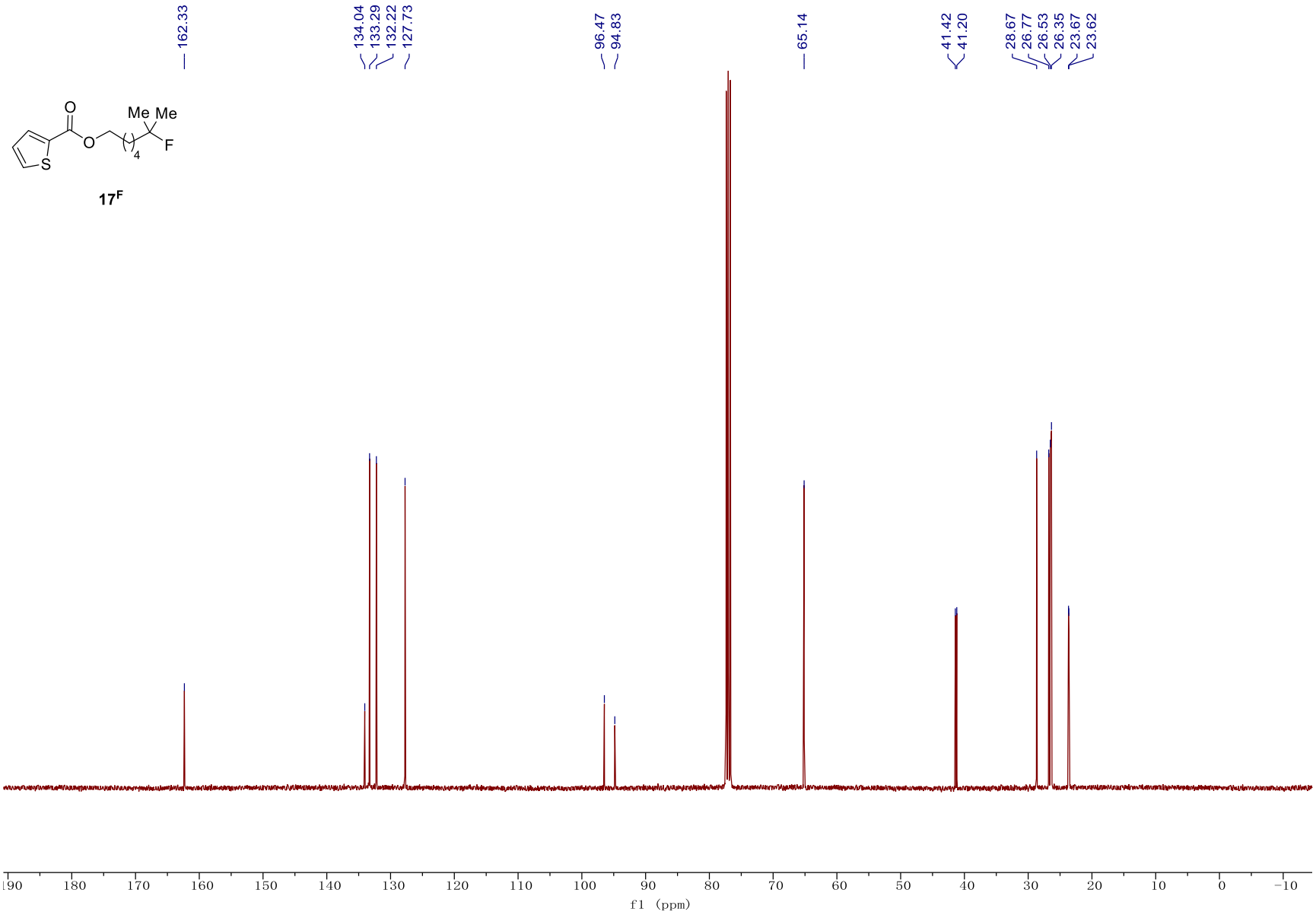
16^{F}

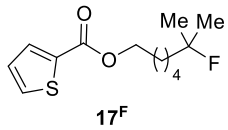
-137.64
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


O
Me Me
O
4
F
S

17^{F}

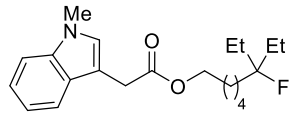
1.00
1.00
1.01
2.01
2.04
2.23
4.00
6.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.33
134.04
133.29
132.22
127.73
96.47
94.83
65.14
41.42
41.20
28.67
26.77
26.53
26.35
23.67
23.62
O
Me Me
O
F
S
4
17F
f1 (ppm)


O
Me Me
O
4
F
S

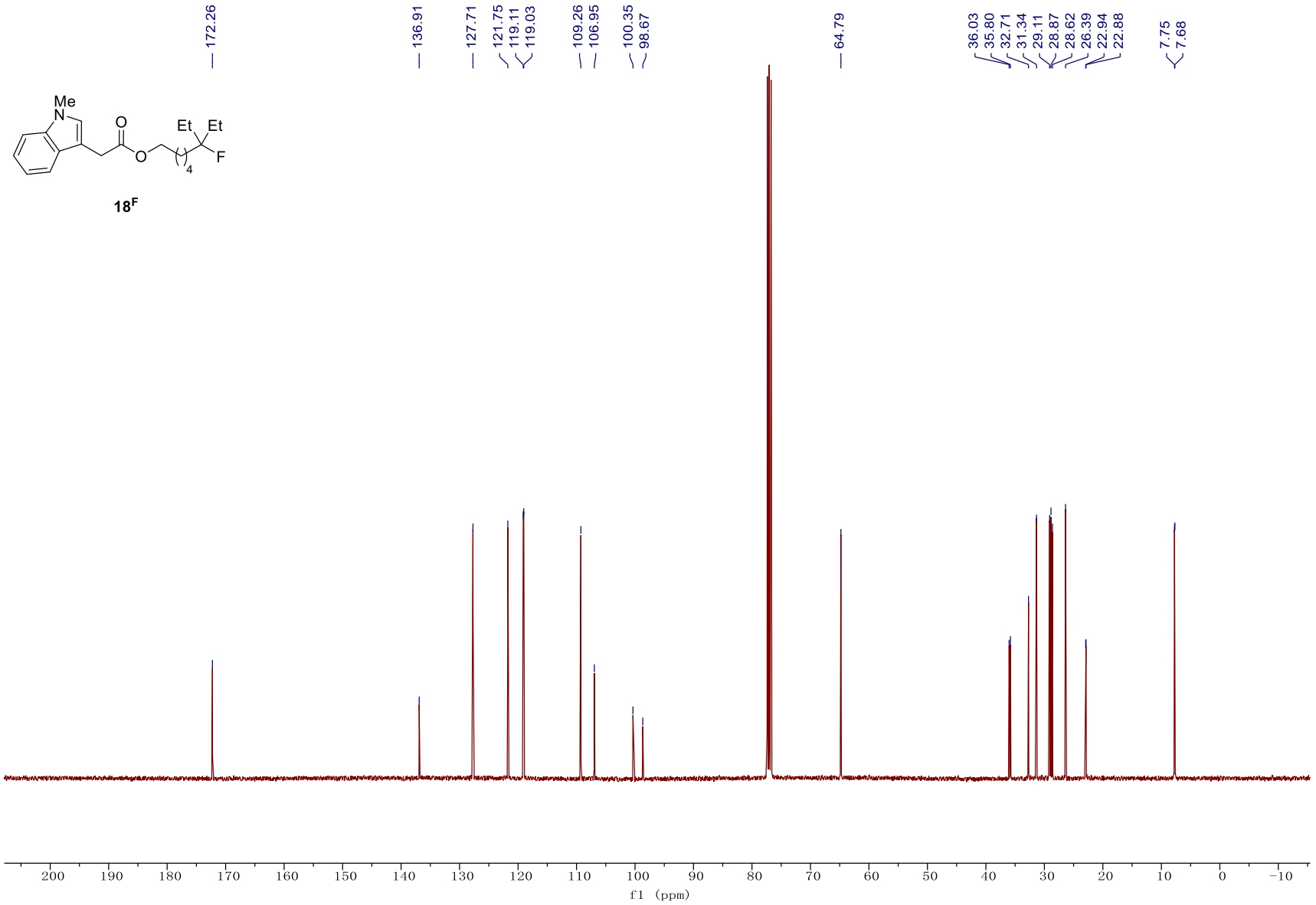
17^{F}

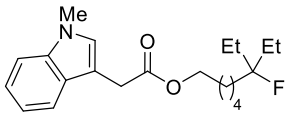
-137.58
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


Me
N
O
O
Et
Et
F
4

18^{F}

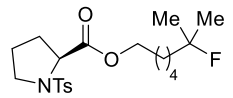
1.00
1.00
1.09
1.01
0.99
2.03
5.14
8.43
4.29
6.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.26
136.91
127.71
121.75
119.11
119.03
109.26
106.95
100.35
98.67
64.79
36.03
35.80
32.71
31.34
29.11
28.87
28.62
26.39
22.94
22.88
7.75
7.68
Me
N
O
O
Et
Et
F
4
18F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
N
O
O
Et
Et
F
4

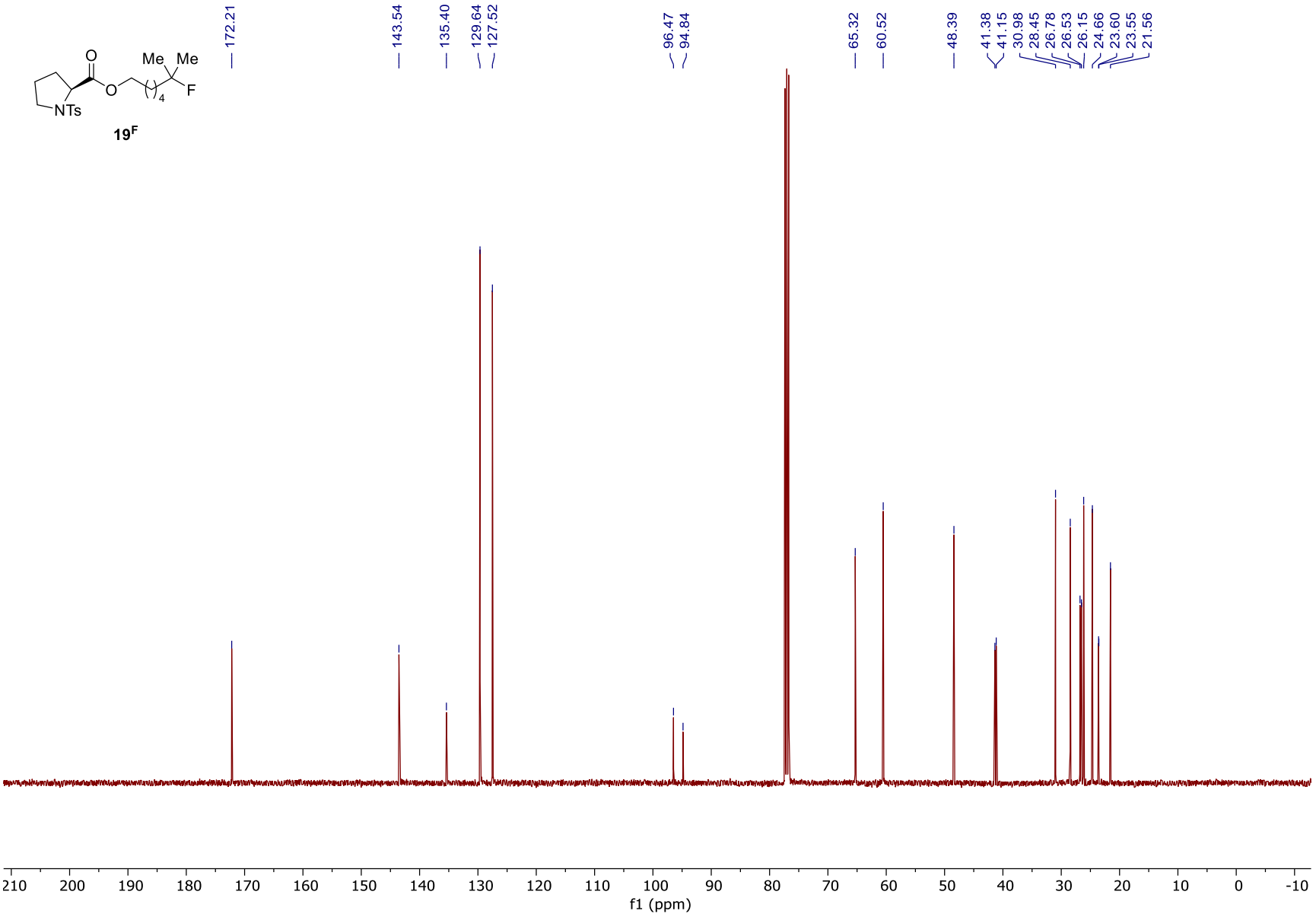
18^{F}

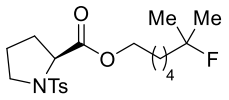
-154.11
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


