Supporting Information

Chromium-Catalyzed Allylic Defluorinative Ketyl Olefin Coupling

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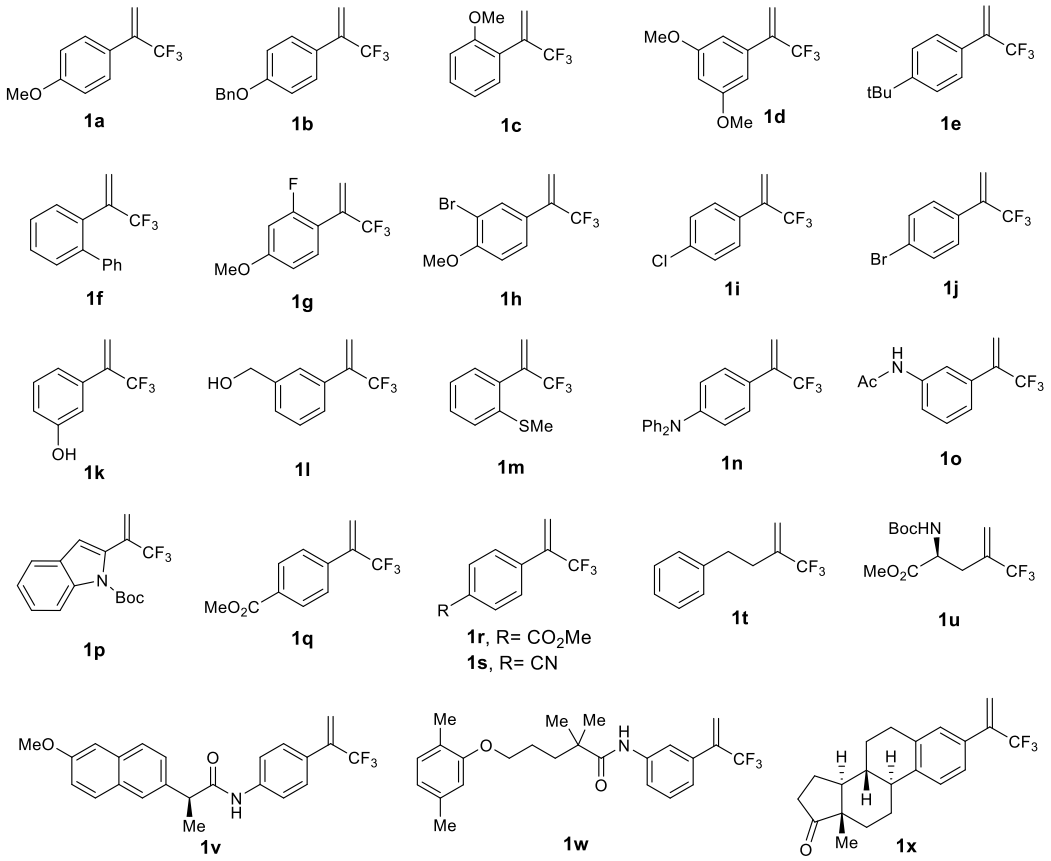
General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$ or CD_3OD at 400 and 101 MHz. ^{19}F NMR were reported as ^{19}F exp. comp. pulse decoupling (F19CPD) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ ($SiMe_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ ($CDCl_3$) = 7.26, ^{13}C: δ ($CDCl_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Unless otherwise noted, all reagents and starting materials were purchased from commercial vendors and used without further purification.

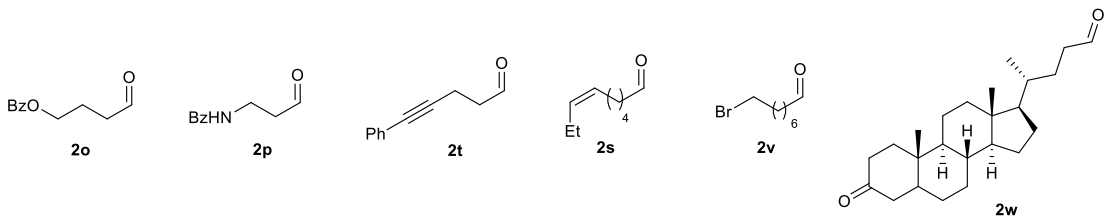
Preparation of Substrates

Synthesis of α-Trifluoromethyl Alkenes



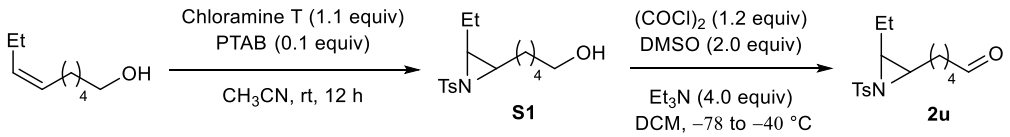
The α-trifuoromethyl alkenes **1a**,[1] **1c–f**,[1] **1i-j**,[1] **1p**,[1] **1r**,[1] **1b**,[2] **1g-h**,[2] **l-n**,[2] **1q**,[2] **1t**,[2] **1v-x,**[3] **1o**,[4] **1k**,[4] **1s**,[4] and **1u**[5] and are known compounds in the literature.

Synthesis of Aldehydes



The aldehydes **2o**,[6] **2p**,[7] **2t**,[8] **2s**,[9] **2v**,[10] and **2w**[11] were synthesized following the reported procedures, and the other aldehydes are commercially available.

Procedure for the Preparation of *cis*-5-(3-Ethyl-1-tosylaziridin-2-yl)pentanal (2u)



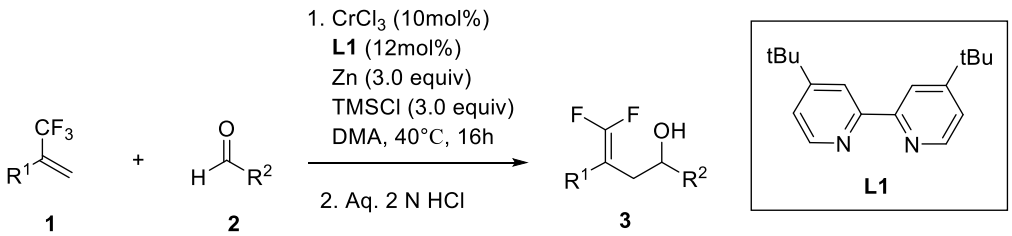
Step1: To a mixture of (*Z*)-non-6-en-1-ol (2.52 g, 30 mmol, 1.0 equiv) and anhydrous Chloramine-T (7.51 g, 33 mmol, 1.1 equiv) in CH_3CN (150 mL) was added phenyltrimethylammonium tribromide (PTAB) (1.13 g, 3 mmol, 0.1 equiv) at 25 ˚C. After vigorous stirring for 12h, aqueous NH_4Cl was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate 1:2) over silica gel, to afford *5-(3-ethyl-1-tosylaziridin-2-yl)pentanal* (**S1**) (8.16 g, 88%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.82 (d, *J*= 7.9 Hz, 2H), 7.33 (d, *J*= 7.9 Hz, 2H), 3.60 (t, *J*= 6.6 Hz, 2H), 2.85-2.76 (m, 1H), 2.74-2.68 (m, 1H), 2.44 (s, 3H), 1.58-1.44 (m, 4H), 1.43-1.30 (m, 6H), 0.84 (t, *J*= 7.5 Hz, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 144.3, 135.3, 129.5 (2C), 128.1 (2C), 62.6, 46.8, 45.1, 32.5, 27.1, 26.5, 25.2, 21.6, 20.1, 11.6 ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{25}NO_3SNa$ $[M+Na]^+$: 334.1447, found: 310.1455.

Step 2: DMSO (3.75 mL, 52.8 mmol, 2.0 equiv) was added dropwise within 5 min to a solution of oxalyl chloride (2.76 mL, 31.7 mmol, 1.2 equiv) in CH_2Cl_2 (264 mL) at –78 °C, and the resultant solution was stirred at this temperature for 5 min. Next, a solution of 5-(3-ethyl-1-tosylaziridin-2-yl)pentan-1-ol (**S1**) (8.16 g, 26.4 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was then added slowly within 10 min, and the resultant mixture was stirred for an additional 5 min at –78 °C. Subsequently, Et_3N (14.6 mL, 106 mmol, 4.0 equiv) was added slowly via syringe, and the reaction contents were allowed to warm slowly to –40 °C within 2 h. Upon completion, the reaction contents were quenched by the addition of water (200 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were then washed with 1 M HCl (100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified purified through column chromatography (petroleum ether/ethyl acetate 1:1) over silica gel, to afford *5-(3-ethyl-1-tosylaziridin-2-yl)pentanal* (**2u**) (6.77 g, 83%)

^{1}H NMR (500 MHz, Chloroform-*d*) δ= 9.72 (t, *J*= 1.7 Hz, 1H), 7.82 (d, *J*= 8.1 Hz, 2H), 7.33 (d, *J*= 8.1 Hz, 2H), 2.80-2.76 (m, 1H), 2.75-2.70 (m, 1H), 2.45 (s, 3H), 2.36 (td, *J*= 7.2, 1.7 Hz, 2H), 1.63-1.57 (m, 2H), 1.55-1.48 (m, 2H), 1.42-1.35 (m, 2H), 1.36-1.28 (m, 2H), 0.85 (t, *J*= 7.5 Hz, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 202.2, 144.4, 135.3, 129.5 (2C), 128.1 (2C), 46.7, 44.8, 43.6, 26.9, 26.4, 21.64, 21.57, 20.1, 11.6 ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{24}NO_3S$ $[M+H]^+$: 310.1471, found: 310.1474.

Standard Procedure for Cr-Catalyzed Allylic Defluorinative Ketyl Olefin Coupling

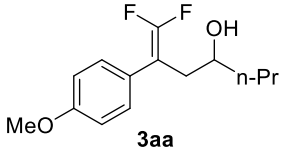


$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol %),[a] the ligand 4,4'-ditertbutyl-2,2'-bipyridine (**L1**)[a] (6.4 mg, 0.024 mmol, 12 mol %) and Zn (39 mg, 0.6 mmol, 3.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, TMSCl (65.2 mg, 78 μ L, 0.6 mmol, 3 equiv) and the aldehydes **2** (0.4 mmol, 2.0 equiv) were added under a positive flow of nitrogen. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before the α-trifluoromethyl alkenes **1** (0.2 mmol, 1.0 equiv) were added under nitrogen atmosphere. The reaction mixture was stirred at 40℃ for 16 hours, before it was quenched by addition of 2 mL aqueous HCl (2 N). After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude materials were then purified through column chromatography over silica gel (petroleum ether/ethyl acetate) to give the *gem*-difluoroalkenes **3** as the products.

[a] 7.5 mol% $CrCl_3$ and 9 mol% 3,4,7,8-Tetramethylphenanthroline (**L4**) were used for compound **3ax**.

Characterization Data of *gem*-Difluoroalkenes 3

1,1-Difluoro-2-(4-methoxyphenyl)hept-1-en-4-ol (3aa)



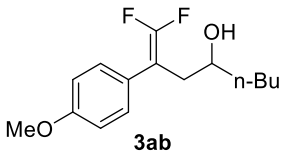
3aa

The title compound **3aa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (48.3 mg, 94%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.33-7.19 (m, 2H), 6.89 (d, *J*= 8.8 Hz, 2H), 3.80 (s, 3H), 3.65-3.49 (m, 1H), 2.50 (dd, *J*= 5.7, 3.2 Hz, 2H), 1.65-1.53 (brs, 1H),

1.50 – 1.27 (m, 4H), 0.88 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 289.7, 287.0 Hz), 129.4 (t, *J*= 3.3 Hz, 2C), 125.5 (dd, *J*= 4.2, 3.0 Hz), 114.0 (2C), 89.3 (dd, *J*= 21.4, 14.6 Hz), 69.6 (t, *J*= 2.8 Hz), 55.2, 39.1, 36.0 (d, *J*= 1.5 Hz), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –91.01 (d, *J*= 43.6 Hz, 1F), –91.40 (d, *J*= 43.6 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{19}F_2O_2$ $[M+H]^+$: 257.1348, found: 257.1365.

1,1-Difluoro-2-(4-methoxyphenyl)oct-1-en-4-ol (3ab)

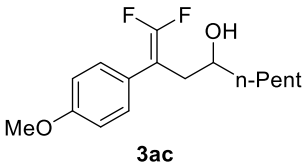


3ab

The title compound **3ab** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (50.7 mg, 94%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.34-7.10 (m, 2H), 6.89 (d, *J*= 8.8 Hz, 2H), 3.81 (s, 3H), 3.66-3.49 (m, 1H), 2.54-2.40 (m, 2H), 1.49-1.24 (m, 6H), 0.87 (t, *J*= 7.0 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 289.8, 286.9 Hz), 129.4 (t, *J*= 3.1 Hz, 2C), 125.5 (dd, *J*= 4.2, 3.0 Hz), 114.0 (2C), 89.3 (dd, *J*= 21.3, 14.6 Hz), 69.9 (t, *J*= 2.7 Hz), 55.3, 36.6, 36.0 (d, *J* = 1.5 Hz), 27.7, 22.7, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.97 (d, *J*= 43.5 Hz, 1F), –91.37 (d, *J*= 43.5 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2O_2Na$ $[M+Na]^+$: 293.1324, found: 293.1335.

1,1-Difluoro-2-(4-methoxyphenyl)non-1-en-4-ol (3ac)



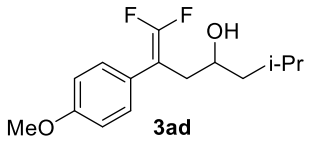
3ac

The title compound **3ac** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (52.8 mg, 93%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.31-7.17 (m, 2H), 6.90 (d, *J*= 8.8 Hz, 2H), 3.81 (s, 3H), 3.65-3.48 (m, 1H), 2.54–2.44 (m, 2H), 1.47-1.25 (m, 8H), 0.87 (t, *J*= 6.9 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 289.7, 287.0 Hz), 129.4 (t, *J*= 3.1 Hz, 2C), 125.5 (dd, *J*= 4.2, 3.0 Hz), 114.0 (2C), 89.3 (dd, *J*= 21.5, 14.7 Hz), 69.9 (t, *J*= 2.7 Hz), 55.3, 36.9, 36.0 (d, *J*= 1.5 Hz), 31.8, 25.2, 22.6, 14.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.97 (d, *J*= 43.6 Hz, 1F), –91.36 (d, *J*= 43.3 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{22}F_2O_2Na$ $[M+Na]^+$: 307.1480, found: 307.1486.

1,1-Difluoro-2-(4-methoxyphenyl)-6-methylhept-1-en-4-ol (3ad)

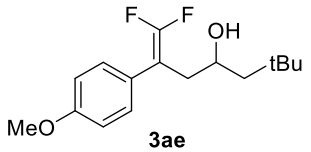


3ad

The title compound **3ad** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (48.6 mg, 90%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.28-7.23 (m, 2H), 6.89 (d, *J*= 8.8 Hz, 2H), 3.80 (s, 3H), 3.72-3.58 (m, 1H), 2.49 (dt, *J*= 6.5, 2.4 Hz, 2H), 1.79-1.67 (m, 1H), 1.63-1.53 (brs, 1H), 1.45-1.34 (m, 2H), 0.88 (d, *J*= 6.7 Hz, 3H), 0.82 (d, *J*= 6.6 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 289.6, 287.0 Hz), 129.4 (t, *J*= 3.1 Hz, 2C), 125.5 (dd, *J*= 4.2, 2.8 Hz), 114.0 (2C), 89.3 (dd, *J*= 21.3, 14.7 Hz), 68.0 (t, *J*= 2.8 Hz), 55.2, 46.1, 36.5 (d, *J*= 1.4 Hz), 24.6, 23.4, 22.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –91.03 (d, *J*= 43.1 Hz, 1F), –91.35 (d, *J*= 43.3 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2O_2Na$ $[M+Na]^+$: 293.1329, found: 293.1333.

1,1-Difluoro-2-(4-methoxyphenyl)-6,6-dimethylhept-1-en-4-ol (3ae)

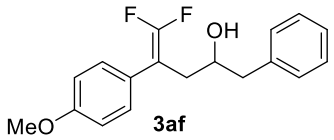


3ae

The title compound **3ae** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (50.5 mg, 89%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.39-7.12 (m, 2H), 6.90 (d, *J*= 8.8 Hz, 2H), 3.81 (s, 3H), 3.76-3.68 (m, 1H), 2.60-2.40 (m, 2H), 1.41-1.35 (m, 2H), 0.89 (s, 9H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.4 (t, *J*= 288.5 Hz), 129.4 (d, *J*= 6.3 Hz, 2C), 125.4 (d, *J*= 1.4 Hz), 114.0 (2C), 89.4 (dd, *J*= 18.5, 17.2 Hz), 67.7 (t, *J*= 2.8 Hz), 55.2, 50.5, 37.8, 30.3, 30.1 (3C) ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –91.13 (s, 2F) ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{22}F_2O_2Na$ $[M+Na]^+$: 307.1480, found: 307.1490.

5,5-Difluoro-4-(4-methoxyphenyl)-1-phenylpent-4-en-2-ol (3af)

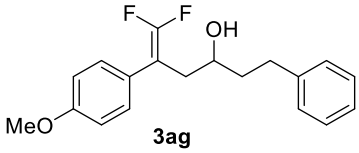


3af

The title compound **3af** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (52.3 mg, 86%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.31-7.20 (m, 5H), 7.16-7.12 (m, 2H), 6.92-6.86 (m, 2H), 3.81 (s, 3H), 3.80-3.76 (m, 1H), 2.83 (dd, *J*= 13.6, 4.3 Hz, 1H), 2.67 (dd, *J*= 13.6, 8.6 Hz, 1H), 2.62-2.53 (m, 2H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 289.8, 287.3 Hz), 138.1 (2C), 129.4 (t, *J*= 3.1 Hz, 2C), 129.3 (2C), 128.6, 126.6, 125.3 (d, *J*= 2.6 Hz), 114.0 (2C), 89.2 (dd, *J*= 21.2, 15.1 Hz), 70.7 (t, *J*= 2.8 Hz), 55.3, 43.5, 35.4 (d, *J*= 1.8 Hz) ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.80 (d, *J*= 43.0 Hz, 1F), –91.10 (d, *J*= 42.9 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{18}H_{18}F_2O_2Na$ $[M+Na]^+$: 327.1173, found: 327.1178.

6,6-Difluoro-5-(4-methoxyphenyl)-1-phenylhex-5-en-3-ol (3ag)

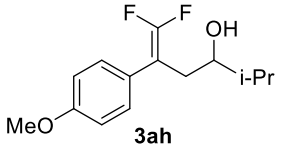


3ag

The title compound **3ag** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (58.5 mg, 92%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.30-7.19 (m, 4H), 7.21-7.14 (m, 1H), 7.14 (d, *J*= 8.1 Hz, 2H), 6.88 (d, *J*= 8.8 Hz, 2H), 3.80 (s, 3H), 3.63 (dd, *J*= 7.2, 4.5 Hz, 1H), 2.84-2.70 (m, 1H), 2.67-2.56 (m, 1H), 2.54 (dt, *J*= 6.4, 2.5 Hz, 2H), 1.86-1.69 (m, 2H), 1.59-1.50 (brs, 1H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.9, 154.3 (dd, *J*= 289.8, 287.3 Hz), 141.8, 129.5 (t, *J*= 3.2 Hz, 2C), 128.4 (2C), 128.4 (2C), 125.9, 125.4 (dd, *J*= 4.0, 2.8 Hz), 114.1 (2C) , 89.1 (dd, *J*= 21.3, 14.9 Hz), 69.4 (t, *J*= 2.7 Hz), 55.3, 38.5, 36.0 (d, *J*= 1.5 Hz), 32.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.73 (d, *J*= 43.1 Hz, 1F), –91.08 (d, *J*= 43.0 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{19}H_{20}F_2O_2Na$ $[M+Na]^+$: 341.1324, found: 341.1322.

6,6-Difluoro-5-(4-methoxyphenyl)-2-methylhex-5-en-3-ol (3ah)

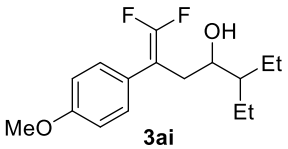


3ah

The title compound **3ah** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (42.5 mg, 83%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.38-7.14 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.48-3.22 (m, 1H), 2.64-2.35 (m, 2H), 1.76-1.57 (m, 1H), 1.51-1.45 (brs, 1H), 0.91 (d, *J*= 6.8 Hz, 3H), 0.90 (d, *J*= 6.8 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 289.5, 286.7 Hz), 129.5 (t, *J*= 3.2 Hz, 2C), 125.5 (dd, *J*= 4.2, 3.2 Hz), 114.0 (2C), 89.5 (dd, *J*= 21.4, 14.4 Hz), 74.2 (t, *J*= 2.5 Hz), 55.2, 33.2, 32.9 (d, *J*= 1.6 Hz), 18.8, 16.9 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.91 (d, *J*= 43.9 Hz, 1F), –91.70 (d, *J*= 44.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{19}F_2O_2$ $[M+H]^+$: 257.1348, found: 257.1365.

5-Ethyl-1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-ol (3ai)

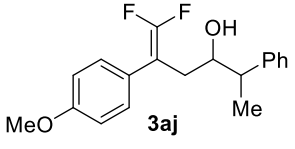


3ai

The title compound **3ai** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (49.4 mg, 87%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.21-7.13 (m, 2H), 6.82 (d, *J*= 8.83 Hz, 2H), 3.73 (s, 3H), 3.52 (dt, *J*= 8.8, 4.5 Hz, 1H), 2.51-2.35 (m, 2H), 1.42-1.31 (m, 2H), 1.27-1.18 (m, 2H), 1.18-1.10 (m, 1H), 0.84-0.70 (m, 6H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 289.8, 286.7 Hz), 129.5 (t, *J*= 3.1 Hz, 2C), 125.5 (dd, *J*= 4.3, 3.1 Hz), 114.0 (2C), 89.7 (dd, *J*= 21.3, 14.3 Hz), 70.9 (t, *J*= 2.5 Hz), 55.2, 46.4, 32.7 (d, *J*= 1.6 Hz), 22.1, 21.2, 11.9, 11.7 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –91.00 (d, *J*= 44.2 Hz, 1F), –91.79 (d, *J*= 44.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{23}F_2O_2$ $[M+H]^+$: 285.1666, found: 285.1669.

6,6-Difluoro-5-(4-methoxyphenyl)-2-phenylhex-5-en-3-ol (3aj)

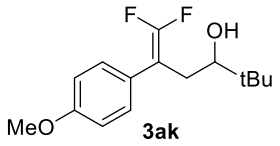


3aj

The title compound **3aj** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil, (54.7 mg, 86%, dr=1.1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ(mixture of two diastereomers)= 7.32-7.26 (m, 2H), 7.24-7.17 (m, 3H), 7.15-7.09 (m, 2H), 6.89-6.83 (m, 2H), 3.79 (s, 3H), 3.67-3.58 (m, 1H), 2.82-2.72 (m, 1H), 2.61-2.33 (m, 2H), 1.29 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 158.8, 154.1 (dd, *J* = 289.4, 287.0 Hz), 144.3, 142.8, 129.5 (t, *J*= 3.1 Hz), 129.4 (t, *J*= 3.3 Hz), 128.6, 128.5, 128.2, 127.7, 126.8, 126.6, 125.5 (dd, *J*= 4.2, 3.1 Hz), 125.1 (dd, *J*= 4.2, 3.1) Hz, 114.0, 89.5 (dd, *J*= 21.3, 14.7Hz), 73.9 (dt, *J*= 5.1, 2.4 Hz), 55.3, 45.8, 45.6, 33.6 (d, *J*= 1.8 Hz), 33.3 (d, *J*= 1.8 Hz), 17.6, 16.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –90.82 (d, *J*= 43.77 Hz, 0.55F), –90.95 (d, *J*= 43.73 Hz, 0.45F), –91.41 (d, *J*= 11.56 Hz, 0.55F), –91.53 (d, *J*= 11.77 Hz, 0.45F) ppm.
HRMS (ESI) m/z calculated for $C_{19}H_{20}F_2O_2Na$ $[M+Na]^+$: 341.1329, found: 341.1337.

6,6-Difluoro-5-(4-methoxyphenyl)-2,2-dimethylhex-5-en-3-ol (3ak)

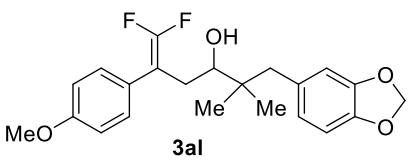


3ak

The title compound **3ak** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (42.1 mg, 78%).

^{1}H NMR(400 MHz, Chloroform-*d*) δ= 7.34-7.20 (m, 2H), 6.90 (d, *J*= 8.8 Hz, 2H), 3.81 (s, 3H), 3.19 (ddd, *J*= 10.5, 2.3, 1.0 Hz, 1H), 2.60-2.28 (m, 2H), 1.51-1.42 (brs, 1H), 0.91 (s, 9H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 289.6, 286.3 Hz), 129.5 (t, *J*= 3.2 Hz, 2C), 125.5 (dd, *J*= 4.3, 3.3 Hz), 114.0(2C), 90.0 (dd, *J*= 21.4, 14.2 Hz), 55.2, 34.8, 30.5 (d, *J*= 1.6 Hz), 25.6 (4C) ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ= –90.84 (d, *J*= 44.7 Hz, 1F), –91.99 (d, *J*= 44.8 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2O_2$ Na $[M+Na]^+$:293.1324, found: 293.1333.

1-(benzo[d][1,3]dioxol-5-yl)-6,6-Difluoro-5-(4-methoxyphenyl)-2,2-dimethylhex-5-en-3-ol (3al)



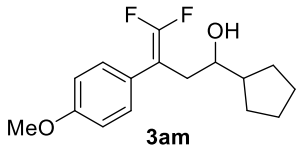
3al

The title compound **3al** was isolated through column chromatography (silica gel,

petroleum ether/ethyl acetate 3:1) as a colorless oil (62.4 mg, 80%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.31-7.17 (m, 2H), 6.90 (d, *J*= 8.8 Hz, 2H), 6.68 (d, *J*= 7.9 Hz, 1H), 6.61 (d, *J*= 1.7 Hz, 1H), 6.56-6.51 (m, 1H), 5.91 (s, 2H), 3.81 (s, 3H), 3.27 (d, *J*= 10.4 Hz, 1H), 2.64-2.53 (m, 2H), 2.52-2.39 (m, 2H), 1.46-1.41 (brs, 1H), 0.88 (s, 3H), 0.82 (s, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 289.8, 286.5 Hz), 147.0, 145.7, 132.2, 129.5 (t, *J*= 3.2 Hz, 2C), 125.4 (dd, *J*= 4.2, 3.2 Hz), 123.5, 114.1 (2C) , 111.1, 107.6, 100.7, 89.9 (dd, *J*= 21.2, 14.3 Hz), 76.0 (t, *J*= 2.3 Hz), 55.3, 44.1, 38.6, 30.5 (d, *J*= 1.7 Hz), 23.2, 22.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.43 (d, *J*= 44.3 Hz, 1F), –91.70 (d, *J*= 44.3 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{22}H_{24}F_2O_4Na$ $[M+Na]^+$: 413.1540, found: 413.1526.

1-Cyclopentyl-4,4-difluoro-3-(4-methoxyphenyl)but-3-en-1-ol (3am)

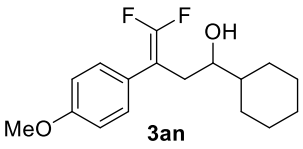


3am

The title compound **3am** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (52.5 mg, 93%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.41-7.14 (m, 2H), 6.90 (d, *J*= 8.8 Hz, 2H), 3.81 (s, 3H), 3.46-3.26 (m, 1H), 2.66-2.53 (m, 1H), 2.51-2.43 (m, 1H), 1.94-1.84 (m, 1H), 1.79-1.63 (m, 2H), 1.61-1.50 (m, 4H), 1.39-1.29 (m, 1H), 1.22-1.12 (m, 1H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 289.7, 286.8 Hz), 129.5 (t, *J*= 3.1 Hz, 2C), 125.5 (dd, *J*= 4.2, 3.2 Hz), 114.0 (2C), 89.4 (dd, *J*= 21.4, 14.4 Hz), 73.6 (t, *J*= 2.5 Hz), 55.3, 45.9, 34.9 (d, *J*= 1.5 Hz), 29.2, 28.3, 25.8, 25.6 ppm .
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.99 (d, *J* = 44.0 Hz, 1F), –91.59 (d, *J* = 44.1 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{20}F_2O_2$ $Na[M+Na]^+$: 305.1329, found: 305.1316.

1-Cyclohexyl-4,4-difluoro-3-(4-methoxyphenyl)but-3-en-1-ol (3an)

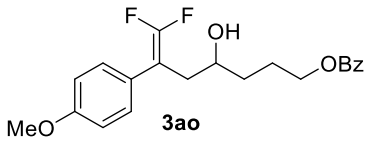


3an

The title compound **3an** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (49.1 mg, 83%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.29-7.22 (m, 2H), 6.89 (d, *J*= 8.8 Hz, 2H), 3.80 (s, 3H), 3.33 (dt, *J*= 9.1, 4.4 Hz, 1H), 2.59-2.51 (m, 1H), 2.50-2.41 (m, 1H), 1.83-1.71 (m, 3H), 1.69-1.60 (m, 2H), 1.51-1.42 (brs, 1H), 1.37-1.30 (m, 1H), 1.27-0.95 (m, 5H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 289.6, 286.7 Hz), 129.5 (t, *J*= 3.1 Hz, 2C), 125.5 (dd, *J*= 4.3, 3.1 Hz), 114.0 (2C), 89.6 (dd, *J* = 21.4, 14.3 Hz), 73.7 (t, *J*= 2.5 Hz), 55.2, 43.3, 32.9 (d, *J*= 1.6 Hz), 29.2, 27.6, 26.5, 26.3, 26.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.82 (d, *J*= 44.3 Hz, 1F), –91.70 (d, *J*= 44.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{17}H_{22}F_2O_2Na$ $[M+Na]^+$: 319.1480, found: 319.1505.

7,7-Difluoro-4-hydroxy-6-(4-methoxyphenyl)hept-6-en-1-yl benzoate (3ao)

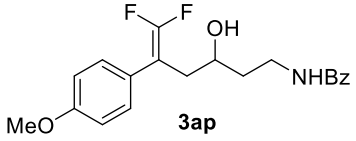


3ao

The title compound **3ao** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (54.9 mg, 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.04-7.97 (m, 2H), 7.59-7.51 (m, 1H), 7.47-7.41 (m, 2H), 7.29-7.21 (m, 2H), 6.88 (d, *J*= 8.8 Hz, 2H), 4.31 (t, *J*= 6.5 Hz, 2H), 3.80 (s, 3H), 3.67 (dt, *J*= 7.5, 3.5 Hz, 1H), 2.62-2.46 (m, 2H), 1.93 (ddd, *J*= 15.7, 7.4, 3.99 Hz, 1H), 1.80 (ddd, *J*= 13.7, 10.0, 6.5 Hz, 1H), 1.71-1.52 (m, 2H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 166.6, 158.9, 154.3 (dd, *J* = 290.9, 287.9 Hz), 132.9, 130.3, 129.5 (2C), 129.4 (t, *J*= 3.3 Hz, 2C), 128.4 (2C), 125.2 (dd, *J*= 4.0, 3.1 Hz), 114.1 (2C), 89.1 (dd, *J*= 21.4, 14.9 Hz), 69.4 (t, *J* = 2.9 Hz), 64.8, 55.3, 36.2 (d, *J*= 1.3 Hz), 33.3, 25.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.67 (d, *J*= 43.2 Hz, 1F), –91.04 (d, *J*= 43.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{21}H_{22}F_2O_4$ Na$[M+Na]^+$: 399.1378, found: 399.1377.

***N*-(6,6-Difluoro-3-hydroxy-5-(4-methoxyphenyl)hex-5-en-1-yl)benzamide (3ap)**



3ap

The title compound **3ap** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) as a colorless oil (50.6 mg, 70%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.70-7.59 (m, 2H), 7.49-7.41 (m, 1H),

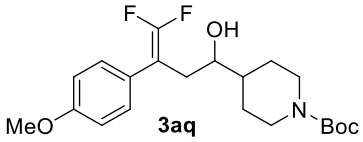
7.39-7.32 (m, 2H), 7.22 (d, *J*= 8.38 Hz, 2H), 6.99 (s, 1H), 6.84 (d, *J*= 8.85 Hz, 2H), 3.82-3.75 (m, 1H), 3.76 (s, 3H), 3.72-3.64 (m, 1H), 3.36-3.22 (m, 1H), 2.66-2.57 (m, 1H), 2.54-2.43 (m, 1H), 1.80-1.69 (m, 1H), 1.65-1.49 (m, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 168.3, 158.8, 154.3 (dd, *J* = 290.9, 288.9 Hz), 134.2, 131.5, 129.4 (t, *J*= 3.1 Hz, 2C), 128.5 (2C), 126.9 (2C), 125.3 (d, *J*= 3.5 Hz), 114.0 (2C), 89.0 (dd, *J*= 21.1, 15.2 Hz), 68.0 (t, *J*= 2.7 Hz), 55.2, 37.3, 36.1, 35.8 (d, *J*= 1.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.73 (d, *J*= 41.6 Hz, 1F), –90.90 (d, *J*= 41.6 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{21}F_2NO_3Na$ $[M+Na]^+$: 384.1382, found: 384.1378.

tert-Butyl4-(4,4-Difluoro-1-hydroxy-3-(4-methoxyphenyl)but-3-en-1-yl)piperidine -1-carboxylate (3aq)



3aq

The title compound **3aq** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) as a colorless oil (68.3 mg, 86%).

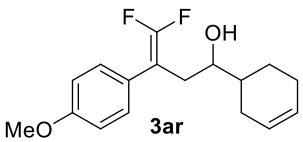
^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.32-7.18 (m, 2H), 6.90 (d, *J*= 8.7 Hz, 2H), 3.81 (s, 3H), 3.46-3.29 (m, 1H), 2.75-2.60 (m, 2H), 2.58-2.43 (m, 2H), 1.80-1.72 (m, 1H), 1.61-1.53 (m, 2H), 1.44 (s, 9H), 1.30-1.15 (m, 4H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 203.0, 158.9, 154.8, 154.2 (dd, *J*= 290.1, 286.8 Hz), 129.4 (t, *J*= 3.1 Hz, 2C), 125.2 (dd, *J*= 4.0, 3.0 Hz)), 114.1 (2C), 89.2 (dd, *J*= 21.3, 14.7 Hz), 79.3, 72.8 (t, *J*= 2.6 Hz), 55.2, 48.0, 41.7, 33.0, 28.4 (3C), 28.3, 26.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.33 (d, *J*= 43.3 Hz, 1F), –91.28 (d, *J*= 43.2 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{29}F_2NO_4Na$ $[M+Na]^+$: 420.1957, found: 420.1968.

1-(Cyclohex-3-en-1-yl)-4,4-difluoro-3-(4-methoxyphenyl)but-3-en-1-ol (3ar)



3ar

The title compound **3ar** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (44.1 mg, 75%, dr=1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.29-7.20 (m, 2H), 6.90 (d, *J*= 8.77 Hz, 2H), 5.71-5.60 (m, 2H), 3.81 (s, 3H), 3.51-3.45 (m, 0.5H),

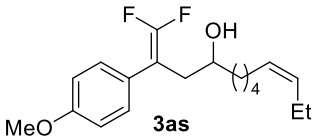
3.43-3.36 (m, 0.5 H), 2.64-2.40 (m, 2H), 2.10 (s, 1H), 2.08-1.77 (m, 4H), 1.69-1.57 (m, 2H), 1.53 (s, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 158.8, 157.5-147.9 (m), 129.5 (t, *J*= 3.7 Hz), 127.3, 126.8, 126.2, 126.0, 125.6-125.2 (m), 114.0 (2C), 89.4 (dd, *J*= 21.6, 14.7), 73.2 (q, *J*= 2.6 Hz), 55.3, 39.4, 39.1, 33.3-32.9 (m), 28.1, 26.0, 25.5, 25.3, 23.7 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –90.66 (d, *J* = 41.4 Hz, 0.5F), –90.69 (d, *J* = 41.4 Hz, 0.5F), −91.45 (d, *J* = 41.4 Hz, 0.5F), −91.53 (d, *J* = 45.1 Hz, 0.5F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{21}F_2O_2$ $[M+H]^+$: 295.1504, found: 295.1498.

(*Z*)-1,1-Difluoro-2-(4-methoxyphenyl)dodeca-1,9-dien-4-ol (3as)



3as

The title compound **3as** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil, (58.3 mg, 90%).

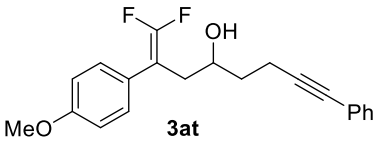
^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.52-7.16 (m, 2H), 6.89 (d, *J*= 8.9 Hz, 2H), 5.57-5.06 (m, 2H), 3.80 (s, 3H), 3.65-3.46 (m, 1H), 2.63-2.42 (m, 2H), 2.08-1.88 (m, 4H), 1.61-1.52 (brs, 1H), 1.51-1.36 (m, 3H), 1.37-1.19 (m, 3H), 0.94 (t, *J*= 7.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.2 (dd, *J*= 291.1, 288.5 Hz), 131.8, 129.4 (t, *J*= 3.2 Hz, 2C), 129.3-128.2 (m), 125.5 (d, *J*= 7.1 Hz), 114.0 (2C), 89.3 (dd, *J*= 21.1, 14.7 Hz), 69.8 (t, *J*= 2.6 Hz), 55.2, 36.8, 36.0, 29.7, 27.0, 25.2, 20.5, 14.4 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –90.96 (d, *J*= 43.4 Hz, 1F), –91.32 (d, *J*= 42.9 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{26}F_2O_2Na$ $[M+Na]^+$: 347.1793, found: 347.1790.

1,1-Difluoro-2-(4-methoxyphenyl)-8-phenyloct-1-en-7-yn-4-ol (3at)



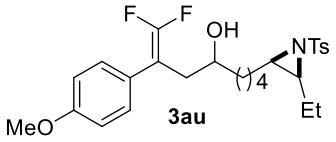
3at

The title compound **3at** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (61.5 mg, 90%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.35-7.12 (m, 7H), 6.98-6.78 (m, 2H), 3.87-3.78 (m, 1H), 3.77 (s, 3H), 2.65-2.54 (m, 2H), 2.54-2.45 (m, 2H), 1.82-1.74 (m, 1H), 1.73-1.67 (m, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.9, 154.3 (dd, *J*= 290.0, 287.3 Hz), 131.6 (2C), 129.5 (t, *J*= 3.1 Hz, 2C), 128.2 (2C), 127.7, 125.3 (dd, *J*= 3.8, 2.5 Hz), 123.6, 114.1 (2C), 89.3, 89.1 (dd, *J*= 21.2, 14.8 Hz), 81.4, 68.9 (t, *J*= 2.8 Hz), 55.2, 35.9, 35.4, 16.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.67 (d, *J* = 43.4 Hz, 1F), –91.10 (d, *J* = 43.4 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{21}H_{20}F_2O_2Na$ $[M+Na]^+$: 365.1324, found: 365.1324.

***cis*-8-(3-Ethyl-1-tosylaziridin-2-yl)-1,1-difluoro-2-(4-methoxyphenyl)oct-1-en-4-ol (3au)**

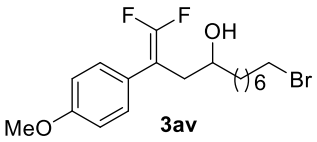


3au

The title compound **3au** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) as a colorless oil (58.2 mg, 59%, dr=1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.91-7.72 (m, 2H), 7.30 (d, *J*= 8.2 Hz, 2H), 7.28-7.22 (m, 2H), 6.92-6.87 (m, 2H), 3.81 (s, 3H), 3.59-3.43 (m, 1H), 2.82-2.74 (m, 1H), 2.74-2.65 (m, 1H), 2.52-2.46 (m, 2H), 2.43 (s, 3H), 1.55-1.27 (m, 10H), 0.88-0.76 (m, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 158.8, 154.3 (dd, *J*= 289.8, 287.1 Hz), 144.3, 135.3 (d, *J* = 2.9 Hz), 129.5, 129.4 (t, *J*= 2.6 Hz), 128.1, 114.0, 89.2 (dd, *J* = 21.3, 14.6 Hz), 69.6 (t, *J* = 2.5 Hz), 69.5 (t, *J* = 2.5 Hz), 55.3, 46.9, 46.7, 45.1, 45.0, 36.6, 36.0, 27.3, 27.2, 26.5, 26.4, 25.0, 24.9, 21.6, 20.1, 11.6 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –90.87 (d, *J*= 42.2 Hz, 1F), –91.3 (d, *J*= 42.9 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{26}H_{33}F_2NO_4SNa$ $[M+Na]^+$: 516.1991, found: 516.1996.

11-Bromo-1,1-difluoro-2-(4-methoxyphenyl)undec-1-en-4-ol (3av)



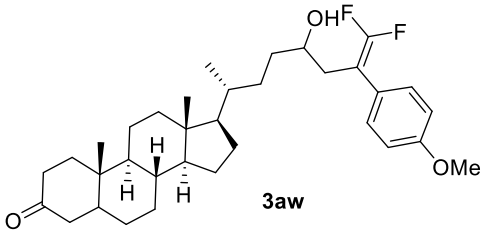
3av

The title compound **3av** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (50.7 mg, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.32-7.16 (m, 2H), 6.90 (d, *J*= 8.9 Hz, 2H), 3.81 (s, 3H), 3.63-3.51 (m, 1H), 3.39 (t, *J*= 6.9 Hz, 2H), 2.56-2.44 (m, 2H), 2.01-1.71 (m, 2H), 1.48-1.29 (m, 10H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 291.0, 288.5 Hz), 129.4 (t, *J*= 2.9 Hz, 2C), 125.5 (dd, *J*= 3.8, 2.5 Hz), 114.1 (2C), 89.3 (dd, *J*= 21.1, 14.7 Hz), 69.8 (t, *J*= 2.8 Hz), 55.3, 36.8, 36.0, 34.0, 32.8, 29.3, 28.7, 28.1, 25.4 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ= –90.91 (d, *J*= 43.4 Hz, 1F), –91.30 (d, *J*= 43.4 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{18}H_{25}F_2O_2BrH$ $[M+H]^+$: 391.1079, found: 391.1090.