O
Me
Me
O
4
F
NTs

19^{F}

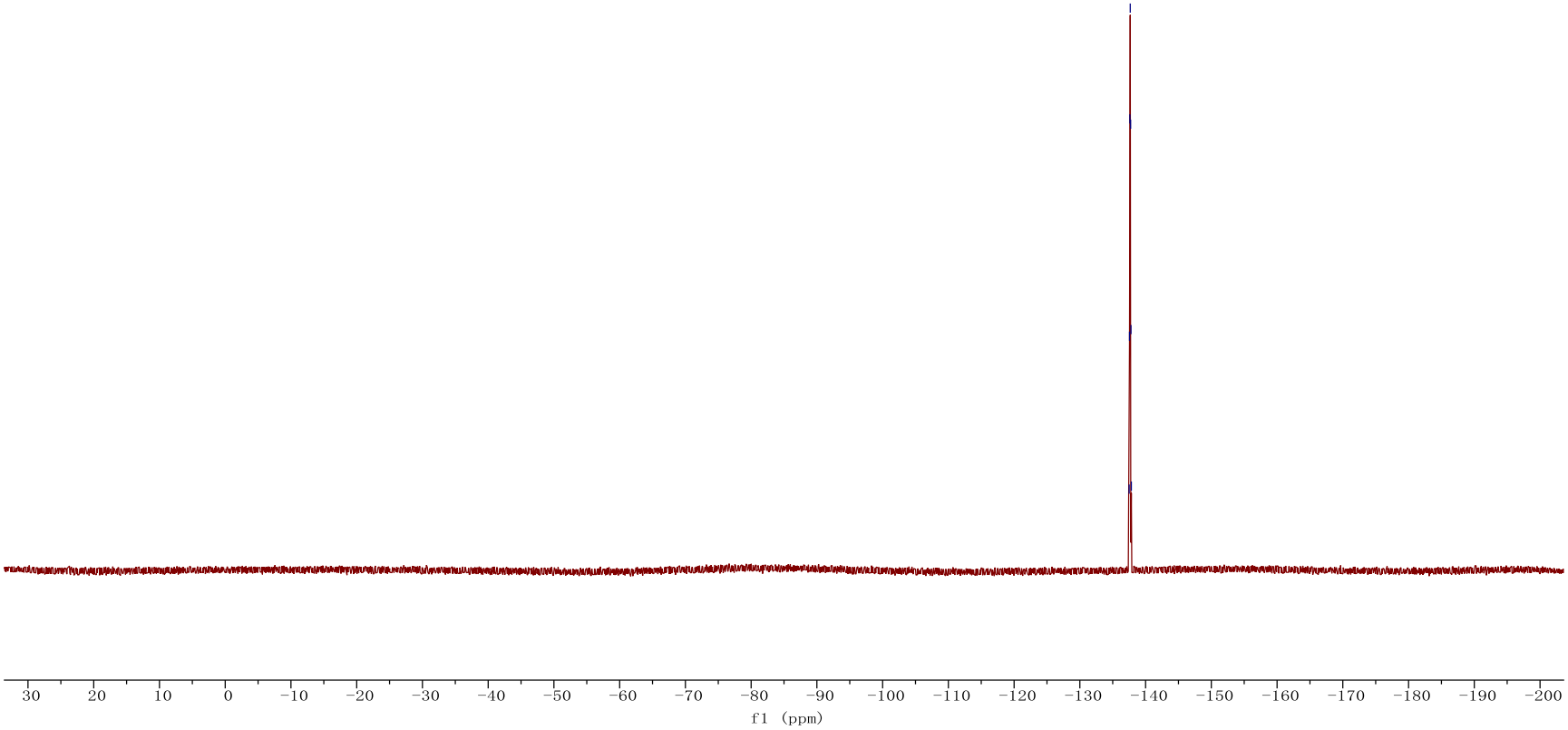
1.99
2.00
1.00
2.02
1.00
0.99
2.99
3.03
1.04
4.16
3.28
6.75
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

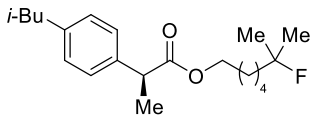

172.21
143.54
135.40
129.64
127.52
96.47
94.84
65.32
60.52
48.39
41.38
41.15
30.98
28.45
26.78
26.53
26.15
24.66
23.60
23.55
21.56
O
Me
Me
O
4
F
NTs
19F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Me
Me
O
4
F
NTs

19^{F}

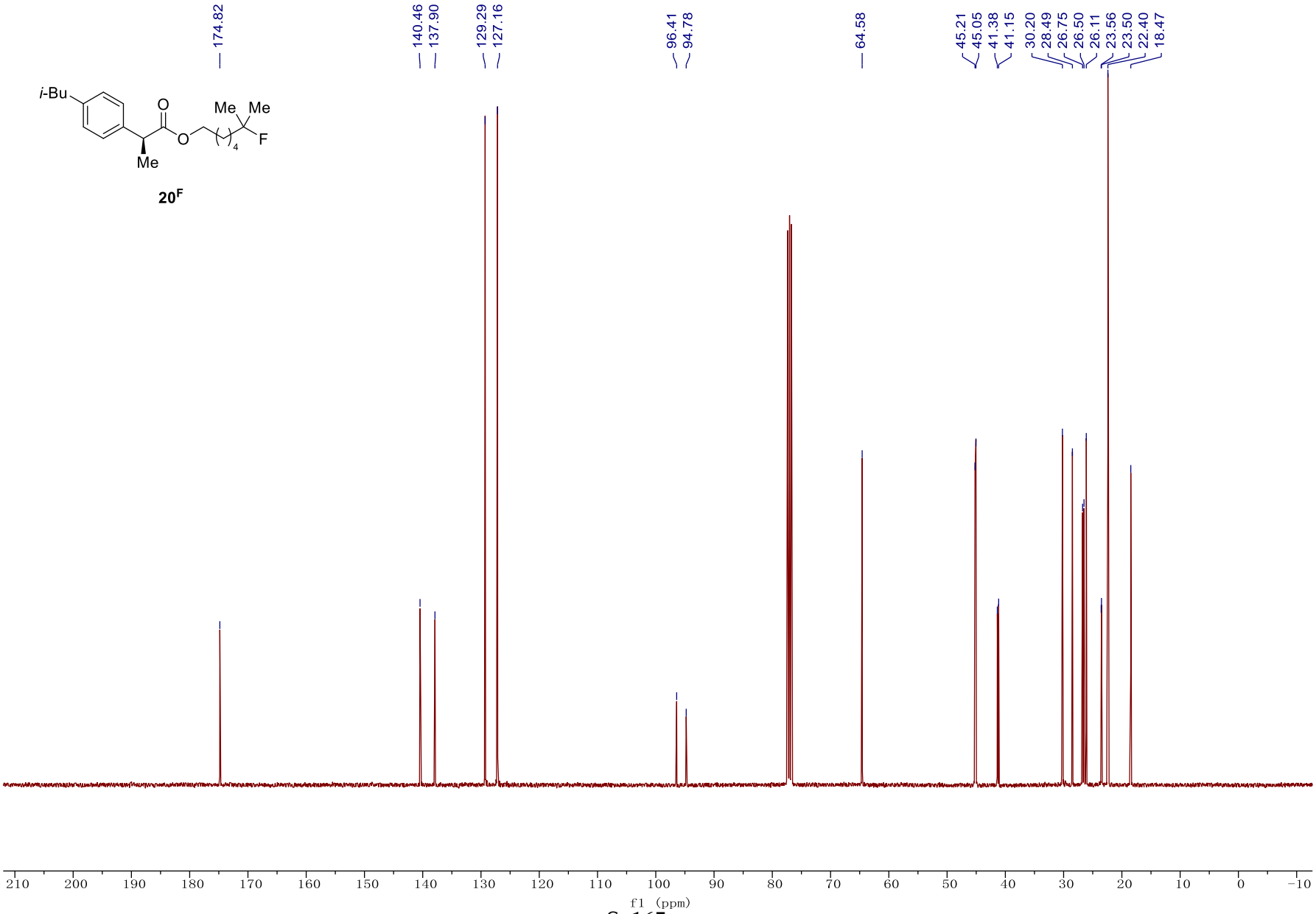

-137.50
-137.55
-137.61
-137.67
-137.72
-137.78
-137.83

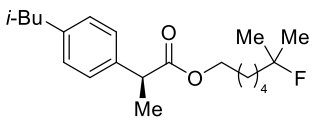

30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)