(8R,9S,10S,13R,14S,17R)-17-((2R)-8,8-Difluoro-5-hydroxy-7-(4-methoxyphenyl)oct-7-en-2-yl)-10,13-dimethylhexadecahydro-3H-cyclopenta[a]phenanthren-3-one (3aw)

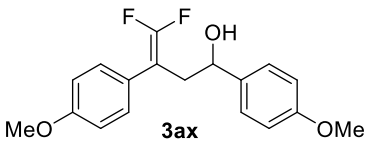


3aw

The title compound **3aw** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a white solid (81.3 mg, 75%, dr=1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.25 (d, *J*= 8.8 Hz, 2H), 6.98-6.82 (m, 2H), 3.81 (s, 3H), 3.60-3.48 (m, 1H), 2.79-2.62 (m, 1H), 2.57-2.42 (m, 2H) 2.39-2.26 (m, 1H), 2.21-2.11 (m, 1H), 2.08-1.97 (m, 3H), 1.91-1.76 (m, 3H), 1.54 (s, 1H), 1.54-1.32 (m, 11H), 1.29-1.16 (m, 4H), 1.14-1.03 (m, 4H), 1.02-1.00 (m, 3H), 0.93-0.85 (m, 3H), 0.72-0.63 (m, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 213.6, 158.8, 154.2 (dd, *J*= 289.5, 287.1 Hz), 129.5 (t, *J*= 3.0 Hz), 125.5, 114.0, 89.3 (dd, *J*= 20.3, 16.0 Hz), 70.3 (d, *J*= 22.0 Hz), 56.4, 56.1, 55.3, 44.3, 42.7, 42.4, 40.7, 40.0, 37.2, 37.0, 36.1, 35.9, 35.7, 35.6, 35.5, 34.9, 33.4, 31.6, 28.3, 28.2, 26.6, 25.8, 24.2, 22.7, 21.2, 18.7, 18.6, 12.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= −90.93 (d, *J*= 37.6 Hz, 0.5F), −90.95 (d, *J*= 37.6 Hz, 0.5F), −91.26 (d, *J*= 37.6 Hz, 0.5F), −91.36 (t, *J*= 37.6 Hz, 0.5F) ppm.
HRMS (ESI) m/z calculated for $C_{34}H_{49}F_2O_3$ $[M+H]^+$: 543.3644, found: 543.3652.

4,4-Difluoro-1,3-bis(4-methoxyphenyl)but-3-en-1-ol (3ax)

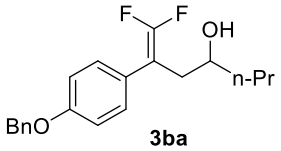


3ax

The title compound **3ax** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (30.7 mg, 48%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.34-7.10 (m, 4H), 6.94-6.77 (m, 4H), 4.57 (dd, *J*= 8.1, 5.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.85 (ddt, *J*= 14.5, 8.2, 2.1 Hz, 1H), 2.70 (ddt, *J*= 14.42, 5.44, 2.51 Hz, 1H), 1.91-1.86 (brs, 1H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 159.3, 158.8, 154.4 (dd, *J*= 288.5, 286.7 Hz), 135.7, 129.5 (t, *J*= 2.9 Hz, 2C), 127.2 (2C), 125.4, 114.0 (2C), 113.8 (2C), 89.1 (dd, *J*= 17.6, 16.4 Hz), 71.9 (t, *J*= 2.7 Hz), 55.3 (2C), 37.6 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = –91.09 (s, 2F) ppm.
HRMS (ESI) m/z calculated for $C_{18}H_{18}F_2O_3Na$ $[M+Na]^+$: 343.1116, found: 343.1103.

2-(4-(Benzyloxy)phenyl)-1,1-difluorohept-1-en-4-ol (3ba)

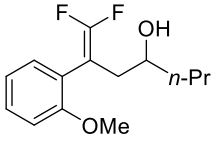


3ba

The title compound **3ba** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (61.1 mg, 92%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ=7.46-7.41 (m, 2H), 7.41-7.36 (m, 2H), 7.36-7.29 (m, 1H), 7.31-7.22 (m, 1H), 6.96-6.94 (m, 1H), 6.93 (dd, *J*= 7.7, 1.3 Hz, 1H), 6.90 (dd, *J*= 8.3, 2.4 Hz, 1H), 5.06 (s, 2H), 3.61-3.49 (m, 1H), 2.54-2.45 (m, 2H), 1.45 -1.26 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ=158.8, 154.4 (dd, *J*= 291.3, 287.7 Hz), 136.8, 134.9 (t, *J*= 4.0 Hz), 129.6, 128.6 (2C), 128.1, 127.6 (2C), 121.0, 115.3-115.1 (m), 113.8, 89.8 (dd, *J*= 21.6, 14.3 Hz), 70.1, 69.6 (d, *J*= 2.9 Hz), 39.1, 36.0, 18.8, 14.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.31 (d, *J*= 39.7 Hz, 1F), –90.09 (d, *J*= 40.1 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{20}H_{22}F_2O_2Na$ $[M+Na]^+$: 355.1480, found: 355.1501.

1,1-Difluoro-2-(2-methoxyphenyl)hept-1-en-4-ol (3ca)



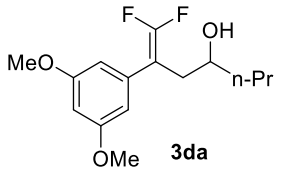
3ca

The title compound **3ca** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (42.5 mg, 83%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.34-7.27 (m, 1H), 7.18-7.11 (m, 2H) 7.00-6.90 (m, 2H), 3.84 (s, 3H), 3.49-3.35 (m, 1H), 2.56-2.28 (m, 2H), 1.50-1.26 (m, 4H), 0.86 (t, *J*= 6.8 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 156.9, 153.9 (dd, *J*= 288.6, 286.7 Hz),

130.8 (dd, *J*= 3.1, 1.6 Hz), 129.4, 122.4 (dd, *J*= 4.8, 1.6 Hz), 121.1, 111.0, 85.5 (dd, *J*= 23.1, 18.3 Hz), 68.8 (t, *J*= 2.6 Hz), 55.7, 38.7, 37.1, 18.9, 14.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –87.38 (d, *J*= 40.2 Hz, 1F), –92.53 (d, *J*= 40.1 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{19}F_2O_2$ $[M+H]^+$: 257.1348, found: 257.1365.

2-(3,5-Dimethoxyphenyl)-1,1-difluorohept-1-en-4-ol (3da)

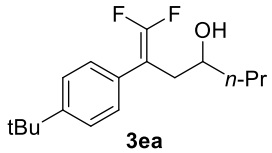


3da

The title compound **3da** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (48.6 mg, 85%).

^{1}H NMR (400 MHz, Chloroform-d) δ= 6.50-6.46 (m, 2H), 6.40 (t, *J* = 2.3 Hz, 1H), 3.79 (s, 6H), 3.67-3.54 (m, 1H), 2.55-2.46 (m, 2H), 1.64-1.54 (brs, 1H), 1.50-1.25 (m, 4H), 0.90 (t, *J*= 6.8 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ=160.8 (2C), 154.4 (dd, *J*= 291.1, 287.4 Hz), 135.4 (dd, *J*= 4.7, 3.0 Hz), 106.7 (t, *J*= 3.2 Hz, 2C), 99.3, 90.0 (dd, *J*= 21.8, 14.1 Hz), 69.6 (t, *J*= 2.6 Hz), 55.3 (2C), 39.1, 36.0 (d, *J*= 1.5 Hz), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ= –88.88 (d, *J*= 40.4 Hz, 1F), –90.17 (d, *J*= 40.4 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2NaO_3$ $[M+Na]^+$: 309.1273, found: 309.1268.

2-(4-(*tert*-Butyl)phenyl)-1,1-difluorohept-1-en-4-ol (3ea)

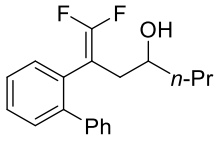


3ea

The title compound **3ea** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (49.6 mg, 88%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.38 (d, *J*= 8.5 Hz, 2H), 7.27 (dd, *J*= 8.5, 1.35 Hz, 2H), 3.67-3.56 (m, 1H), 2.58-2.49 (m, 2H), 1.49-1.39 (m, 4H), 1.32 (s, 9H), 0.89 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.4 (dd, *J*= 290.9, 287.2 Hz), 150.4, 130.3 (dd, *J*= 4.0, 2.0 Hz), 127.9 (t, *J*= 3.3 Hz, 2C), 125.5 (2C), 89.5 (dd, *J* = 21.0, 14.2 Hz), 69.7 (t, *J*= 2.6 Hz), 39.1, 35.8 (d, *J* = 1.5 Hz), 34.5, 31.3 (3C), 18.8, 14.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.14 (d, *J*= 41.8 Hz, 1F), –90.48 (d, *J*= 41.5 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{17}H_{24}F_2ONa$ $[M+Na]^+$: 305.1687, found: 305.1687.

2-([1,1'-Biphenyl]-2-yl)-1,1-difluorohept-1-en-4-ol (3fa)

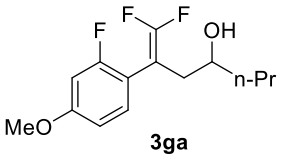


3fa

The title compound **3fa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a white solid (56.2 mg, 93%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.57-7.26 (m, 9H), 3.44-3.16 (m, 1H), 2.04-1.75 (m, 2H), 1.30-1.11 (m, 4H), 0.79 (t, *J*= 7.0 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.4 (dd, *J*= 288.3, 286.2 Hz), 141.6 (d, *J*= 3.7 Hz), 141.1, 131.8 (d, *J*= 4.8 Hz), 131.0, 130.5, 128.7 (2C), 128.4 (2C), 128.3, 127.5, 127.4, 90.1 (dd, *J*= 21.6, 17.0 Hz), 69.1, 39.1, 36.3, 18.7, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = –88.3 (s, 1F), –92.73 (d, *J*= 42.7 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{19}H_{20}F_2OH$ $[M+H]^+$: 303.1555, found: 303.1575.

1,1-Difluoro-2-(2-fluoro-4-methoxyphenyl)hept-1-en-4-ol (3ga)

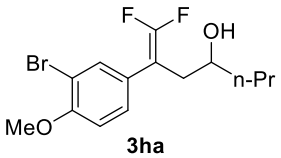


3ga

The title compound **3ga** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (49.9 mg, 91%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.16 (t, *J*= 8.5 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.65 (dd, *J*= 11.8, 2.6 Hz, 1H), 3.81 (s, 3H), 3.52 (td, *J*= 6.1, 5.5, 2.2 Hz, 1H), 2.50-2.40 (m, 2H), 1.63-1.53 (brs, 1H), 1.47-1.27 (m, 4H), 0.88 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 160.7 (d, *J*= 245.8 Hz), 160.7 (d, *J*= 11.0 Hz), 154.2 (t, *J*= 288.7 Hz), 131.3 (dt, *J*= 5.1, 2.6 Hz), 113.0 (ddd, *J*= 15.8, 5.0, 1.8 Hz), 110.3 (d, *J* = 2.9 Hz), 101.8 (d, *J*= 26.0 Hz), 84.1 (dd, *J*= 24.6, 17.2 Hz), 69.4 (t, *J*= 2.8 Hz), 55.6, 39.0, 36.2, 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –87.49 (dd, *J*= 38.1, 10.3 Hz, 1F), –91.18 (dd, *J*= 38.1, 2.1 Hz, 1F), -112.03 (dd, *J*= 10.1, 1.9 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{17}F_3O_2Na$ $[M+Na]^+$: 297.1073, found: 297.1052.

2-(3-Bromo-4-methoxyphenyl)-1,1-difluorohept-1-en-4-ol (3ha)

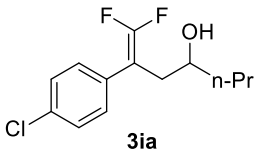


3ha

The title compound **3ha** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (60.1 mg, 90%).

^{1}H NMR (400 MHz, Chloroform-d) δ= 7.34 (d, *J*= 8.2 Hz, 1H), 6.92 (s, 1H), 6.89-6.84 (m, 1H), 3.90 (s, 3H), 3.64-3.52 (m, 1H), 2.55-2.46 (m, 2H), 1.60-1.51 (brs, 1H), 1.47-1.29 (m, 4H), 0.90 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-d) δ= 154.9, 154.4 (dd, *J*= 291.3, 288.2 Hz), 133.4 (dd, *J*= 4.7, 3.1 Hz), 130.1, 121.7, 121.2 (t, *J*= 3.2 Hz), 112.3 (t, *J*= 3.4 Hz), 89.6 (dd, *J*= 22.2, 14.0 Hz), 69.6 (t, *J*= 2.6 Hz), 56.1, 39.3, 35.9 (d, *J*= 1.4 Hz), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ= –88.90 (d, *J*= 39.5 Hz, 1F), –89.61 (d, *J*= 39.5 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{17}F_2O_2BrNa$ [M+Na]+: 357.0272, found: 357.0297.

2-(4-Chlorophenyl)-1,1-difluorohept-1-en-4-ol (3ia)

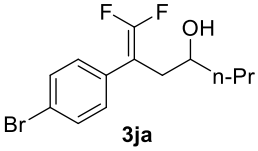


3ia

The title compound **3ia** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (38.0 mg, 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.33 (d, *J*= 8.7 Hz, 2H), 7.27 (d, *J*= 8.6 Hz, 2H), 3.62-3.52 (m, 1H), 2.54-2.48 (m, 2H), 1.46-1.27 (m, 4H), 0.89 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.4 (dd, *J*= 291.2, 288.3 Hz), 133.3, 132.0 (dd, *J* = 4.1, 2.8 Hz), 129.6 (t, *J*= 3.1 Hz, 2C), 128.8 (2C), 89.2 (dd, *J*= 21.8, 14.5 Hz), 69.6 (t, *J*= 2.8 Hz), 39.2, 35.8 (d, *J*= 1.5 Hz), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.34 (d, *J*= 39.6 Hz, 1F), –89.56 (d, *J*= 39.5 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{13}H_{16}F_2OCl$ $[M+H]^+$: 261.0852, found: 261.0848.

2-(4-Bromophenyl)-1,1-difluorohept-1-en-4-ol (3ja)

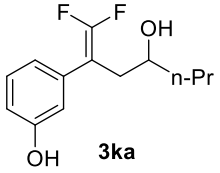


3ja

The title compound **3ja** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (34.1 mg, 56%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.41 (d, *J*= 8.5 Hz, 2H), 7.14 (d, *J*= 8.2 Hz, 2H), 3.56-3.39 (m, 1H), 2.50-2.35 (m, 2H), 1.45-1.18 (m, 4H), 0.82 (t, *J*= 6.8 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 153.3 (dd, *J*= 291.2, 288.5 Hz), 131.43 (dd, *J* = 3.8, 2.6 Hz), 130.7 (2C), 128.9 (t, *J*= 3.2 Hz, 2C), 120.4, 88.2 (dd, *J*= 21.6, 14.6 Hz), 68.5 (t, *J*= 2.6 Hz), 38.2, 34.7, 17.7, 13.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.21 (d, *J*= 39.4 Hz, 1F), –89.39 (d, *J*= 39.4 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{13}H_{16}BrF_2O$ $[M+H]^+$: 305.0347, found: 305.0345.

3-(1,1-Difluoro-4-hydroxyhept-1-en-2-yl)phenol (3ka)

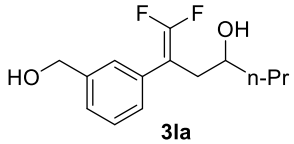


3ka

The title compound **3ka** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (29 mg, 60%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.25-7.18 (m, 1H), 6.92-6.83 (m, 1H), 6.84-6.80 (m, 1H), 6.75 (dd, *J*= 8.1, 2.40 Hz, 1H), 6.20-5.91 (brs, 1H), 3.73-3.47 (m, 1H), 2.61-2.45 (m, 2H), 1.67-1.61 (brs, 1H), 1.48-1.24 (m, 4H), 0.89 (t, *J*= 6.90 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 155.9, 154.4 (d, *J* = 3.9 Hz), 134.9 (dd, *J*= 4.3, 3.1 Hz), 129.8, 120.5 (t, *J* = 3.1 Hz), 115.4 (t, *J* = 3.3 Hz), 114.6, 89.6 (dd, *J* = 21.8, 14.1 Hz), 69.9 (t, *J* = 2.6 Hz), 39.1, 35.8 (d, *J* = 1.4 Hz), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.21 (d, *J*= 40.3 Hz, 1F), –89.98 (d, *J*= 40.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{13}H_{16}F_2O_2H$ $[M+H]^+$: 243.1191, found: 243.1194.

1,1-Difluoro-2-(3-(hydroxymethyl)phenyl)hept-1-en-4-ol (3la)



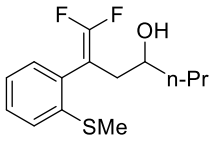
3la

The title compound **3la** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (29.7 mg, 58%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.41-7.32 (m, 2H), 7.30-7.25 (m, 2H), 4.70 (s, 2H), 3.70-3.47 (m, 1H), 2.59-2.42 (m, 2H), 1.67-1.62 (brs, 2H), 1.48-1.21 (m, 4H), 0.89 (t, *J*= 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.4 (dd, *J*= 291.9, 288.9 Hz), 141.3, 133.8 (dd, *J*= 4.4, 3.0 Hz), 128.8, 127.6 (t, *J*= 3.1 Hz), 126.9 (t, *J*= 3.1 Hz), 126.1, 89.8 (dd, *J*= 21.5, 14.5 Hz), 69.7 (t, *J*= 2.8 Hz), 65.0, 39.1, 35.9 (d, *J*= 1.5 Hz), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.83 (d, *J*= 40.2 Hz, 1F), –90.24 (d, *J*= 40.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{19}F_2O_2Na$ $[M+Na]^+$: 279.1167, found: 279.1183.

1,1-Difluoro-2-(2-(methylthio)phenyl)hept-1-en-4-ol (3ma)

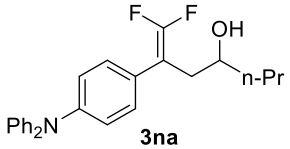


3ma

The title compound **3ma** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (47.3 mg, 87%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.35-7.29 (m, 1H), 7.23 (d, *J*= 7.96 Hz, 1H), 7.18-7.14 (m, 2H), 3.56-3.38 (m, 1H), 2.48 (s, 3H), 2.44-2.23 (m, 2H), 1.46-1.29 (m, 4H), 0.87 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 153.8 (dd, *J*= 290.5, 287.9 Hz), 138.1 (t, *J*= 2.2 Hz), 132.0 (d, *J*= 4.8 Hz), 129.9, 128.8, 125.3, 125.2, 87.9 (d, *J*= 5.4 Hz), 68.8 (t, *J*= 2.8 Hz), 38.9, 37.6, 19.0, 15.7, 14.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –85.55 (s, 1F), –91.15(s, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{18}F_2OSNa$ $[M+Na]^+$: 295.0939, found: 295.0950.

2-(4-(Diphenylamino)phenyl)-1,1-difluorohept-1-en-4-ol (3na)



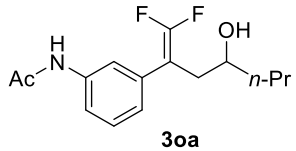
3na

The title compound **3na** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 1:2) as a colorless oil (73.9 mg, 94%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.28-7.22 (m, 4H), 7.19 (dd, *J*= 8.7, 1.3 Hz, 2H), 7.11-7.07 (m, 4H), 7.05-7.00 (m, 4H), 3.73-3.54 (m, 1H), 2.56-2.45 (m, 2H), 1.48-1.29 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.4 (dd, *J*= 290.9, 287.2 Hz), 147.5 (2C), 147.0, 129.3 (4C), 128.9 (t, *J*= 3.5 Hz, 2C), 126.80 (t, *J* = 3.7 Hz)), 124.6 (4C), 123.2 (2C), 123.1 (2C), 89.4 (dd, *J*= 21.3, 13.9 Hz), 69.8 (t, *J*= 2.8 Hz), 39.1, 35.8 (d, *J* = 1.8 Hz), 18.8, 14.1 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ = –90.04 (d, *J*= 42.2 Hz, 1F), –90.44 (d, *J*=

41.9 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{25}H_{25}F_2NONa$ $[M+Na]^+$: 416.1796, found: 416.1795.

***N*-(3-(1,1-Difluoro-4-hydroxyhept-1-en-2-yl)phenyl)acetamide (3oa)**

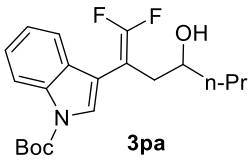


3oa

The title compound **3oa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 1:2) as a colorless oil (47.5 mg, 84%).

^{1}H NMR (400 MHz, Chloroform-d) δ= 7.50 (s, 1H), 7.45 (dt, *J*= 8.2, 1.4 Hz, 1H), 7.37 (s, 1H), 7.31 (t, *J*= 7.9 Hz, 1H), 7.08 (dd, *J*= 7.7, 1.7 Hz, 1H), 3.67-3.51 (m, 1H), 2.59-2.45 (m, 2H), 2.18 (s, 3H), 1.52-1.20 (m, 4H), 0.89 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR 13C NMR (101 MHz, Chloroform-d) δ= 168.4, 154.4 (dd, *J*= 292.9, 288.9 Hz), 138.1, 134.4 (d, *J*= 3.0 Hz), 129.2, 124.2, 119.7 (t, *J*= 3.2 Hz), 118.9, 89.7 (dd, *J*= 21.5, 13.8 Hz), 69.6 (t, *J*= 2.5 Hz), 39.2, 35.9, 24.6, 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ= –89.40 (d, *J*= 40.1 Hz, 1F), –89.93 (d, *J*= 40.1 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{19}F_2NO_2Na$ $[M+Na]^+$: 306.1276, found: 306.1273.

tert-Butyl 3-(1,1-Difluoro-3-hydroxyhex-1-en-2-yl)-1*H*-indole-1-carboxylate (3pa)

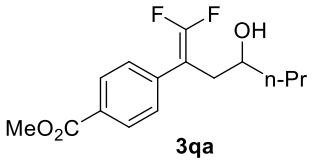


3pa

The title compound **3pa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) as a colorless oil (52.7mg, 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.21-8.07 (m, 1H), 7.61-7.55 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.38-7.29 (m, 1H), 7.30-7.22 (m, 1H), 3.75-3.45 (m, 1H), 2.67-2.45 (m, 2H), 1.68 (s, 9H), 1.45-1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.6 (dd, *J*= 290.9 Hz, *J*= 289.8 Hz), 149.5, 135.3, 129.1, 124.7 (2C), 122.9, 119.9 (d, *J* = 2.9 Hz), 115.4, 113.5 (dd, *J* = 5.3, 2.0 Hz), 84.1, 82.3 (dd, *J* = 25.1, 16.7 Hz), 69.7 (t, *J* = 2.8 Hz), 39.2, 36.4, 28.2 (3C), 18.8, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –85.80 (d, *J* = 38.8 Hz), –90.22 (d, *J* = 38.1 Hz) ppm.
.**HRMS (ESI)** m/z calculated for $C_{20}H_{25}F_2NO_3Na$ $[M+Na]^+$: 388.1695, found: 388.1700.

Methyl 4-(1,1-difluoro-4-hydroxyhept-1-en-2-yl)benzoate (3qa)

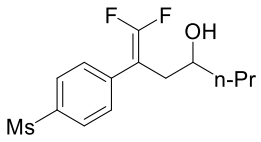


3qa

The title compound **3qa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (39.7 mg, 70%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.02 (d, *J*= 8.2 Hz, 2H), 7.43 (d, *J*= 8.2 Hz, 2H), 3.92 (s, 3H), 3.66-3.43 (m, 1H), 2.62-2.52 (m, 2H), 1.49-1.25 (m, 4H), 0.88 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 166.7, 154.6 (dd, *J*= 292.9 Hz, *J*= 290.9 Hz), 138.5, 129.8 (2C), 129.0 (d, J= 5.5 Hz), 128.2 (t, J= 3.3 Hz, 2C), 89.7 (dd, J = 18.7, 17.2 Hz), 69.6 (t, J= 2.5 Hz), 52.2, 39.2, 35.6, 18.7, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ= –88.08 (s, 2F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{18}F_2O_3Na$ $[M+Na]^+$: 307.1116, found: 307.1118.

1,1-Difluoro-2-(4-(methylsulfonyl)phenyl)hept-1-en-4-ol (3ra)

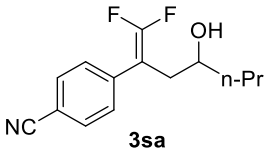


3ra

The title compound **3ra** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (41.9 mg, 69%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.92 (d, *J*= 8.3 Hz, 2H), 7.57 (d, *J*= 8.3 Hz, 2H), 3.69-3.49 (m, 1H), 3.07 (s, 3H), 2.70-2.50 (m, 2H), 1.61-1.53 (brs, 1H), 1.48-1.30 (m, 4H), 0.90 (t, *J* -= 7.0 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.8 (dd, *J*= 293.4, 289.8 Hz), 139.8 (dd, *J* = 4.8, 3.6 Hz), 139.2, 129.3 (t, *J*= 3.5 Hz, 2C), 127.6 (2C), 89.5 (dd, *J*= 22.7, 13.2 Hz), 69.6 (t, *J*= 2.6 Hz), 44.5, 39.4, 35.6, 18.7, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ=–86.95 (d, *J* = 34.1 Hz, 1F), –87.49 (d, *J* = 34.1 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{18}F_2O_3SNa$ $[M+Na]^+$: 327.0837, found: 327.0838.

4-(1,1-Difluoro-4-hydroxyhept-1-en-2-yl)benzonitrile (3sa)

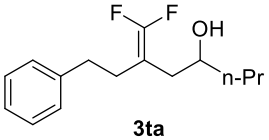


3sa

The title compound **3sa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (25.6mg, 51%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.65 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 3.65-3.51 (m, 1H), 2.59-2.52 (m, 2H), 1.67-1.62 (brs, 1H), 1.49-1.27 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –86.76 (d, *J* = 34.1 Hz, 1F), –87.20 (d, *J* = 34.1 Hz, 1F) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.7 (dd, *J*= 293.9, 290.4 Hz), 138.9 (dd, *J*= 4.0, 3.6 Hz), 132.3 (2C), 129.0 (t, *J*= 3.5 Hz, 2C), 118.6, 111.0, 89.6 (dd, *J*= 23.1, 13.2 Hz), 69.6 (t, *J*= 2.6 Hz), 39.4, 35.4, 18.7, 14.0 ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{15}F_2NOH$ $[M+H]^+$: 252.1194, found: 252.1204.

6-(Difluoromethylene)-8-phenyloctan-4-ol (3ta)

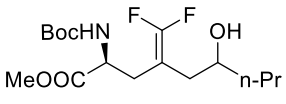


3ta

The title compound **3 ta** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (41.7 mg, 82%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.32-7.24 (m, 2H), 7.25-7.14 (m, 3H), 3.74-3.62 (m, 1H), 2.72 (t, *J*= 8.0 Hz, 2H), 2.42-2.24 (m, 2H), 2.19-1.98 (m, 2H), 1.55 – 1.29 (m, 4H), 0.93 (t, *J*= 7.1 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 154.5 (dd, *J*= 286.0, 283.5 Hz), 141.1, 128.5 (2C), 128.4 (2C), 126.2, 86.1 (d, *J*= 34.2 Hz), 69.6 (t, *J*= 2.8 Hz), 39.3, 34.5 (d, *J*= 3.7 Hz), 34.0 (t, *J*= 2.5 Hz), 28.6 (d, *J*= 2.8 Hz), 18.9, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –93.00 (d, *J*= 52.5 Hz, 1F), –93.98 (d, *J*= 52.5 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2OH$ $[M+H]^+$:255.1555, found: 255.1553.

Methyl(2*S*)-2-((tert-butoxycarbonyl)amino)-4-(difluoromethylene)-6-hydroxynonanoate (3ua)



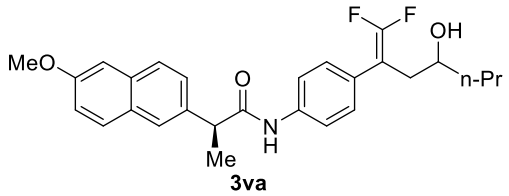
3ua

The title compound **3 ua** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) as a colorless oil (28.1 mg, 40%, dr=1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 5.31-5.16 (m, 1H), 4.53-4.39 (m, 1H), 3.77-3.70 (m, 1H), 3.74 (s, 3H), 2.49-2.37 (m, 2H), 2.27-2.13 (m, 1H), 2.11-1.98 (m, 1H), 1.42 (s, 9H), 1.46-1.35 (m, 4H), 0.92 (t, *J*= 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ(mixture of two diastereomers)= 172.4, 172.3, 156.4 (dd, *J*= 286.8, 260.6 Hz), 83.1 (d, *J*= 36.4 Hz), 80.4, 80.2, 69.6, 69.2, 52.52, 52.48, 52.3, 51.9, 39.5, 35.7, 35.1, 31.8, 31.3, 28.20, 28.19, 18.93, 18.86, 14.02, 14.00 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –90.85 - –91.85 (m, 2F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2OH$ $[M+H]^+$:255.1555, found: 255.1553.

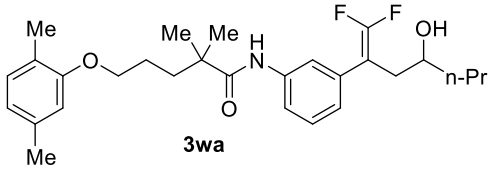
(2*S*)-*N*-(4-(1,1-Difluoro-4-hydroxyhept-1-en-2-yl)phenyl)-2-(6-methoxynaphthal-en-2-yl)propanamide (3va)



3va

The title compound **3va** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a white solid (81.6mg, 90%, dr=1:1).
^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers) = 7.79-7.67 (m, 3H), 7.50-7.41 (m, 2H), 7.37 (d, *J*= 3.9 Hz, 1H), 7.35-7.29 (m, 1H), 7.24-7.11 (m, 3H), 7.01 (d, *J*= 7.7 Hz, 1H), 3.92 (s, 3H), 3.88-3.77 (m, 1H), 3.61-3.43 (m, 1H), 2.53 -2.40 (m, 2H), 1.87-1.74 (brs, 1H), 1.64 (d, *J*= 7.2 Hz, 3H), 1.44-1.25 (m, 4H), 0.85 (t, *J*= 6.2 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ(mixture of two diastereomers)= 172.6, 157.9, 154.3 (dd, *J*= 290.8, 287.6 Hz), 138.1, 135.8, 134.3 (dd, *J*= 4.4, 3.0 Hz), 133.9, 129.3, 129.0 (d, *J*= 5.9 Hz), 127.9, 126.4, 126.1, 124.2, 119.6 (t, *J*= 2.9 Hz), 119.4, 118.8, 105.7, 89.7 (dd, *J*= 21.8, 14.1 Hz), 69.5, 55.4, 48.1, 39.1, 35.9, 18.7, 18.6, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –89.50 (d, *J*= 41.4 Hz, 0.5F), –89.52 (d, *J*= 41.4 Hz, 0.5F), –90.19 (d, *J* = 41.4 Hz, 0.5F), –90.20 (d, *J* = 41.4 Hz, 0. 5F) ppm.
HRMS (ESI) m/z calculated for $C_{27}H_{29}F_2NO_3Na$ $[M+Na]^+$: 476.2008, found: 476.2022.

***N*-(3-(1,1-Difluoro-4-hydroxyhept-1-en-2-yl)phenyl)-5-(2,5-dimethylphenoxy)-2,2 -dimethylpentanamide (3wa)**



3wa

The title compound **3wa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a white solid (68.2 mg, 72%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.56-7.48 (m, 2H), 7.45-7.39 (m, 1H),

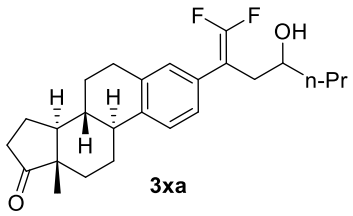
7.31-7.23 (m, 1H), 7.05 (dd, *J*= 7.85, 1.42 Hz, 1H), 6.99 (d, *J*= 7.44 Hz, 1H), 6.65 (dd, *J*= 7.44, 1.50 Hz, 1H), 6.60 (d, *J*= 1.60 Hz, 1H), 3.93 (t, *J*= 4.6 Hz, 2H), 3.63-3.48 (m, 1H), 2.54-2.45 (m, 2H), 2.28 (s, 3H), 2.16 (s, 3H), 2.14-2.08 (brs, 1H), 1.85-1.78 (m, 4H), 1.45-1.37 (m, 3H), 1.32 (s, 6H), 1.29-1.24 (m, 1H), 0.86 (t, *J*= 6.94 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ= 176.0, 156.9, 154.4 (dd, *J*= 290.5, 287.6 Hz), 138.2, 136.6, 134.4 (dd, *J*= 4.3, 3.1 Hz), 130.4, 129.1, 124.4 (t, *J*= 2.9 Hz), 123.5, 120.9, 120.3 (t, *J*= 3.3 Hz), 119.4, 112.2, 89.9 (dd, *J*= 22.0, 13.9 Hz), 69.5 (t, *J*= 2.9 Hz), 67.9, 42.9, 39.1, 37.7, 36.0, 25.6 (2C), 25.2, 21.4, 18.8, 15.8, 14.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –89.64 (d, *J*= 40.5 Hz, 1F), –90.26 (d, *J*= 40.4 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{28}H_{37}F_2NO_3Na$ $[M+Na]^+$: 496.2634, found: 496.2644.

(8R,9S,13S,14S)-3-(1,1-Difluoro-4-hydroxyhept-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3xa)



3xa

The title compound **3xa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a white solid (46.7 mg, 58%, dr=1:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.32-7.23 (m, 1H), 7.15-7.02 (m, 2H), 3.70-3.55 (m, 1H), 3.00-2.85 (m, 2H), 2.56-2.47 (m, 3H), 2.45-2.38 (m, 1H), 2.34-2.24 (m, 1H), 2.21-2.11 (m, 1H), 2.09-2.00 (m, 2H), 2.00-1.91 (m, 1H), 1.70-1.57 (m, 3H), 1.57-1.39 (m, 6H), 1.36-1.28 (m, 1H), 0.97-0.84 (m, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 221.1, 154.4 (dd, *J*= 290.5, 287.1 Hz), 139.1, 136.7, 130.8 (dd, *J*= 4.0, 3.0 Hz), 128.8 (dd, *J*= 6.5, 3.1 Hz), 125.6, 89.6 (dd, *J* = 20.9, 14.1 Hz), 69.6, 50.5, 48.0, 44.3, 39.1, 38.0, 35.90, 35.87, 31.6, 29.4, 26.5, 25.6, 21.6, 18.8, 14.1, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –90.10 (d, *J*= 41.4 Hz, 0.5F), –90.12 (d, *J*= 41.4 Hz, 0.5F), –90.55 (d, *J* = 41.4 Hz, 0.5F), –90.58 (d, *J* = 41.4 Hz, 0. 5F) ppm.

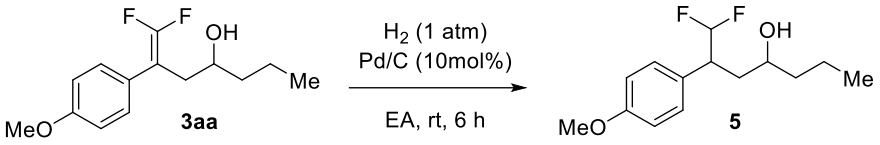
HRMS (ESI) m/z calculated for $C_{25}H_{33}F_2O_2H$ $[M+H]^+$: 403.2443, found: 403.2441.

Procedure for 5-mmol-Scale Reaction

$CrCl_3$ (80 mg, 0.5 mmol, 10 mol %), the ligand 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (160 mg, 0.6 mmol, 12 mol %) and Zn (975 mg, 15 mmol, 3.0 equiv) were placed in a

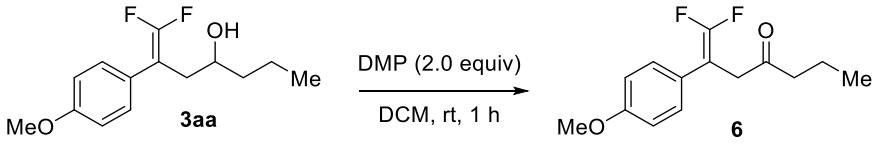
Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (25.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, TMSCl (1630 mg, 2 mL, 15 mmol, 3 equiv) and butanal (**2a**) or 8-bromooctanal (**2v**) (10 mmol, 2.0 equiv) were added under a positive flow of nitrogen. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1a** (1.01 g, 5 mmol, 1.0 equiv) were added under nitrogen atmosphere. The reaction mixture was stirred at 40℃ for 16 hours and subsequently filtered through Celite, before it was quenched by addition of 25 mL aqueous HCl (2 N). After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified through column chromatography (petroleum ether/ethyl acetate 5:1) over silica gel, to afford *1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-ol* (**3aa**) (1.14 g, 89%) or *11-bromo-1,1-difluoro-2-(4-methoxyphenyl)undec-1-en-4-ol* (**3av**) (1.31 g, 67%).

Procedures for Derivatizations



A flask is charged with the *gem*-difluoroalkene **3aa** (102.4 mg, 0.4 mmol, 1.0 equiv), and Pd/C (4.3 mg, 10mol%) in ethyl acetate (4.0 mL) with a H_2 ballon. The reaction mixture was stirred for 6 h at room temperature. Then the reaction mixture was diluted with ethyl acetate, filtered, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified through column chromatography (petroleum ether/ethyl acetate 5:1) over silica gel, to afford *1,1-difluoro-2-(4-methoxyphenyl)heptan-4-ol* (**5**) (100.1 mg, 97%, dr= 1.4:1) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.19 (dd, *J*= 8.6, 1.9 Hz, 2H), 6.88 (dd, *J*= 8.7, 1.6 Hz, 2H), 6.02-5.66 (m, 1H), 3.81-3.78 (m, 3H), 3.72-3.64 (m, 0.4H), 3.39-3.26 (m, 1H), 3.25- 3.07 (m, 0.6H), 2.14-1.99 (m, 0.4H), 1.94 -1.81 (m, 1.6H), 1.50-1.26 (m, 4H), 0.95-0.78 (m, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 159.04, 159.02, 130.1, 129.8, 129.2 (dd, *J*= 6.4, 4.9 Hz), 128.4 (dd, *J*= 5.2, 2.9 Hz), 118.1 (t, *J*= 244.3Hz), 118.0 (t, *J*= 244.3Hz), 114.2, 114.1, 69.7, 68.3, 55.3, 55.2, 45.9 (t, *J*= 19.8 Hz), 45.6 (t, *J*= 19.8 Hz), 40.6, 39.5, 36.7 (dd, *J*= 4.4, 2.9 Hz), 35.5 (dd, *J*= 4.4, 2.9 Hz), 18.8, 18.6, 14.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –118.64 (d, *J*= 275 Hz, 0.4F), –119.45 (d, *J*= 275 Hz, 0.6F), –122.22 (d, *J*= 275 Hz, 0.6F), –122.88 (d, *J*= 275 Hz, 0.4F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{21}F_2O_2$ $[M+H]^+$: 259.1504, found: 259.1517.



To a stirred solution of the alcohol **3aa** (51.2 mg, 0.2mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) at room temperature was added Dess-Martin periodinane (DMP) (170 mg, 0.4 mmol, 2.0 equiv), and the mixture was stirred for an additional 1 hour. The mixture was quenched by sat. aqueous $Na_2S_2O_3$ and sat. aqueous $NaHCO_3$ successively, and diluted by CH_2Cl_2. The organic phase was collected, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate 10:1) over silica gel, to afford *1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-one* (**6**) (41.7 mg, 82%) as a colorless oil.

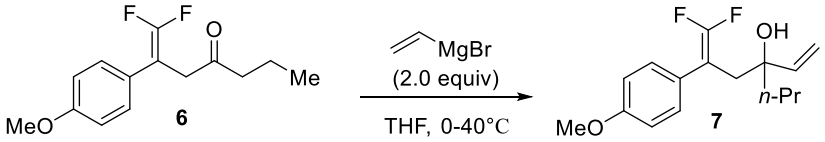
^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.22 (dd, *J*= 8.9, 1.2 Hz, 2H), 6.88 (dd, 2H),

3.79 (s, 3H), 3.42 (d, *J*= 2.3 Hz, 2H), 2.41 (t, *J*= 7.3 Hz, 2H), 1.63-1.48 (m, 2H), 0.88 (t, *J*= 7.4 Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ= 206.9, 158.8, 154.6(dd, *J*=292.3, 288.5 Hz), 129.0 (t, *J*= 3.7 Hz, 2C), 125.3 (t, *J*= 4.0 Hz), 114.0 (2C), 86.8 (dd, *J*= 22.1, 16.5 Hz), 55.3, 43.9, 42.3, 17.1, 13.6 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.35 (d, *J*= 39.4 Hz, 1F), –90.38 (d, *J*= 39.5 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{17}F_2O_2$ $[M+H]^+$: 255.1191, found: 255.1198.



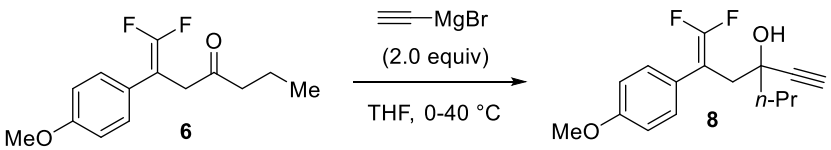
To a stirred solution of the ketone **6** (50.8 mg, 0.2 mmol, 1 equiv) in dry THF (1 mL) was added vinyl magnesium bromide (1.0 M in THF, 0.4 mL, 0.4 mmol, 2 equiv) dropwise at 0 °C. After stirring for 20 min, the reaction mixture was heated to 40℃. The resulting mixture was stirred for 4 hours and then quenched by saturated aqueous NH_4Cl solution (5 mL). The organic phase was extracted with ethyl acetate (2 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to afford the crude product, which was further purified through column chromatography (petroleum ether/ethyl acetate 5:1) over silica gel, to afford *1,1-difluoro-2-(4-methoxyphenyl)-4-vinylhept-1-en-4-ol* (**7**) (45.1mg, 80%) as a colorless oil.