i-Bu
O
O
Me
Me
Me
F
4
Me

20^{F}

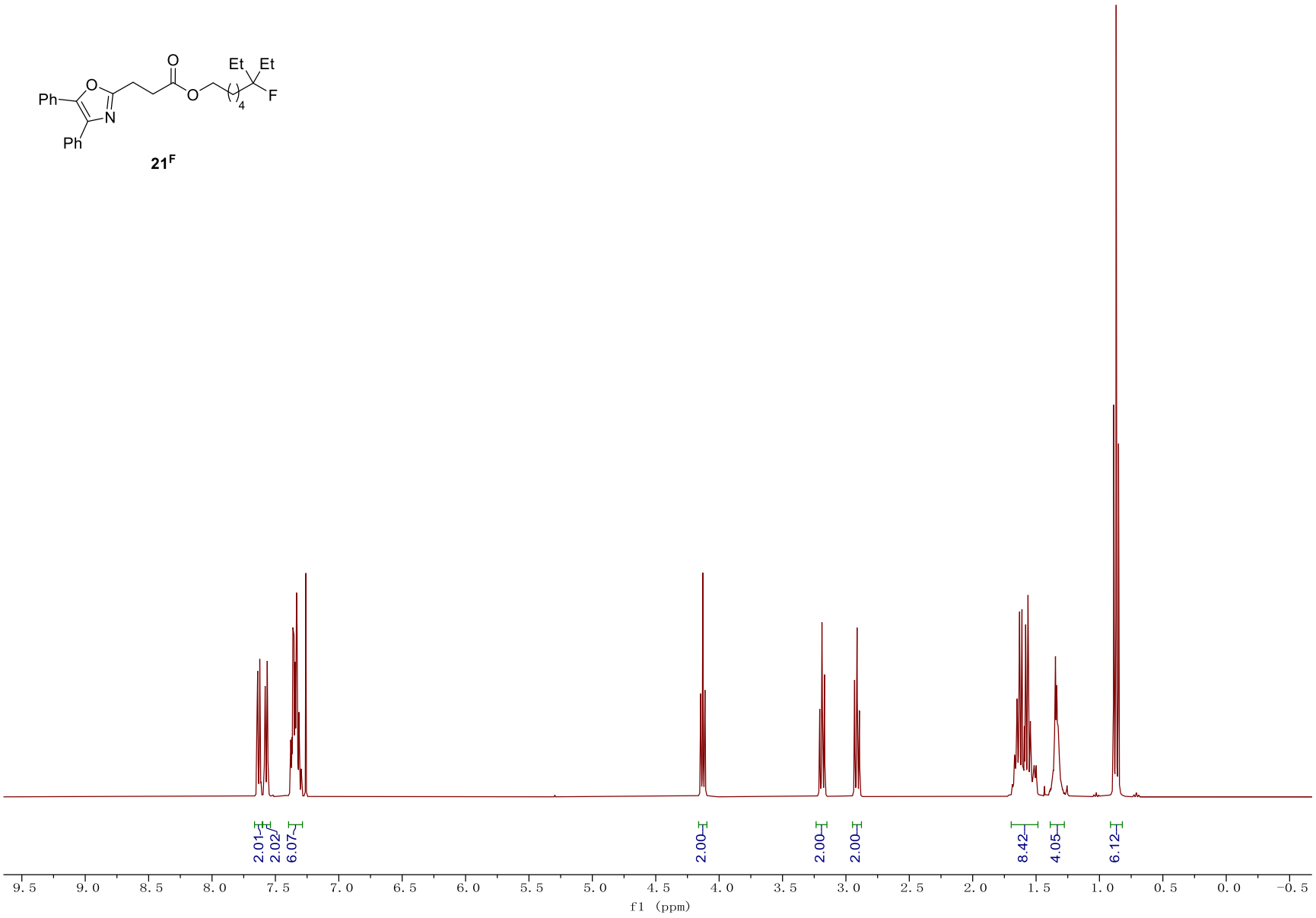
2.01
2.02
1.99
0.99
2.00
0.97
3.76
3.39
10.31
6.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

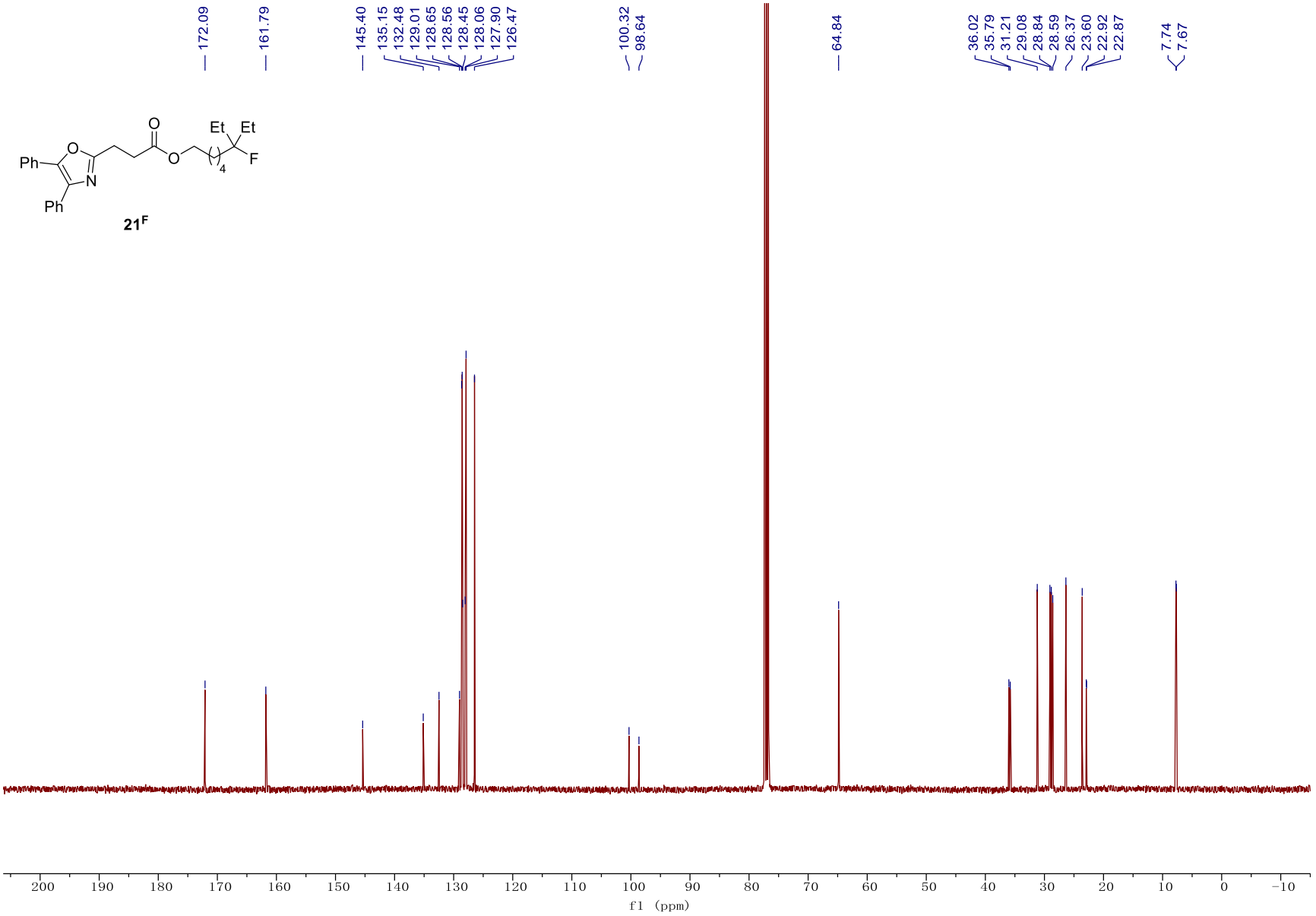

174.82
140.46
137.90
129.29
127.16
96.41
94.78
64.58
45.21
45.05
41.38
41.15
30.20
28.49
26.75
26.50
26.11
23.56
23.50
22.40
18.47
i-Bu
O
O
Me
Me
Me
F
4
Me
20F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

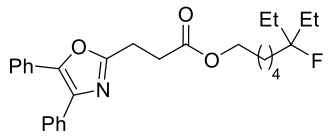

i-Bu
O
Me
Me
O
4
F
Me

20^{F}

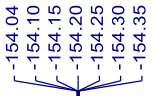
-137.51
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)

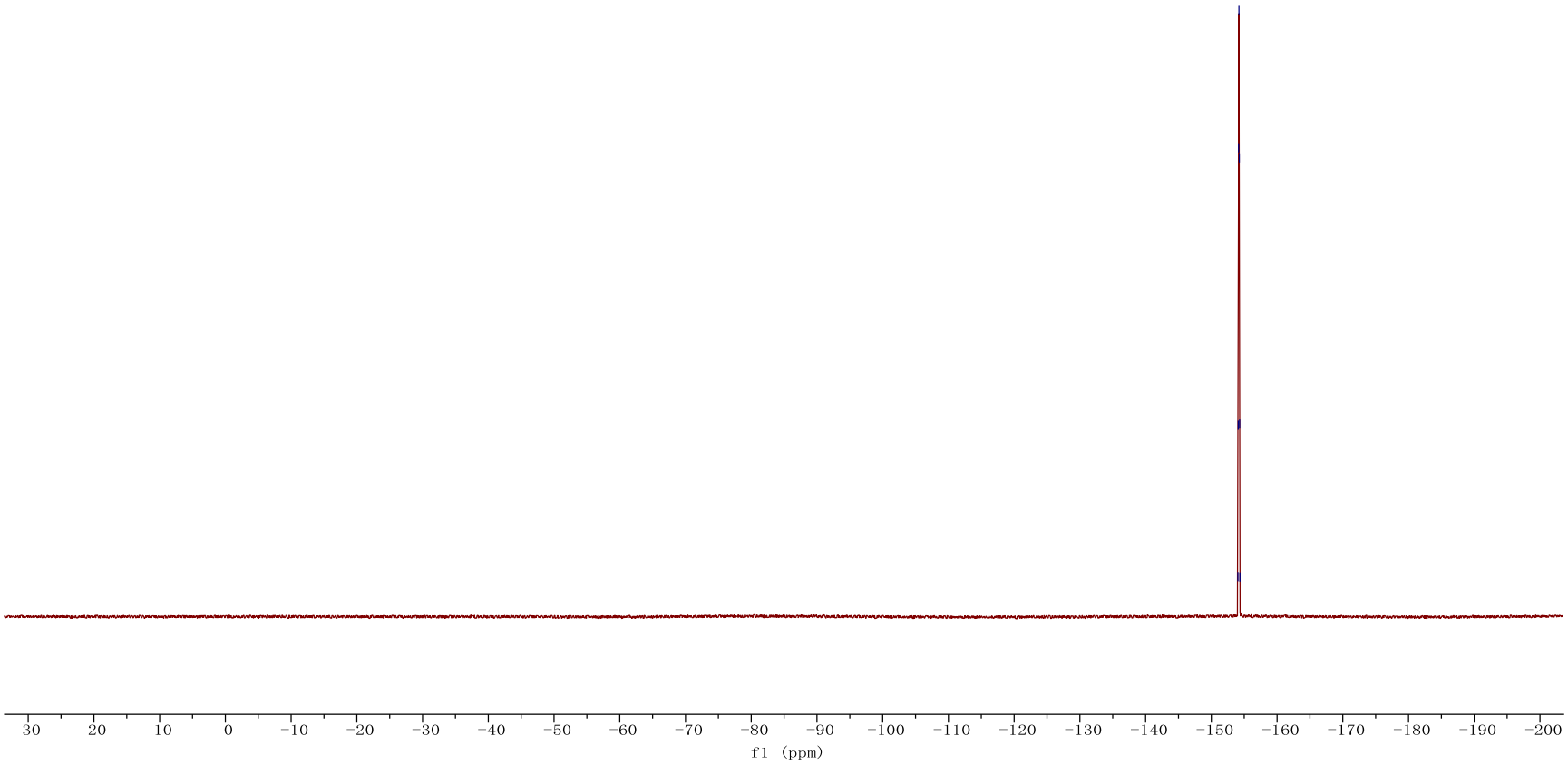

Ph
O
N
Ph
O
O
Et
Et
F
4
21F
2.01
2.02
6.07
2.00
2.00
2.00
8.42
4.05
6.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