H NMR (500 MHz, Chloroform-*d*) δ= 7.22 (d, *J*= 7.5 Hz, 2H), 6.88 (d, *J*= 8.9 Hz, 2H), 5.76-5.67 (m, 1H), 5.19-4.96 (m, 2H), 3.80 (s, 3H), 2.62 (t, *J*= 2.3 Hz, 2H), 1.54-1.47 (m, 1H), 1.46-1.38 (m, 1H), 1.31-1.27 (m, 1H), 1.25-1.19 (m, 1H), 0.83 (t, *J*= 7.3 Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ= 158.8, 154.5 (dd, *J*= 290.0, 288.5 Hz), 143.0, 129.8 (t, *J*= 3.1 Hz, 2C), 126.4 (dd, *J*= 3.8, 2.5 Hz),), 114.0 (2C), 112.7, 88.6 (dd, *J*= 21.1, 14.7 Hz), 76.6 (t, *J*= 2.7 Hz), 55.2, 43.1, 39.5, 16.6, 14.4 ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ= –89.88 (d, *J*= 41.5 Hz, 1F), –91.69 (d, *J*= 40.7 Hz, 1F) ppm.

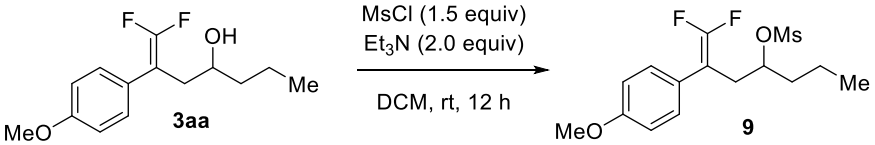
HRMS (ESI) m/z calculated for $C_{16}H_{20}F_2O_2Na$ $[M+Na]^+$: 305.1324, found: 305.1314.



To a stirred solution of the ketone **6** (50.8 mg, 0.2 mmol, 1 equiv) in dry THF (1 mL) was added ethynyl magnesium bromide (1.0 M in THF, 0.4 mL, 0.4 mmol, 2 equiv)

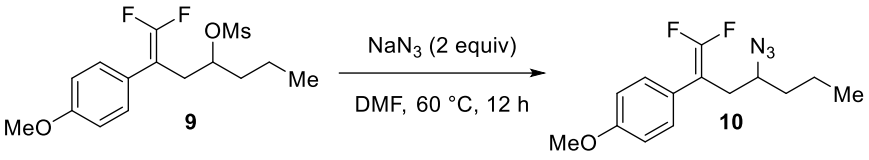
dropwise at 0 °C. After stirring for 20 min, the reaction mixture was heated to 40℃. The resulting mixture was stirred for 4 hours and then quenched by saturated aqueous NH_4Cl solution (5 mL). The organic phase was extracted with ethyl acetate (2 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to afford the crude product, which was further purified through column chromatography (petroleum ether/ethyl acetate 5:1) over silica gel, to afford *4-ethynyl-1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-ol* (**8**) (31.4mg, 56%) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.28 (d, *J*= 7.8 Hz, 2H), 6.89 (d, *J*= 8.8 Hz, 2H), 3.80 (s, 3H), 2.86-2.78 (m, 1H), 2.76-2.66 (m, 1H), 2.36 (s, 1H), 1.79 (s, 1H), 1.62-1.47 (m, 4H), 0.88 (t, *J*= 7.2 Hz, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 158.9, 154.9 (dd, *J*= 291.0, 289.5 Hz), 129.9 (t, *J*= 2.7 Hz, 2C), 126.1 (dd, *J* = 4.1, 2.8 Hz), 114.0 (2C), 88.4 (dd, *J*= 21.1, 16.5 Hz), 85.6, 73.2, 71.5 (dd, *J*= 3.8, 2.5 Hz), 55.3, 43.9, 40.4, 17.5, 14.1 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ= –89.12 (d, *J*= 38.2 Hz, 1F), –90.69 (d, *J*= 38.3 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{18}F_2O_2Na$ $[M+Na]^+$: 303.1167, found: 303.1173.



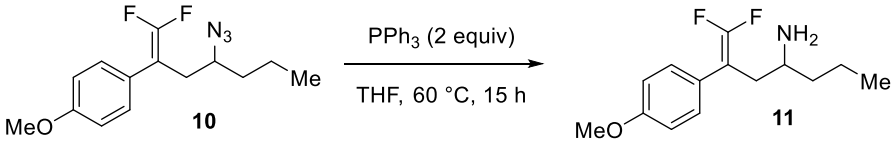
A solution of the alcohol **3aa** (51.2 mg, 0.2 mmol, 1.0 equiv) in DCM (1 mL) was cooled in an ice water bath and treated with Et_3N (40.4 mg, 0.4 mmol, 2.0 equiv, 56 μL) and mesyl chloride (34.4 mg, 0.3 mmol, 1.5 equiv, 23 μL). Afer the resulting solution was stirred at room temperature for 12 hours, the reaction was diluted with ethyl acetate and washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified through column chromatography (petroleum ether/ethyl acetate 5:1) over silica gel, to afford *1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-yl methanesulfonate* (**9**) (63mg, 95%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.39-7.18 (m, 2H), 6.91 (d, *J*= 8.9 Hz, 2H), 4.73 – 4.56 (m, 1H), 3.81 (s, 3H), 2.90-2.82 (m, 1H), 2.85 (s, 3H), 2.76-2.67 (m, 1H), 1.72-1.55 (m, 2H), 1.49-1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 159.0, 154.4 (dd, *J*= 291.9, 288.9 Hz), 129.4 (t, *J*= 3.3 Hz, 2C), 124.5 (t, *J*= 3.7 Hz), 114.1 (2C), 88.1 (dd, *J*= 21.1, 16.0 Hz), 80.9 (dd, *J*= 4.0, 3.0 Hz), 55.3, 38.3, 36.3, 33.2 (d, *J*= 1.8 Hz), 18.2, 13.7 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –89.69 (d, *J*= 39.6 Hz, 1F), –90.06 (d, *J*= 39.8 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{15}H_{20}F_2O_4Na$ $[M+Na]^+$: 357.0943, found: 357.0935.



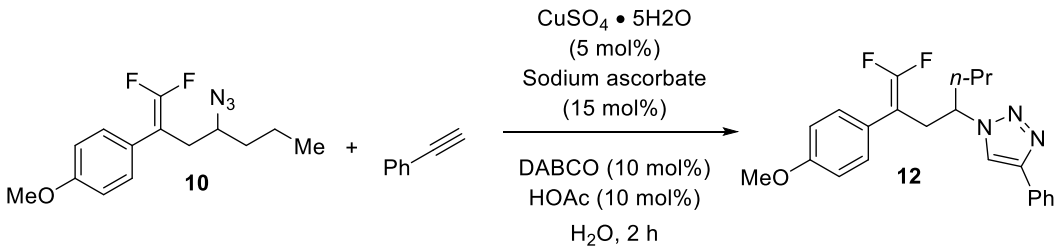
A mixture of the mesylate **9** (66.8 mg, 0.2 mmol, 1.0 equiv) and NaN_3 (26 mg, 0.4 mmol, 2 equiv) in DMF (1 mL) was stirred at 60 ℃ for 12h. Next, the mixure was diluted with ethyl acetate, washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified through column chromatography (petroleum ether/ethyl acetate 10:1) over silica gel, to afford *1-(4-azido-1,1-difluorohept-1-en-2-yl)-4-methoxybenzene* (**10**) (55 mg, 98%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.34-7.03 (m, 2H), 6.84 (d, *J*= 8.47 Hz, 2H), 3.74 (s, 3H), 3.22-3.01 (m, 1H), 2.58-2.36 (m, 2H), 1.44-1.18 (m, 4H), 0.81 (t, *J*= 6.9 Hz, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 158.9, 154.2 (dd, *J* = 290.0, 287.7 Hz), 129.4 (t, *J*= 3.1 Hz, 2C), 124.8-124.7 (m), 114.1 (2C), 89.1 (dd, *J*= 21.3, 15.8 Hz), 60.6 (t, *J*= 2.9 Hz), 55.3, 36.3, 33.5 (d, *J*= 2.2 Hz), 19.3, 13.8 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –90.54 (d, *J*= 41.9 Hz, 1F), –90.94 (d, *J*= 41.7 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{18}F_2N_3O$ $[M+H]^+$: 282.1412, found: 282.1414.



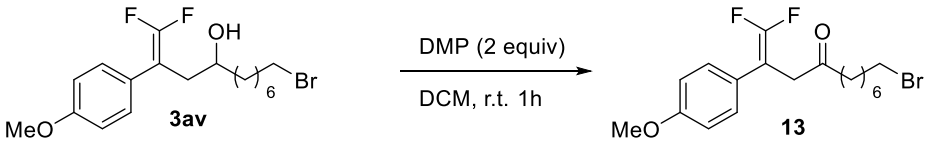
A mixture of the azide **10** (56.2 mg, 0.2 mmol, 1.0 equiv) and PPh_3 (104.8 mg, 0.4 mmol, 2.0 equiv) in THF (1 mL) was stirred at 60℃ for 15h. Next, the mixture was diluted with EA, washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified through column chromatography (ethyl acetate) over silica gel, to afford *1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-amine* (**11**) (45.9 mg, 90%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.27-7.23 (m, 2H), 6.89 (d, *J*= 8.82 Hz, 2H), 3.81 (s, 3H), 2.78-2.57 (m, 1H), 2.50-2.41 (m, 1H), 2.38-2.25 (m, 1H), 1.42-1.25 (m, 4H), 0.87 (t, *J*= 6.6 Hz, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 158.8, 154.3 (dd, *J*= 291.0, 287.3 Hz), 129.4 (t, *J*= 3.2 Hz, 2C), 125.5 (dd, *J*= 5.1, 2.5 Hz), 114.0 (2C), 89.9 (dd, *J*= 21.4, 13.9 Hz), 55.3, 49.1, 39.7, 36.6, 19.3, 14.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ= –91.35 (d, *J*= 44.3 Hz, 1F), –91.66 (d, *J*= 44.2 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{14}H_{19}F_2NONa$ $[M+Na]^+$: 278.1327, found: 278.1330.



A mixture of $CuSO_4$•$5H_2O$ (3.8 mg, 0.015 mmol, 0.05 equiv), sodium ascorbate (9.0 mg, 0.045 mmol, 0.15 equiv) and DABCO (3.4 mg, 0.03 mmol, 0.1 equiv) in water (1 mL) was stirred vigorously at room temperature for 5 min. Acetic acid (1.8 mg, 0.03 mmol, 0.1 equiv, 1.8 μL), phenyl acetylene (51 mg, 0.5 mmol, 1.6equiv, 55 μL) and the azide **10** (84.3 mg, 0.3 mmol, 1.0 equiv) were added sequentially. After the resulting solution was stirred at room temperature for 2 hours, the reaction mixture was diluted by adding EtOAc (5 mL) and aqueous NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 minutes and two layers were separated. The aqueous layer was extracted with EtOAc (2x5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified through column chromatography (petroleum ether/ethyl acetate 10:1) over silica gel, to afford *1-(1,1-difluoro-2-(4-methoxyphenyl)hept-1-en-4-yl)-4-phenyl-1H-1,2,3-triazole* (**12**) (68.9 mg, 92%) as a colorless oil.

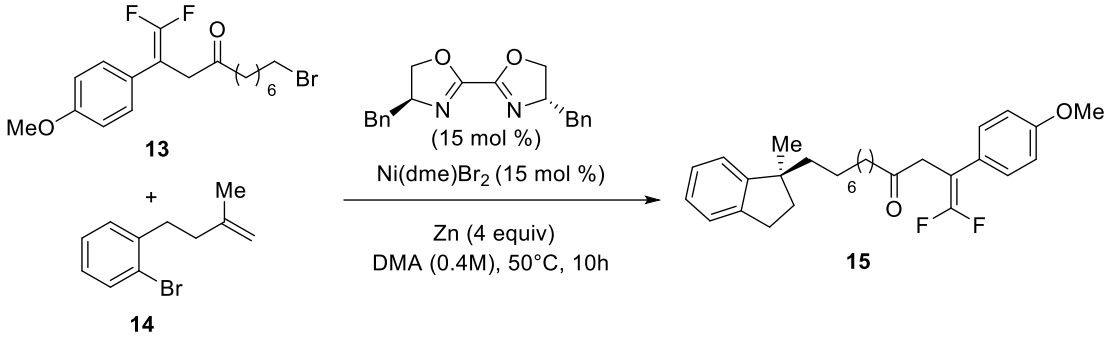
^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.73-7.66 (m, 2H), 7.44 (s, 1H), 7.33 (t, *J*= 7.58 Hz, 2H), 7.24 (t, *J*= 7.41 Hz, 1H), 7.02 (d, *J*= 8.38 Hz, 2H), 6.76 (d, *J*= 8.72 Hz, 2H), 4.46-4.31 (m, 1H), 3.64 (s, 3H), 2.97-2.82 (m, 2H), 1.94-1.84 (m, 1H), 1.82 – 1.72 (m, 1H), 1.14-1.01 (m, 2H), 0.76 (t, *J*= 7.37 Hz, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 159.1, 154.2 (dd, *J*= 290.4, 288.7 Hz), 147.4, 130.7, 129.4 (t, *J*= 2.7 Hz, 2C), 128.8 (2C), 128.1, 125.7 (2C), 124.1 (d, *J*= 6.9 Hz), 118.2, 114.2 (2C), 88.6 (dd, *J*= 20.2, 16.5 Hz), 59.9 (t, *J*= 2.8 Hz), 55.2, 37.0, 34.5, 19.1, 13.5 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ= –90.23 (d, *J*= 41.02 Hz, 1F), –90.68 (d, *J*= 39.92 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{22}H_{23}F_2N_3ONa$ $[M+Na]^+$: 406.1701, found: 406.1700.



To a stirred solution of the alcohol **3av** (1.31 g, 3.35 mmol, 1.0 equiv) in CH_2Cl_2 (35 mL) at room temperature was added Dess-Martin periodinane (DMP) (2.84 g, 6.7 mmol, 2.0 equiv), and the mixture was stirred for 1 hour. The mixture was quenched by sat. aqueous $Na_2S_2O_3$ and sat. aqueous $NaHCO_3$ successively, and diluted by CH_2Cl_2. The organic phase was collected, and the aqueous phase was extracted with

CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate 20:1) over silica gel, to afford *11-bromo-1,1-difluoro-2-(4-methoxyphenyl)undec-1-en-4-one* (**13**) (1092 mg, 84%) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.21 (d, *J*= 8.6 Hz, 2H), 6.86 (d, *J*= 8.9 Hz, 2H), 3.78 (s, 3H), 3.40 (t, *J*= 2.3 Hz, 2H), 3.37 (t, *J*= 6.9 Hz, 2H), 2.41 (t, *J*= 7.3 Hz, 2H), 1.84-1.77 (m, 2H), 1.56-1.49 (m, 2H), 1.42-1.35 (m, 2H), 1.29-1.19 (m, 4H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 206.9 (t, *J*= 3.2 Hz), 158.9, 154.5 (dd, *J*= 292.3, 287.7 Hz), 129.0 (t, *J*= 3.7 Hz, 2C), 125.3 (t, *J*= 3.7 Hz), 114.0 (2C), 86.8 (dd, *J*= 22.1, 16.5 Hz), 55.3, 42.3, 41.8, 34.0, 32.7, 28.8, 28.5, 27.9, 23.4 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ= –89.27 (d, *J*= 38.1 Hz, 1F), –90.28 (d, *J*= 38.1 Hz, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{18}H_{23}F_2O_2BrH$ $[M+H]^+$: 389.0922, found: 389.0923.



A sealed test tube charged with $NiBr_2$(dme) (9.3 mg, 0.03 mmol, 15mol%), BiOX ligand (9.6 mg, 0.03 mmol, 15 mol%), Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) and a stir bar was evacuated and filled with nitrogen (three cycles) before adding DMA (0.5 mL) under nitrogen atmosphere. Then the reaction mixture was stirred at 50 °C for 15 minutes. Next, *1-bromo-2-(3-methylbut-3-en-1-yl)benzene* (**14**) (44.8 mg, 0.2 mmol, 1.0 equiv) and the alkyl bromide **13** (116.4 mg, 0.3 mmol, 1.5 equiv) were added, and the resulting mixture was stirred at 50 °C for 10 hours. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography (petroleum ether/ethyl acetate 30:1) over silica gel, to afford *(S)-1,1-difluoro-2-(4-methoxyphenyl)-12-(1-methyl-2,3-dihydro-1H-inden-1-yl)dodec-1-en-4-one* (**15**) (27.1 mg, 30%, 90% *ee*) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.25-7.07 (m, 6H), 6.88 (d, *J*= 8.8 Hz, 2H), 3.80 (s, 3H), 3.41 (t, *J*= 2.3 Hz, 2H), 2.88 (t, *J*= 7.3 Hz, 2H), 2.41 (t, *J*= 7.4 Hz, 2H), 2.08-1.96 (m, 1H), 1.89-1.76 (m, 1H), 1.60-1.45 (m, 4H), 1.31-1.11 (m, 10H), 1.23 (s, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 207.1 (t, *J*= 2.8 Hz), 158.8, 154.5 (dd, *J*=

292.0, 287.2 Hz), 151.8, 143.2, 129.0 (t, *J*= 3.7 Hz, 2C), 126.13, 126.08, 125.3 (t, *J*= 3.8 Hz), 124.5, 122.6, 114.0 (2C), 86.8 (dd, *J*= 21.8, 16.7 Hz), 55.3, 47.3, 42.3 (d, *J*= 2.2 Hz), 42.0, 41.4, 38.6, 30.34, 30.29, 29.41, 29.37, 29.1, 26.8, 24.9, 23.6 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ= –89.2 (d, *J*= 38.8 Hz, 1F), –90.2 (d, *J*= 38.8 Hz, 1F) ppm.

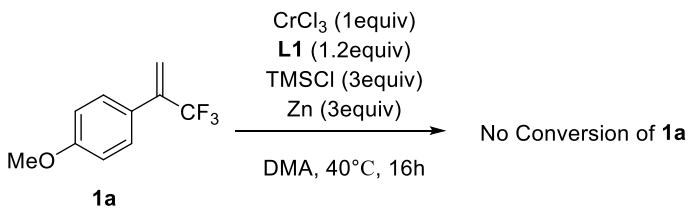
HRMS (ESI) m/z calculated for $C_{29}H_{36}F_2O_2Na$ $[M+Na]^+$: 477.2576, found: 477.2588.

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 98/2, flow rate = 0.4 mL/min): t_R= 16.7 (minor), 17.8 (major).

The absolute configuration of compound **15** was assigned assuming a common reaction pathway as reported in the literature.[12]

Control Experiments

A)



1a

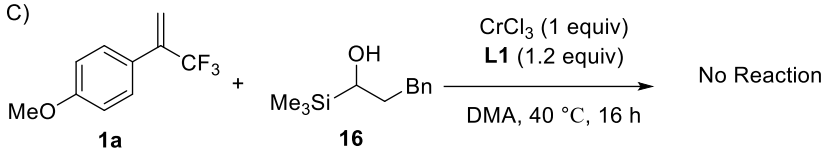
$CrCl_3$ (32 mg, 0.2 mmol, 1 equiv), 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (64 mg, 0.24 mmol, 1.2 equiv) and Zn (39 mg, 0.6 mmol, 3.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, TMSCl (65.2 mg, 78 μL, 0.6 mmol, 3 equiv) was added under a positive flow of nitrogen. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before the α-trifluoromethyl alkenes **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 ℃ for 16 hours, before it was quenched by addition of 2 mL aqueous HCl (2 N). After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. According to the analyses based on TCL and ^{1}H-NMR spectroscopy, no conversion of **1a** was observed.

B)

1a 2g

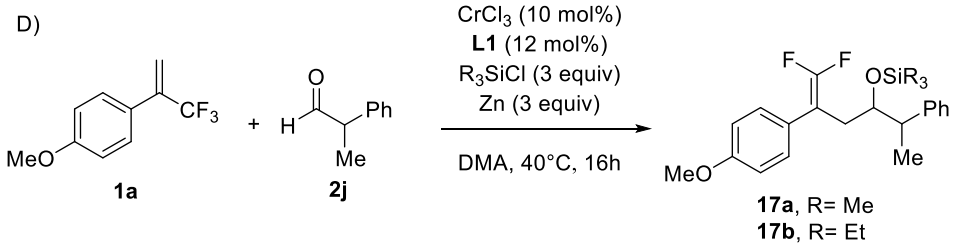
$CrCl_2$ (49.2 mg, 0.4 mmol, 2 equiv) and 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (130 mg, 0.48 mmol, 2.4 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, TMSCl (65.2 mg, 78 μL, 0.6 mmol, 3 equiv) and the 3-phenylpropanal (**2g**) (53.6 mg, 0.4 mmol, 2 equiv) were added under a positive flow of nitrogen. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before the α-trifluoromethyl alkene **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40℃ for 16 hours, before it was quenched by addition of 2 mL aqueous HCl (2 N). After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. According to the analyses based on TCL and ^{1}H-NMR spectroscopy, compound **3ag** was not formed.

C)



$CrCl_3$ (32 mg, 0.2 mmol, 1 equiv) and 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (64 mg, 0.24 mmol, 1.2 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before the α-trifluoromethyl alkene **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) and 3-phenyl-1-(trimethylsilyl)propan-1-ol **16**[13] (83.2 mg, 0.4 mmol, 2.0 equiv) were added under nitrogen atmosphere. The reaction mixture was stirred at 40℃ for 16 hours, before it was quenched by addition of 2 mL aqueous HCl (2 N). After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. According to the analyses based on TCL and ^{1}H-NMR spectroscopy, conversion of either **1a** or **13** was not observed.

D)



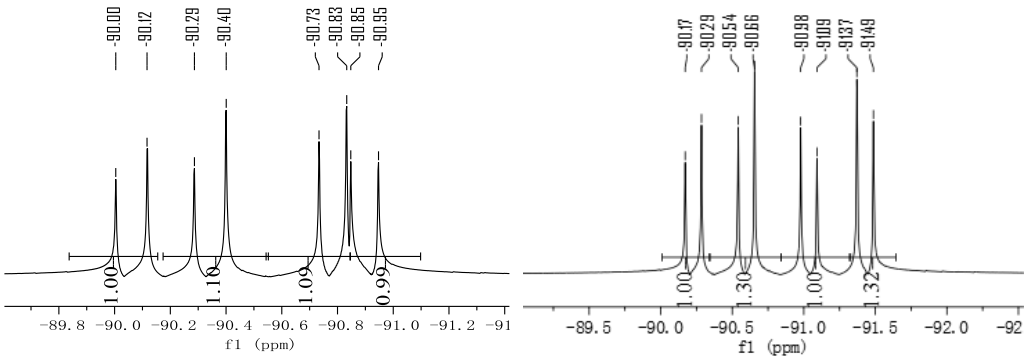
$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol %), 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (6.4 mg, 0.024 mmol, 12 mol %) and Zn (39 mg, 0.6 mmol, 3.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, R_3SiCl (0.6 mmol, 3 equiv) and 2-phenylpropanal **2j** (53.6 mg, 0.4 mmol, 2.0 equiv) were added under a positive flow of nitrogen. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before the α-trifluoromethyl alkenes **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) were added under nitrogen atmosphere. The reaction mixture was stirred at 40℃ for 16 hours, before it was quenched by addition of 2 mL aqueous $NaHCO_3$. After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified through column chromatography (petroleum ether/ethyl acetate 50:1) over silica gel, to afford *((6,6-difluoro-5-(4-methoxyphenyl)-2-phenylhex-5-en-3-yl)oxy)trimethylsilane* (**17a**) (R= Me, 69.4 mg, 89%, dr=1:1.1) or *((6,6-difluoro-5-(4-methoxyphenyl)-2-phenylhex-5-en-3-yl)oxy)triethylsilane* (**17b**) (R= Et, 35.5 mg, 59%, dr=1:1.3).

Compound **17a**

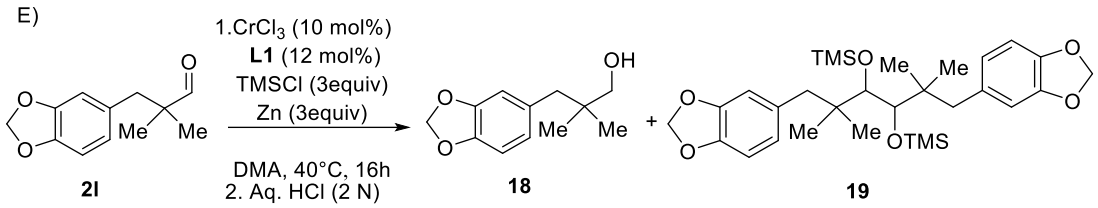
^{1}H NMR (500 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.40-7.35 (m, 2H), 7.34-7.27 (m, 2H), 7.22 (t, *J*= 8.7 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.96 (m, 2H), 3.92 (s, 3H), 3.88-3.76 (m, 1H), 2.96-2.83 (m, 1H), 2.68-2.47 (m, 2H), 1.38 (m, 3H), 0.02 (s, 9H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 158.7, 158.6, 154.2 (dd, *J*= 291.0, 287.3 Hz), 145.1, 143.7, 129.4 (t, *J*= 3.2 Hz, 2C), 128.7, 128.3, 128.1, 128.1, 126.40, 126.39, 125.8 (t, *J*= 3.8 Hz), 125.5 (t, *J*= 3.8 Hz), 114.0, 113.9, 89.5 (dd, *J*= 21.3, 13.1 Hz), 75.6 (t, *J*= 2.5 Hz), 75.4 (t, *J*= 2.4 Hz), 55.4, 45.6, 45.1, 34.1, 32.5, 16.6, 15.6, 0.3 (3C) ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= – 90.06 (d, *J*= 42.2 Hz, 0.48 F), – 90.34 (d, *J*= 42.9 Hz, 0.52 F), – 90.78 (d, *J*= 37.5 Hz, 0.52 F), – 90.90 (d, *J*= 37.5 Hz, 0.48 F) ppm.
HRMS (ESI) m/z calculated for $C_{22}H_{28}F_2O_2SiNa$ $[M+Na]^+$: 413.1719, found: 413.1714.

Compound **17b**

^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 7.23-7.06 (m, 5H), 7.01-6.94 (m, 1H), 6.91- 6.85 (m, 1H), 6.83-6.77 (m, 1H), 6.72-6.66 (m, 1H), 3.75 (s, 3H), 3.68-3.57 (m, 1H), 2.89-2.64 (m, 1H), 2.57-2.14 (m, 2H), 1.28-1.11 (m, 3H), 0.91-0.64 (m, 9H), 0.50-0.16 (m, 6H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 158.8, 158.6, 154.5 (dd, *J*= 296.1, 291.0 Hz), 145.3, 143.2, 129.6 (t, *J*= 3.7 Hz), 129.4 (t, *J*= 3.7 Hz), 128.68, 128.69, 128.3, 128.20, 128.15, 126.4, 126.3, 125.6 (d, *J*= 3.8 Hz), 125.5 (d, *J*= 7.3 Hz), 114.0, 113.8, 89.5 (dd, *J*= 22.7, 10.1 Hz), 75.0 (t, *J*= 2.5Hz), 74.8 (t, *J*= 2.4Hz), 55.39, 55.35, 44.9, 43.8, 34.0, 31.1, 14.7, 13.9, 7.04, 6.99, 5.2, 5.1 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= –90.23 (d, *J*= 42.9 Hz, 0.43 F), –90.60 (d, *J*= 42.9 Hz, 0.57 F), –91.04 (d, *J*= 42.9 Hz, 0.43 F), –91.43 (d, *J*= 43.6 Hz, 0.57 F) ppm.
HRMS (ESI) m/z calculated for $C_{12}H_{16}F_2O_3H$ $[M+H]^+$: 209.1172, found: 209.1170.



17a **17b**



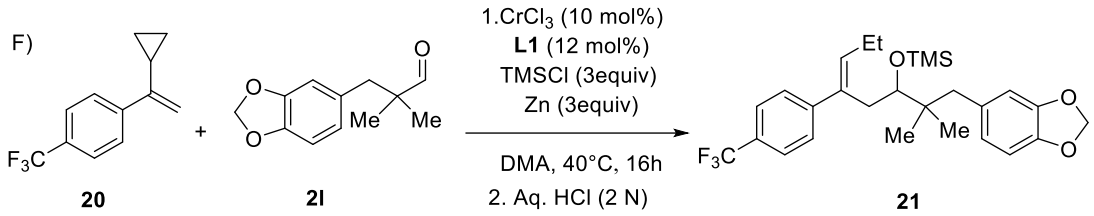
$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol %), 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (6.4 mg, 0.024 mmol, 12 mol %) and Zn (39 mg, 0.6 mmol, 1.5 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, TMSCl (65.2 mg, 76 μL, 0.6 mmol, 1.5 equiv) and the aldehydes **2l** (82.4 mg, 0.4 mmol, 1.0 equiv) were added under a positive flow of nitrogen. The reaction mixture was stirred at 40℃ for 16 hours, before it was quenched by addition of 2 mL aqueous HCl (2 N). After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified through column chromatography (petroleum ether/ethyl acetate 30:1) over silica gel, to afford *3-(Benzo[d][1,3]dioxol-5-yl)-2,2-dimethylpropan-1-ol* (**18**) (26.6 mg, 32%,) and *4,5-Bis(1-(benzo[d][1,3]dioxol-5-yl)-2-methylpropan-2-yl)-2,2,7,7-tetramethyl-3,6-di oxa-2,7-disilaoctane* (**19**) (40.2 mg, 36%).

Compound **18**

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 6.73 (d, *J*= 7.9 Hz, 1H), 6.67 (d, *J*= 1.8 Hz, 1H), 6.63-6.58 (m, 1H), 5.92 (s, 2H), 3.30 (s, 2H), 2.50 (s, 2H), 0.87 (s, 6H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ= 147.1, 145.8, 132.5, 123.3, 110.9, 107.7, 100.7, 71.0, 44.3, 36.4, 24.0 (2C) ppm..
HRMS (ESI) m/z calculated for $C_{12}H_{16}F_2O_3H$ $[M+H]^+$: 209.1172, found: 209.1170.

Compound **19**

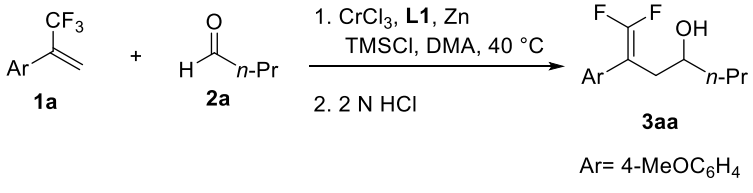
^{1}H NMR (400 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 6.74 (dd, *J*= 7.9, 2.3 Hz, 2H), 6.64 (dd, *J*= 5.4, 1.7 Hz, 2H), 6.58 (ddd, *J*= 7.9, 4.4, 1.8 Hz, 2H), 5.95-5.92 (m, 4H), 3.78 (s, 1.1H), 3.64 (s, 0.9H), 2.64 (s, 2.2H), 2.53 (s, 1.8H), 0.92 (s, 3.1H), 0.85 (s, 3.1H), 0.78 (s, 5.8H), 0.22 (s, 9.9H), 0.20 (s, 8.1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ (mixture of two diastereomers)= 147.1, 147.0, 145.8, 145.7, 133.2, 133.0, 124.0, 123.8, 111.6, 111.4, 107.7, 107.6, 100.85, 100.82, 85.9, 77.5, 44.4, 43.7, 40.5, 40.2, 25.2 , 24.5, 24.2, 22.7, 1.8, 1.4 ppm.
HRMS (ESI) m/z calculated for $C_{30}H_{46}O_6Si_2H$ $[M+H]^+$: 559.2906, found: 559.2900.



$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol %), 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (6.4 mg, 0.024 mmol, 12 mol %) and Zn (39 mg, 0.6 mmol, 3.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, DMA (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, TMSCl (64.8 mg, 76 μL, 0.6 mmol, 3 equiv) and the aldehyde **2l** (82.4 mg, 0.4 mmol, 2.0 equiv) were added under a positive flow of nitrogen. The resultant mixture was stirred at 40 ℃ for another 5 minutes, before *1-(1-cyclopropylvinyl)-4-(trifluoromethyl)benzene* (**20**) (42.4 mg, 0.2 mmol, 1.0 equiv) was added under nitrogen atmosphere. The reaction mixture was stirred at 40℃ for 16 hours, before it was quenched by addition of 2 mL aqueous HCl . After stirring for 1 hour, the aqueous phase was extracted with ethyl acetate (3×25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified through column chromatography (petroleum ether/ethyl acetate 3:1) over silica gel, to afford *((1-(benzo[d][1,3]dioxol-5-yl)-2,2-dimethyl-5-(4- (trifluoromethyl)phenyl)oct-5-en-3-yl)oxy)trimethylsilane* (**21**) (55.1 mg, 56%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ= 7.64 (d, *J*= 8.4 Hz, 2H), 7.56 (d, *J*= 8.4 Hz, 2H), 6.79 (d, *J*= 7.9 Hz, 1H), 6.69 (s, 1H), 6.63 (d, *J*= 7.5 Hz, 1H), 6.00 (s, 2H), 5.98 -5.96 (m, 1H), 3.51-3.43 (m, 1H), 2.89-2.76 (m, 2H), 2.64-2.52 (m, 2H), 2.46-2.25 (m, 2H), 1.16 (t, *J*= 7.6 Hz, 3H), 0.91 (s, 3H), 0.86 (s, 3H), 0.00 (s, 9H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ= 147.1, 146.4, 145.8, 136.1, 135.6 (2C), 132.9 (2C), 126.7 (2C), 125.3 (q, *J*= 3.7 Hz), 123.8 (2C), 111.4, 107.7, 100.9, 80.1, 43.4, 40.0, 31.9, 23.9, 23.0, 22.5, 14.2, 1.1 (3C) ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ= – 62.29 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{27}H_{35}F_3O_3SiNa$ $[M+Na]^+$: 515.2200, found: 515.2230.

Kinetic Studies



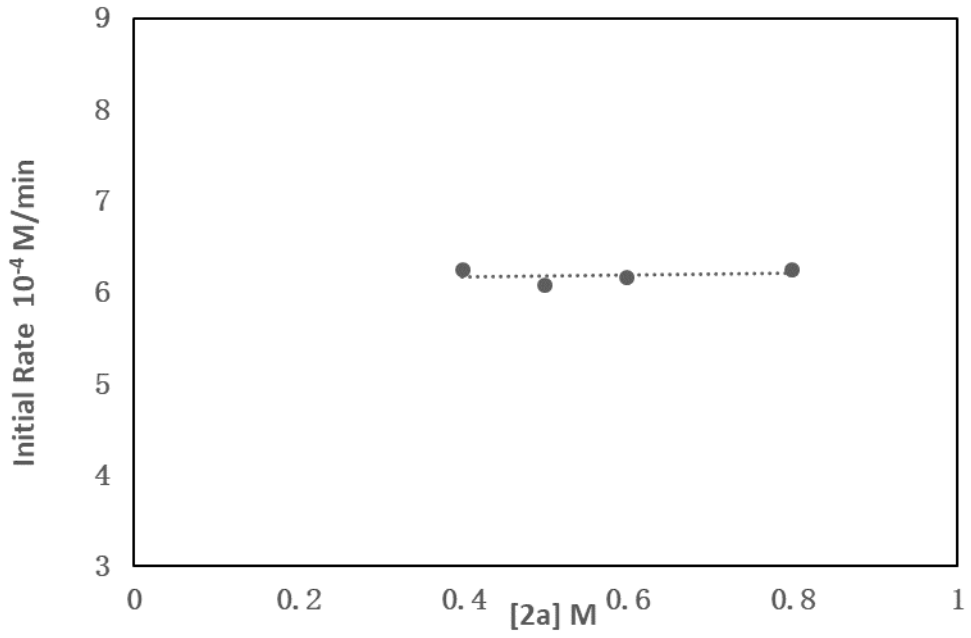
A Schlenk tube was charged with the indicated concentration of butyraldehyde (**2a**), the trifluoromethyl alkene **1a**, $CrCl_3$, the ligand 4,4'-ditertbutyl-2,2'-bipyridine (**L1**),

TMSCl and Zn in DMA. After stirring for 25 min at 40 ˚C, the reaction was quenched by addition of aqueous HCl (2 N). The reaction mixture was analyzed by ^{19}F NMR, and the molar concentration of **3aa** was determined by the integration of the characteristic peak against the internal standard (4-fluoroanisole). The initial rates were calculated and plotted against the reactant or catalyst concentration to determine the reaction orders.

Determination of the Reaction Order in Butyraldehyde (2a)

The reaction was performed with the trifluoromethyl alkene **1a** (40.4 mg, 0.2 mmol, 0.2 M, 1 equiv), $CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol %), the ligand 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (6.4 mg, 0.024 mmol, 12 mol %), TMSCl (65.2 mg, 78 μ L, 0.6 mmol, 3 equiv) and Zn (39 mg, 0.6 mmol, 3.0 equiv) in DMA (1.0 mL) in the presence of 0.4 M, 0.5 M, 0.6 M and 0.8 M butyraldehyde (**2a**). The initial rates at various [**2a**] were similar, showing the reaction exhibits zero-order rate dependence on the concentration of **2a**.

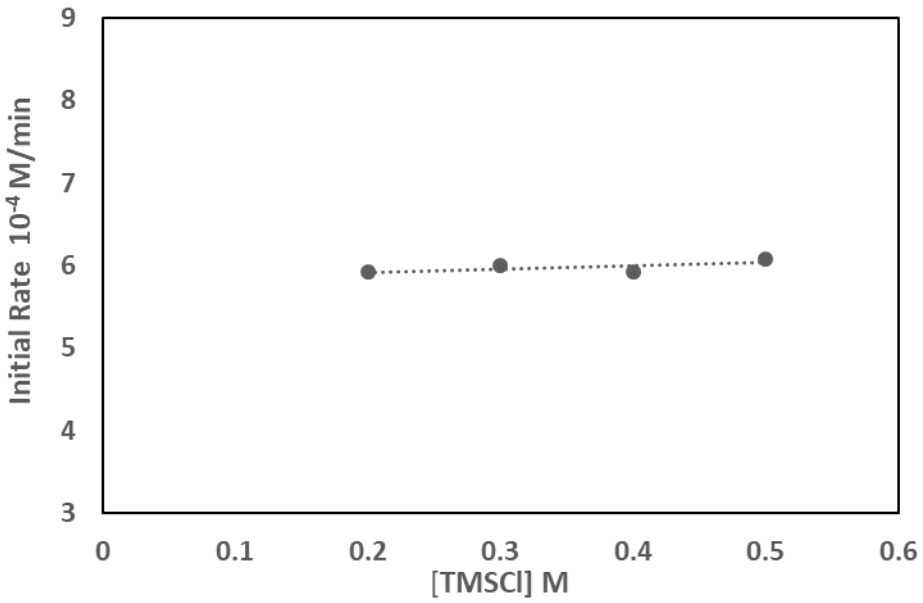
[**2a**] (M)	Conversion of **1a** (%)	[**3aa**] (10^{-2}M)	Initial Rate (10^{-4}M/min)
0.4	7.8	1.56	6.24
0.5	7.6	1.52	6.08
0.6	7.7	1.54	6.16
0.8	7.8	1.56	6.24



Determination of the Reaction Order in TMSCl

The reaction was performed with the trifluoromethyl alkene **1a** (40.4 mg, 0.2 mmol, 0.2 M, 1 equiv), butyraldehyde (**2a**) (28.8 mg, 0.4 mmol, 2 equiv), $CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol %), the ligand 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (6.4 mg, 0.024 mmol, 12 mol %) and Zn (39 mg, 0.6 mmol, 3.0 equiv) in DMA (1.0 mL) in the presence of 0.2 M, 0.3 M, 0.4 M and 0.5 M TMSCl. The initial rates at various [TMSCl] were similar, showing the reaction exhibits a first-order rate dependence on the concentration of **2a**.

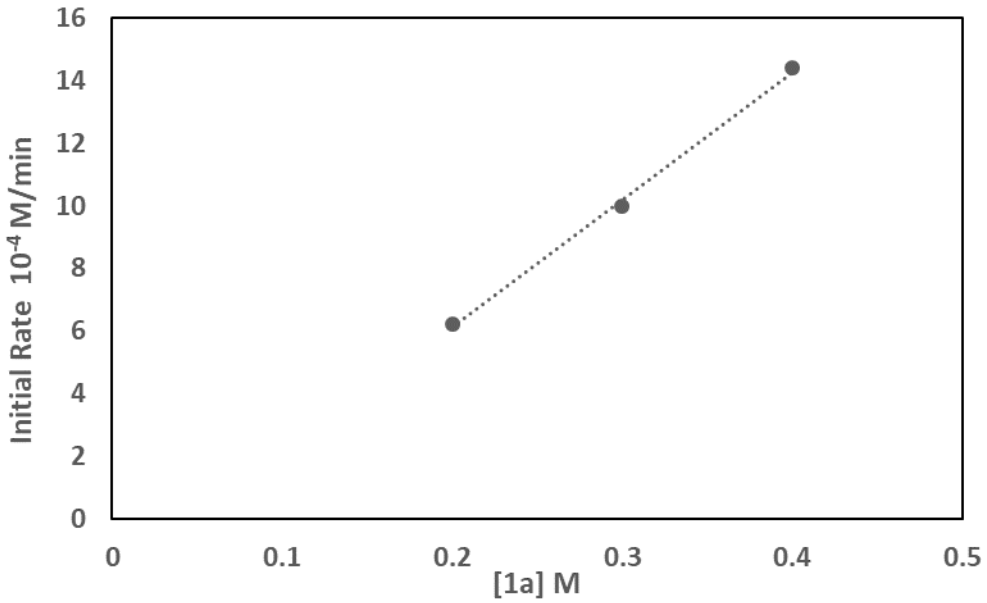
[TMSCl] (M)	Conversion of **1a** (%)	[**3aa**] (10^{-2}M)	Initial Rate (10^{-4}M/min)
0.2	7.4	1.48	5.92
0.3	7.5	1.50	6.00
0.4	7.4	1.48	5.92
0.5	7.6	1.52	6.08



Determination of the Reaction Order in the Trifluoromethyl Alkene 1a

The reaction was performed with butyraldehyde (**2a**) (28.8 mg, 0.4 mmol, 0.4 M, 1 equiv), $CrCl_3$ (3.2 mg, 0.02 mmol, 5 mol %), the ligand 4,4'-ditertbutyl-2,2'-bipyridine (**L1**) (6.4 mg, 0.024 mmol, 6 mol %), TMSCl (65.2 mg, 78 µ L, 0.6 mmol, 1.5 equiv) and Zn (39 mg, 0.6 mmol, 1.5 equiv) in DMA (1.0 mL) in the presence of 0.2 M, 0.3 M, and 0.4 M the trifluoromethyl alkene **1a**. The relationship between the initial rates and [**1a**] was linear, showing the reaction exhibits a first-order rate dependence on the concentration of **1a**.