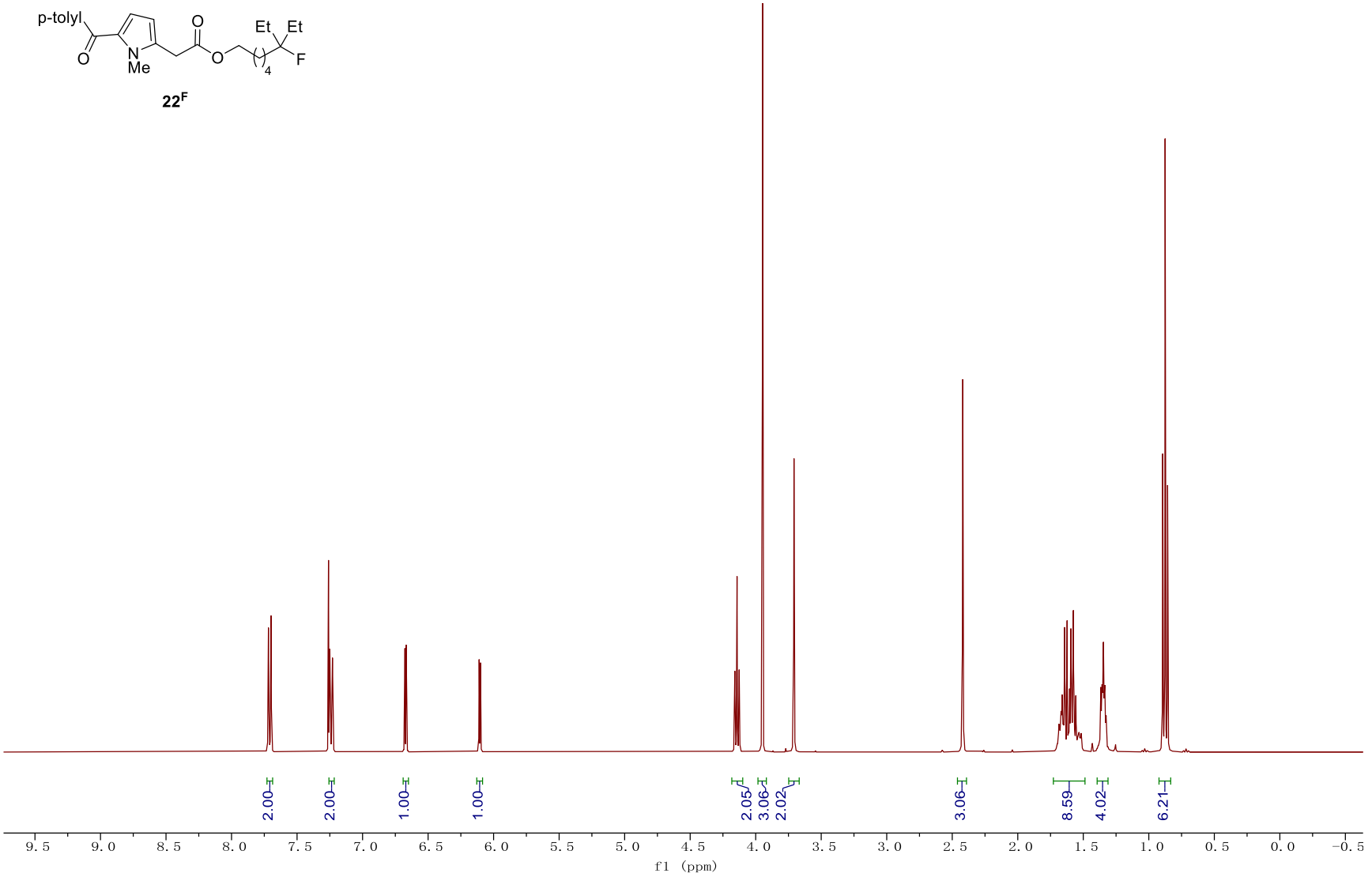

172.09
161.79
145.40
135.15
132.48
129.01
128.65
128.56
128.45
128.06
127.90
126.47
100.32
98.64
64.84
36.02
35.79
31.21
29.08
28.84
28.59
26.37
23.60
22.92
22.87
7.74
7.67
O
Et
Et
Ph
O
O
F
N
Ph
4
21F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

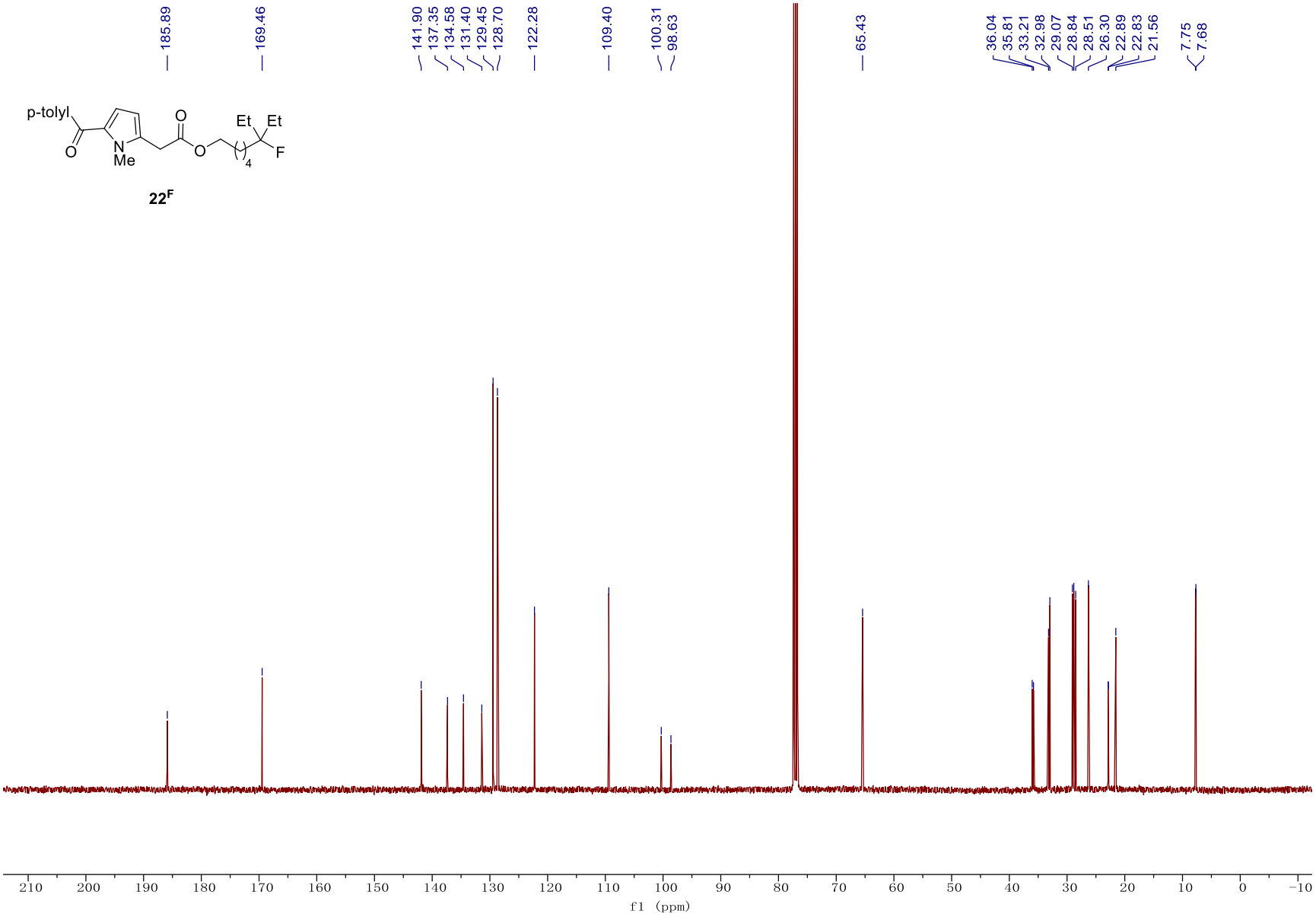

O
Et
Et
O
O
4
F
Ph
N
Ph

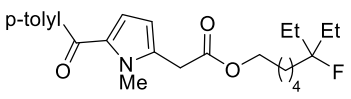
21^{F}


-154.04
-154.10
-154.15
-154.20
-154.25
-154.30
-154.35


30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

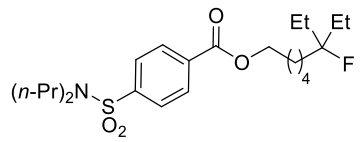

p-tolyl
O
N
Me
O
O
Et
Et
F
4
22F
2.00
2.00
1.00
1.00
2.05
3.06
2.02
3.06
8.59
4.02
6.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


185.89
169.46
141.90
137.35
134.58
131.40
129.45
128.70
122.28
109.40
100.31
98.63
65.43
36.04
35.81
33.21
32.98
29.07
28.84
28.51
26.30
22.89
22.83
21.56
7.75
7.68
p-tolyl
O
N
Me
O
O
Et
Et
F
4
22F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


p-tolyl
O
N
Me
O
O
Et
Et
F
4

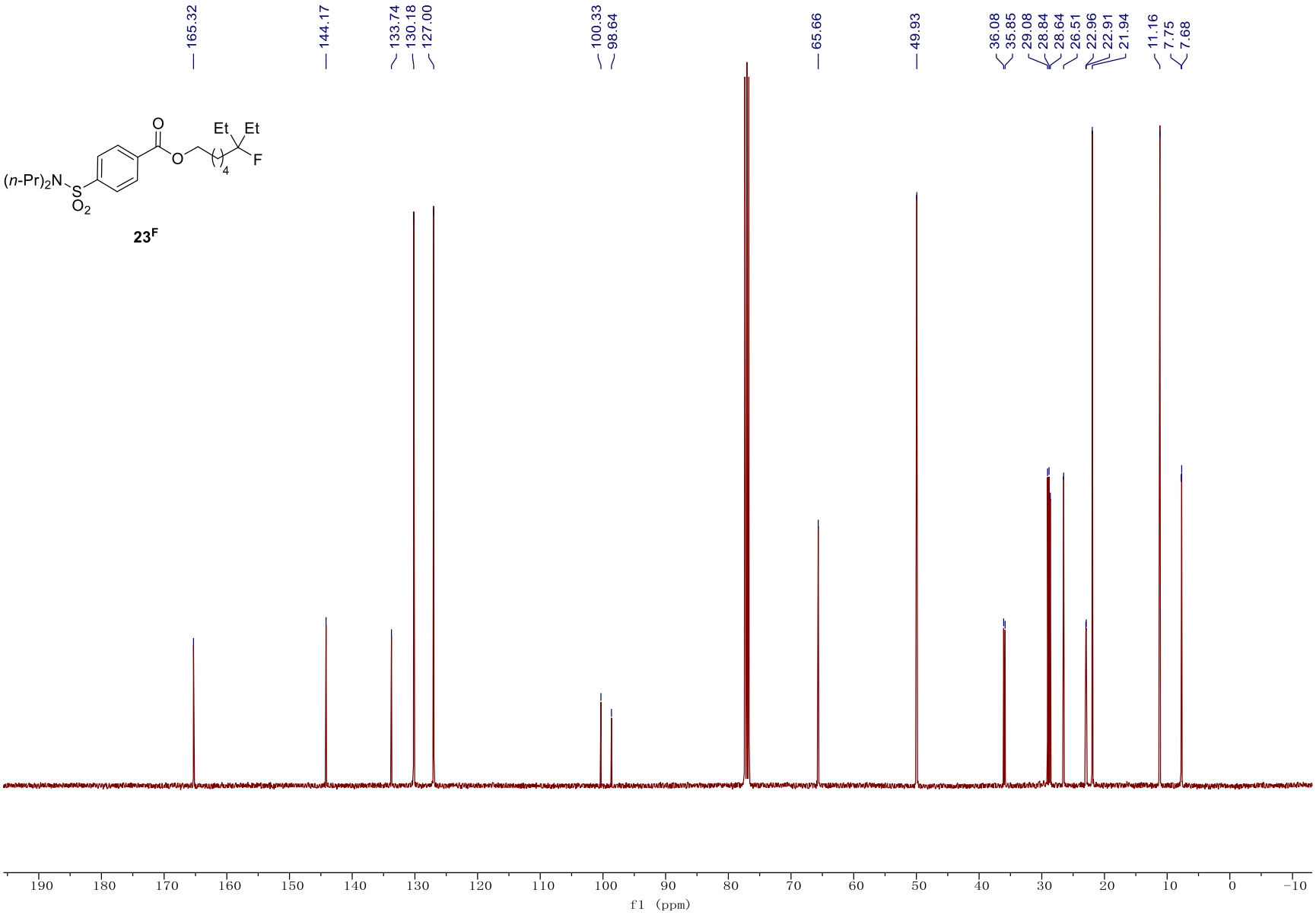
22^{F}

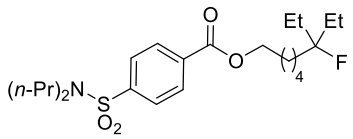
-154.02
-154.07
-154.13
-154.18
-154.23
-154.28
-154.33
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)


O
Et
Et
O
4
F
(n-Pr)2N
S
O2

23^{F}

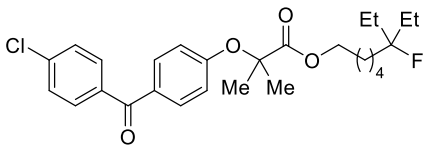
2.00
2.00
1.99
4.02
2.02
14.51
12.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


165.32
144.17
133.74
130.18
127.00
100.33
98.64
65.66
49.93
36.08
35.85
29.08
28.84
28.64
26.51
22.96
22.91
21.94
11.16
7.75
7.68
(n-Pr)2N
S
O2
O
O
Et
Et
F
4
23F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

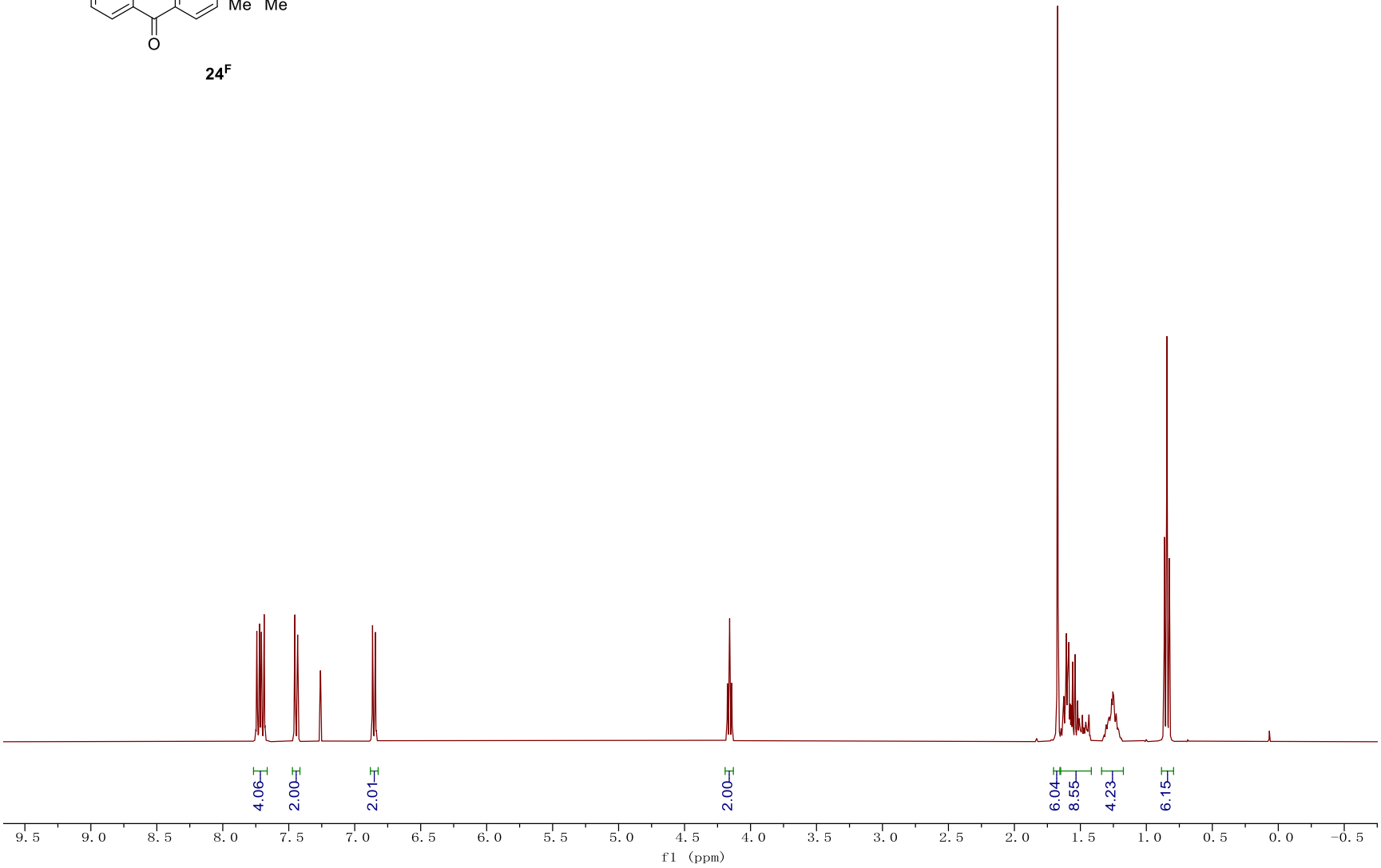

O
Et
Et
O
4
F
(n-Pr)2N
S
O2

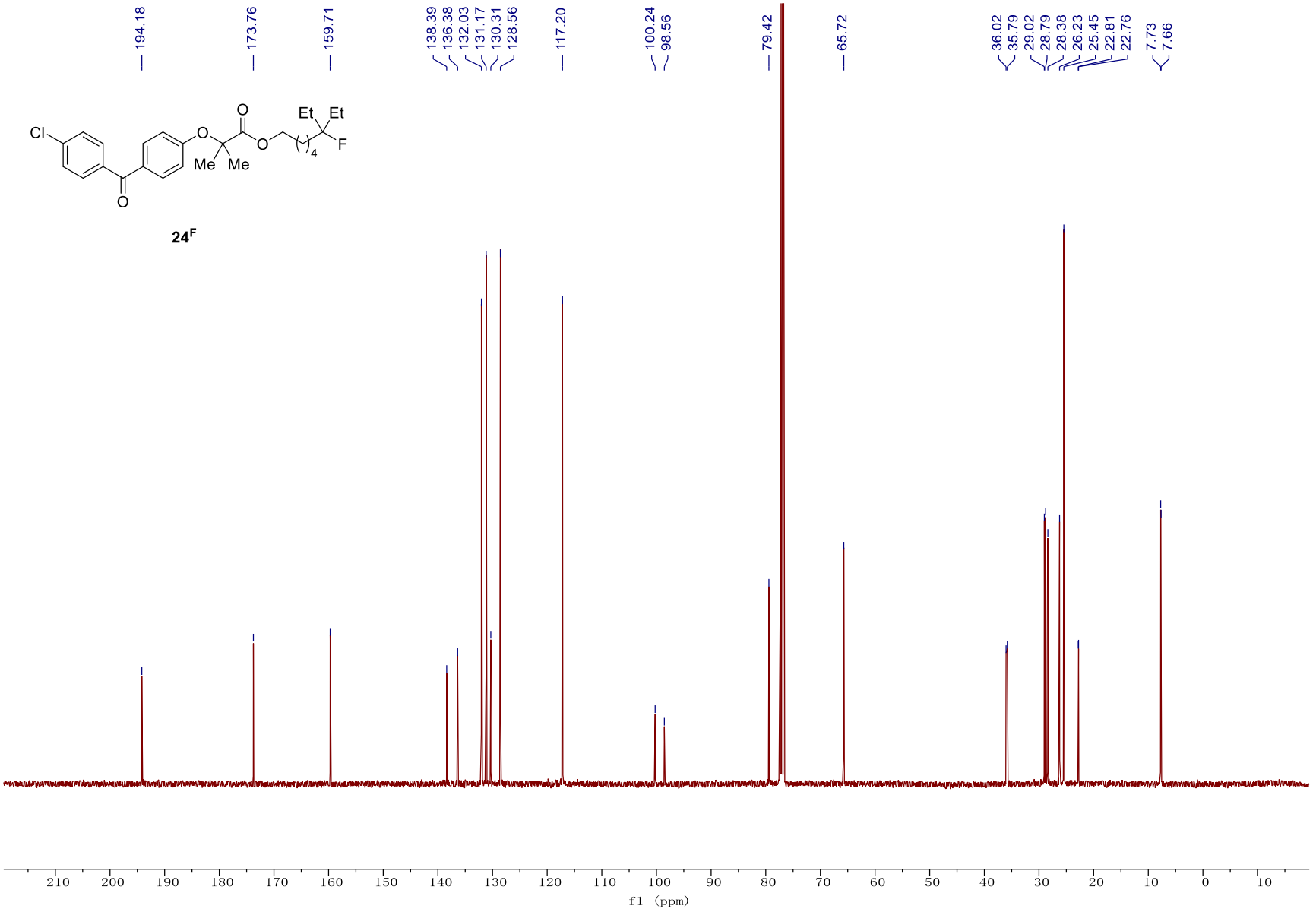
23^{F}

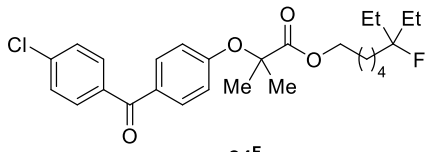
-154.04
-154.05
-154.09
-154.10
-154.14
-154.15
-154.19
-154.20
-154.25
-154.25
-154.28
-154.30
-154.30
-154.35
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)