[**1a**] (M)	Conversion of **1a** (%)	[**3aa**] (10^{-2}M)	Initial Rate (10^{-4}M/min)
0.2	7.8	1.56	6.24
0.3	8.3	2.50	10.0
0.4	9.0	3.60	14.4
0.2[a]	7.7	1.54	6.16

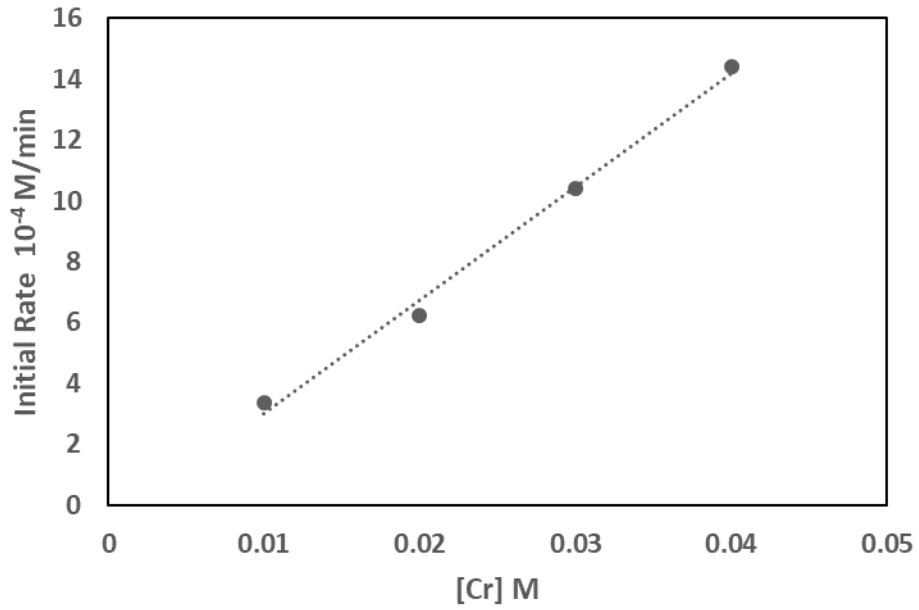


[a] Reaction was performed with 1.0 equiv of $ZnCl_2$.

Determination of the Reaction Order in $CrCl_3$

The reaction was performed with the trifluoromethyl alkene **1a** (40.4 mg, 0.2 mmol, 0.2 M, 1 equiv), butyraldehyde (**2a**) (28.8 mg, 0.4 mmol, 2 equiv), TMSCl (65.2 mg, 78 μ L, 0.6 mmol, 3 equiv) and Zn (39 mg, 0.6 mmol, 3.0 equiv) in DMA (1.0 mL) in the presence of 0.01 M, 0.02 M, 0.03 M and 0.04 M $CrCl_3$ with 0.012 M, 0.024 M, 0.036 M and 0.048 M 4,4'-ditertbutyl-2,2'-bipyridine (**L1**), respectively. The relationship between the initial rates and [$CrCl_3$] was linear, showing the reaction exhibits a first-order rate dependence on the concentration of $CrCl_3$.

[$CrCl_3$] (M)	Conversion of **1a** (%)	[**3aa**] (10^{-2}M)	Initial Rate (10^{-4}M/min)
0.01	4.2	0.84	3.36
0.02	7.8	1.56	6.24
0.03	13	2.60	10.4
0.04	18	3.60	14.4



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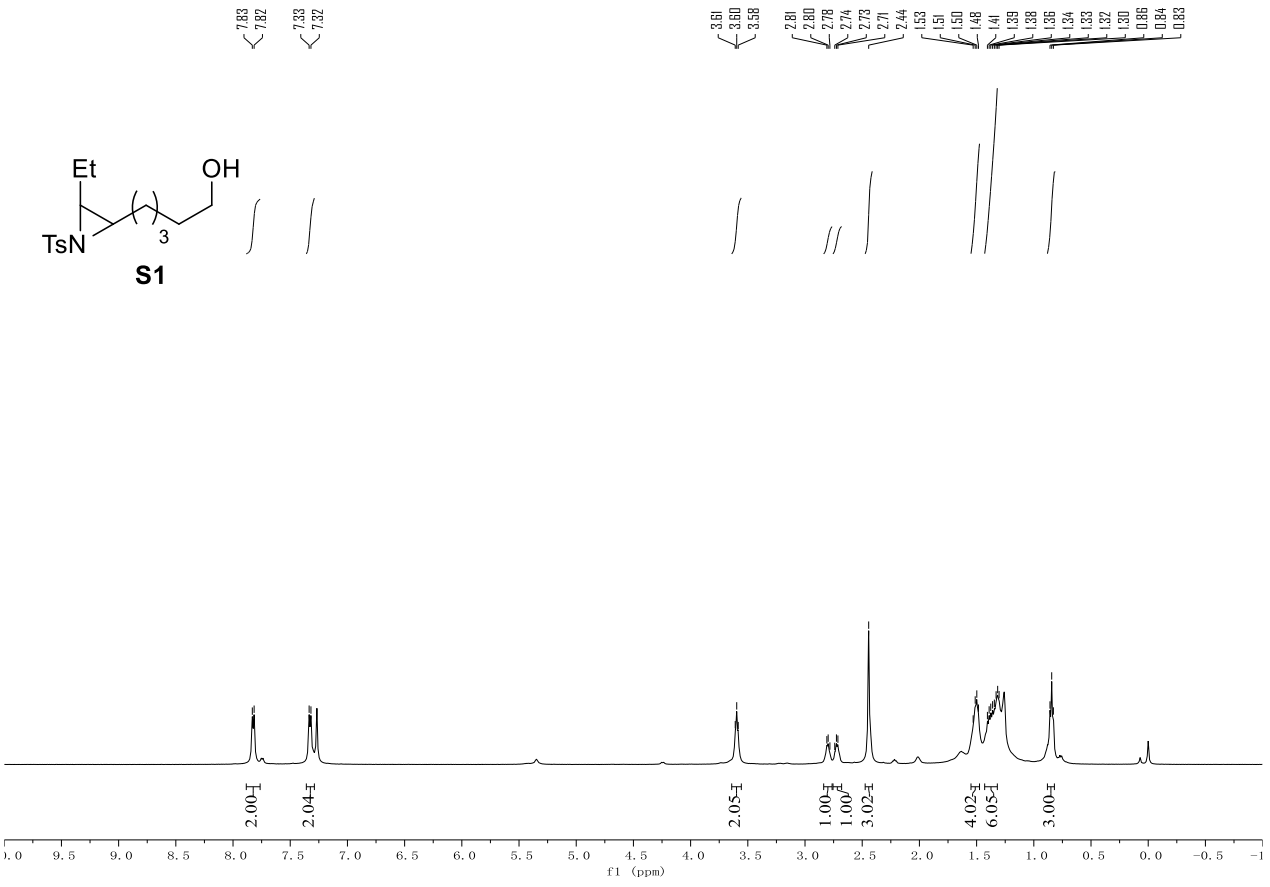
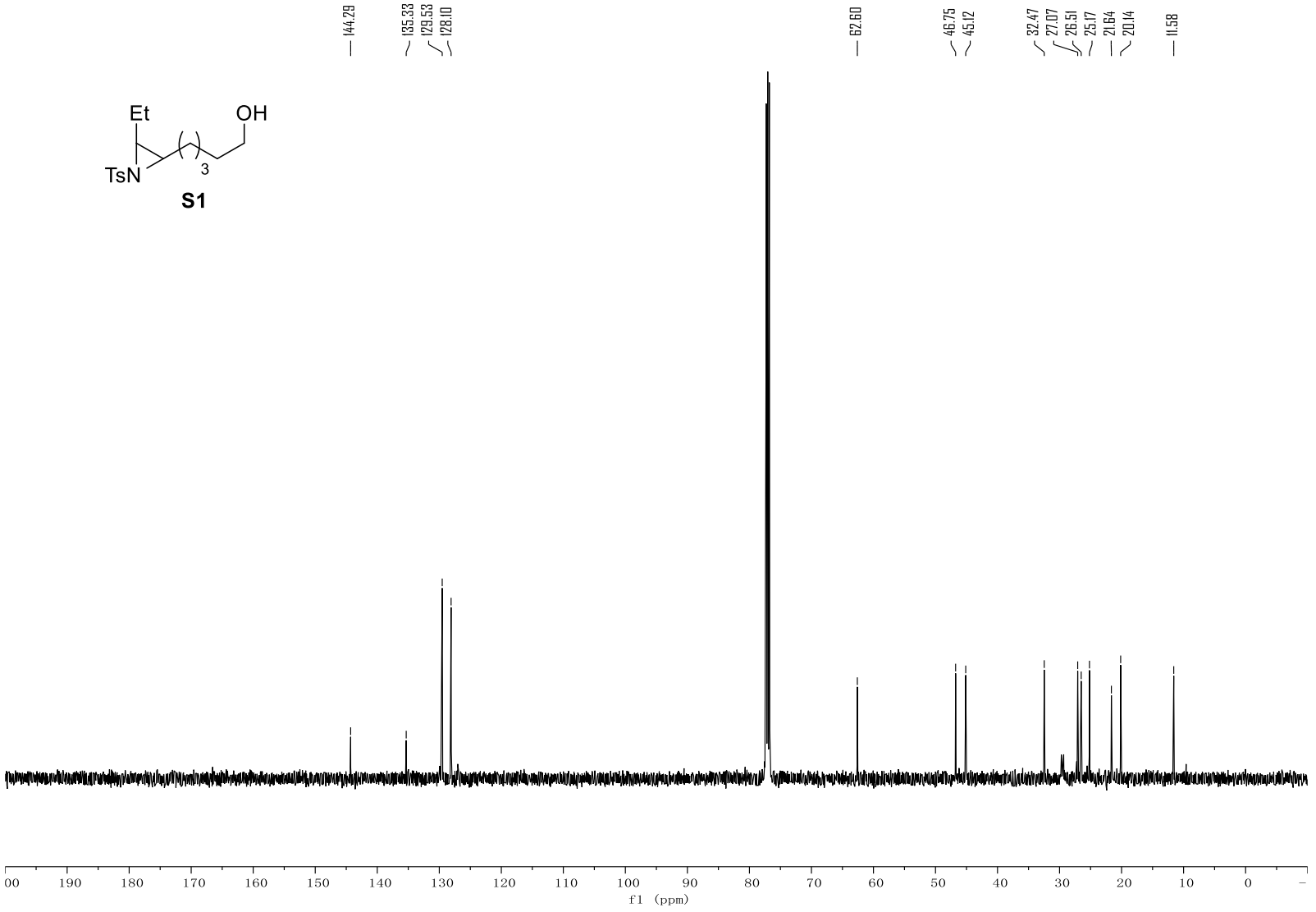
^{1}H, ^{13}C and ^{19}F-NMR Spectra

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TsN
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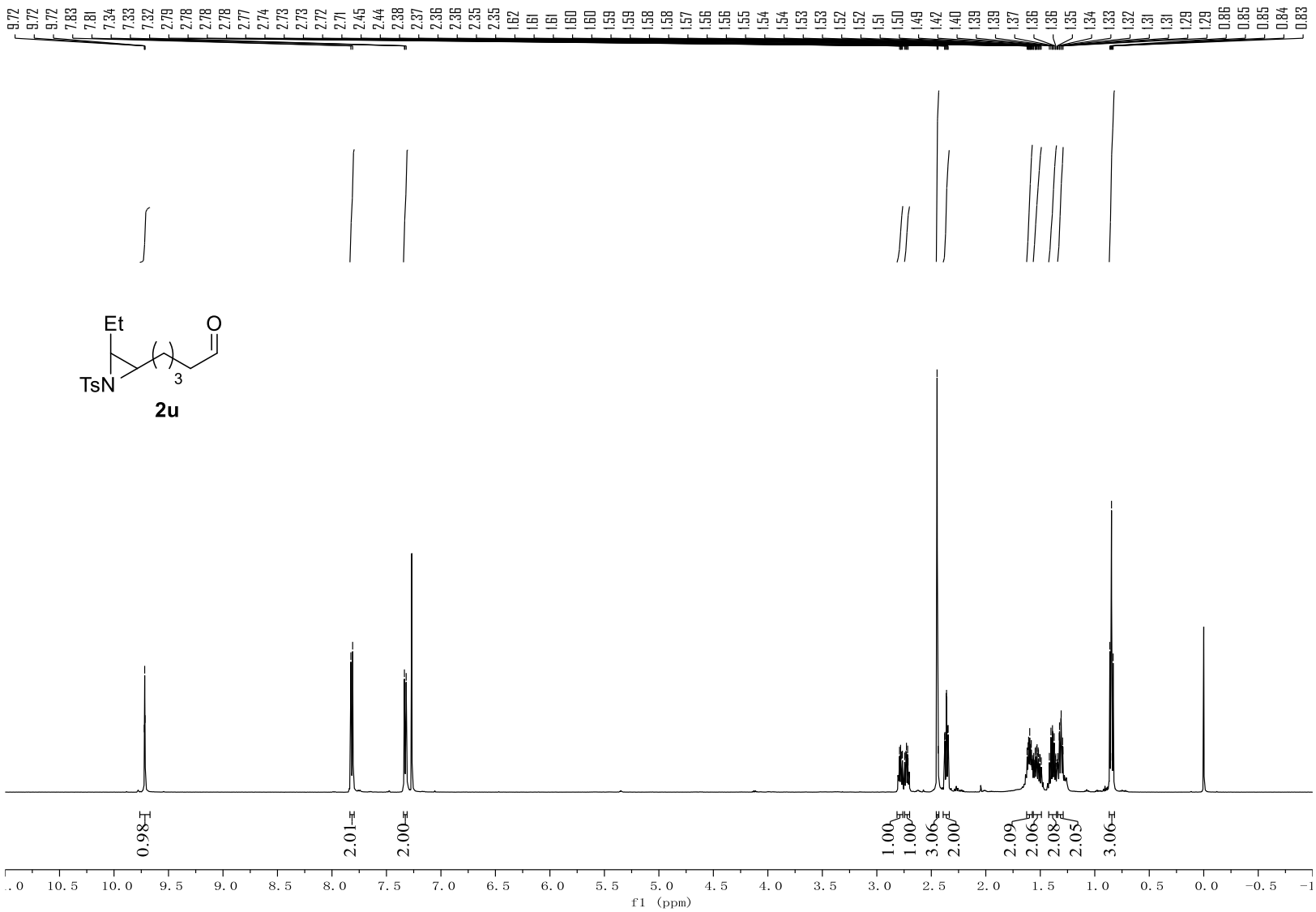
S1
f1 (ppm)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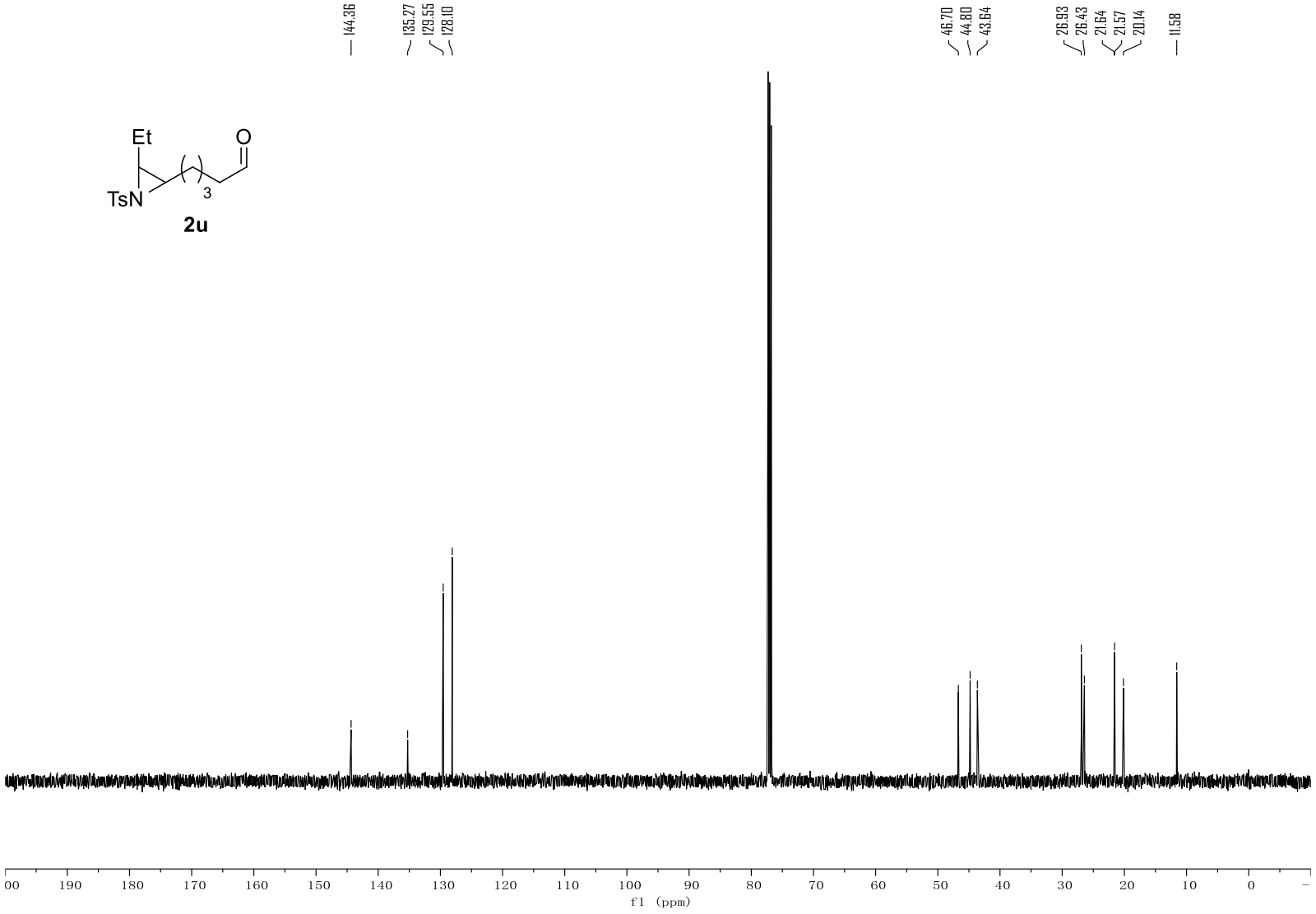
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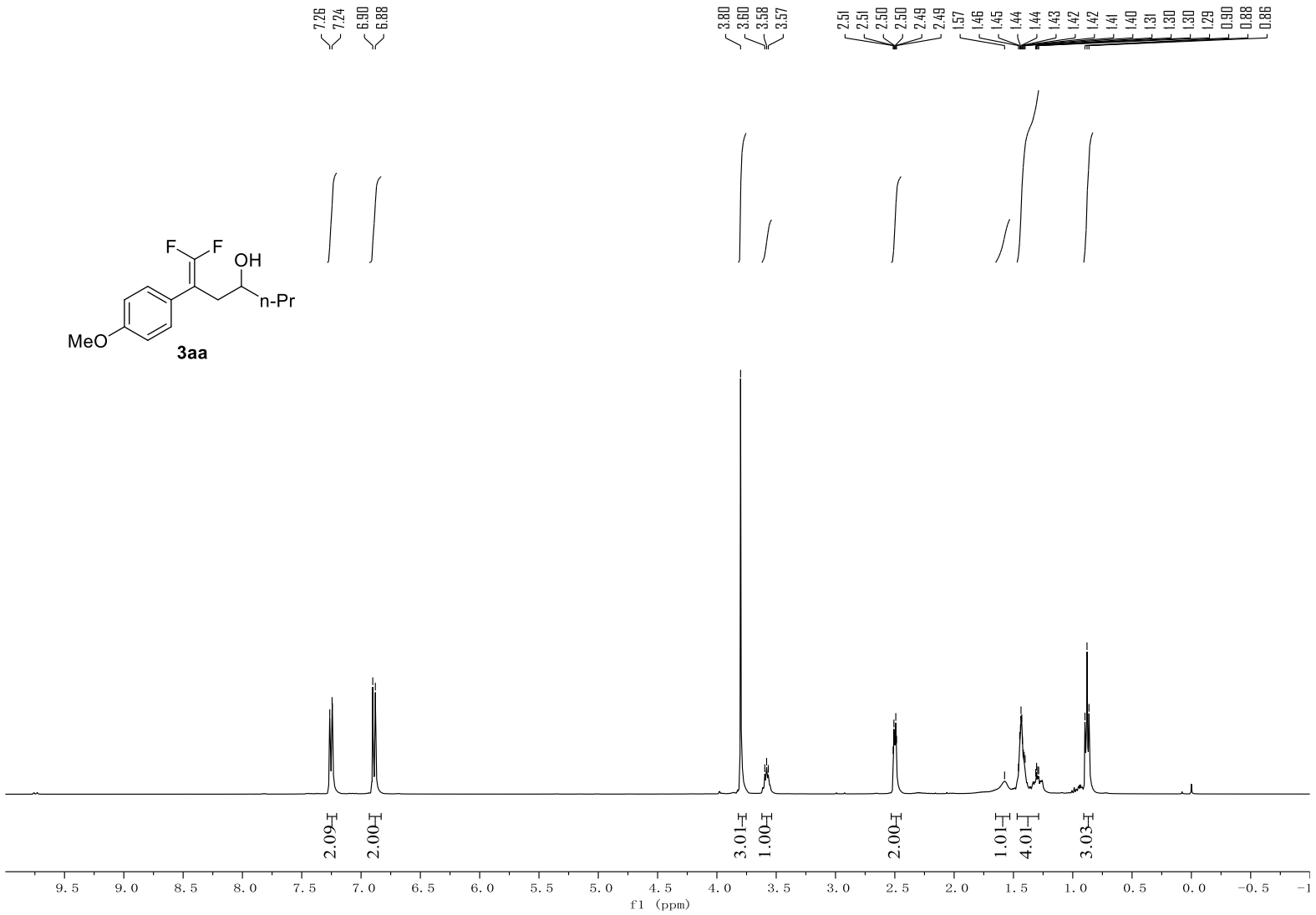
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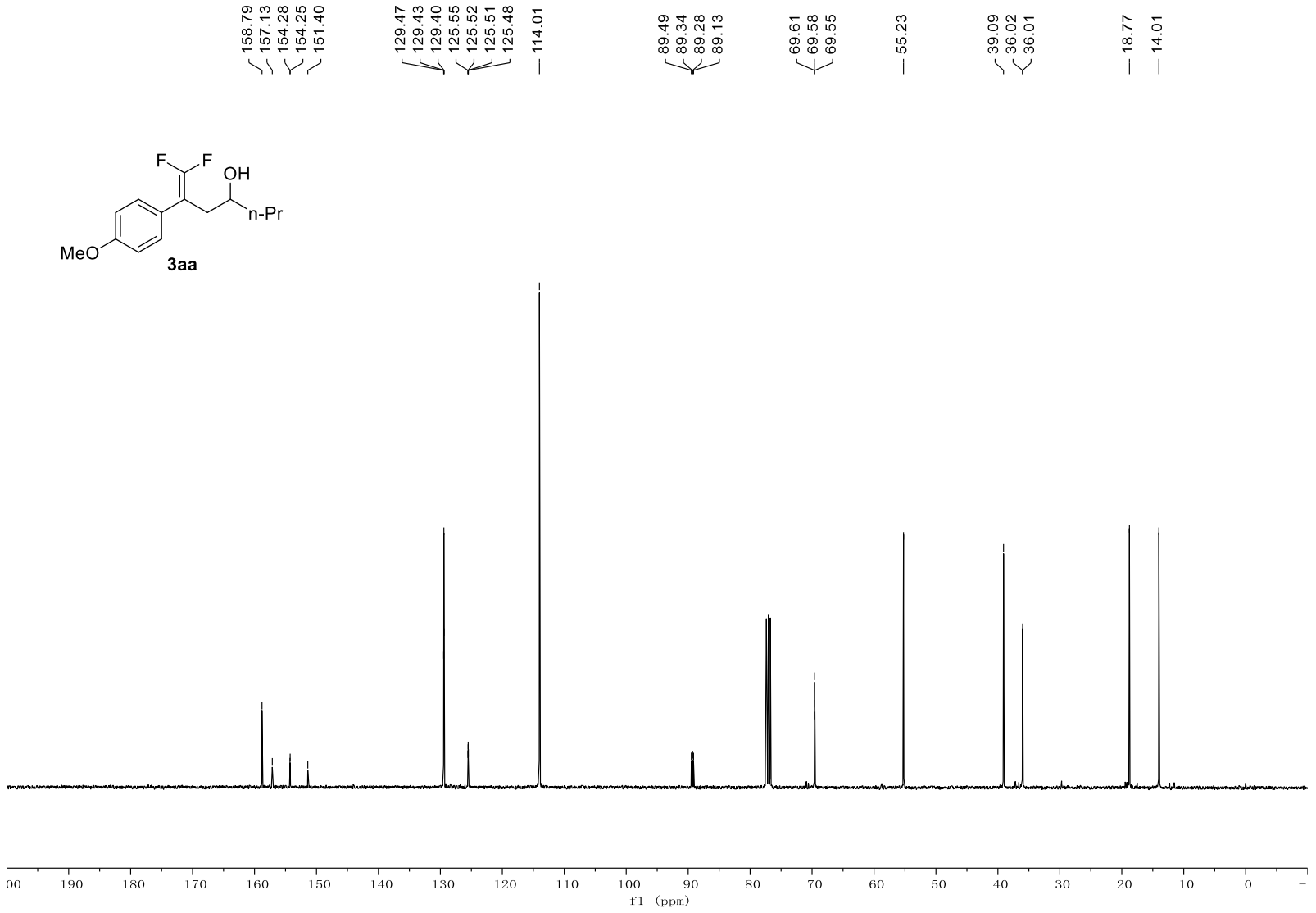
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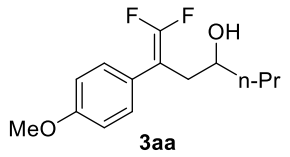
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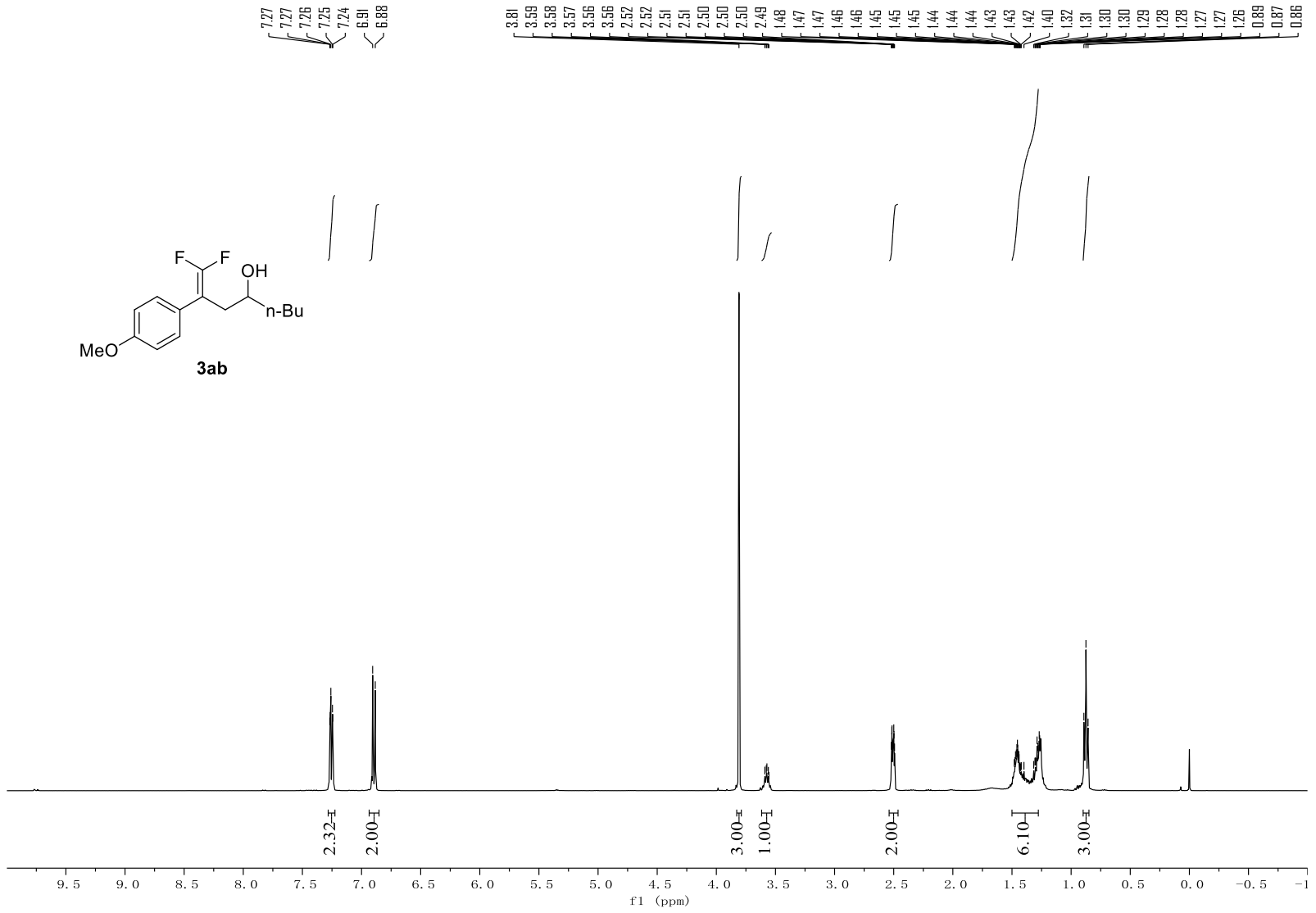
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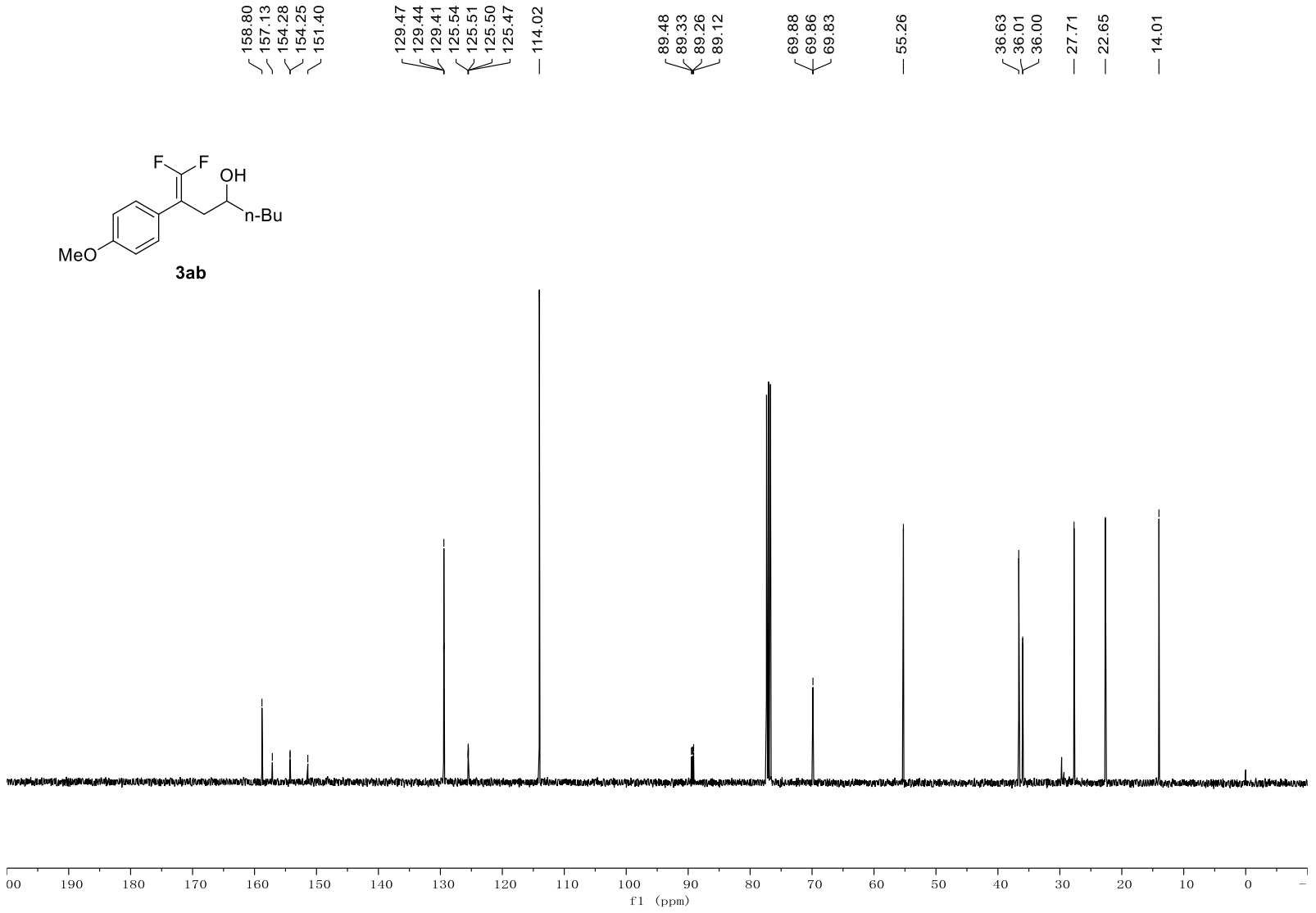
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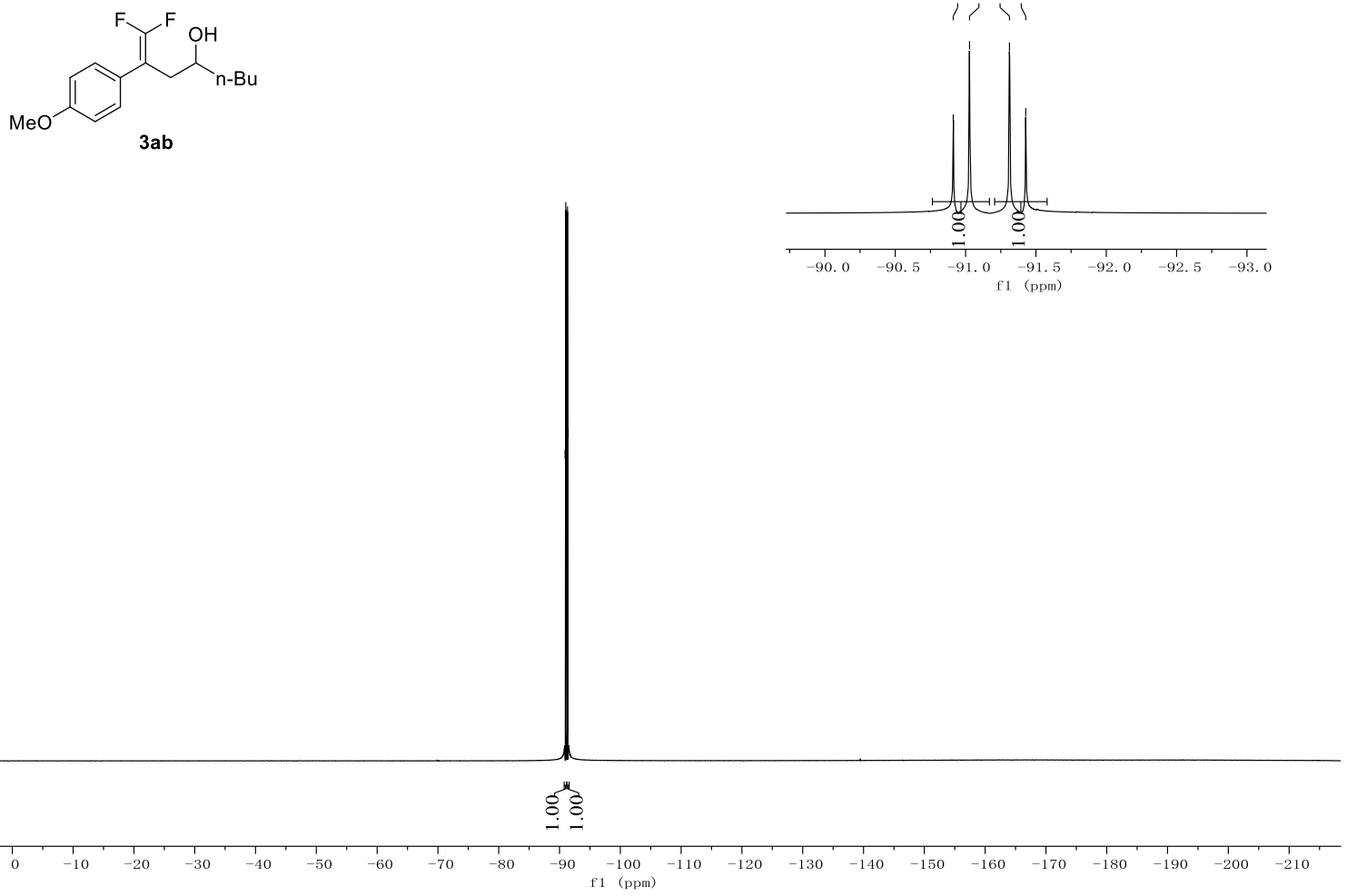
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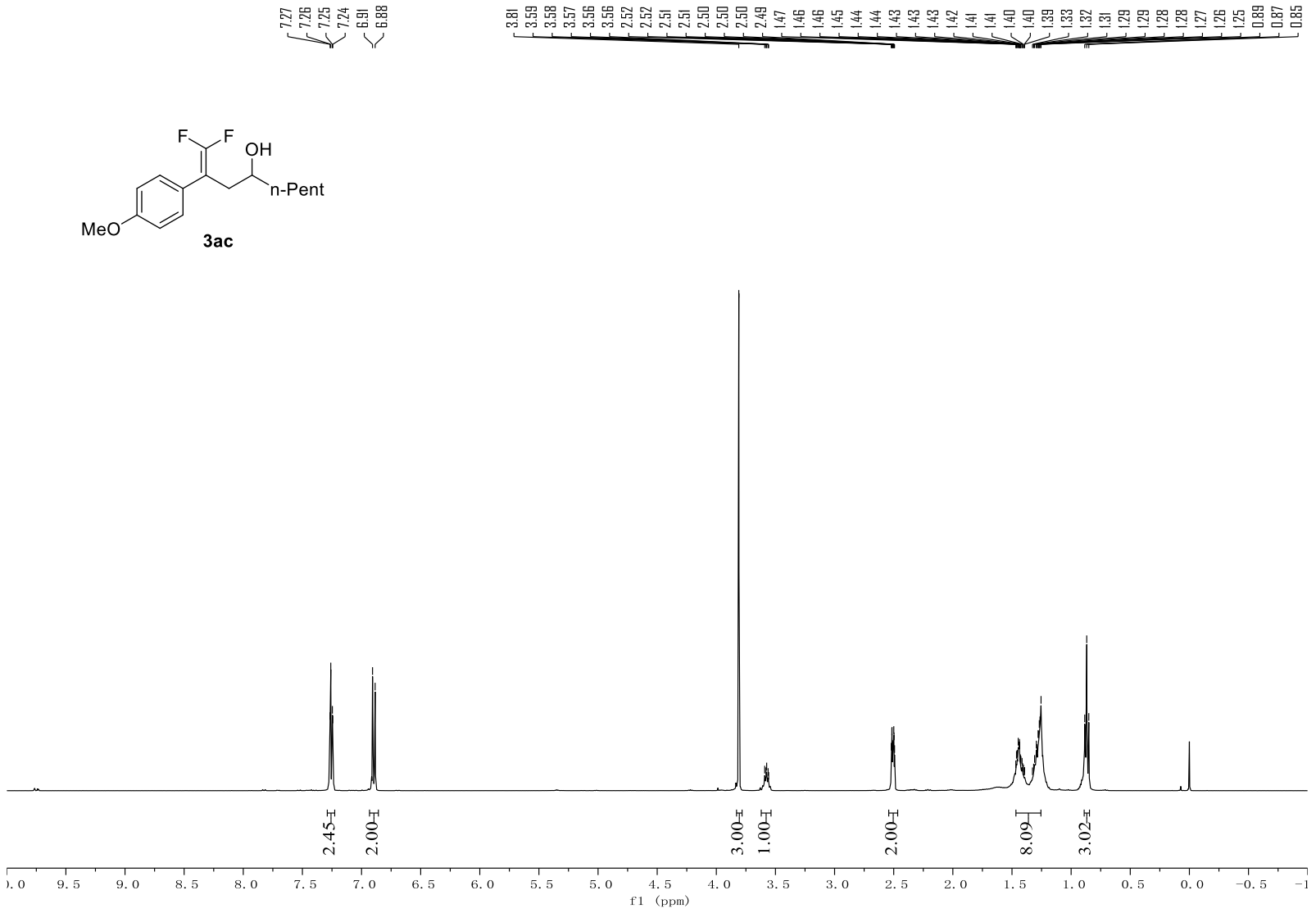
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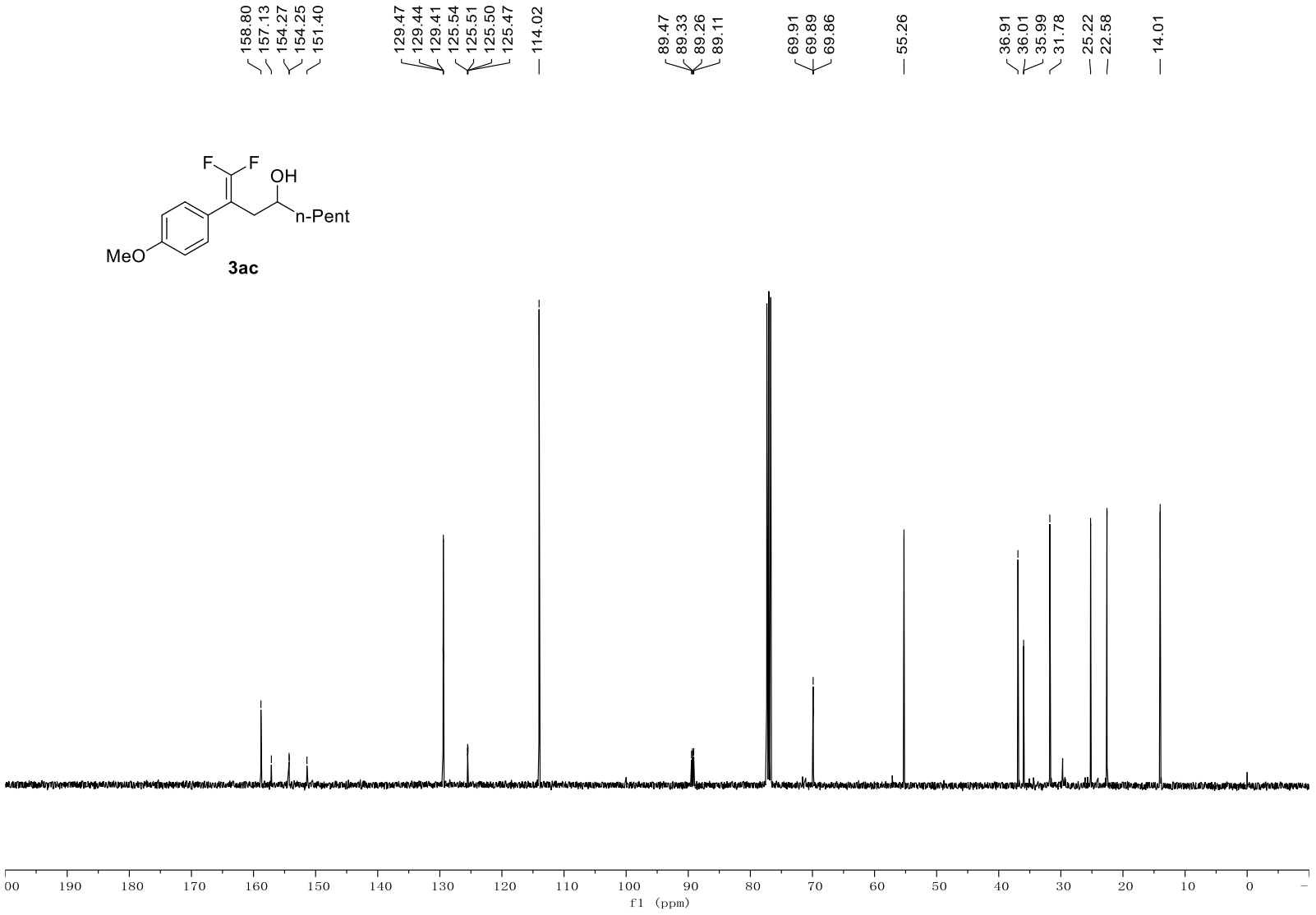
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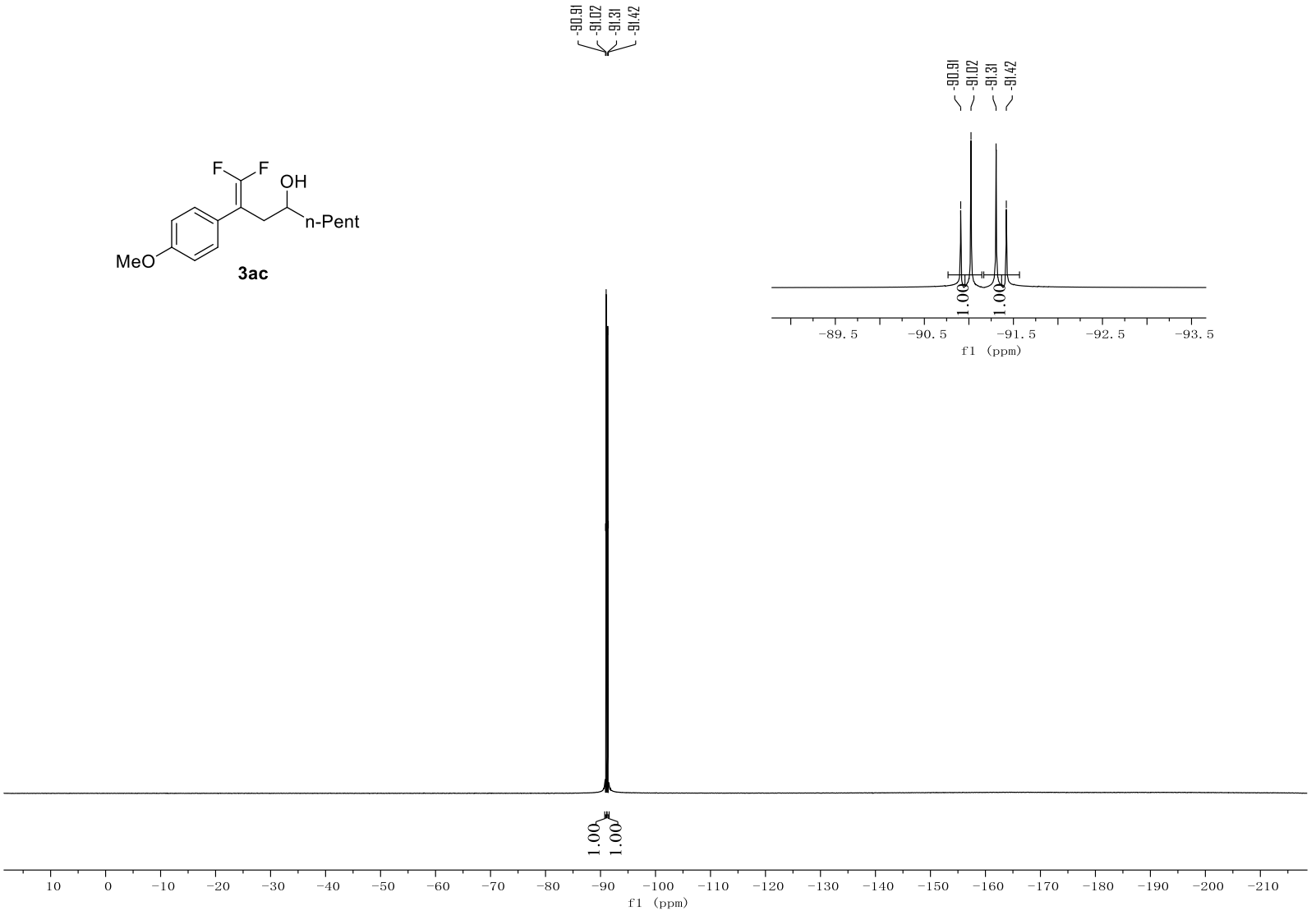
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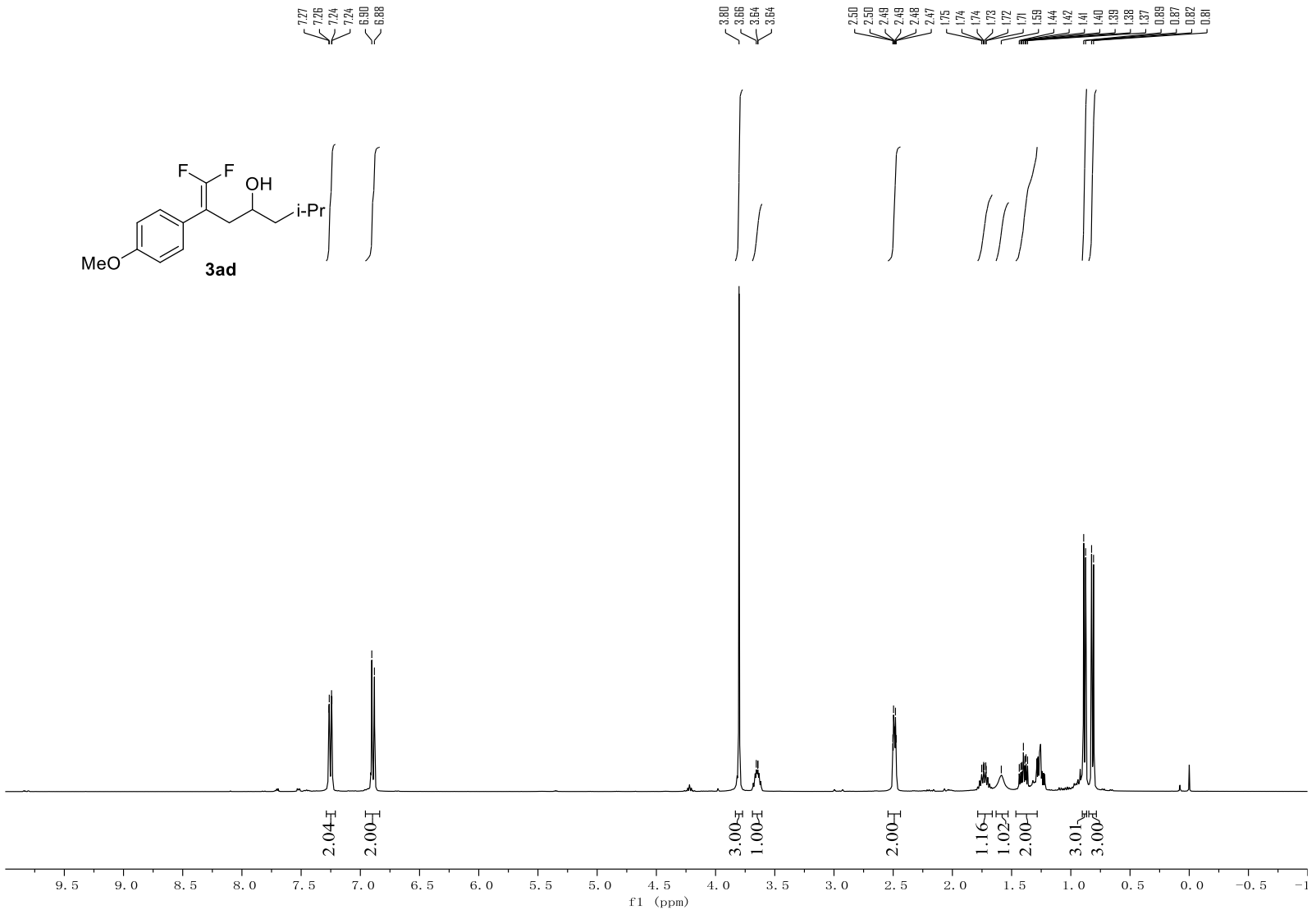
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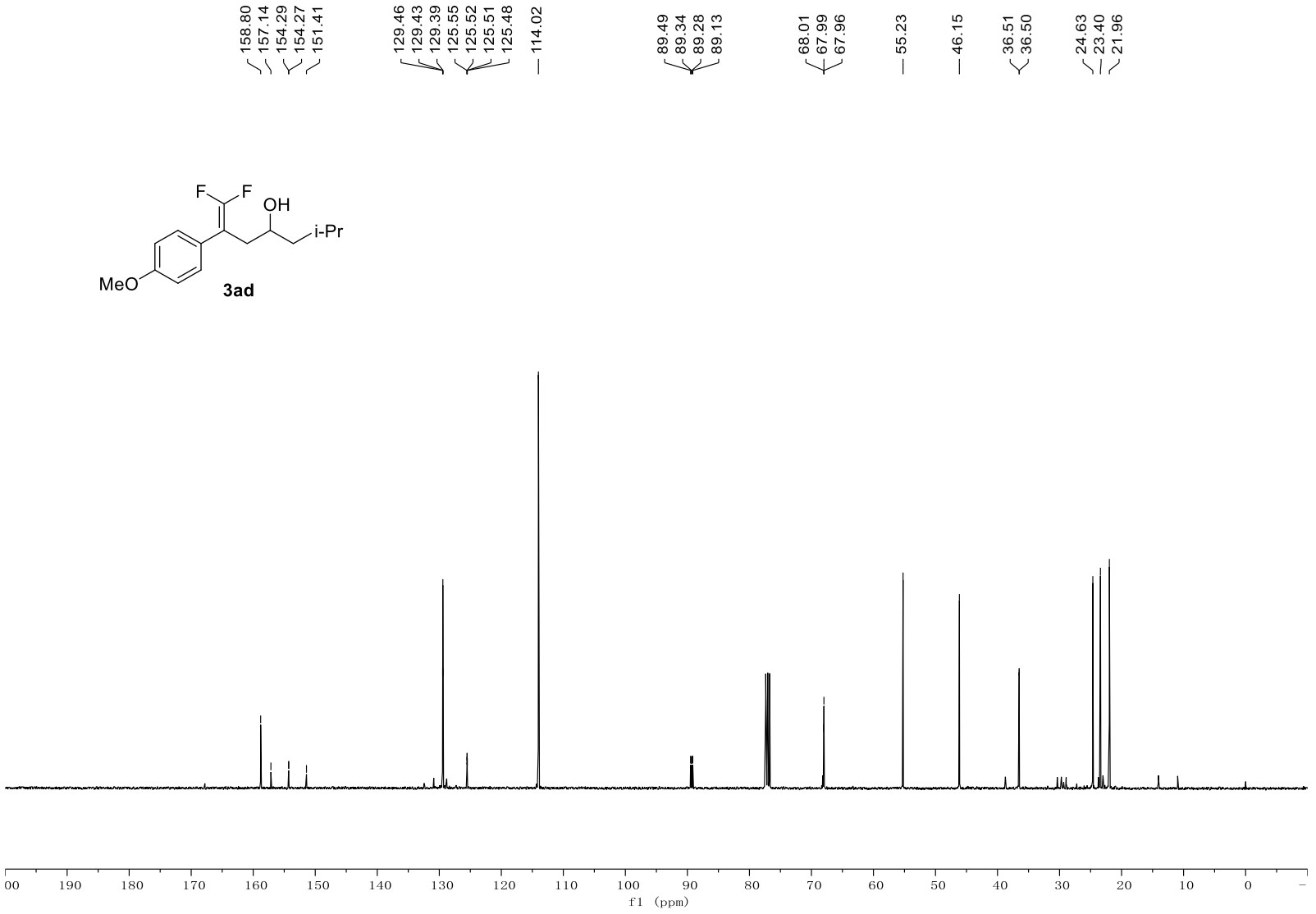
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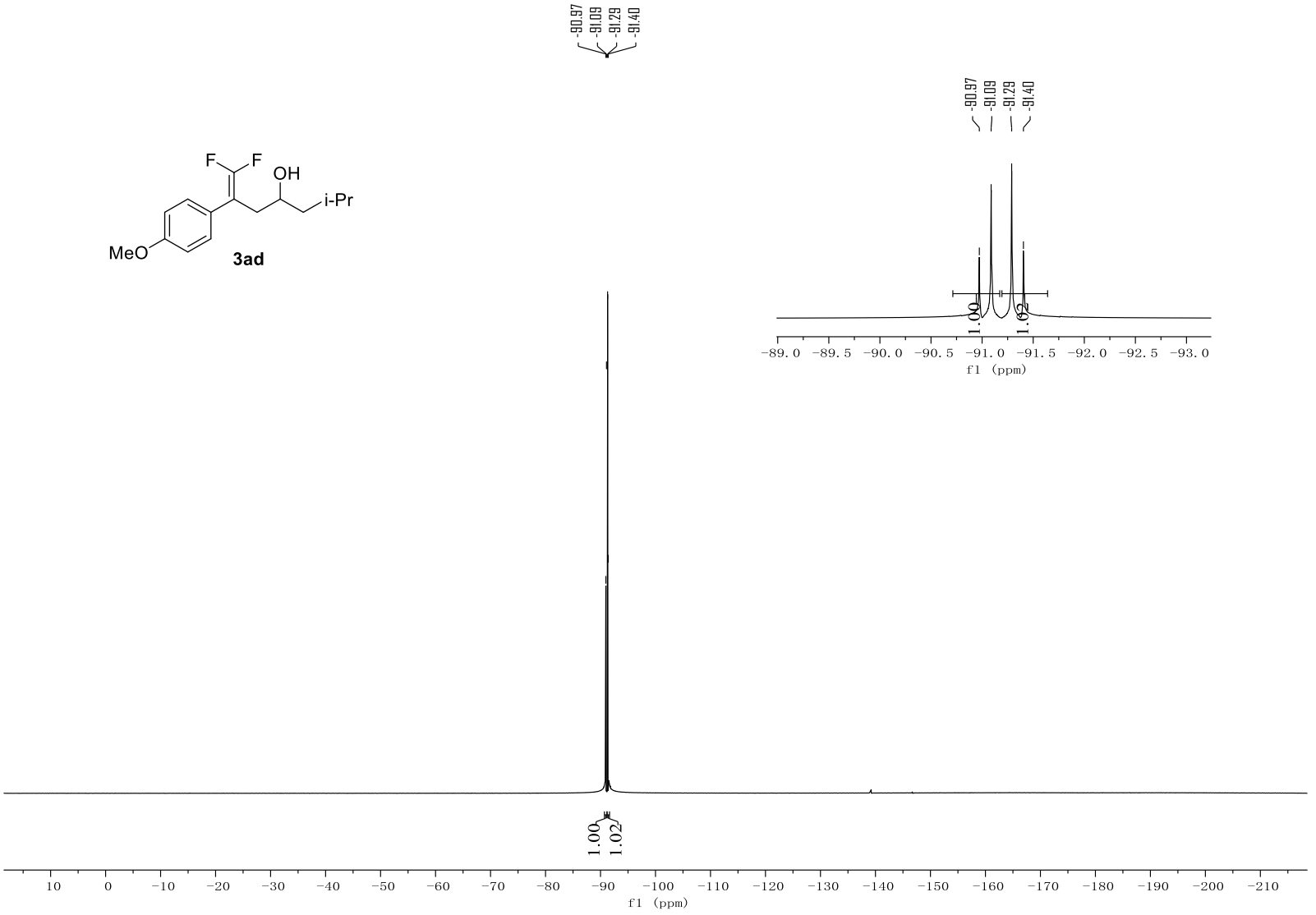
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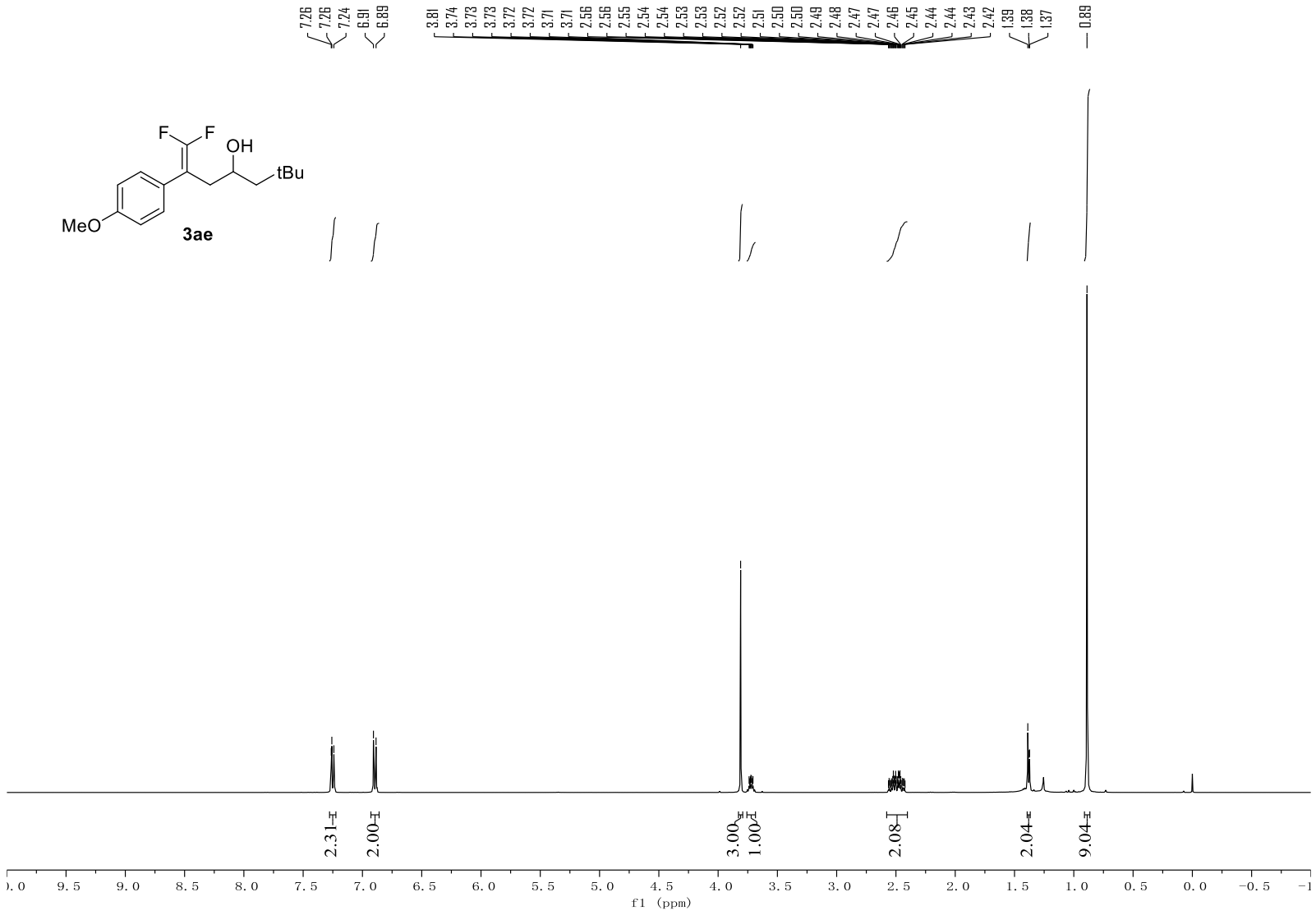
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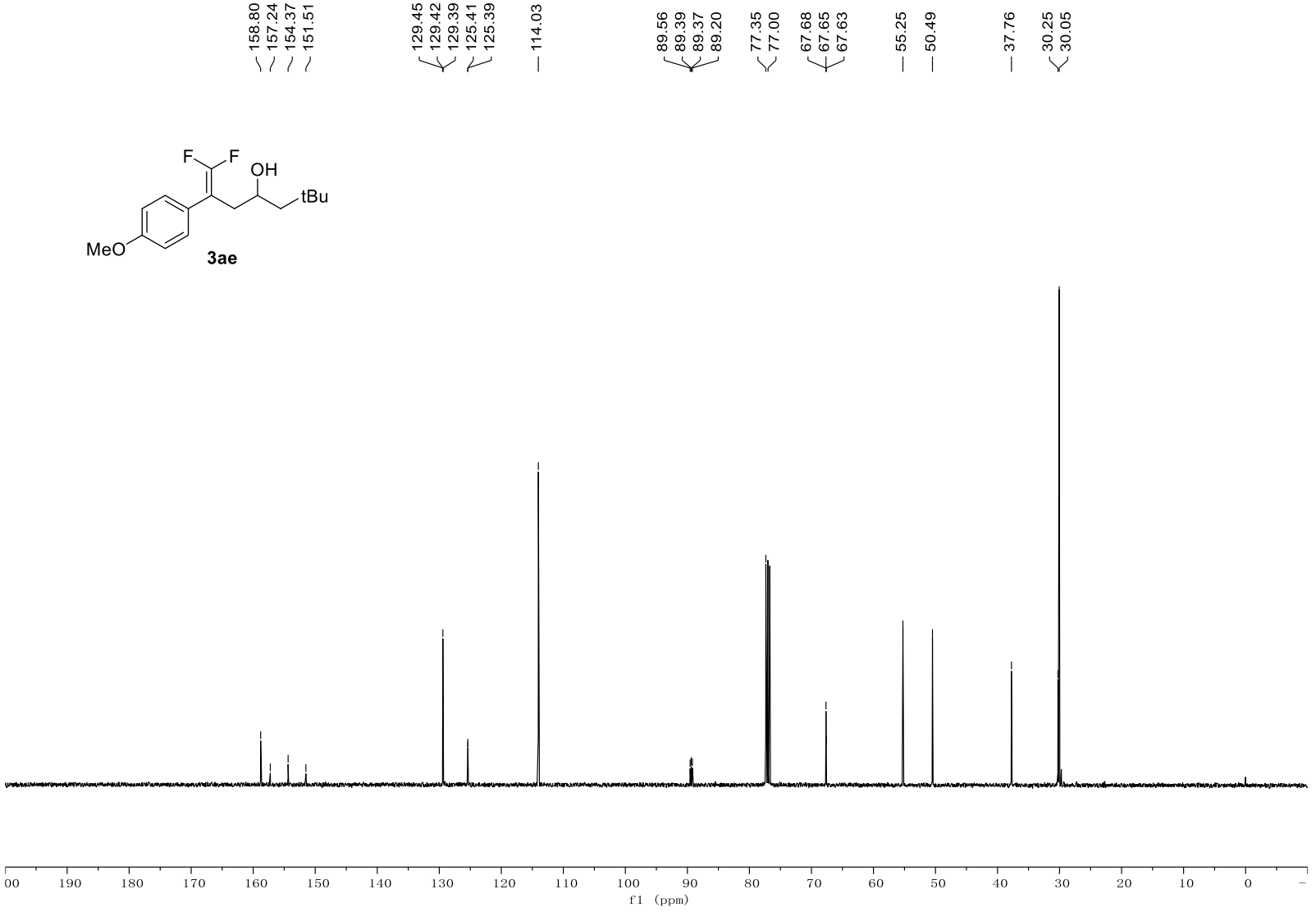
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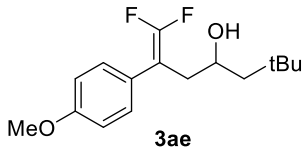
F
F
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MeO