Cl
O
O
Me
Me
O
O
Et
Et
F
4

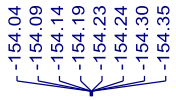
24^{F}

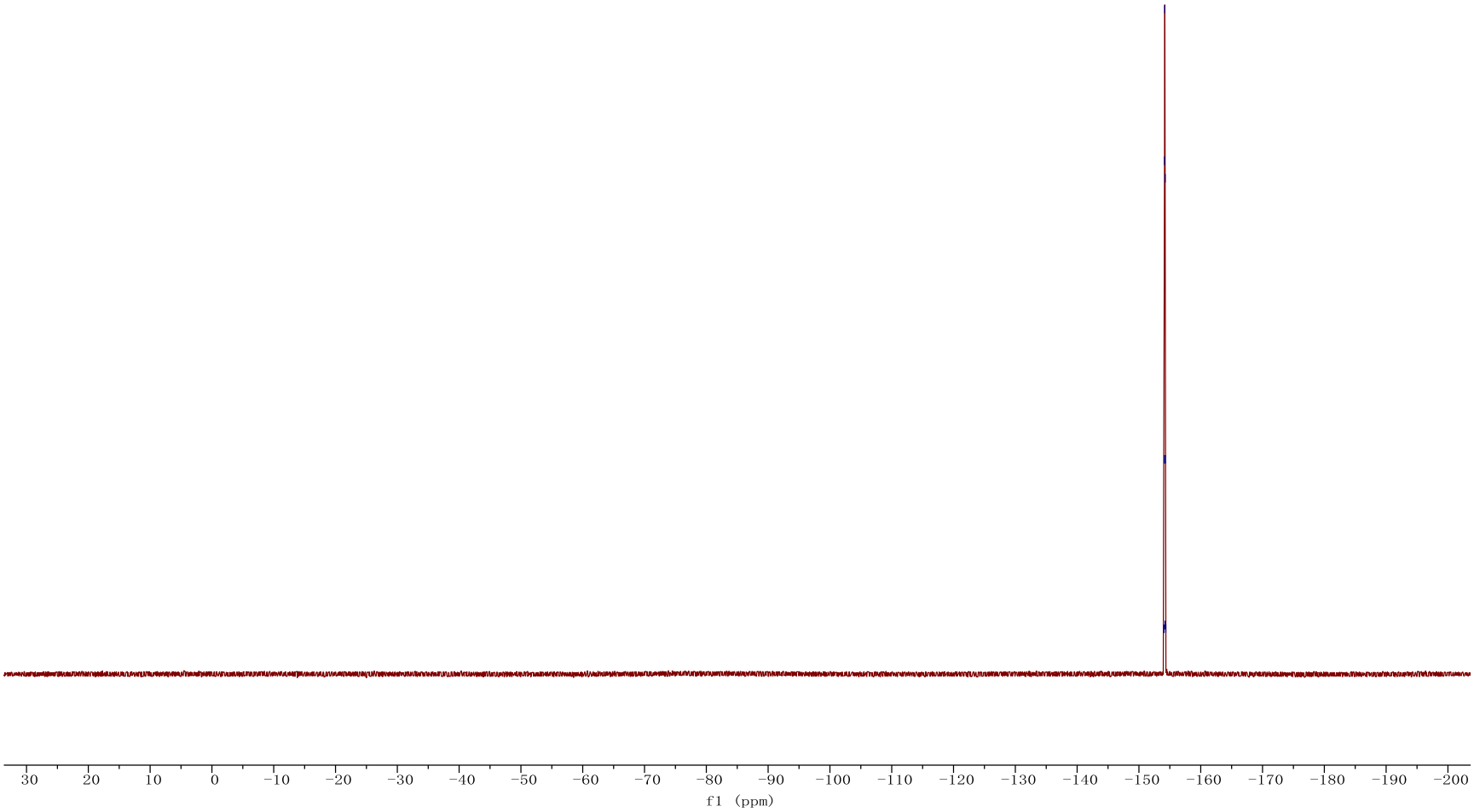

4.06
2.00
2.01
2.00
6.04
8.55
4.23
6.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

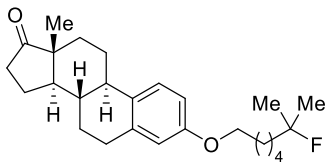

194.18
173.76
159.71
138.39
136.38
132.03
131.17
130.31
128.56
117.20
100.24
98.56
79.42
65.72
36.02
35.79
29.02
28.79
28.38
26.23
25.45
22.81
22.76
7.73
7.66
Cl
O
O
Et
Et
O
O
F
Me
Me
4
O
24F
f1 (ppm)