3ae

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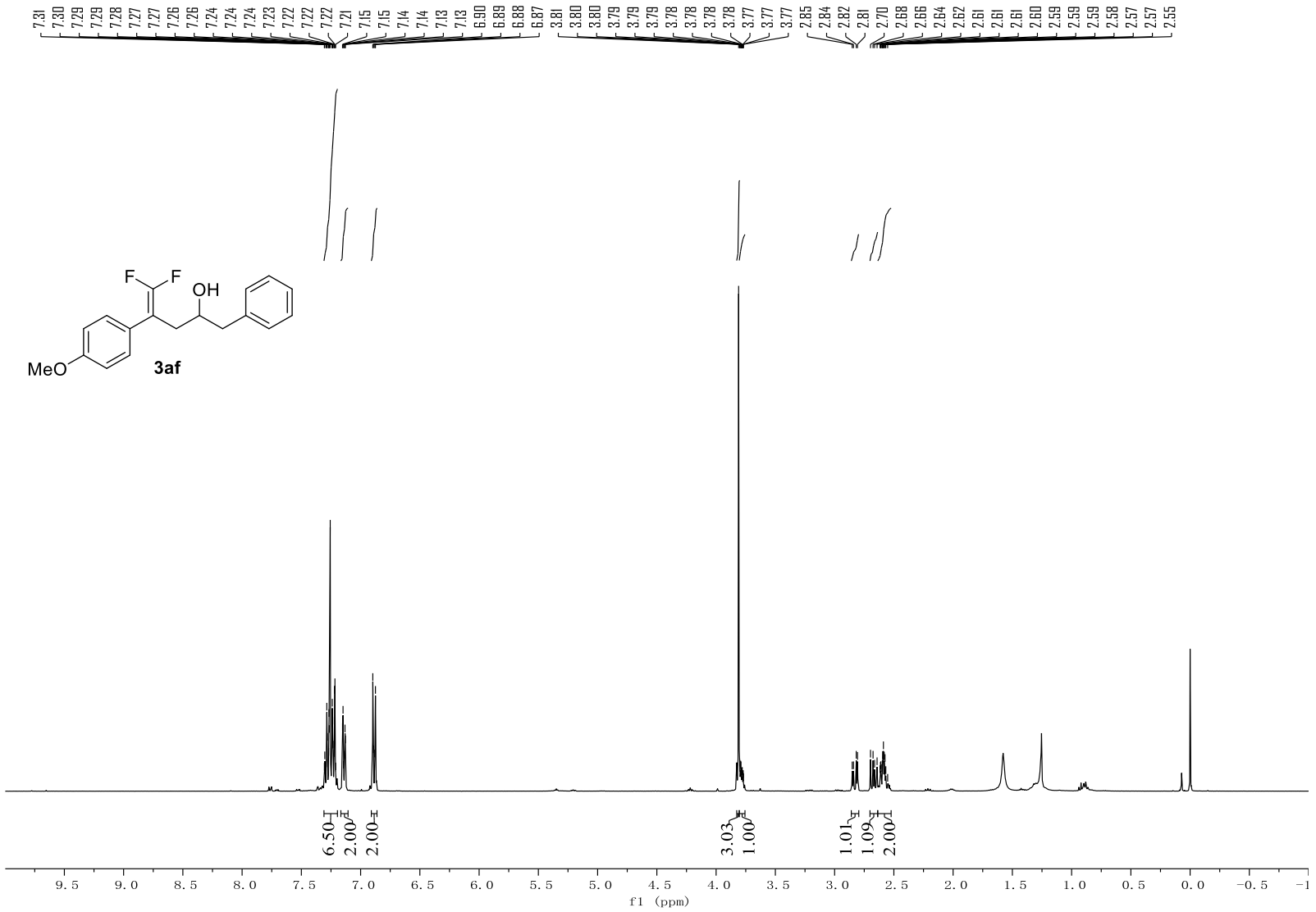
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7.27
7.27
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7.26
7.24
7.24
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7.23
7.22
7.22
7.22
7.21
7.15
7.15
7.14
7.14
7.13
7.13
6.90
6.89
6.88
6.87
3.81
3.80
3.80
3.79
3.79
3.79
3.78
3.78
3.78
3.78
3.77
3.77
3.77
2.85
2.84
2.82
2.81
2.70
2.68
2.66
2.64
2.62
2.61
2.61
2.61
2.60
2.59
2.59
2.59
2.58
2.57
2.57
2.55
F
F
OH
MeO
3af
6.50
2.00
2.00
3.03
1.00
1.01
1.09
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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1.5
1.0
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0.0
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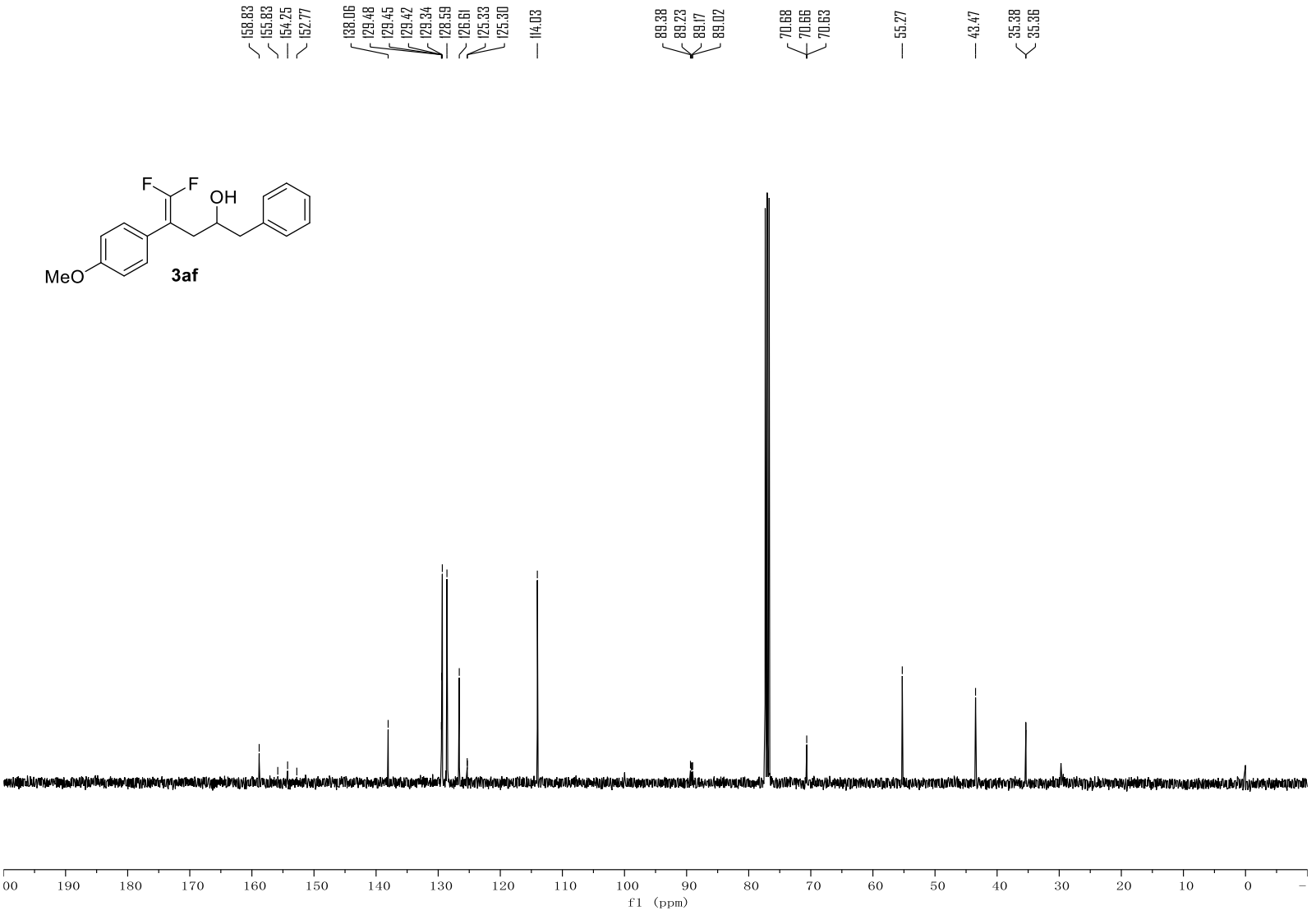
−1
f1 (ppm)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129.48
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129.42
129.34
128.59
126.61
125.33
125.30
114.03
89.38
89.23
89.17
89.02
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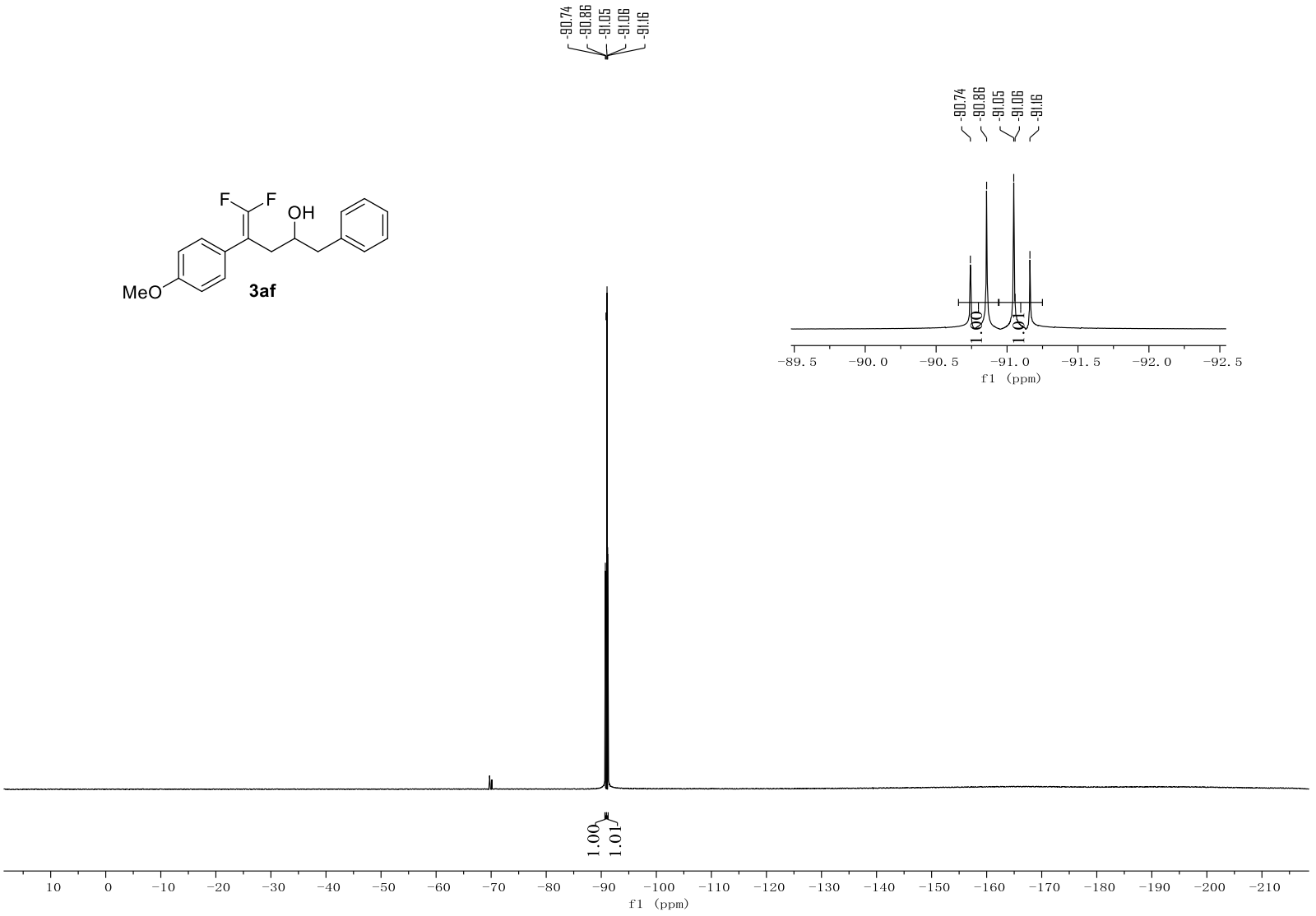
70.66
70.63
55.27
43.47
35.38
35.36
F
F
OH
MeO
3af
f1 (ppm)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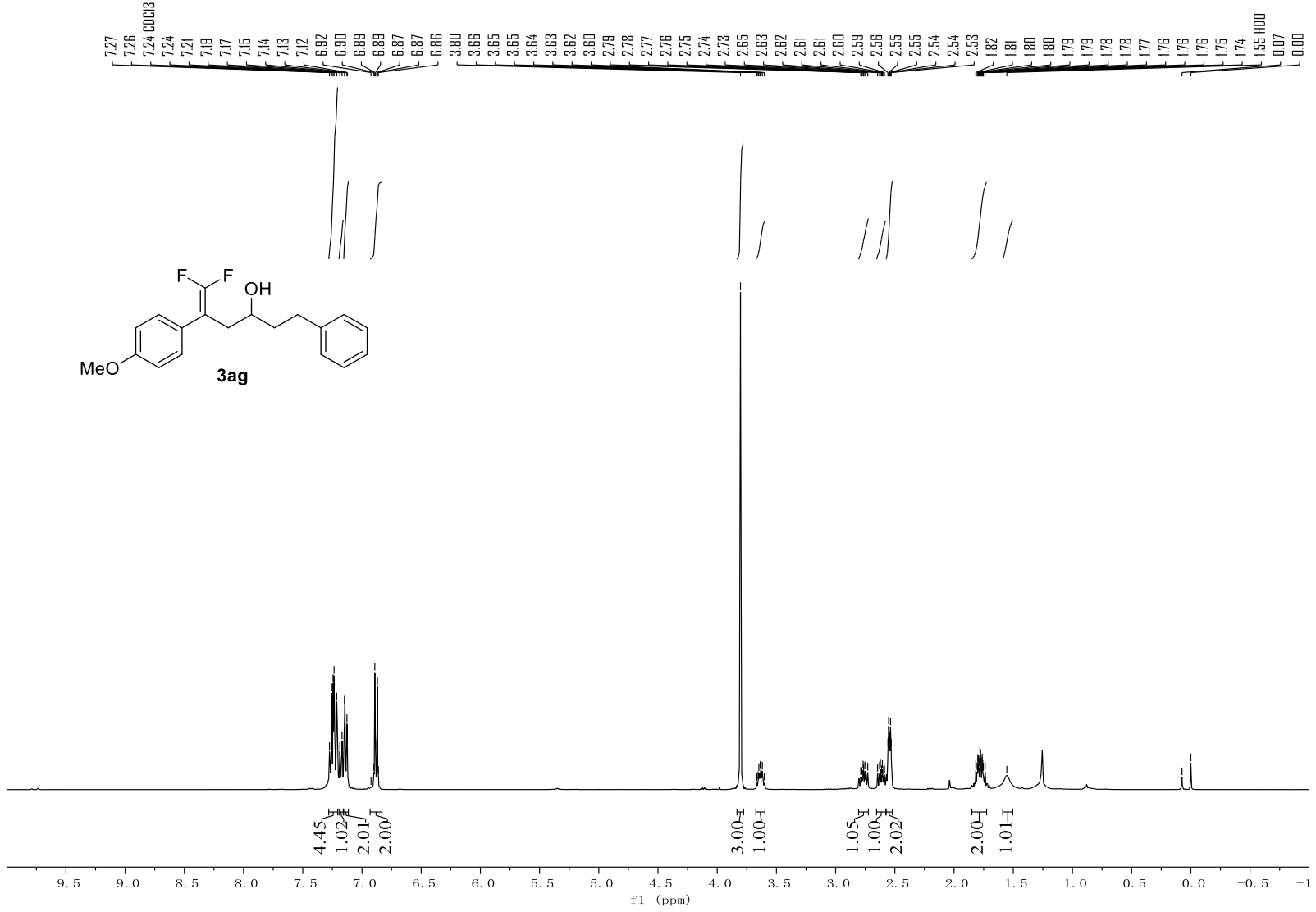
-91.05
-91.06
-91.16
F
F
OH
MeO
3af
1.00
1.01
-89.5
-90.0
-90.5
-91.0
-91.5
-92.0
-92.5
f1 (ppm)
1.00
1.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.27
7.26
7.24 CDCl3
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7.21
7.19
7.17
7.15
7.14
7.13
7.12
6.92
6.90
6.89
6.89
6.87
6.87
6.86
3.80
3.66
3.65
3.65
3.64
3.63
3.62
3.60
2.79
2.78
2.77
2.76
2.75
2.74
2.73
2.65
2.63
2.62
2.61
2.61
2.60
2.59
2.56
2.55
2.55
2.54
2.54
2.53
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1.81
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1.80
1.79
1.79
1.78
1.78
1.77
1.76
1.76
1.76
1.75
1.74
1.55 HDO
0.07
0.00
F
F
OH
MeO
3ag
4.45
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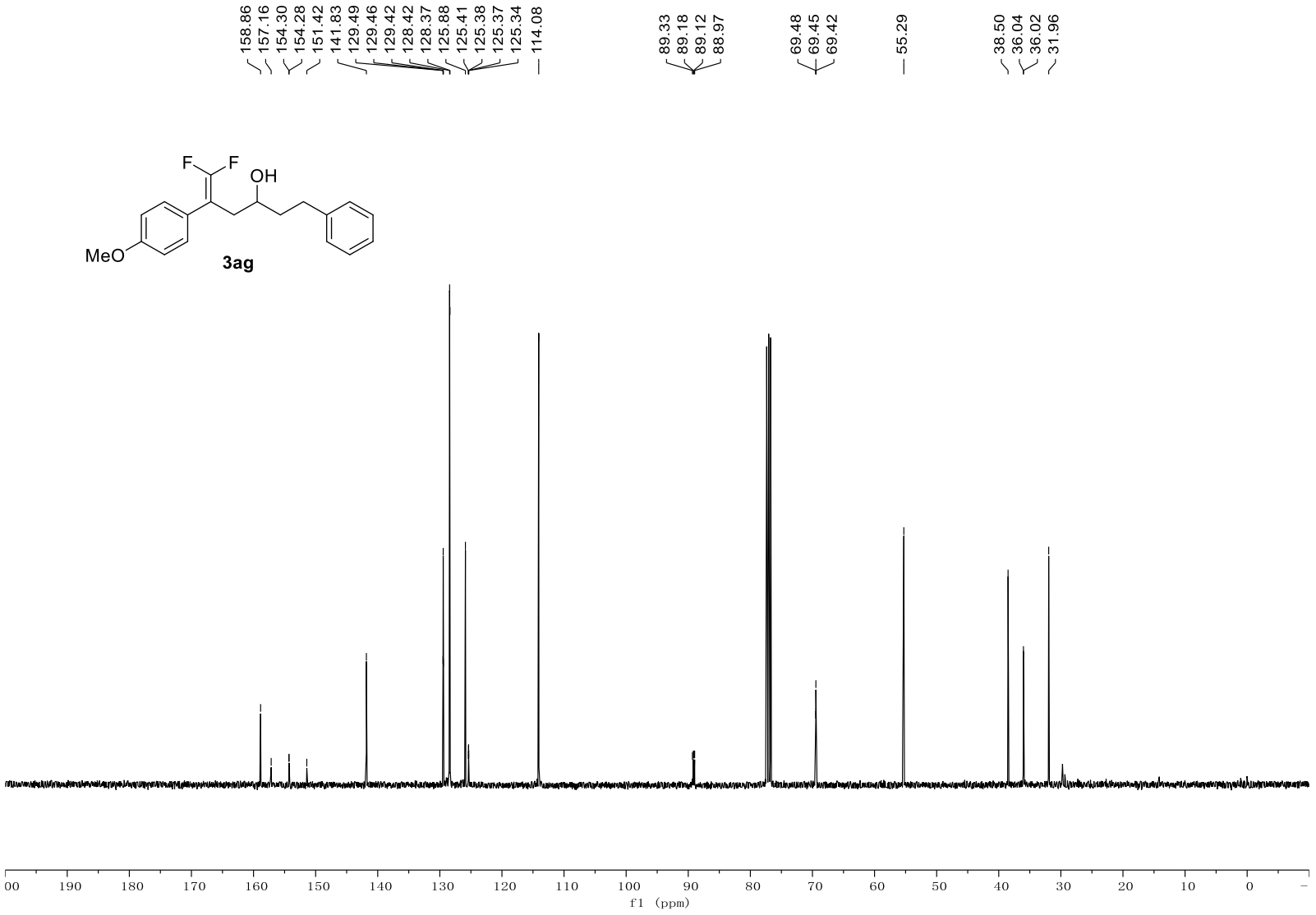
2.00
3.00
1.00
1.05
1.00
2.02
2.00
1.01
f1 (ppm)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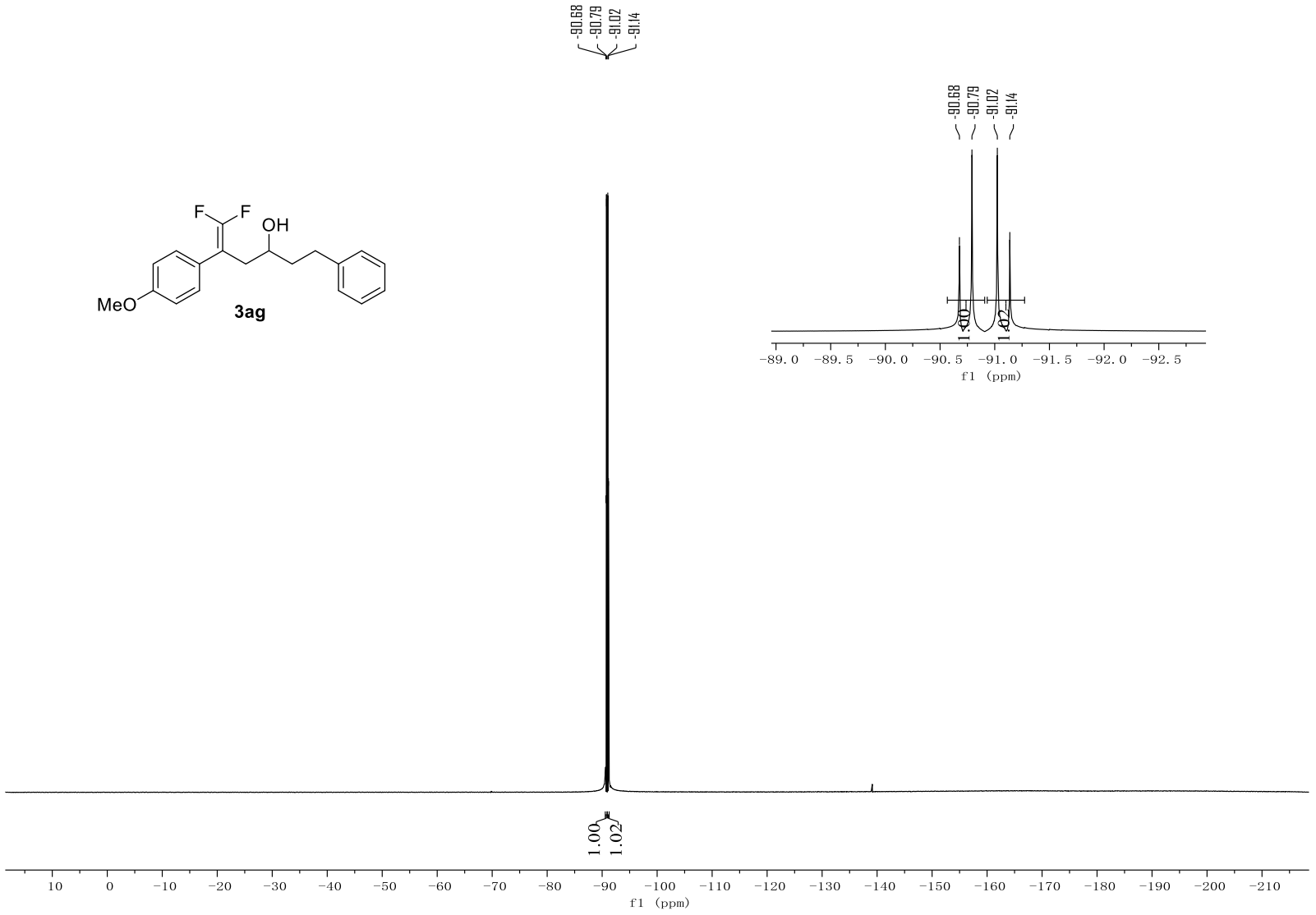
141.83
129.49
129.46
129.42
128.42
128.37
125.88
125.41
125.38
125.37
125.34
114.08
89.33
89.18
89.12
88.97
69.48
69.45
69.42
55.29
38.50
36.04
36.02
31.96
F
F
OH
MeO
3ag
f1 (ppm)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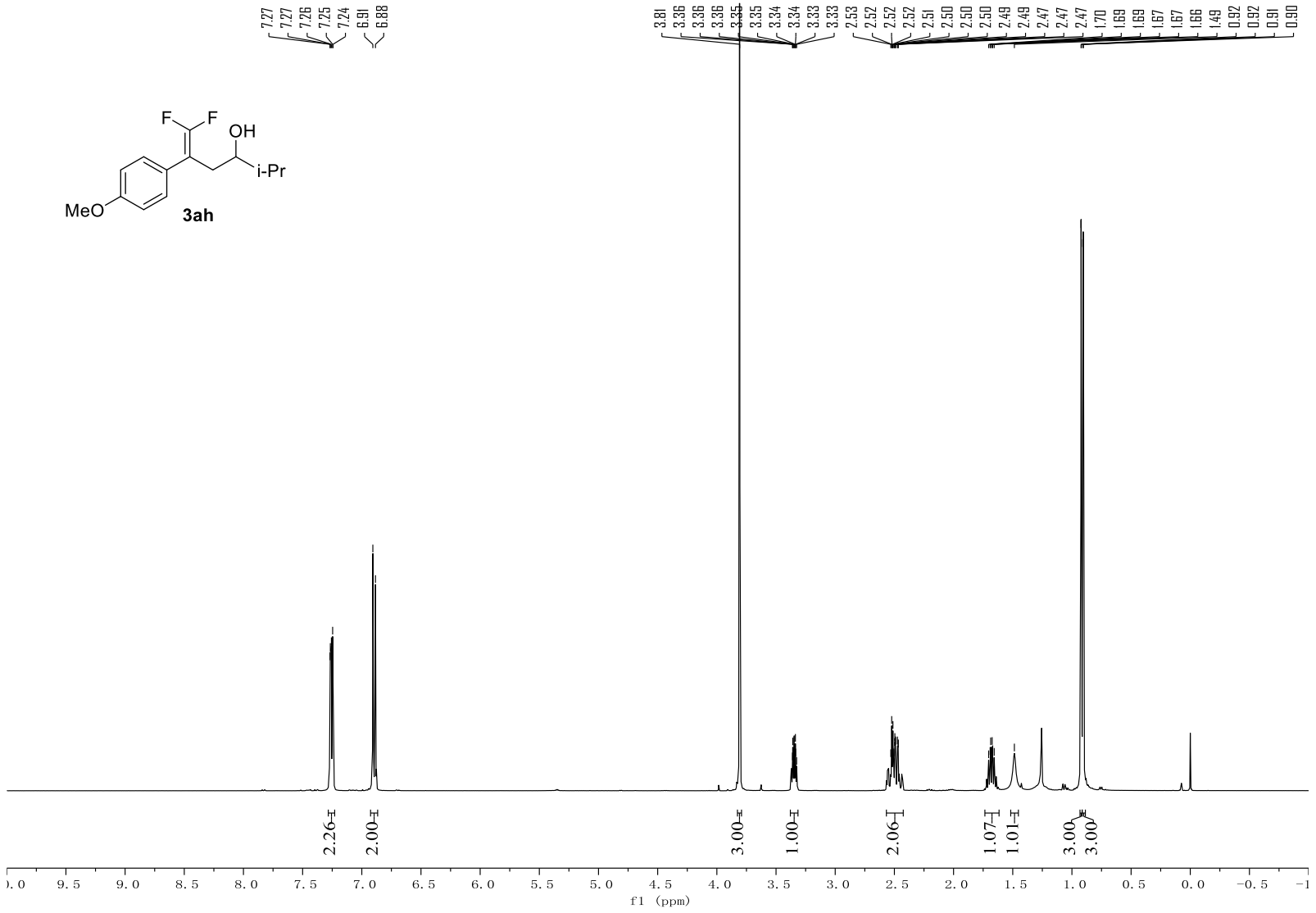
-91.14
F
F
OH
MeO
3ag
1.00
1.02
f1 (ppm)


F
F
OH
i-Pr
MeO
3ah
7.27
7.27
7.26
7.25
7.24
6.91
6.88
3.81
3.38
3.38
3.38
3.35
3.35
3.34
3.34
3.33
3.33
2.53
2.52
2.52
2.52
2.51
2.50
2.50
2.50
2.49
2.49
2.47
2.47
2.47
1.70
1.69
1.69
1.67
1.67
1.66
1.49
0.92
0.92
0.91
0.90
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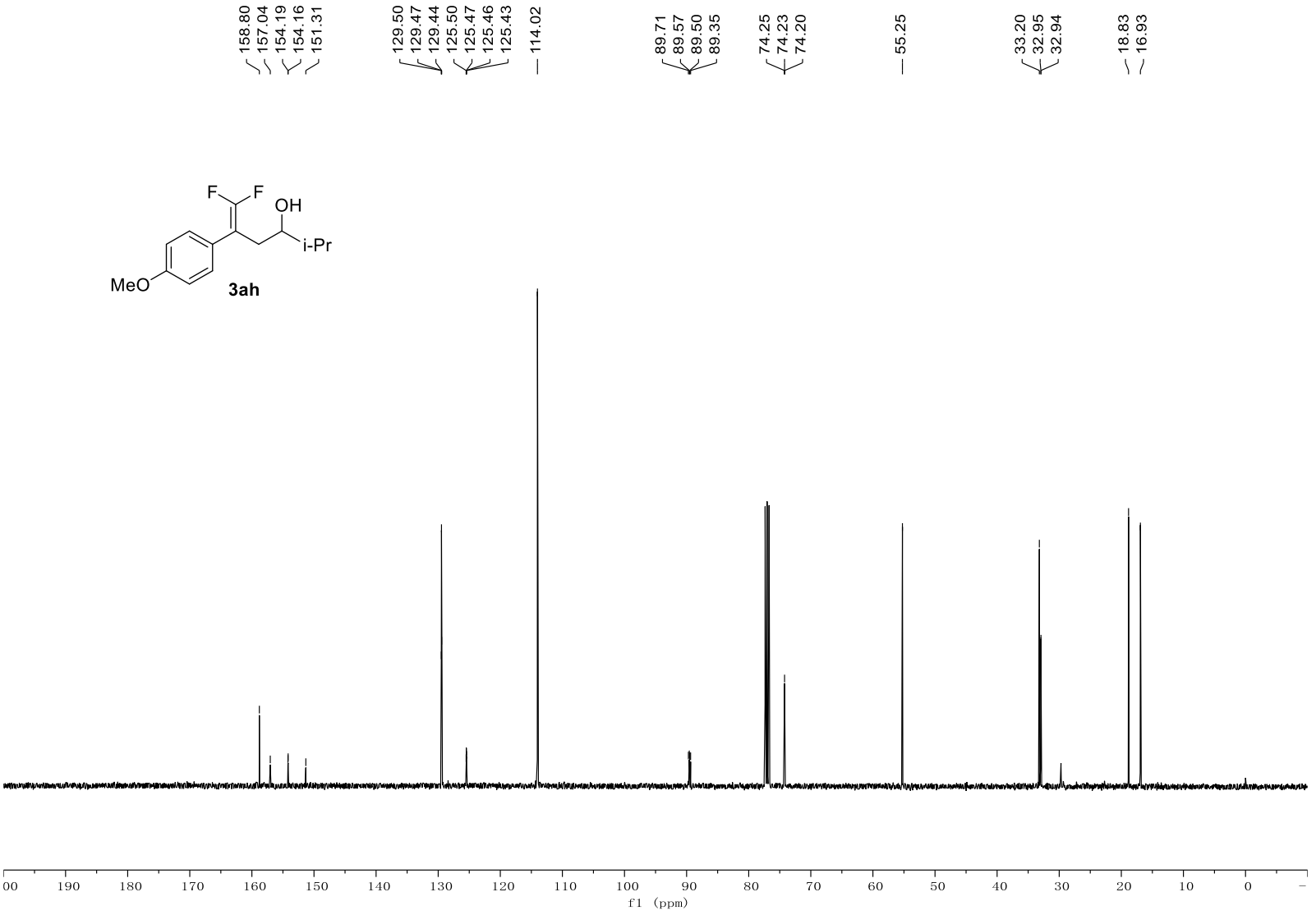
2.00
3.00
1.00
2.06
1.07
1.01
3.00
3.00
f1 (ppm)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154.16
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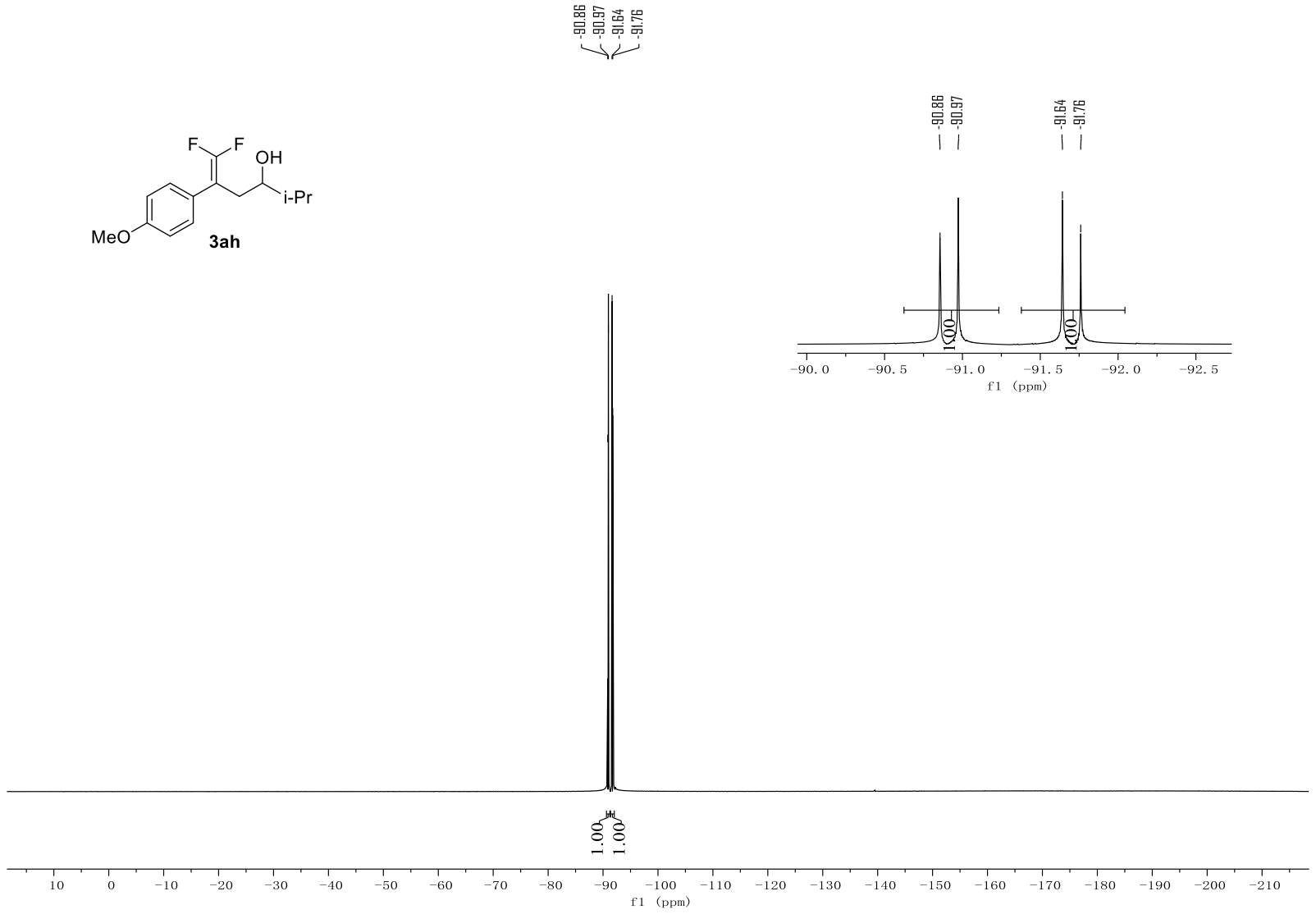
129.50
129.47
129.44
125.50
125.47
125.46
125.43
114.02
89.71
89.57
89.50
89.35
74.25
74.23
74.20
55.25
33.20
32.95
32.94
18.83
16.93
F
F
OH
i-Pr
MeO
3ah
f1 (ppm)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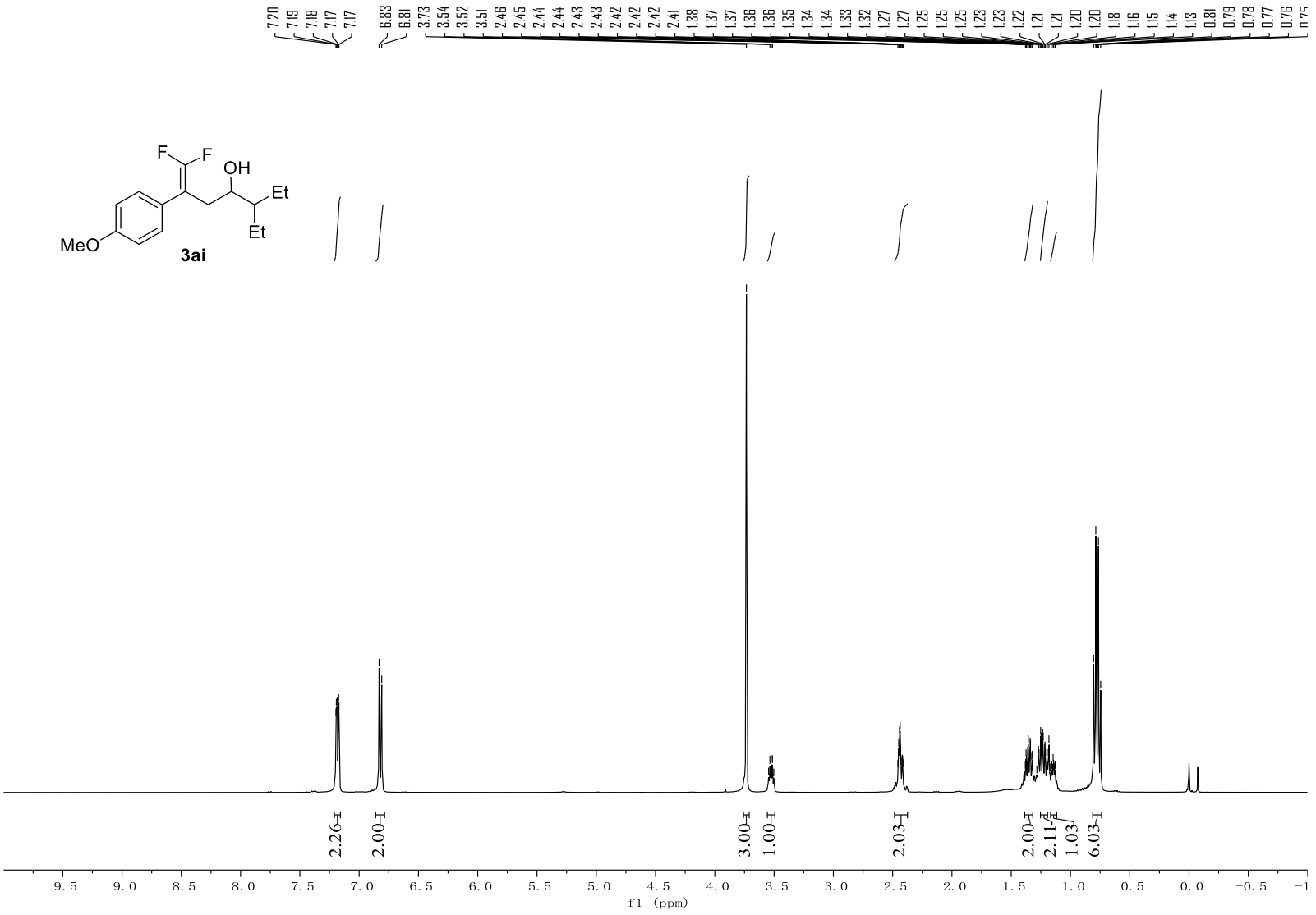
-90.97
-91.64
-91.76
F
F
OH
i-Pr
MeO
3ah
1.00
1.00
f1 (ppm)
1.00
1.00
f1 (ppm)


F
F
OH
Et
Et
MeO
3ai
7.20
7.19
7.18
7.17
7.17
6.83
6.81
3.73
3.54
3.52
3.51
2.46
2.45
2.44
2.44
2.43
2.43
2.42
2.42
2.42
2.41
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1.37
1.37
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1.36
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1.34
1.33
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1.25
1.25
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1.23
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1.22
1.21
1.21
1.20
1.20
1.18
1.16
1.15
1.14
1.13
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0.79
0.78
0.77
0.76
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3.00
1.00
2.03
2.00
2.11
1.03
6.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
1.5
1.0
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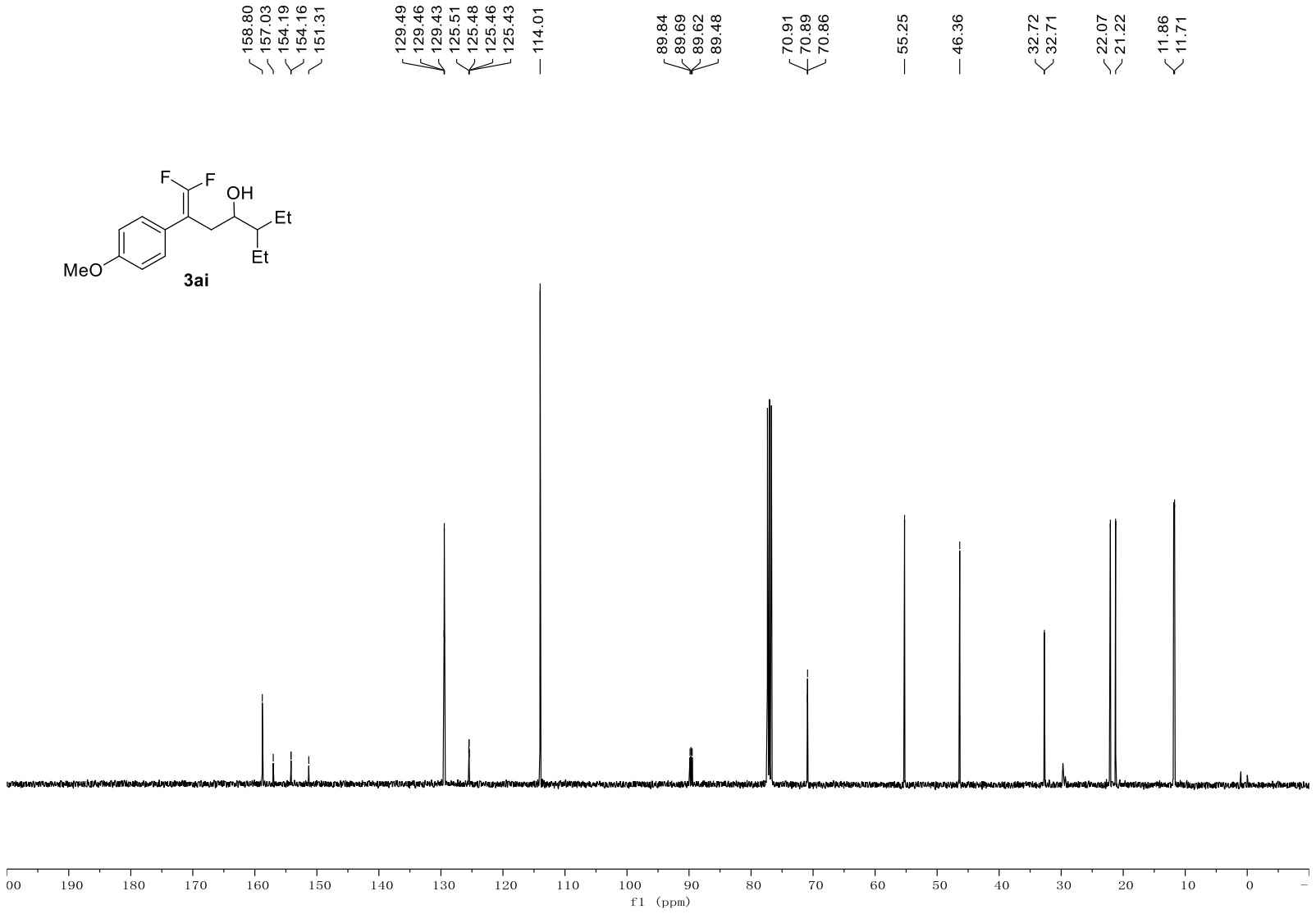
0.0
−0.5
−1
f1 (ppm)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129.43
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125.48
125.46
125.43
114.01
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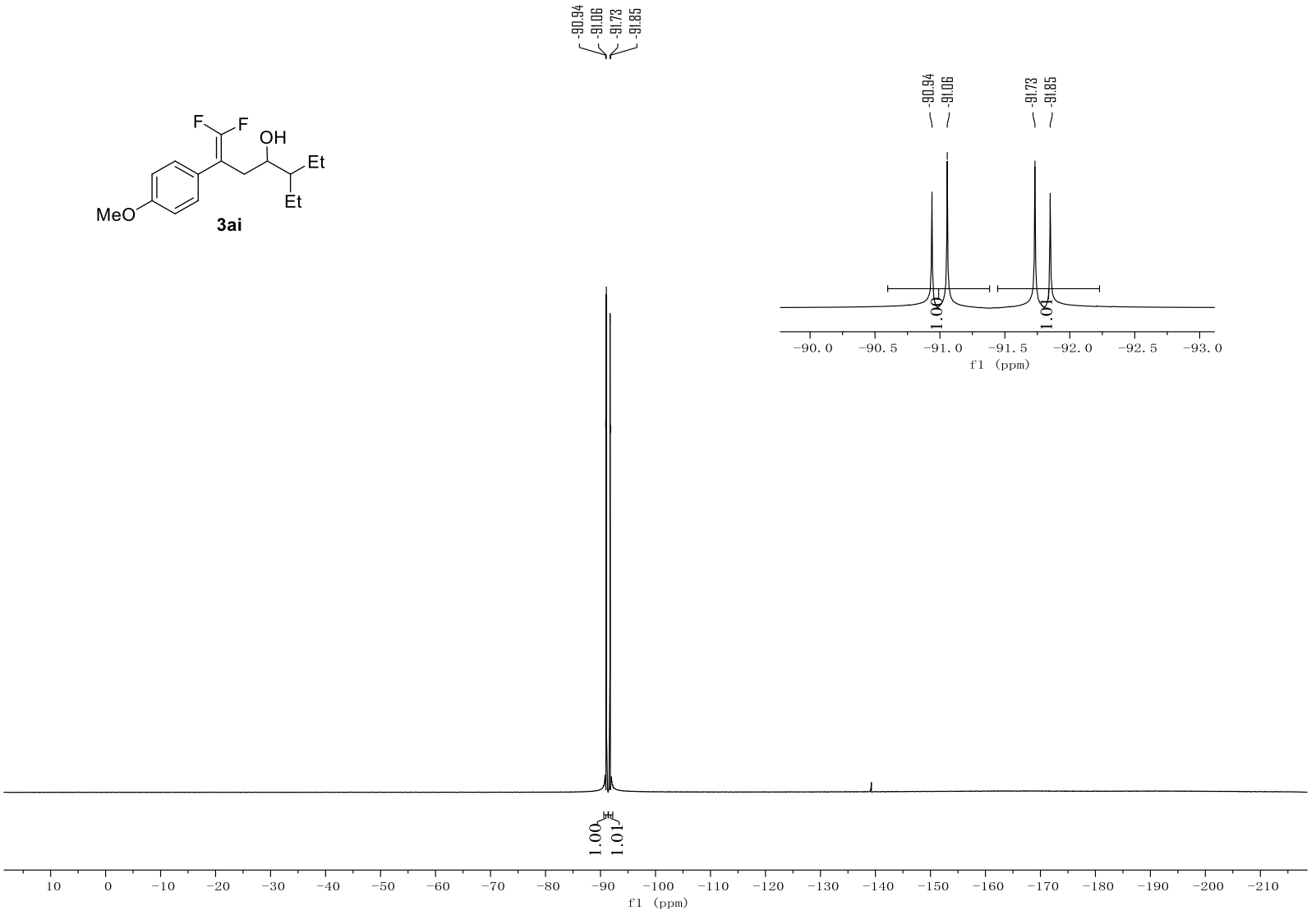
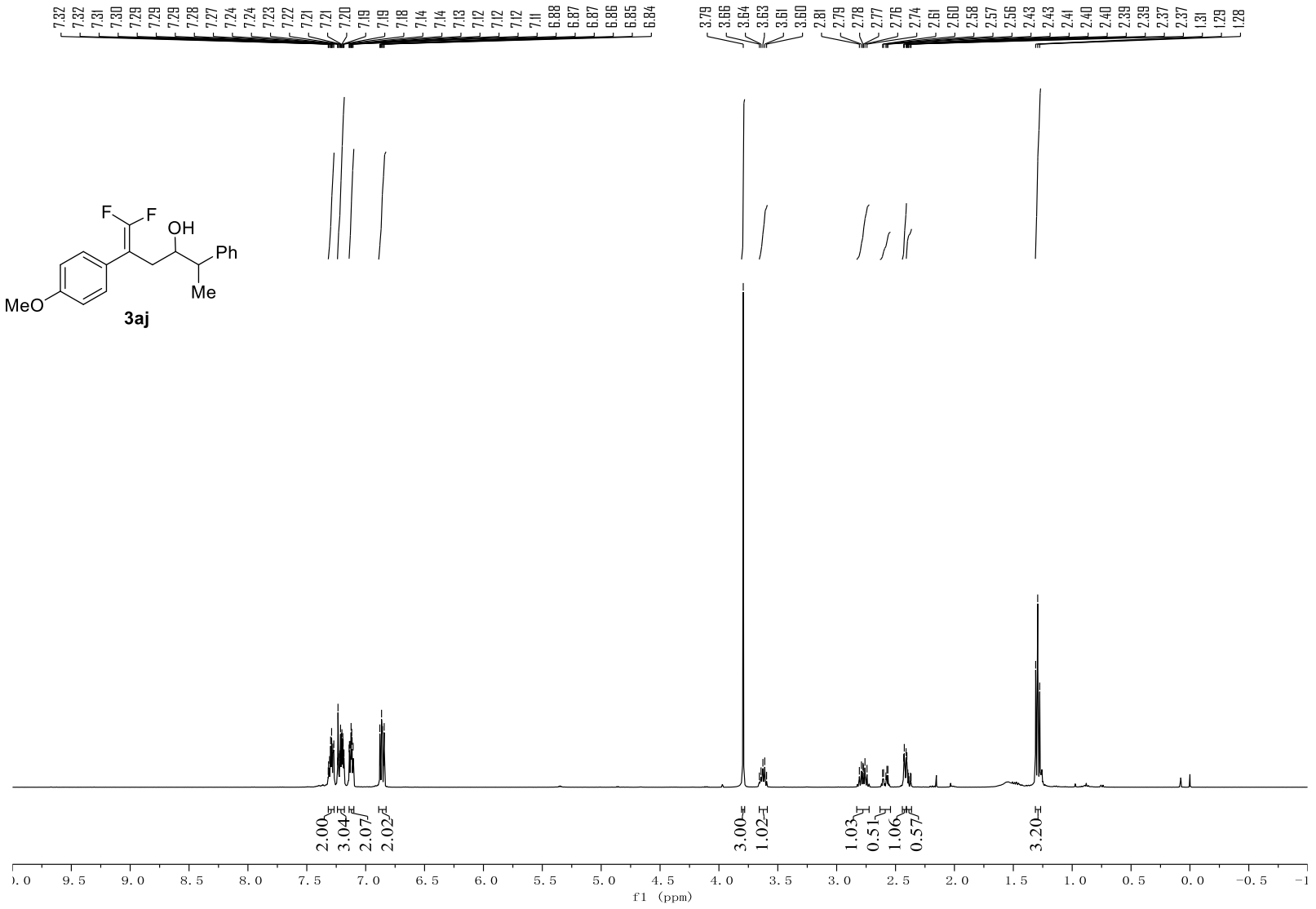
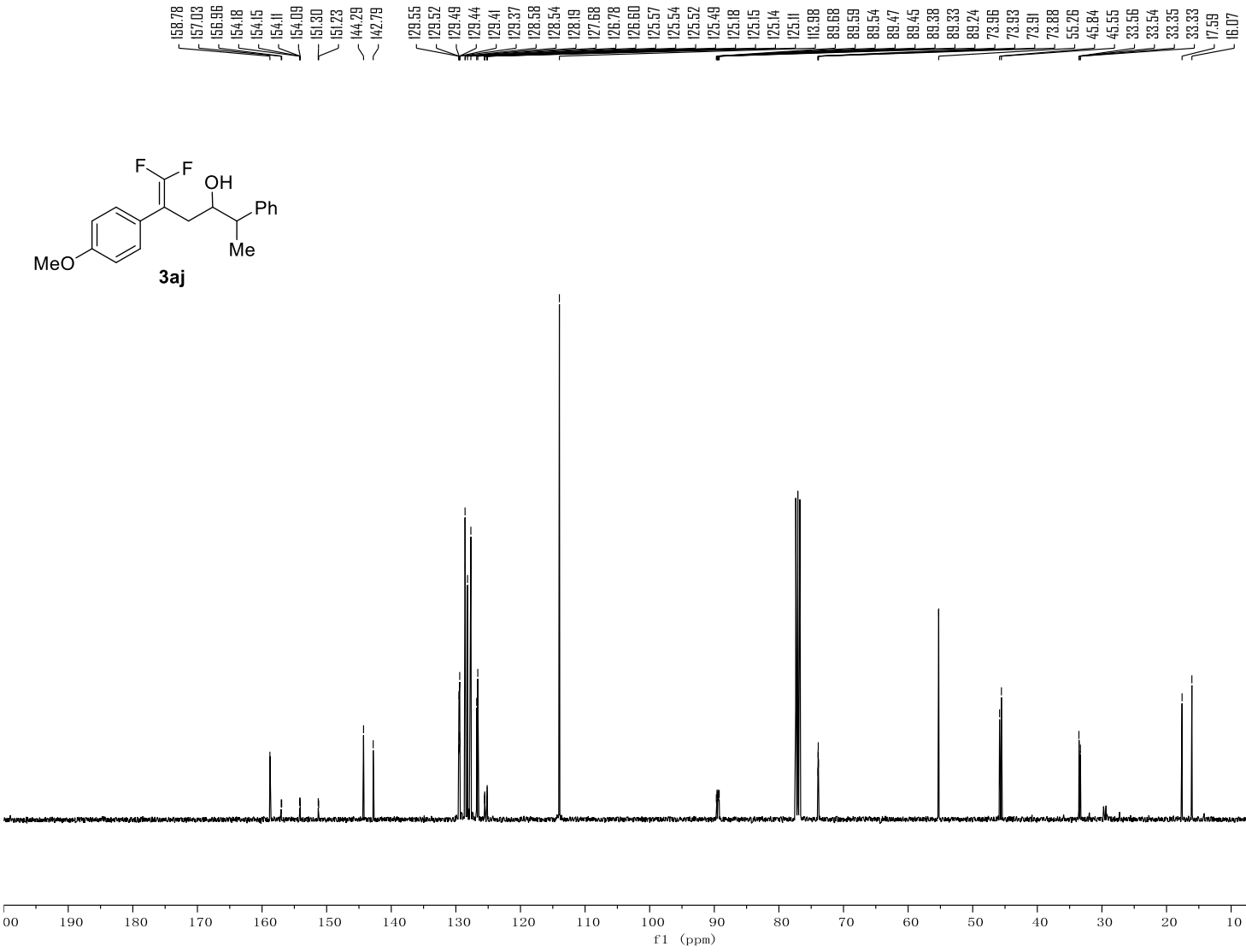
89.69
89.62
89.48
70.91
70.89
70.86
55.25
46.36
32.72
32.71
22.07
21.22
11.86
11.71
F
F
OH
Et
Et
MeO
3ai
f1 (ppm)


F
F
OH
Et
Et
MeO
3ai
-90.94
-91.06
-91.73
-91.85
1.00
1.01
f1 (ppm)