Cl
O
O
Me
Me
O
O
Et
Et
F
4

24^{F}

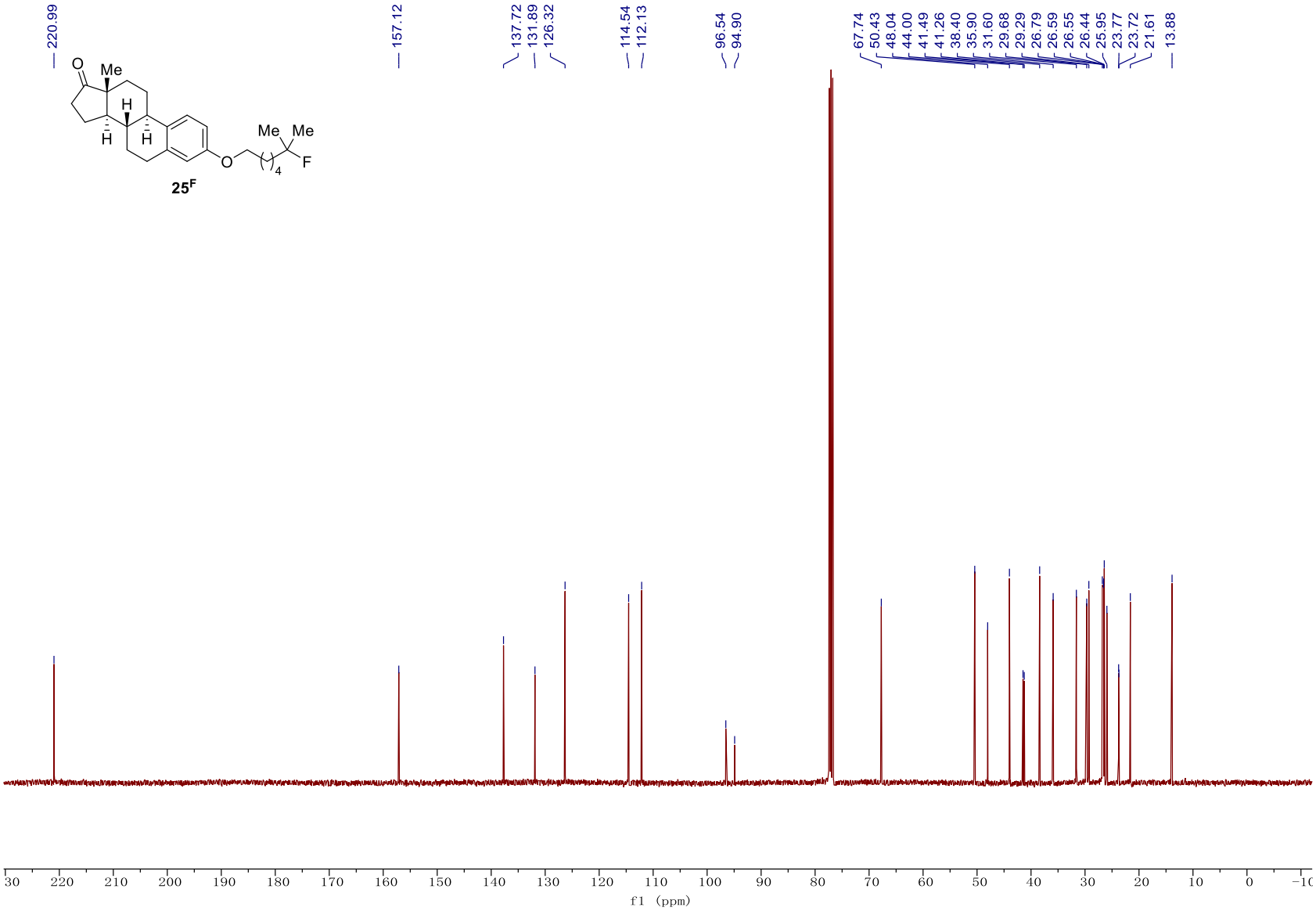

-154.04
-154.09
-154.14
-154.19
-154.23
-154.24
-154.30
-154.35

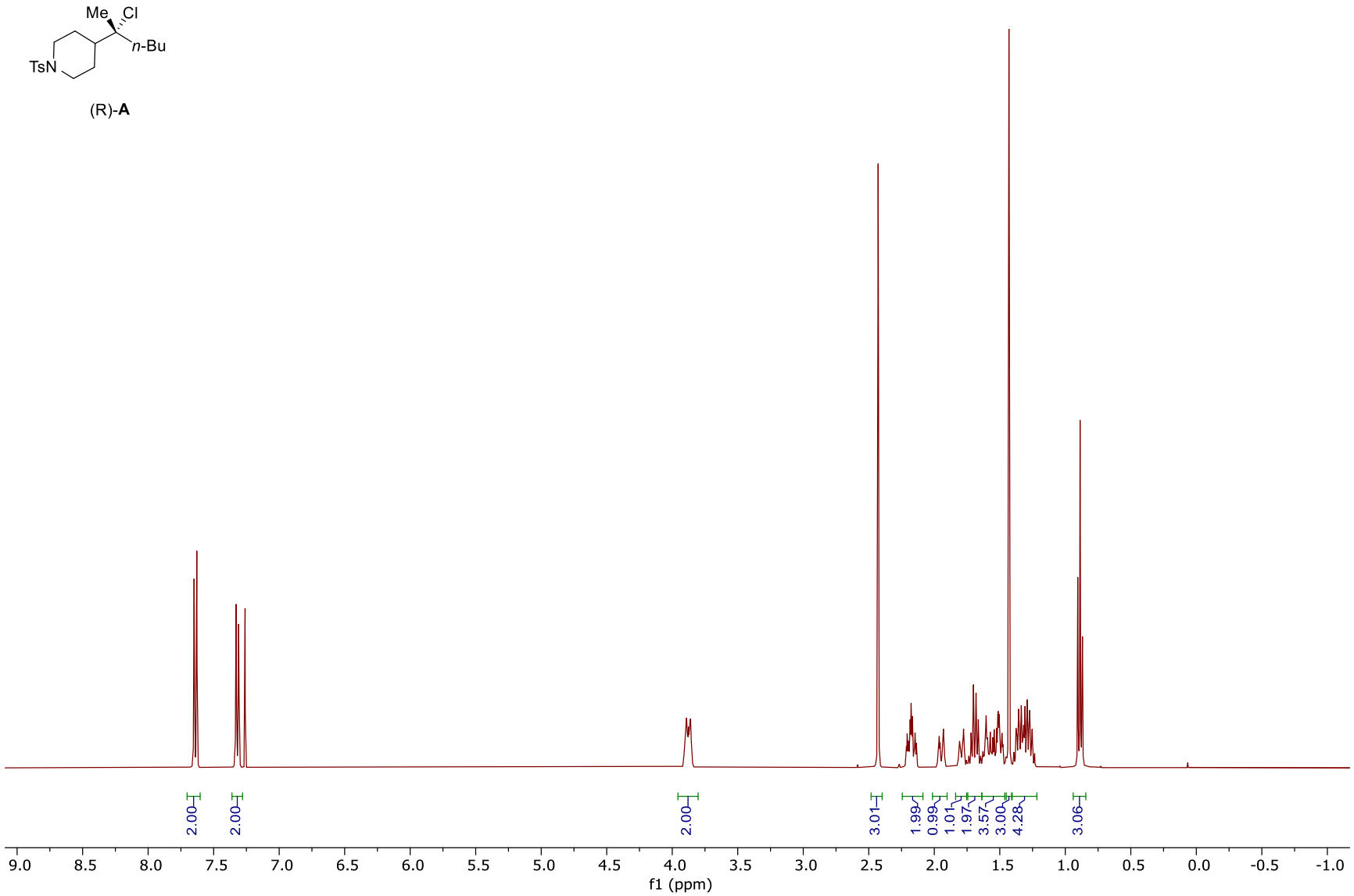

30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

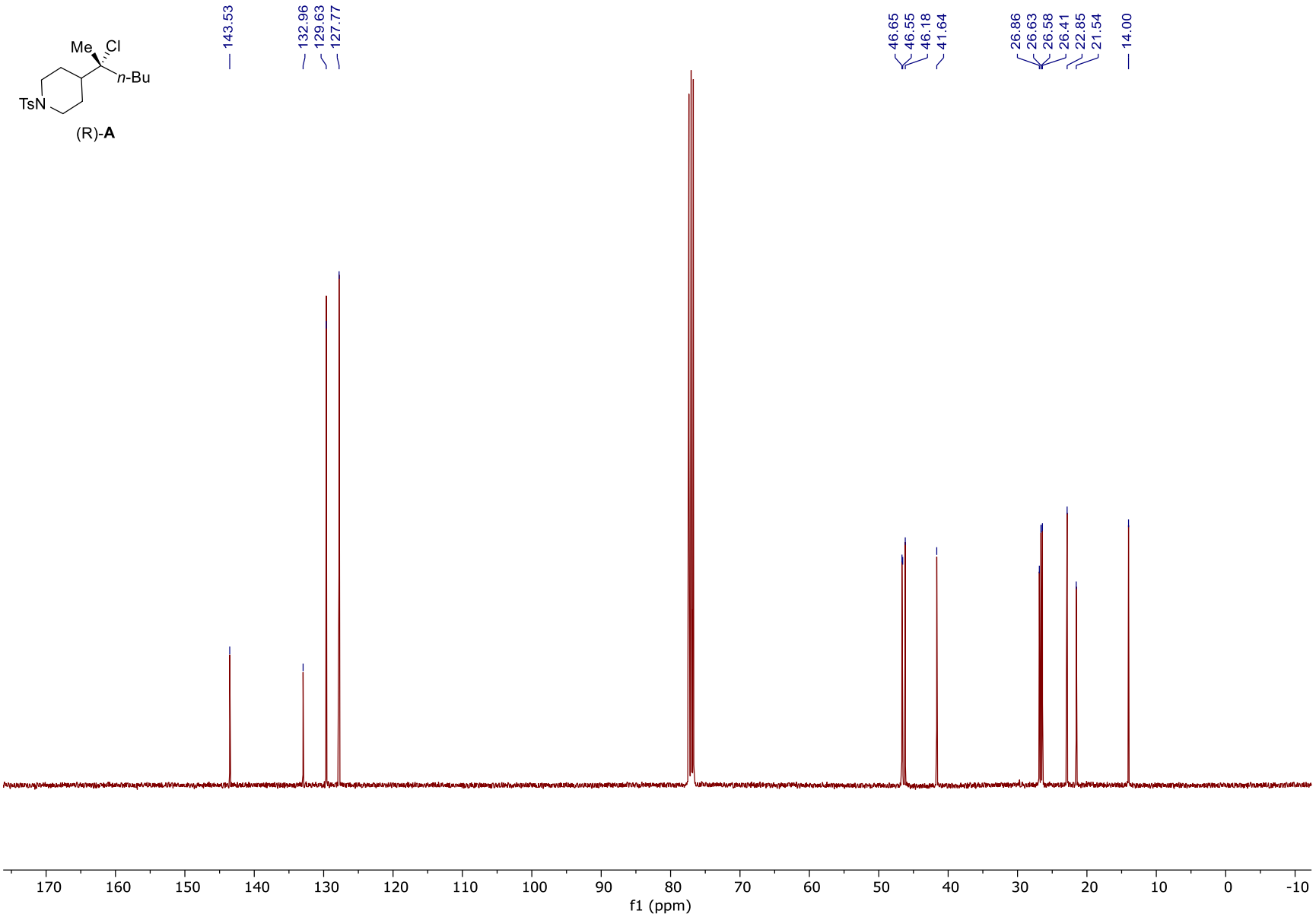

O
Me
H
H
H
Me
Me
O
4
F

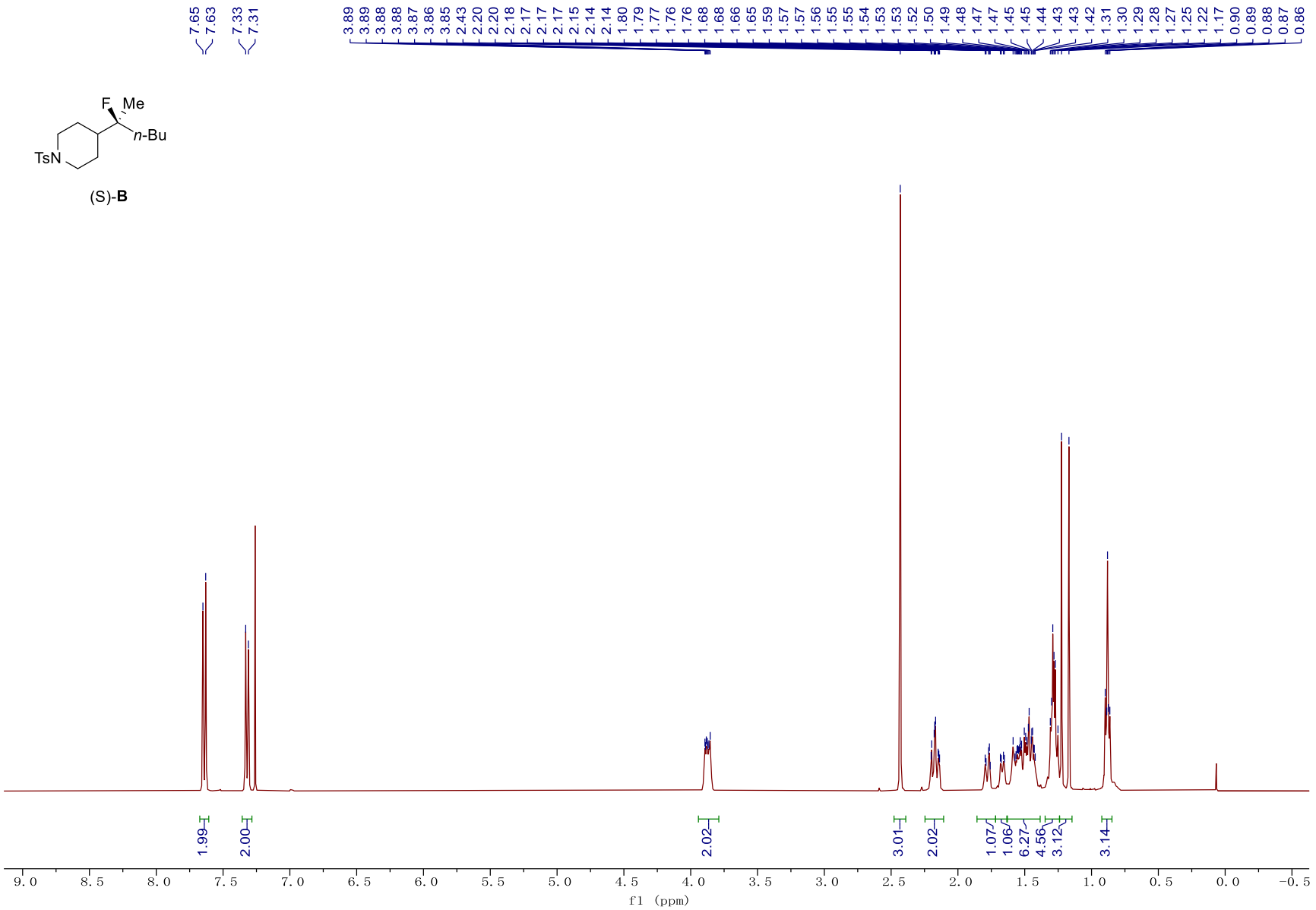
25^{F}

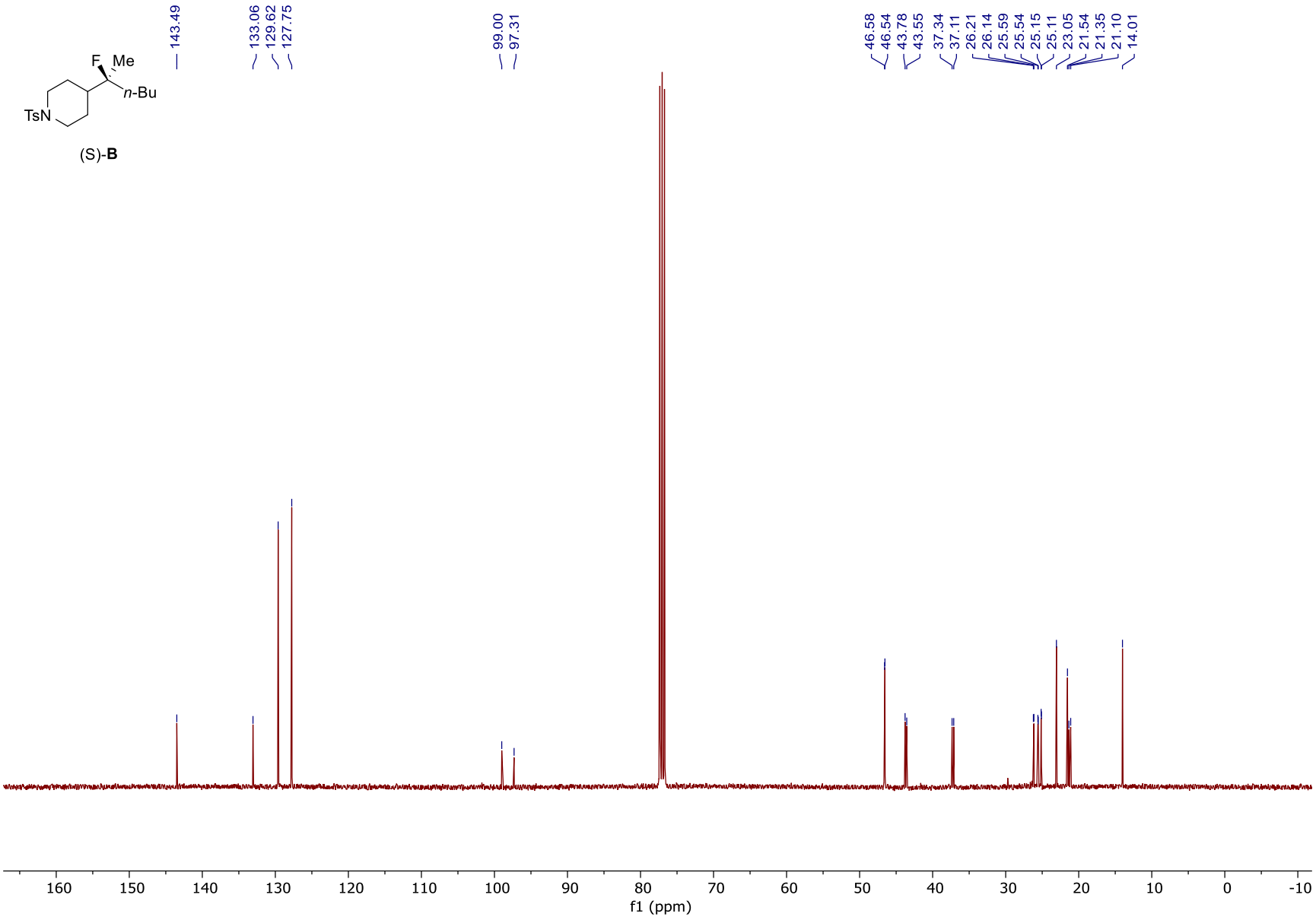
1.00
1.02
1.01
2.04
2.00
1.00
0.98
1.03
4.12
2.01
12.73
6.30
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