F
F
OH
Ph
Me
MeO
3aj
f1 (ppm)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142.79
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129.44
129.41
129.37
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128.54
128.19
127.68
126.78
126.60
125.57
125.54
125.52
125.49
125.18
125.15
125.14
125.11
113.98
89.68
89.59
89.54
89.47
89.45
89.38
89.33
89.24
73.96
73.93
73.91
73.88
55.26
45.84
45.55
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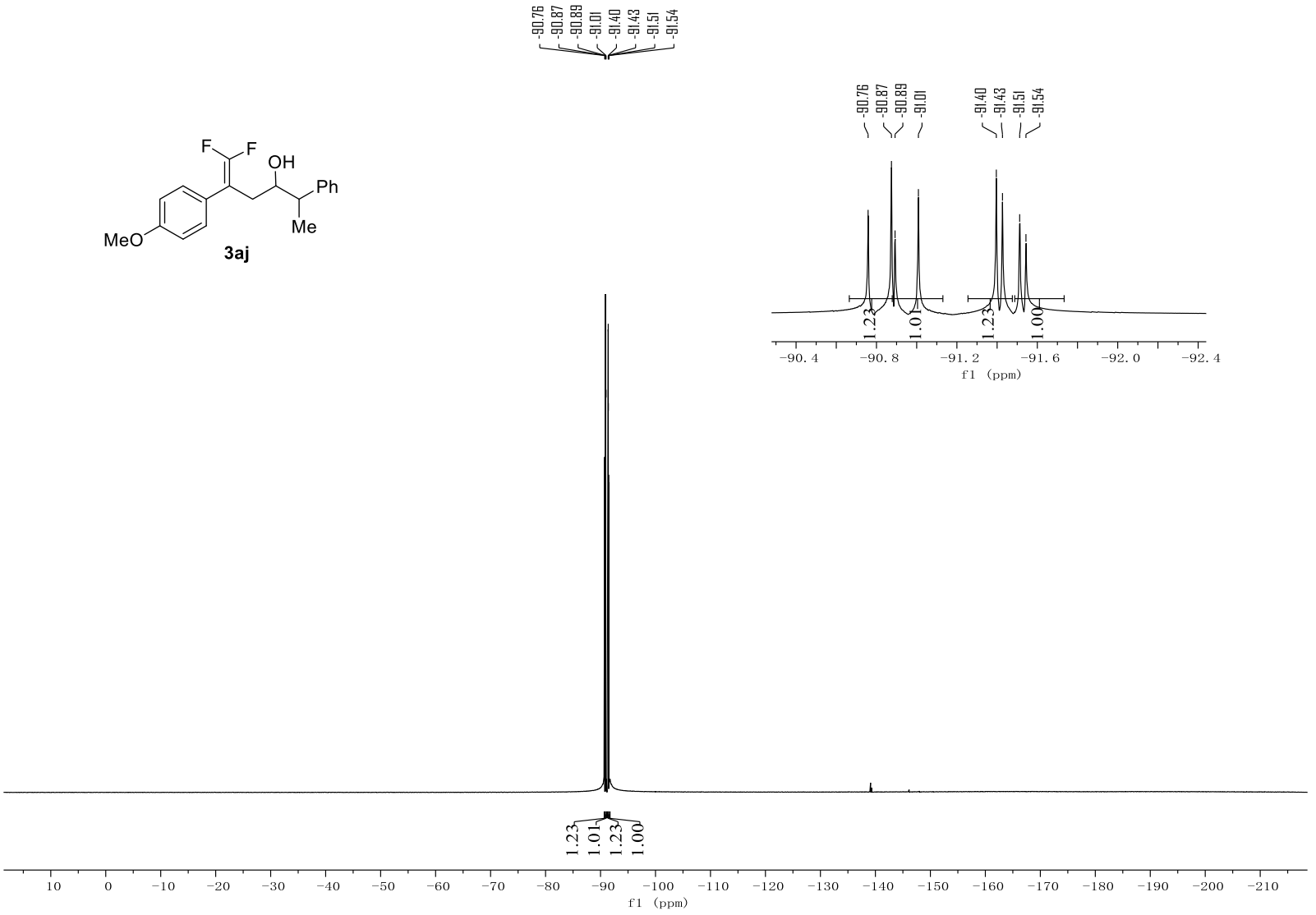
33.35
33.33
17.59
16.07
F
F
OH
Ph
Me
MeO
3aj
f1 (ppm)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-90.89
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-91.43
-91.51
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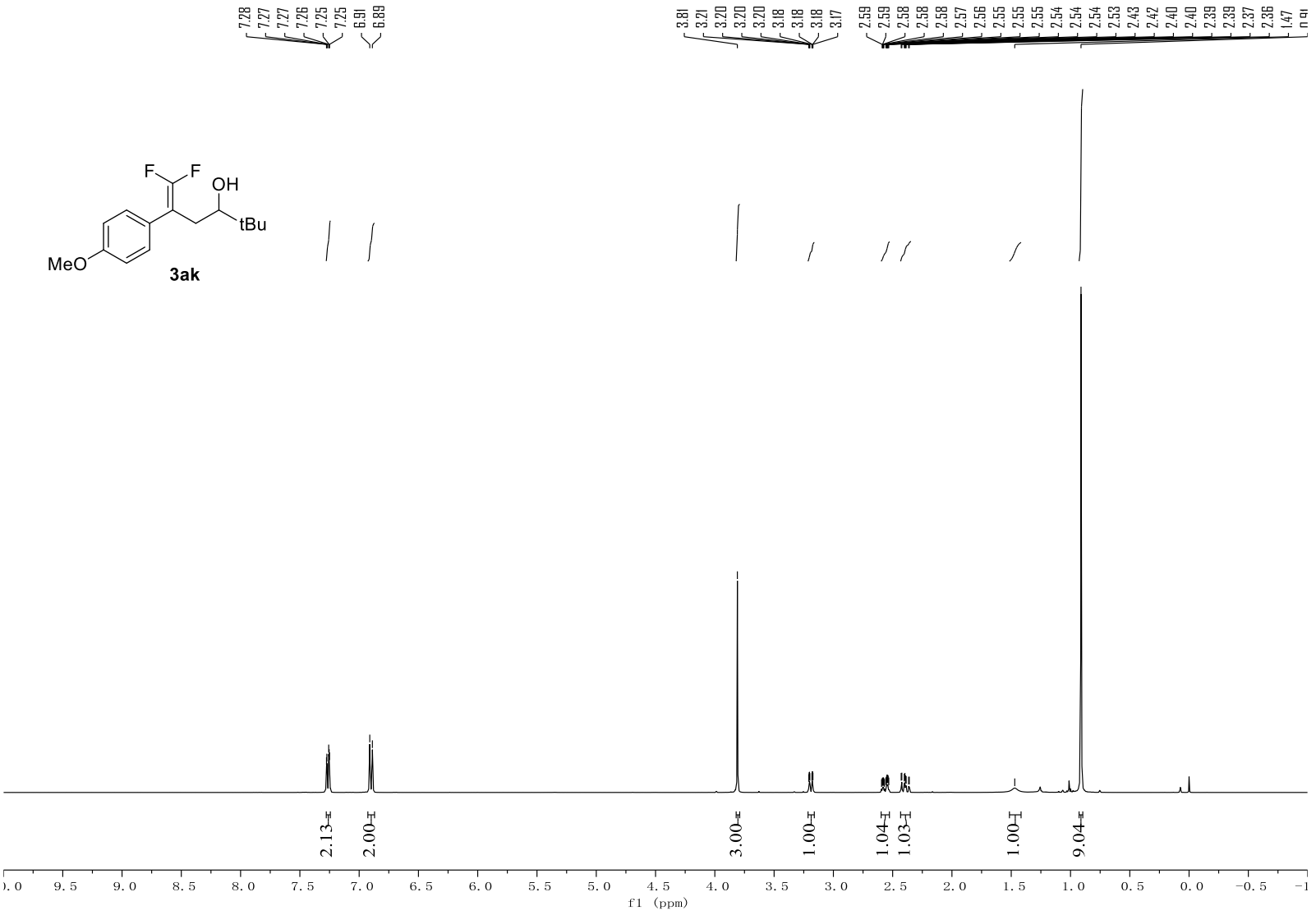
F
F
OH
Ph
Me
MeO
3aj
1.23
1.01
1.23
1.00
f1 (ppm)


F
F
OH
tBu
MeO
3ak
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7.25
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6.89
3.81
3.21
3.20
3.20
3.20
3.18
3.18
3.18
3.17
2.59
2.59
2.58
2.58
2.58
2.57
2.56
2.55
2.55
2.55
2.54
2.54
2.54
2.53
2.43
2.42
2.40
2.40
2.39
2.39
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2.13
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3.00
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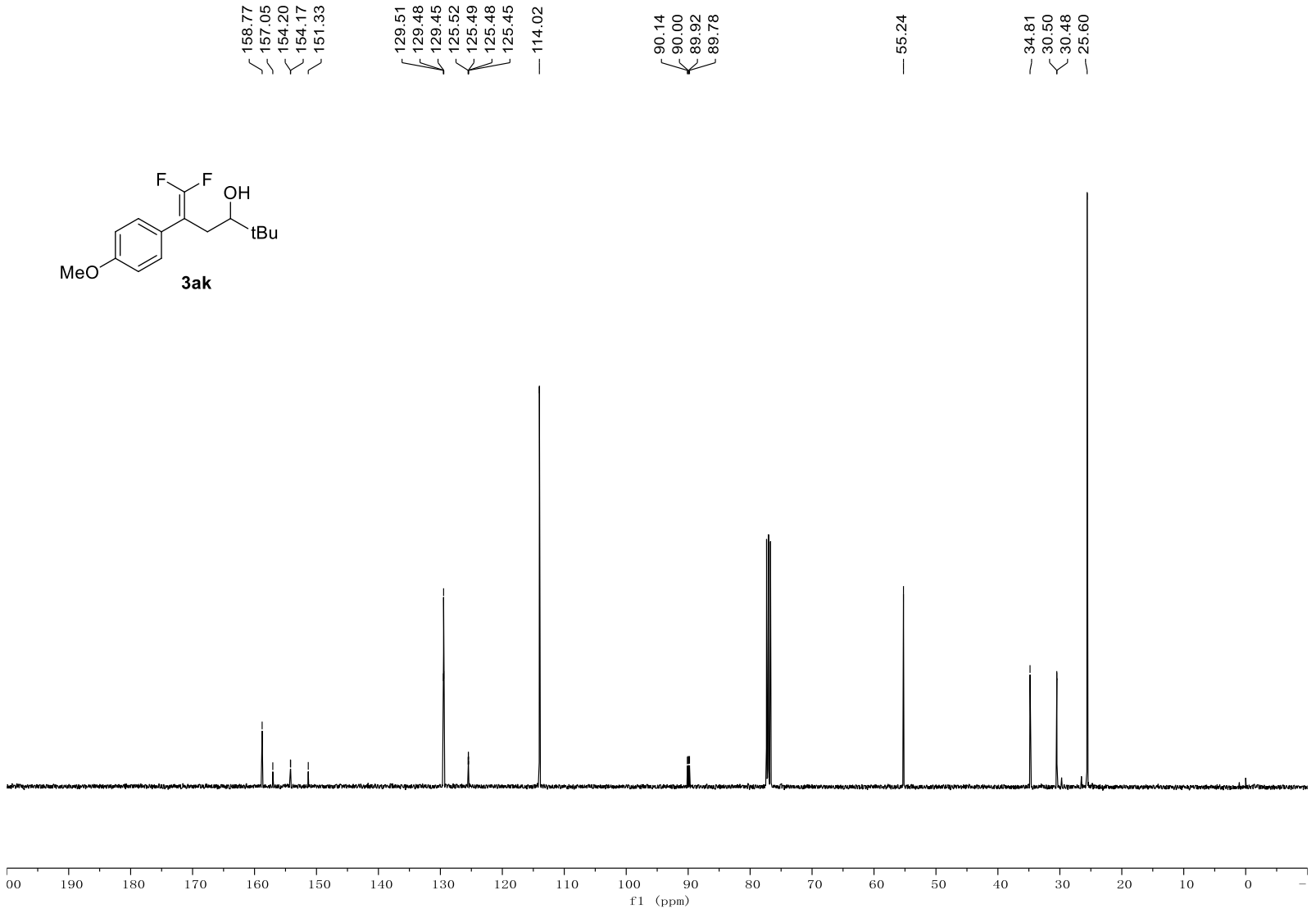
1.03
1.00
9.04
f1 (ppm)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125.49
125.48
125.45
114.02
90.14
90.00
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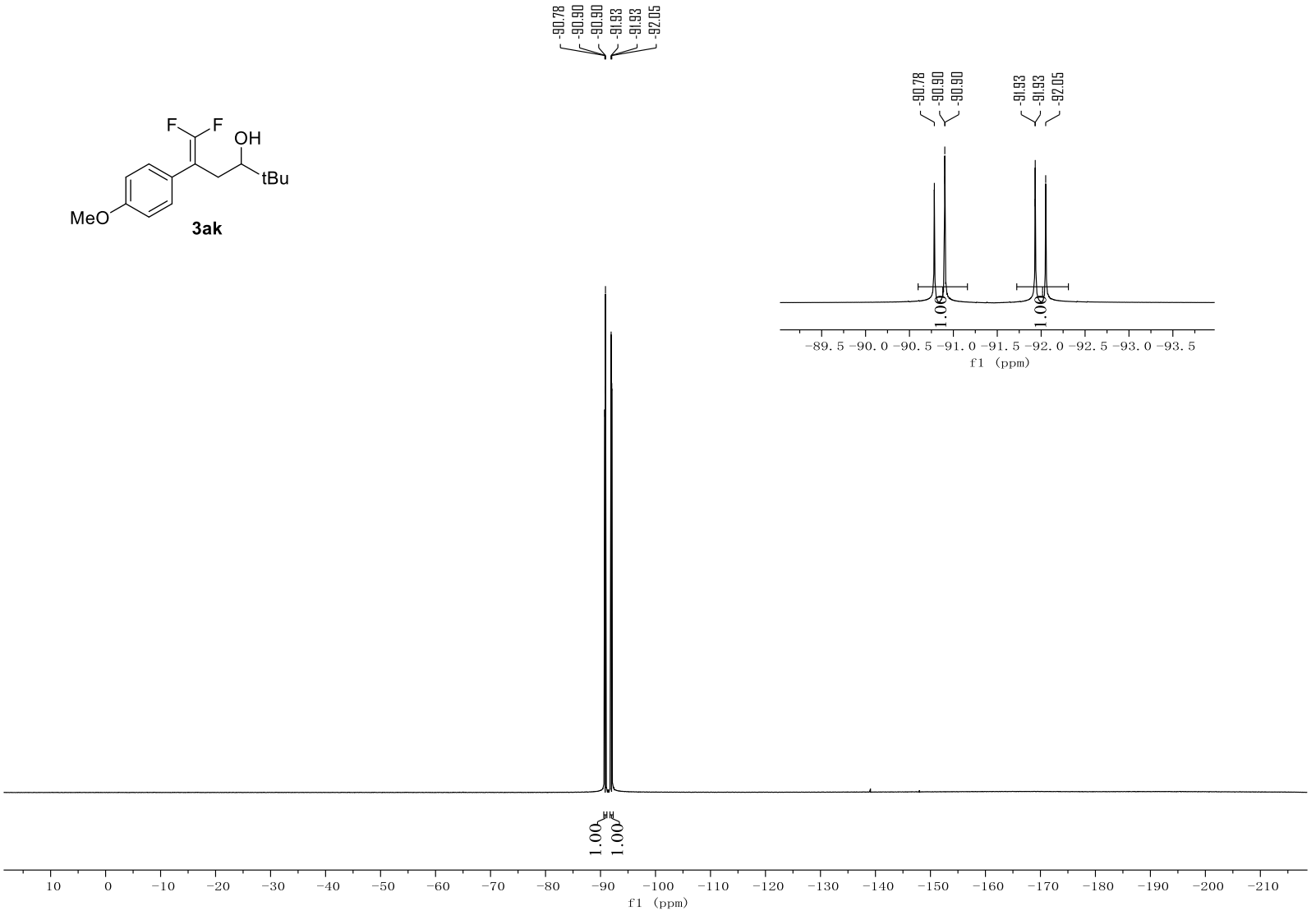
34.81
30.50
30.48
25.60
F
F
OH
tBu
MeO
3ak
f1 (ppm)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F
OH
tBu
MeO
3ak
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-90.90
-90.90
-91.93
-91.93
-92.05
1.00
1.00
f1 (ppm)
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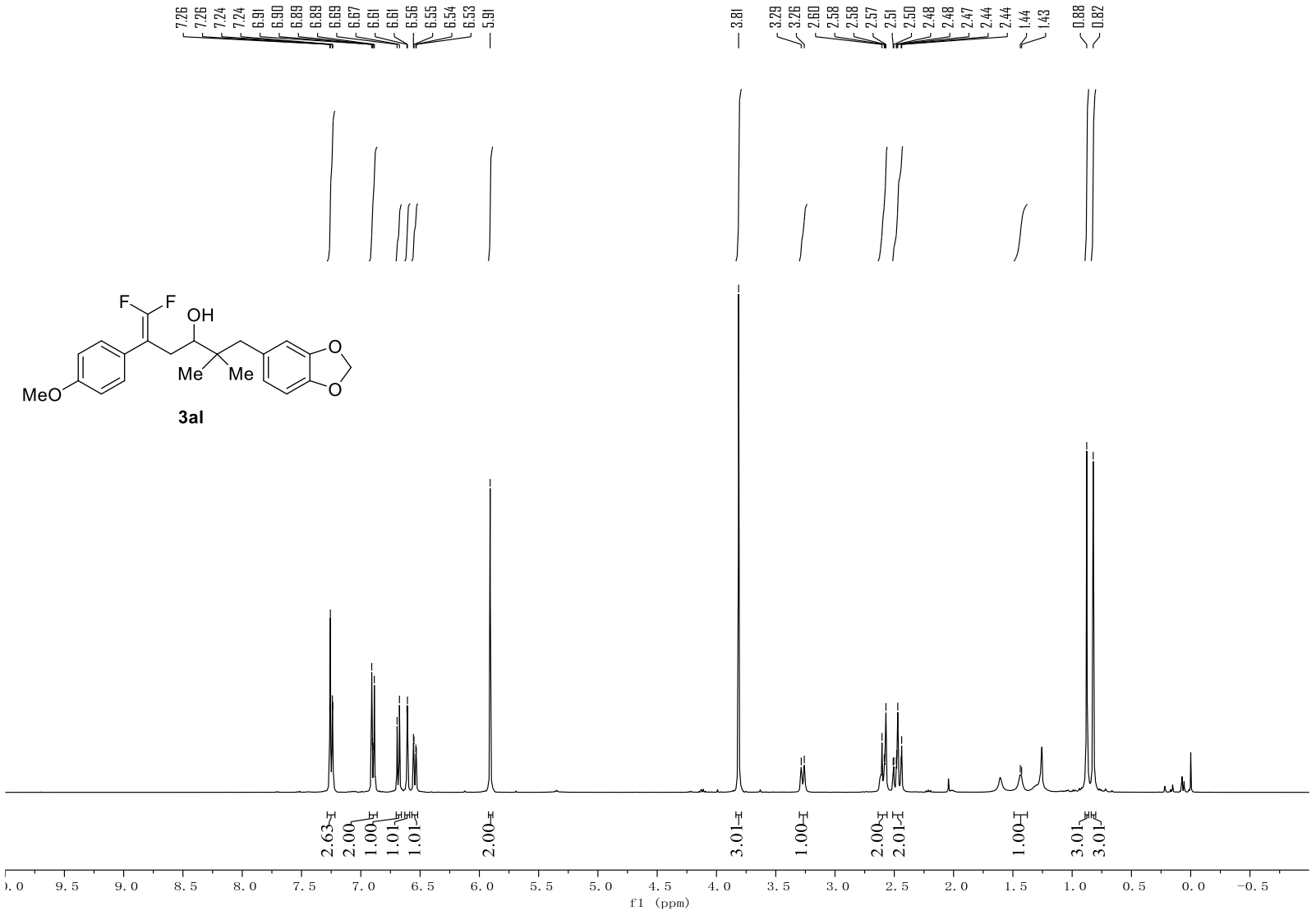
-90.90
-90.90
-91.93
-91.93
-92.05
1.06
1.06
f1 (ppm)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6.56
6.55
6.54
6.53
5.91
3.81
3.29
3.26
2.60
2.58
2.58
2.57
2.51
2.50
2.48
2.48
2.47
2.44
2.44
1.44
1.43
0.88
0.82
F
F
OH
Me
Me
O
O
MeO
3al
2.63
2.00
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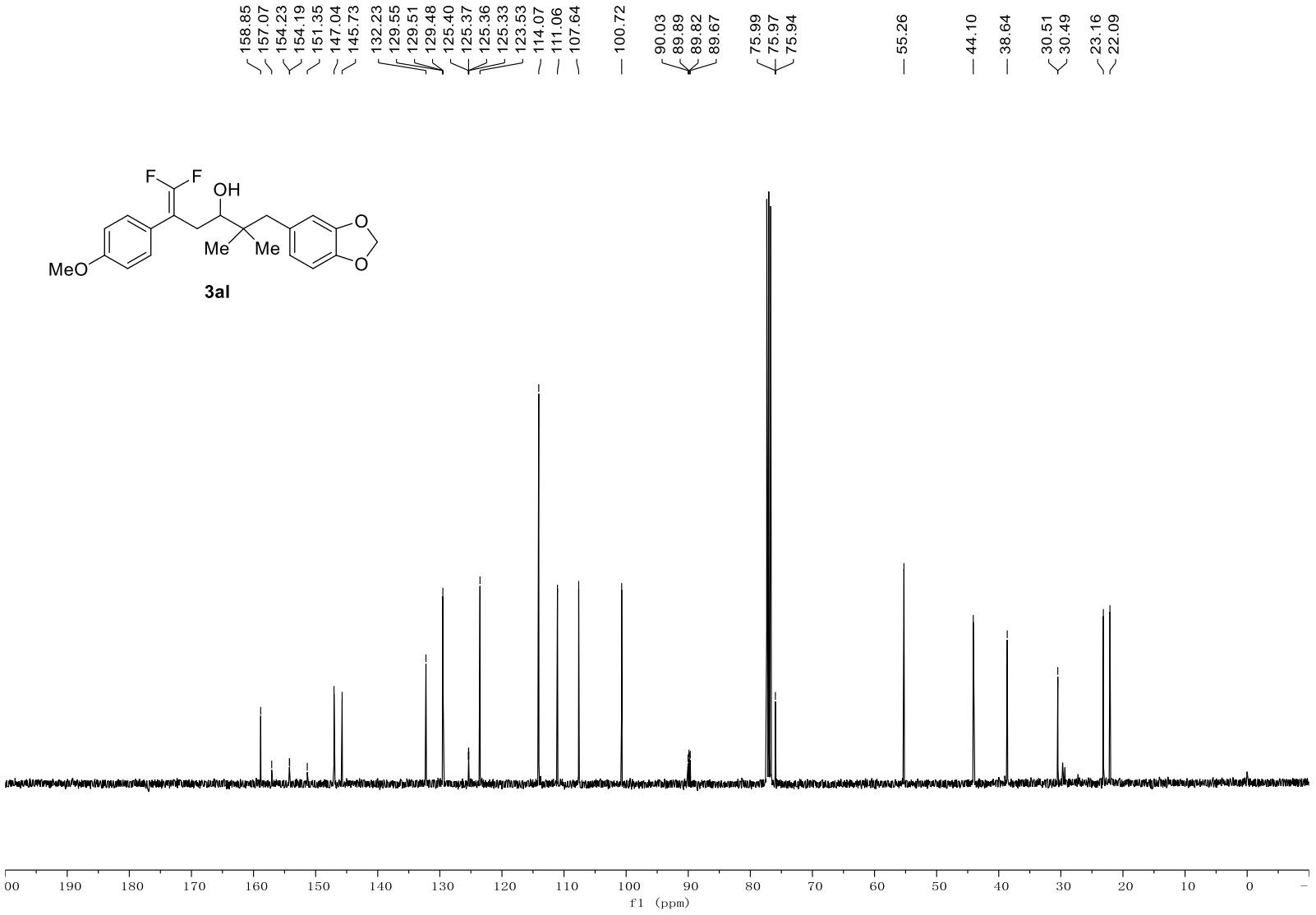
1.01
2.00
3.01
1.00
2.00
2.01
1.00
3.01
3.01
f1 (ppm)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129.48
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125.37
125.36
125.33
123.53
114.07
111.06
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89.82
89.67
75.99
75.97
75.94
55.26
44.10
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23.16
22.09
F
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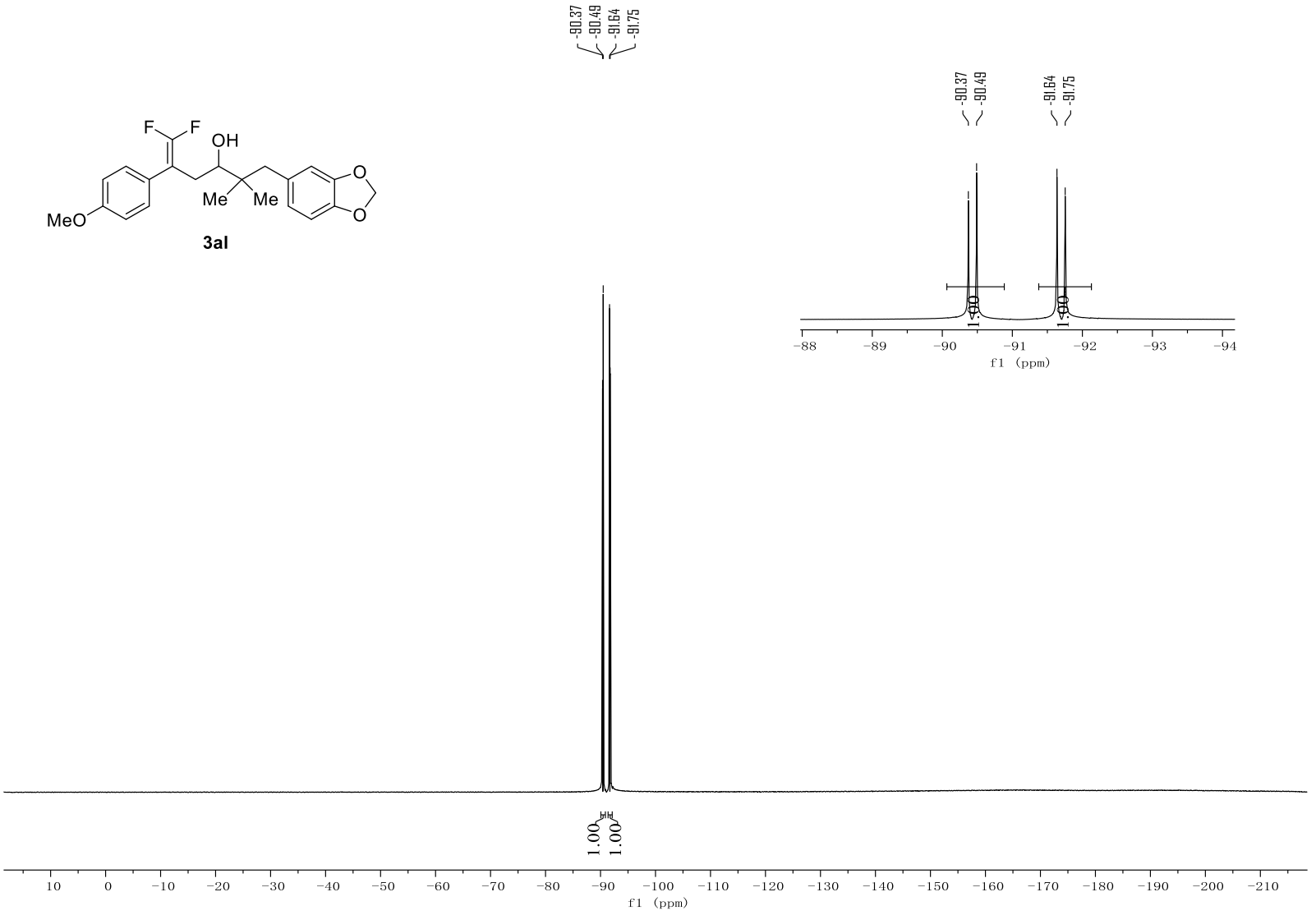
OH
Me
Me
MeO
O
O
3al
f1 (ppm)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F
OH
Me
Me
O
O
MeO
3al
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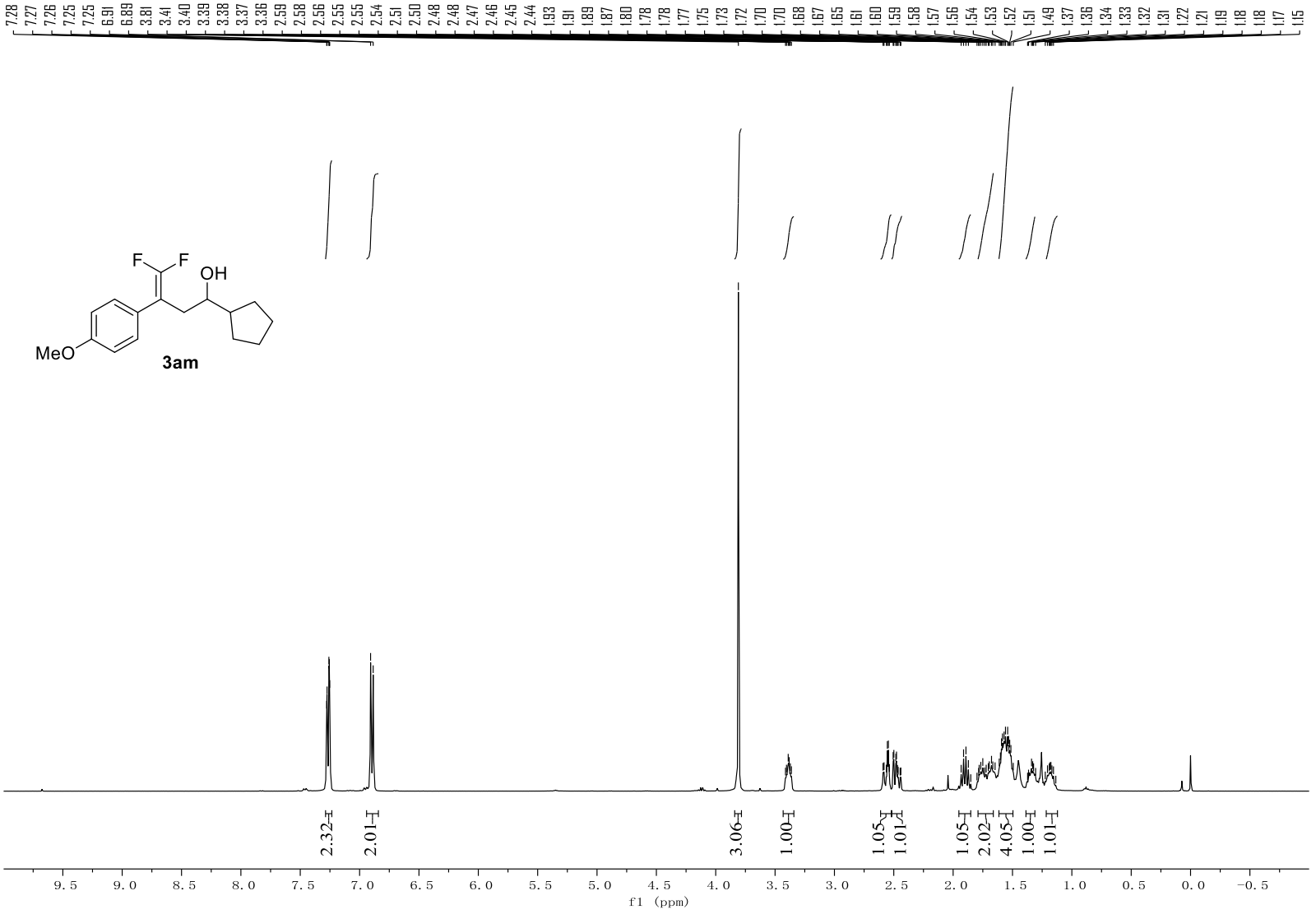
1.00
f1 (ppm)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1.33
1.32
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1.22
1.21
1.19
1.18
1.18
1.17
1.15
F
F
OH
MeO
3am
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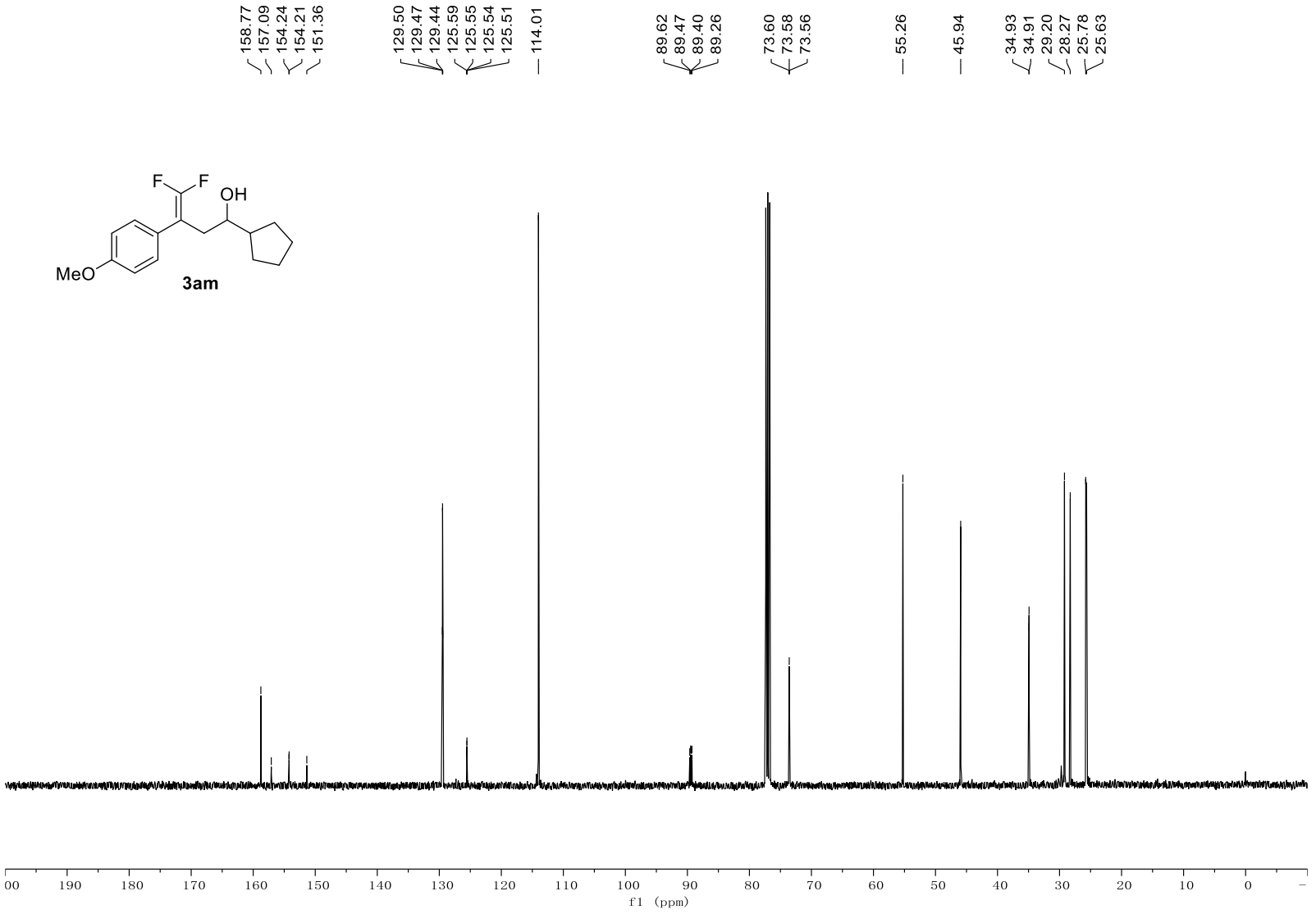
1.05
1.01
1.05
2.02
4.05
1.00
1.01
f1 (ppm)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129.47
129.44
125.59
125.55
125.54
125.51
114.01
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89.47
89.40
89.26
73.60
73.58
73.56
55.26
45.94
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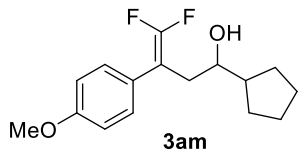
34.91
29.20
28.27
25.78
25.63
F
F
OH
MeO
3am
f1 (ppm)


F
F
OH
MeO

3am

-90.93
-91.05
-91.53
-91.64
-90.93
-91.05
-91.53
-91.64
1.00
1.01
-90.0
-90.5
-91.0
-91.5
-92.0
-92.5
f1 (ppm)
1.00
1.01
10
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-10
-20
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-50
-60
-70
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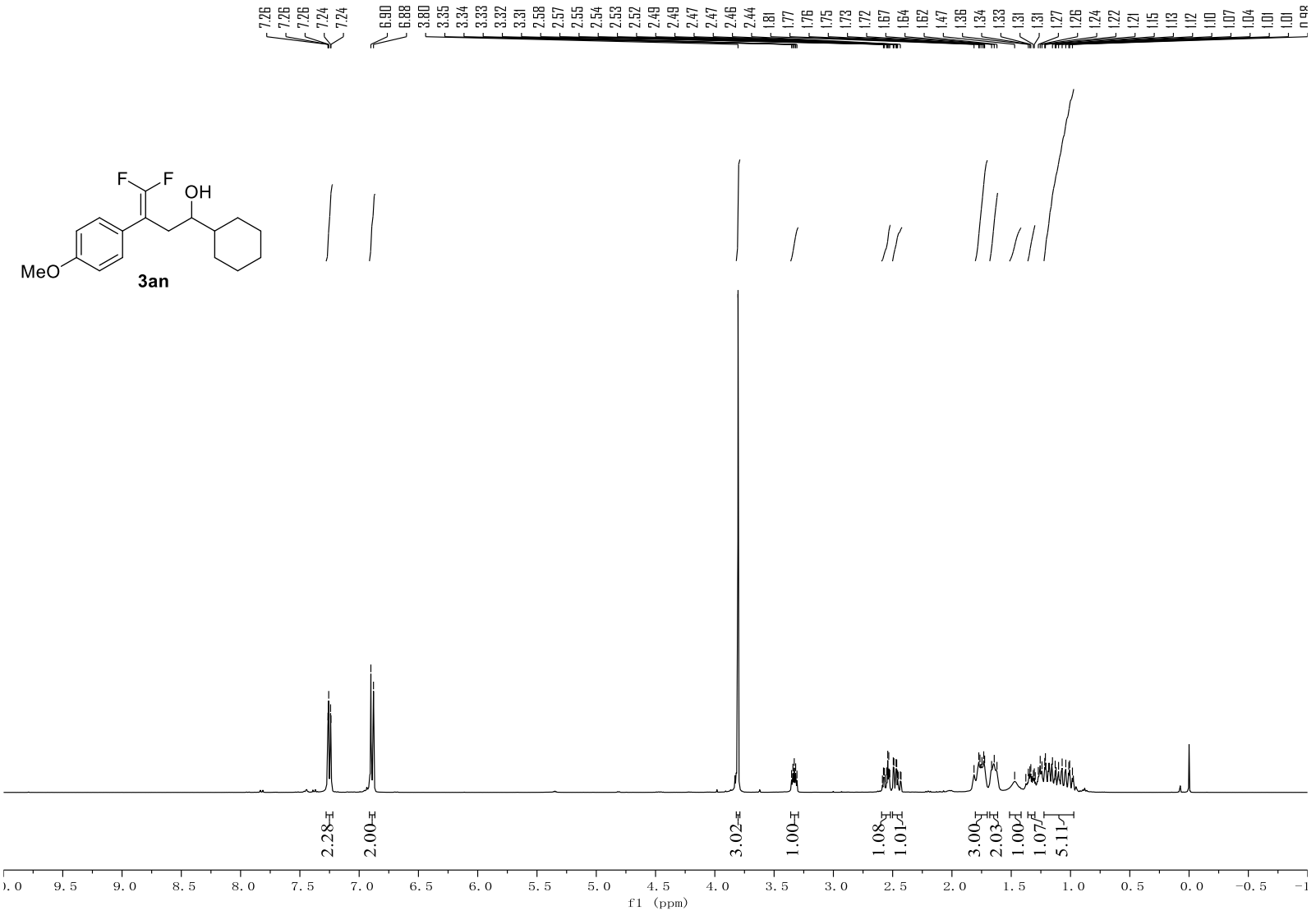
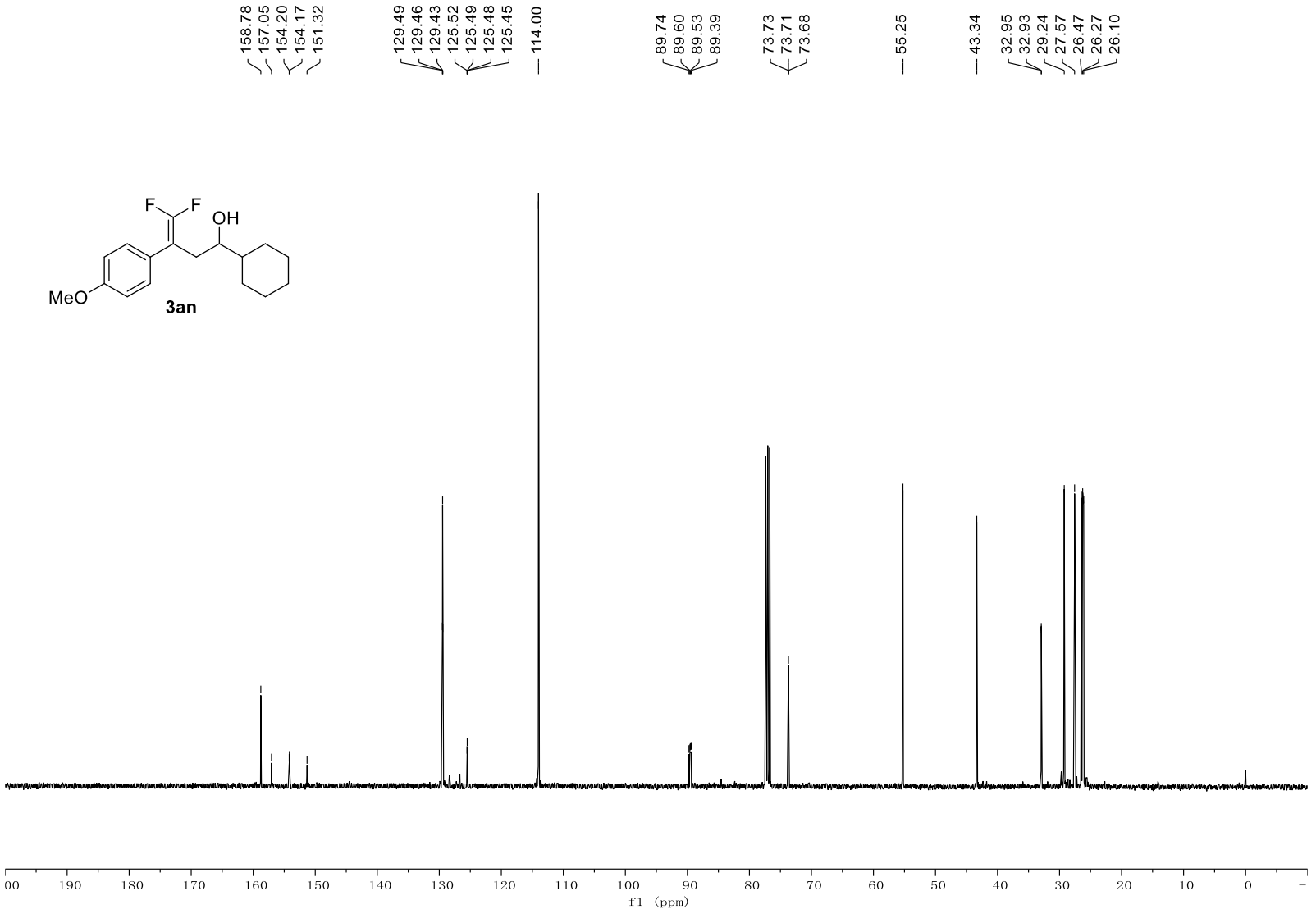
-160
-170
-180
-190
-200
-210
f1 (ppm)