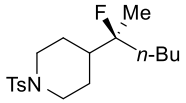

220.99
157.12
137.72
131.89
126.32
114.54
112.13
96.54
94.90
67.74
50.43
48.04
44.00
41.49
41.26
38.40
35.90
31.60
29.68
29.29
26.79
26.59
26.55
26.44
25.95
23.77
23.72
21.61
13.88
O
Me
H
H
H
Me
Me
O
4
F
25F
f1 (ppm)


Me
Cl
n-Bu
TsN
(R)-A
2.00
2.00
2.00
3.01
1.99
0.99
1.01
1.97
3.57
3.00
4.28
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

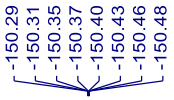

Me
Cl
n-Bu
TsN
(R)-A
143.53
132.96
129.63
127.77
46.65
46.55
46.18
41.64
26.86
26.63
26.58
26.41
22.85
21.54
14.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

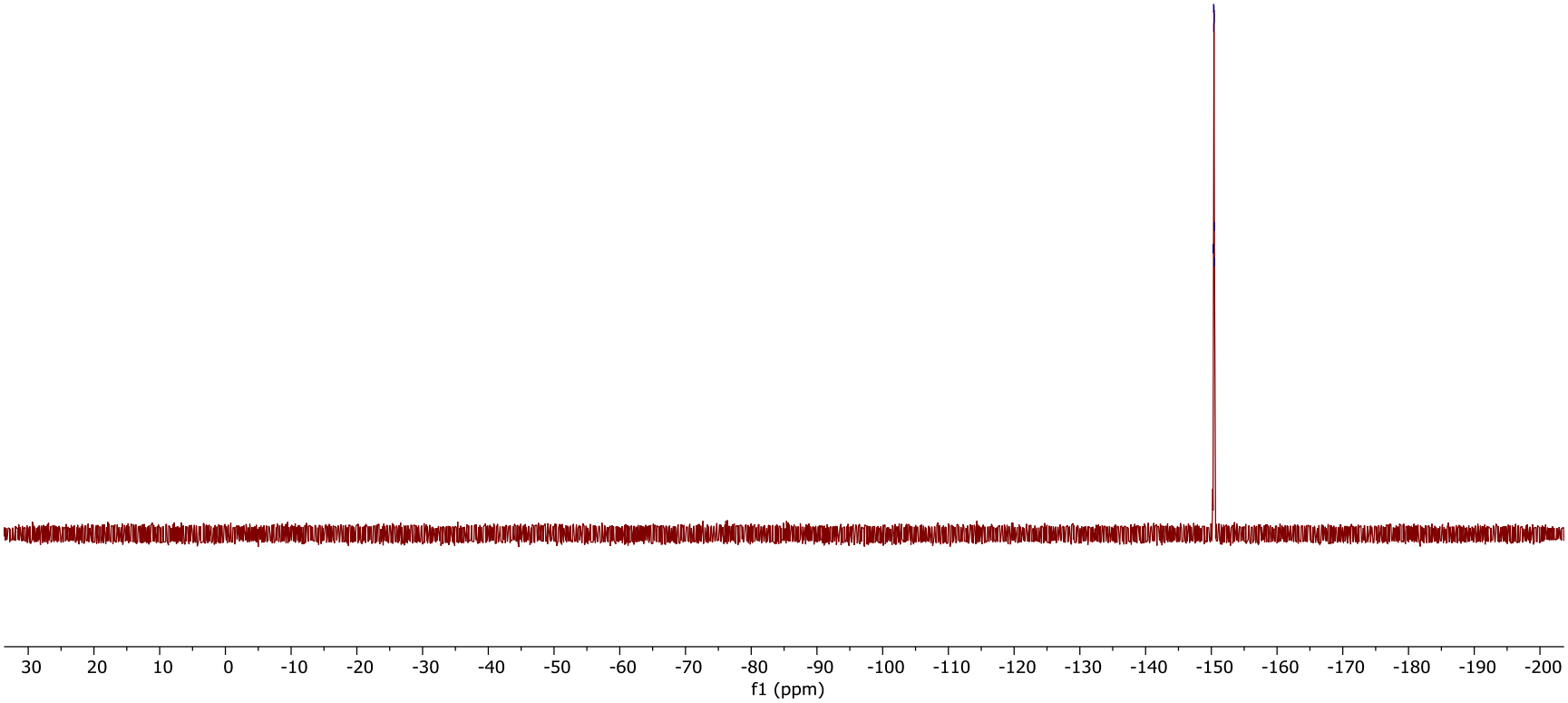

7.65
7.63
7.33
7.31
3.89
3.89
3.88
3.88
3.87
3.86
3.85
2.43
2.20
2.20
2.18
2.17
2.17
2.17
2.15
2.14
2.14
1.80
1.79
1.77
1.76
1.76
1.68
1.68
1.66
1.65
1.59
1.57
1.57
1.56
1.55
1.55
1.54
1.53
1.53
1.52
1.50
1.49
1.48
1.47
1.47
1.45
1.45
1.44
1.43
1.43
1.42
1.31
1.30
1.29
1.28
1.27
1.25
1.22
1.17
0.90
0.89
0.88
0.87
0.86
F
Me
n-Bu
TsN
(S)-B
1.99
2.00
2.02
3.01
2.02
1.07
1.06
6.27
4.56
3.12
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

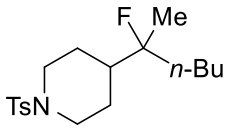

143.49
133.06
129.62
127.75
99.00
97.31
46.58
46.54
43.78
43.55
37.34
37.11
26.21
26.14
25.59
25.54
25.15
25.11
23.05
21.54
21.35
21.10
14.01
F
Me
n-Bu
TsN
(S)-B
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
Me
n-Bu
TsN

(S)-**B**

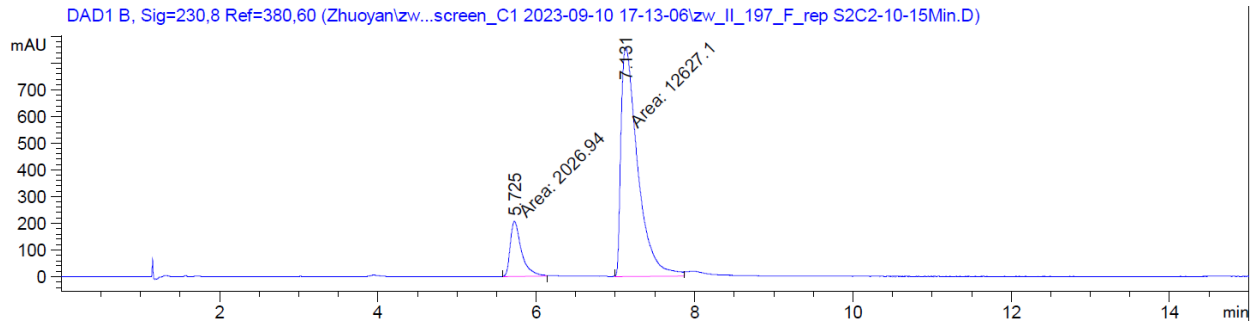

-150.29
-150.31
-150.35
-150.37
-150.40
-150.43
-150.46
-150.48


30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)



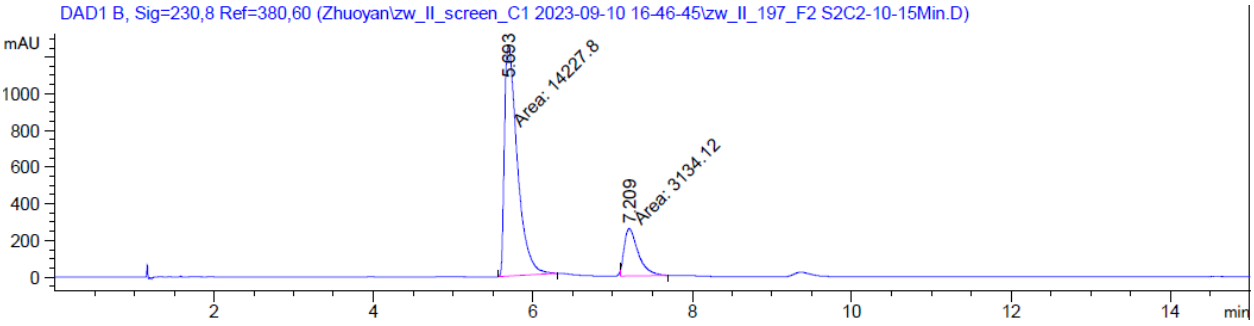
4-(2-Fluorohexan-2-yl)-1-tosylpiperidine (B)

(S)-**B**: from (R)-**A** (>99% ee), 72% ee



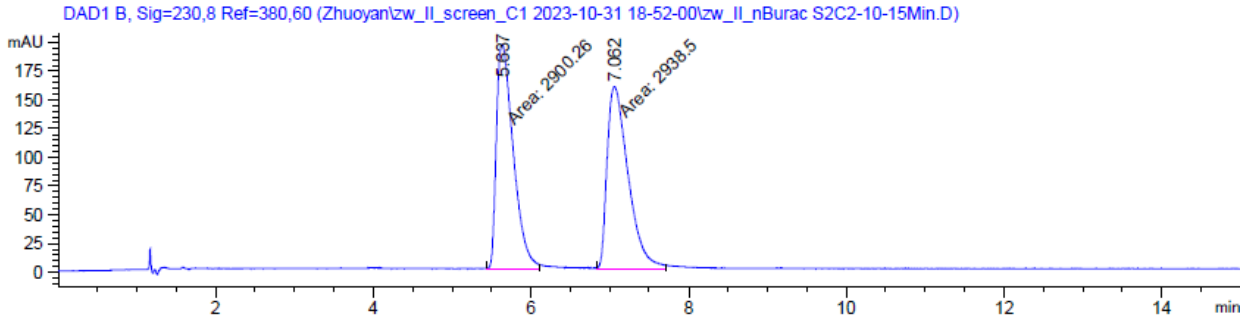
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.725	FM	0.1634	2026.94214	206.68449	13.8320
2	7.131	FM	0.2449	1.26271e4	859.50641	86.1680

(R)-**B**: from (S)-**A** (>90% ee), 64% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.693	FM	0.1883	1.42278e4	1259.24854	81.9484
2	7.209	FM	0.2025	3134.11743	257.89359	18.0516

rac-**B**: from *rac*-**A**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.637	MM T	0.2476	2900.25513	195.22202	49.6725
2	7.062	MM T	0.3086	2938.49756	158.72342	50.3275