F
F
OH
MeO
3an
7.26
7.26
7.26
7.24
7.24
6.90
6.88
3.80
3.35
3.34
3.33
3.32
3.31
2.58
2.57
2.55
2.54
2.53
2.52
2.49
2.49
2.47
2.47
2.46
2.44
1.81
1.77
1.76
1.75
1.73
1.72
1.67
1.64
1.62
1.47
1.36
1.34
1.33
1.31
1.31
1.27
1.26
1.24
1.22
1.21
1.15
1.13
1.12
1.10
1.07
1.04
1.01
1.01
2.28
2.00
3.02
1.00
1.08
1.01
3.00
2.03
1.00
1.07
5.11
f1 (ppm)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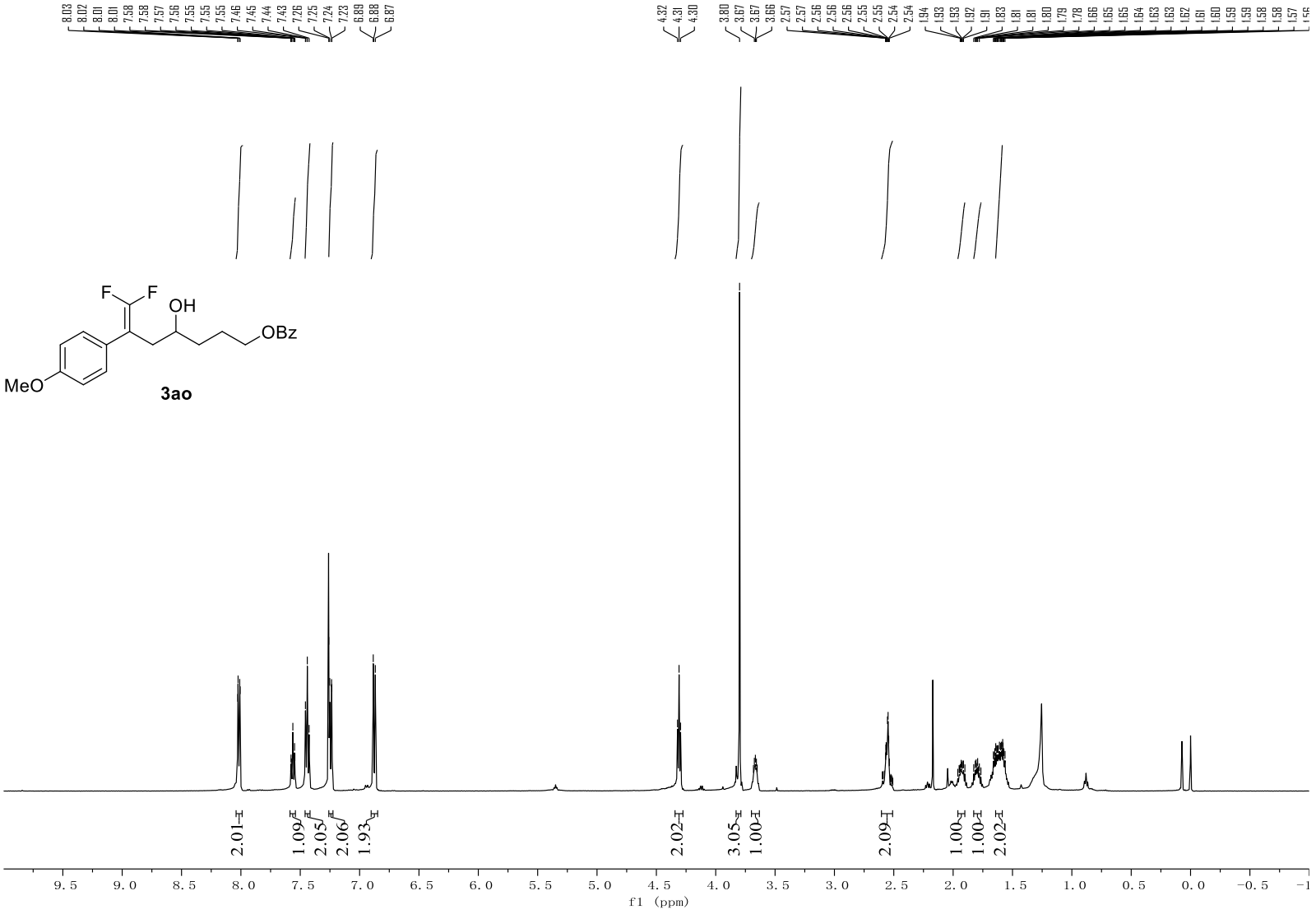
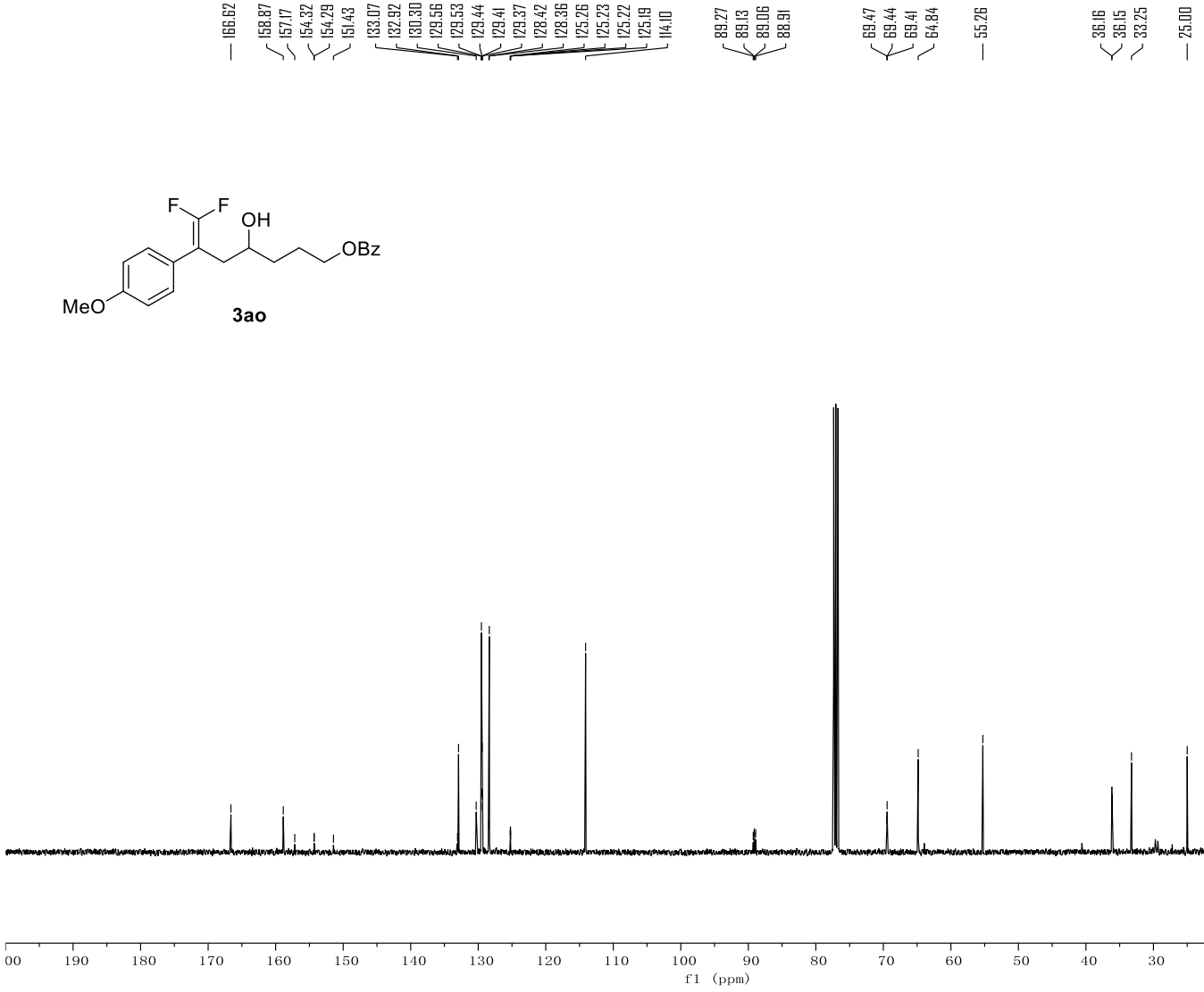
157.05
154.20
154.17
151.32
129.49
129.46
129.43
125.52
125.49
125.48
125.45
114.00
89.74
89.60
89.53
89.39
73.73
73.71
73.68
55.25
43.34
32.95
32.93
29.24
27.57
26.47
26.27
26.10
F
F
OH
MeO
3an
f1 (ppm)


-90.76
-90.88
-91.65
-91.76
F
F
OH
MeO
3an
1.00
1.01
f1 (ppm)


F
F
OH
OBz
MeO
3ao
f1 (ppm)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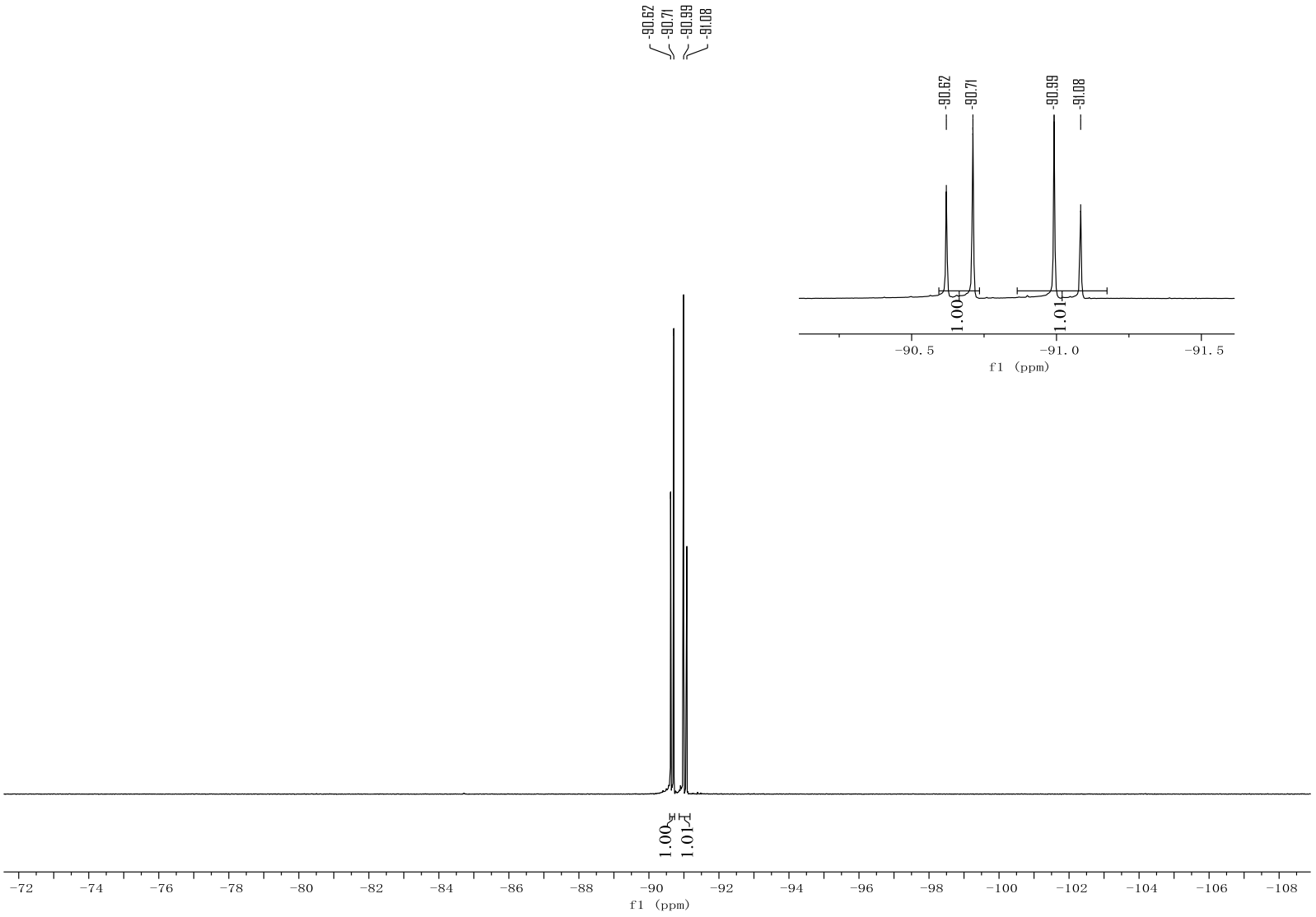
158.87
157.17
154.32
154.29
151.43
133.07
132.92
130.30
129.56
129.53
129.44
129.41
129.37
128.42
128.36
125.26
125.23
125.22
125.19
114.10
89.27
89.13
89.06
88.91
69.47
69.44
69.41
64.84
55.26
36.16
36.15
33.25
25.00
F
F
OH
OBz
MeO
3ao
f1 (ppm)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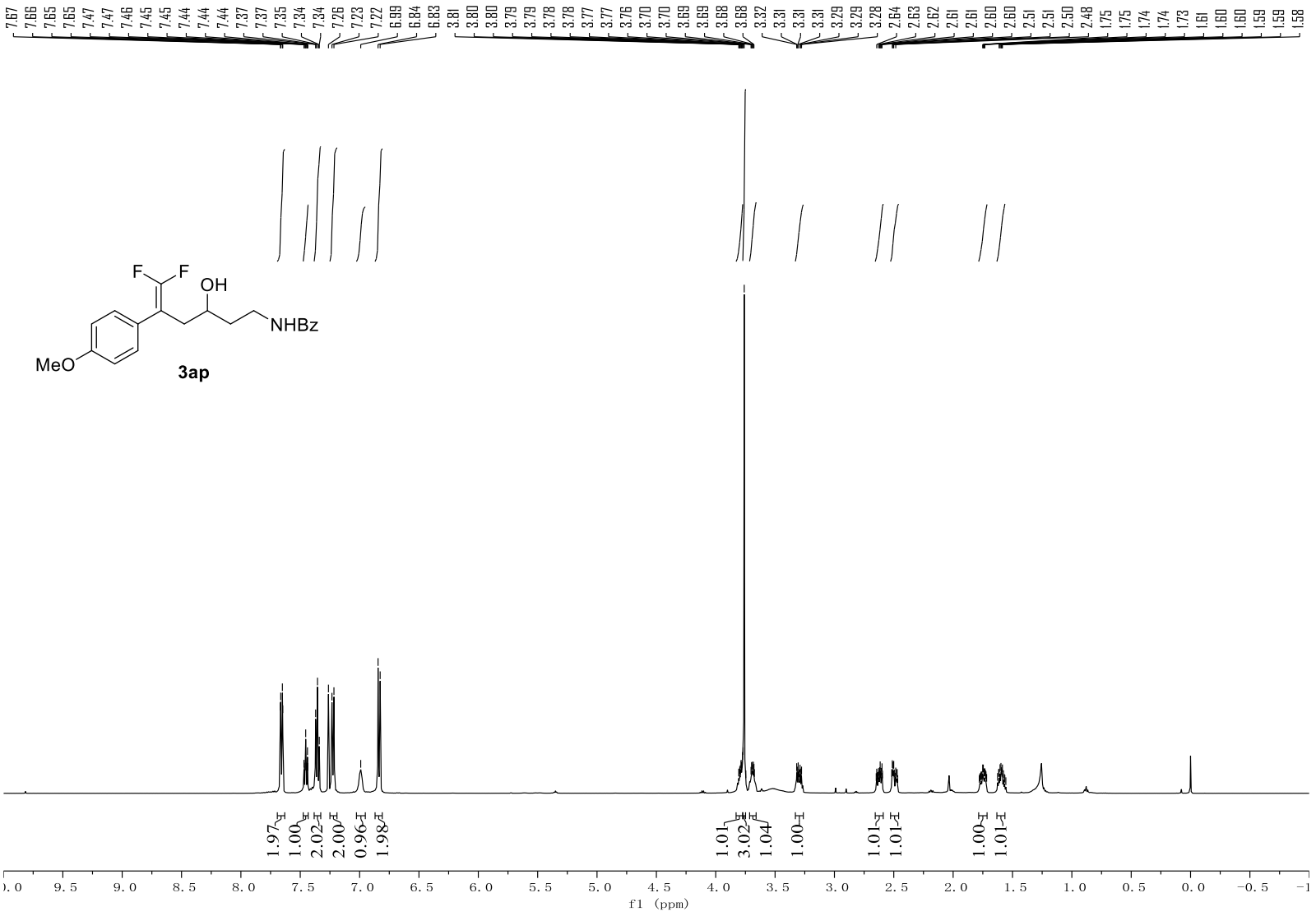
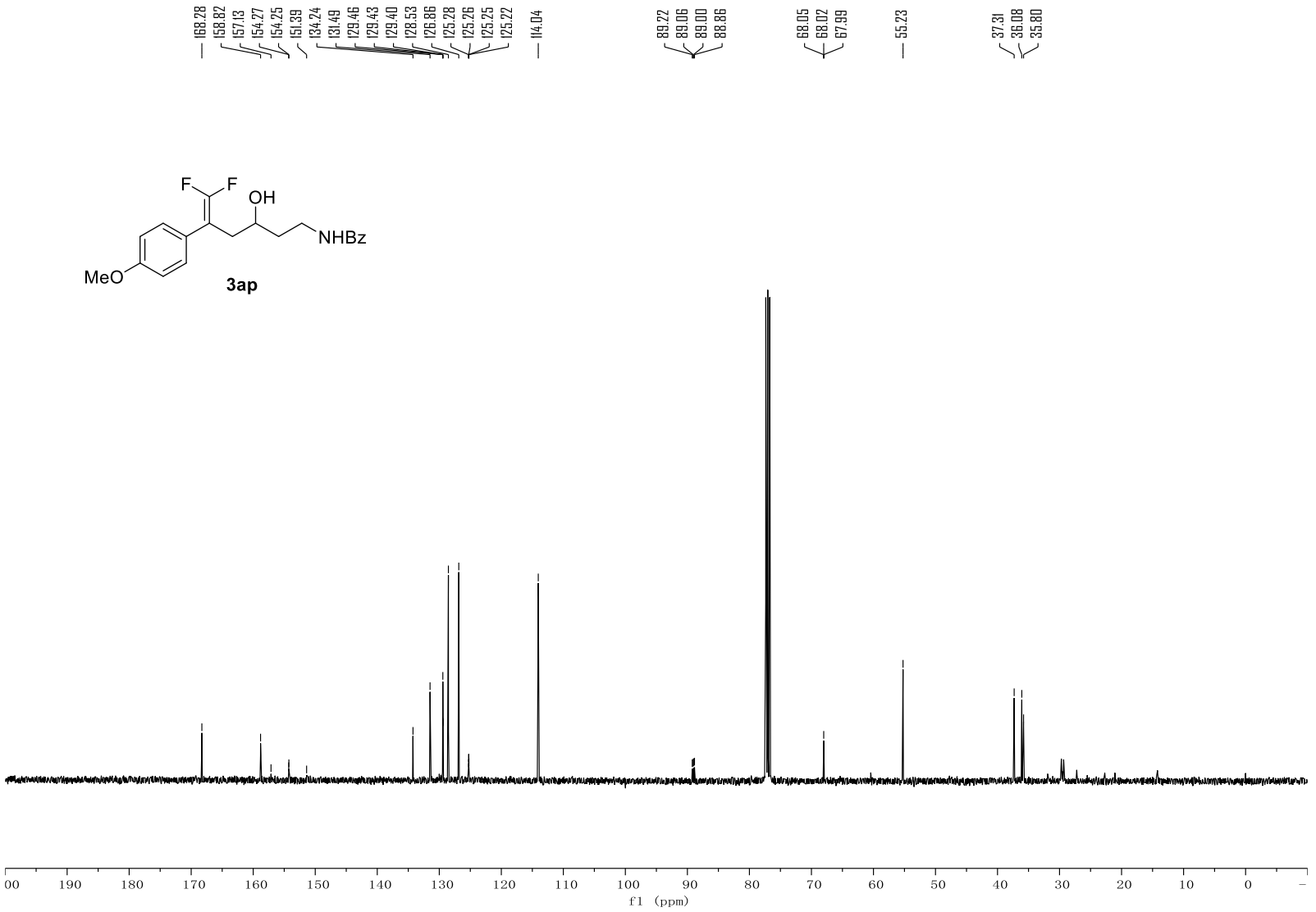
-90.99
-91.08
1.00
1.01
f1 (ppm)
-90.5
-91.0
-91.5


F
F
OH
NHBz
MeO
3ap
f1 (ppm)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157.13
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151.39
134.24
131.49
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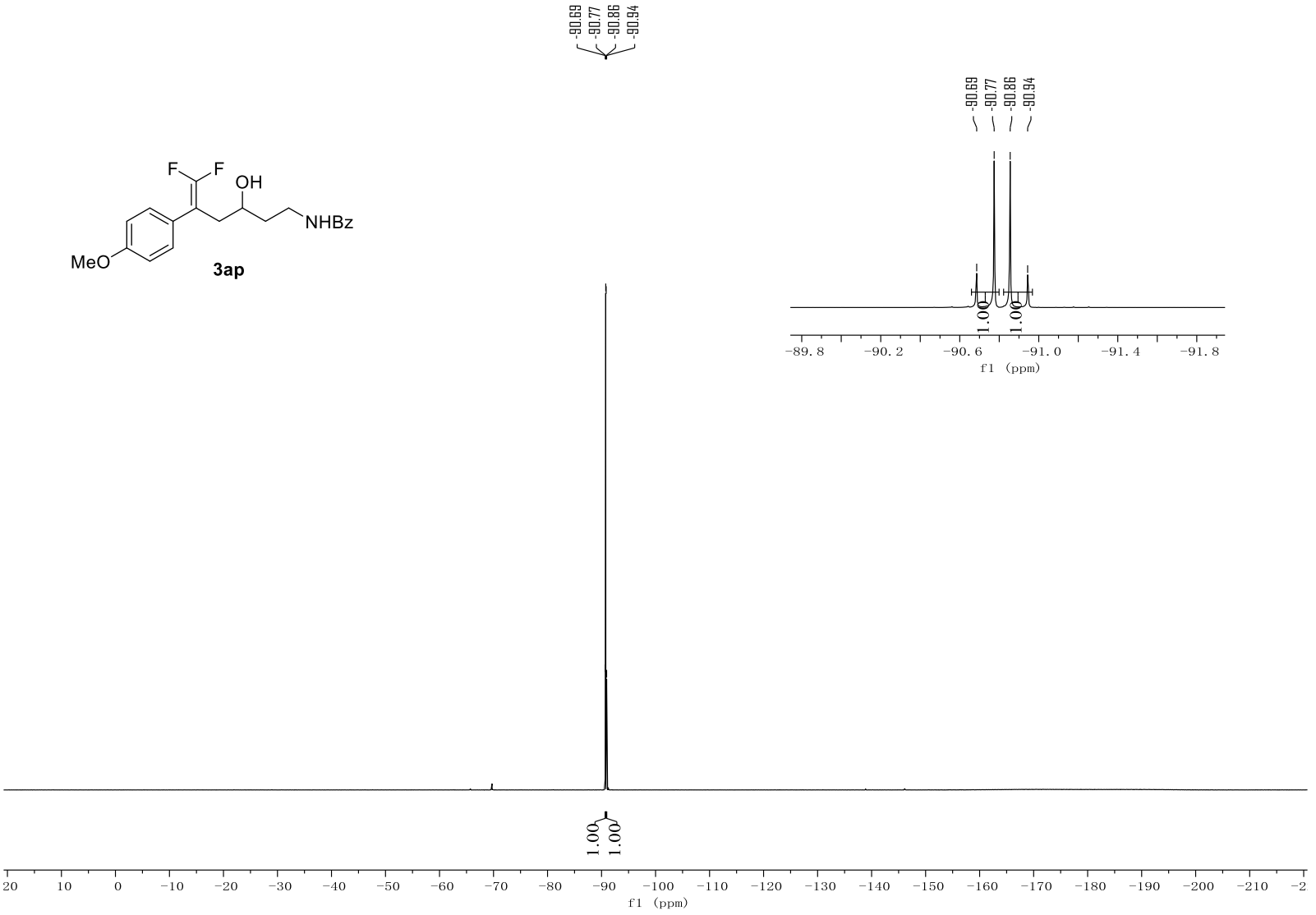
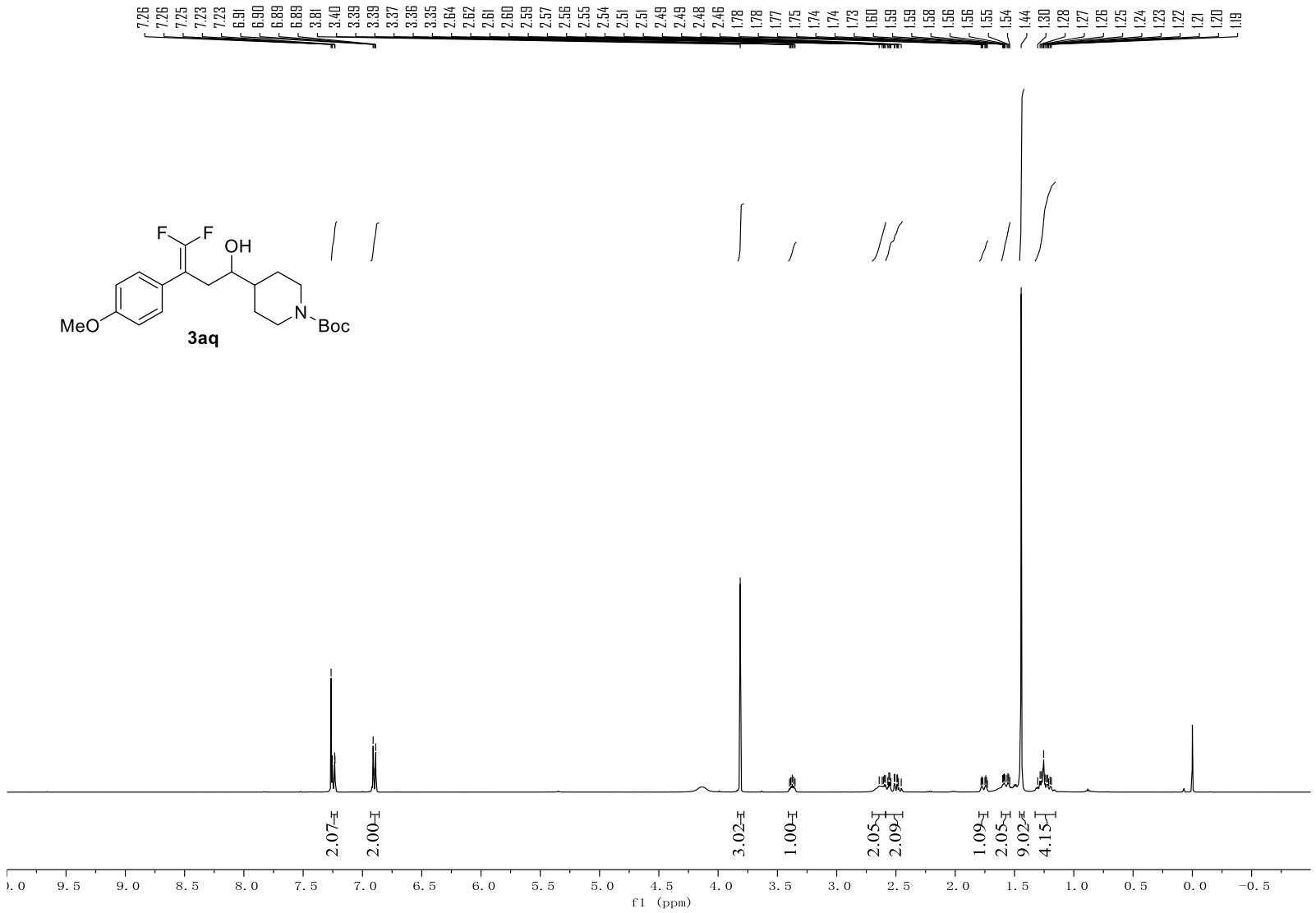
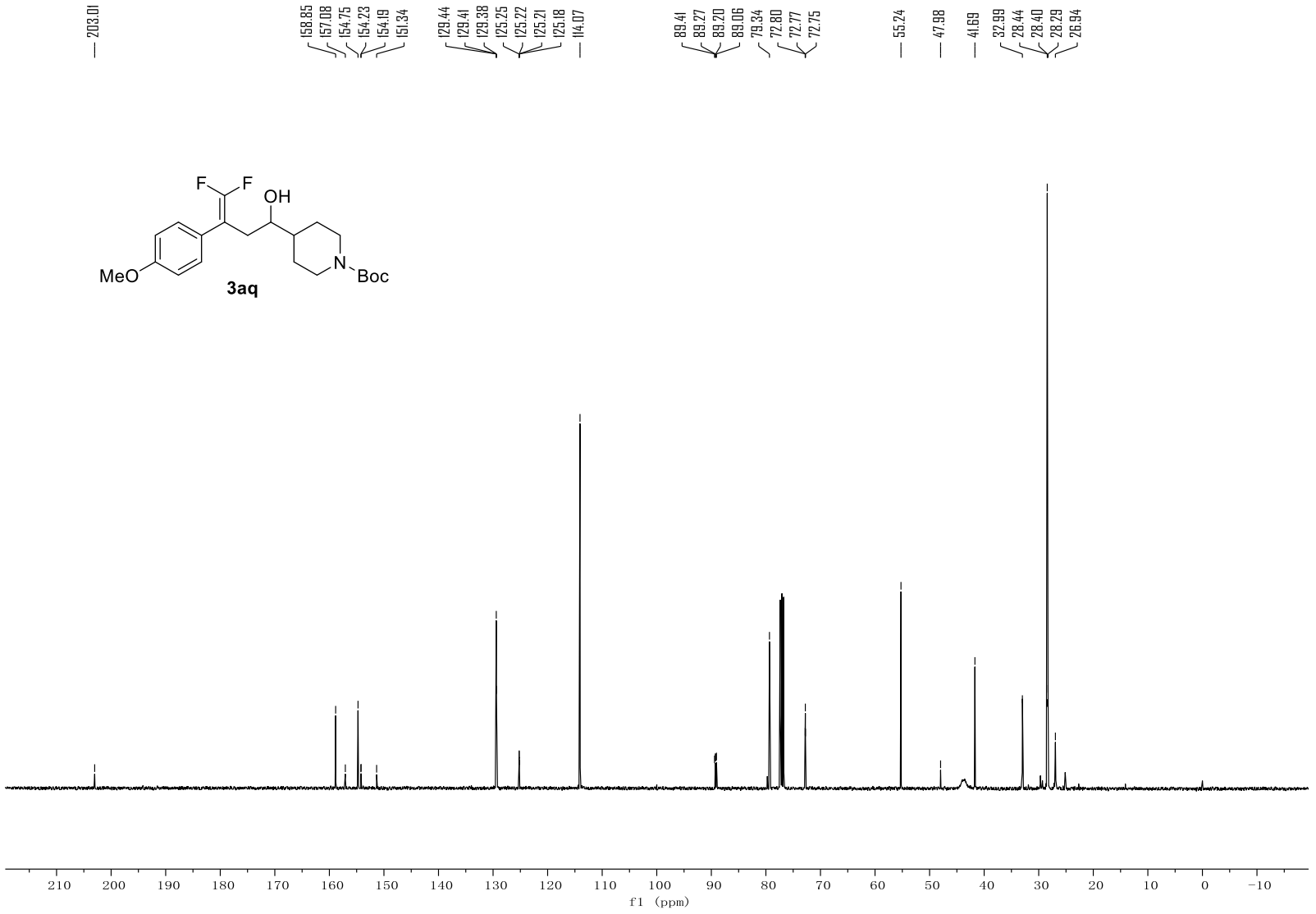
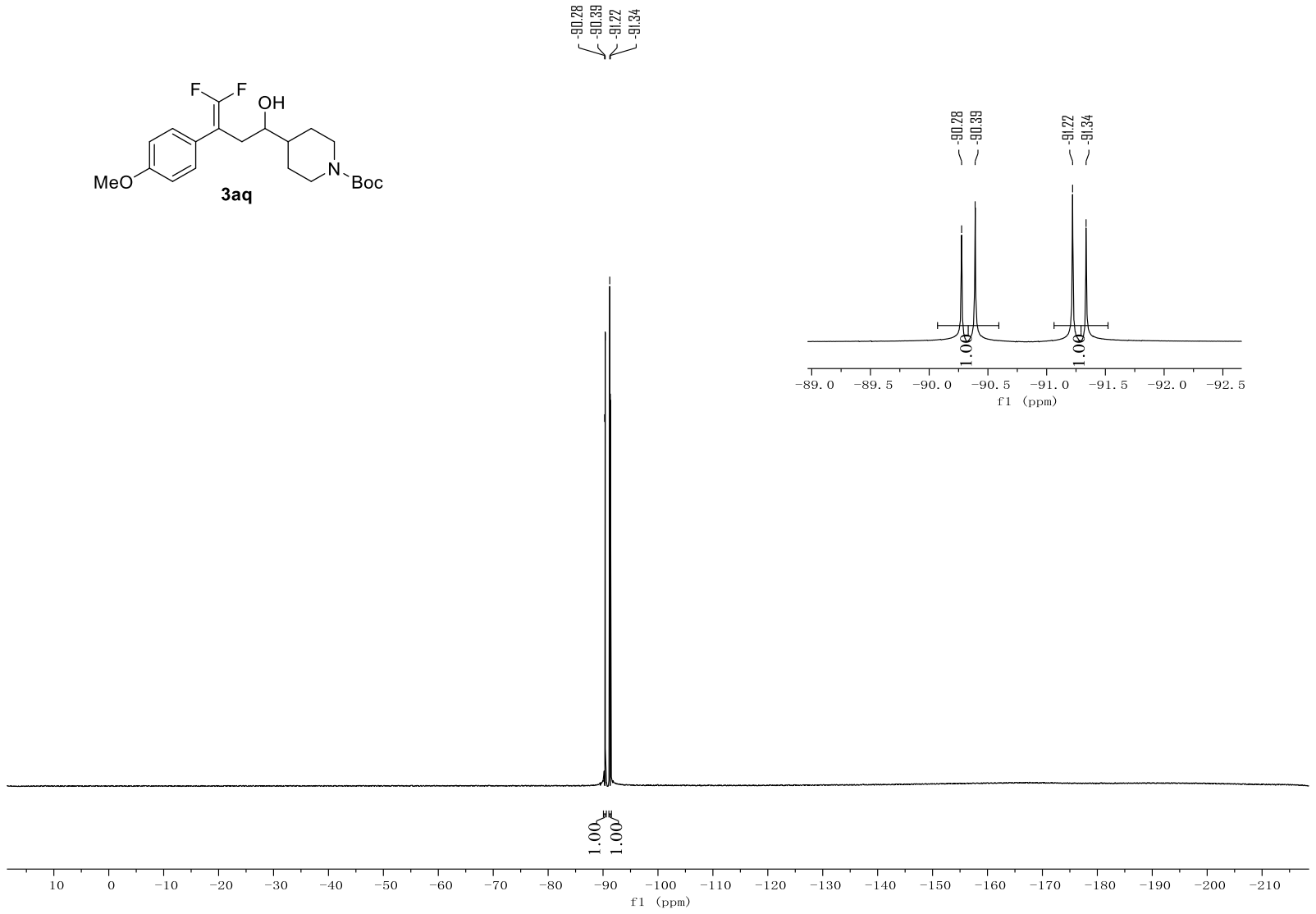
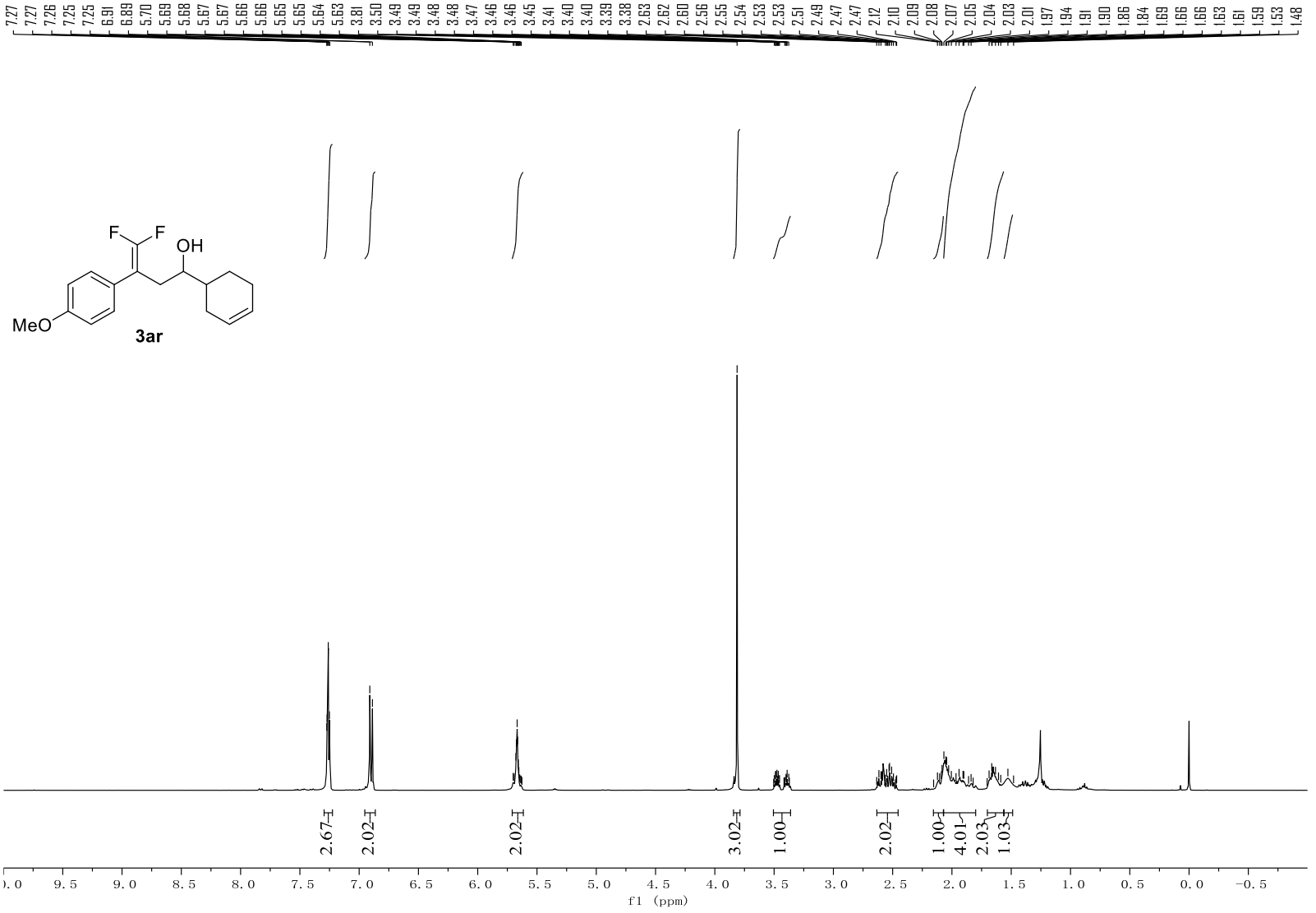
129.43
129.40
128.53
126.86
125.28
125.26
125.25
125.22
114.04
89.22
89.06
89.00
88.86
68.05
68.02
67.99
55.23
37.31
36.08
35.80
F
F
OH
NHBz
MeO
3ap
f1 (ppm)

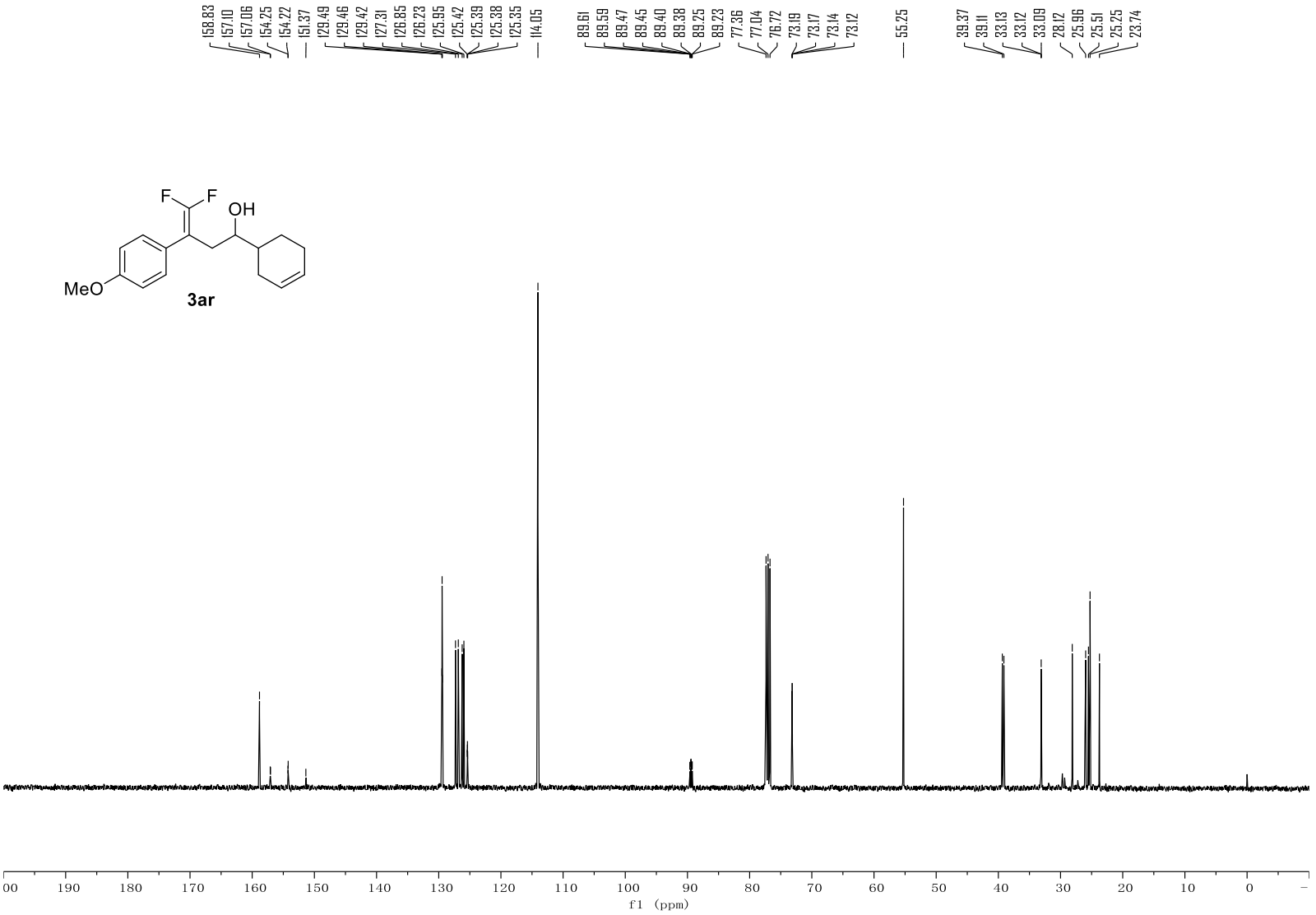

-90.69
-90.77
-90.86
-90.94
F
F
OH
NHBz
MeO
3ap
1.00
1.00
-89.8
-90.2
-90.6
-91.0
-91.4
-91.8
f1 (ppm)
1.00
1.00
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

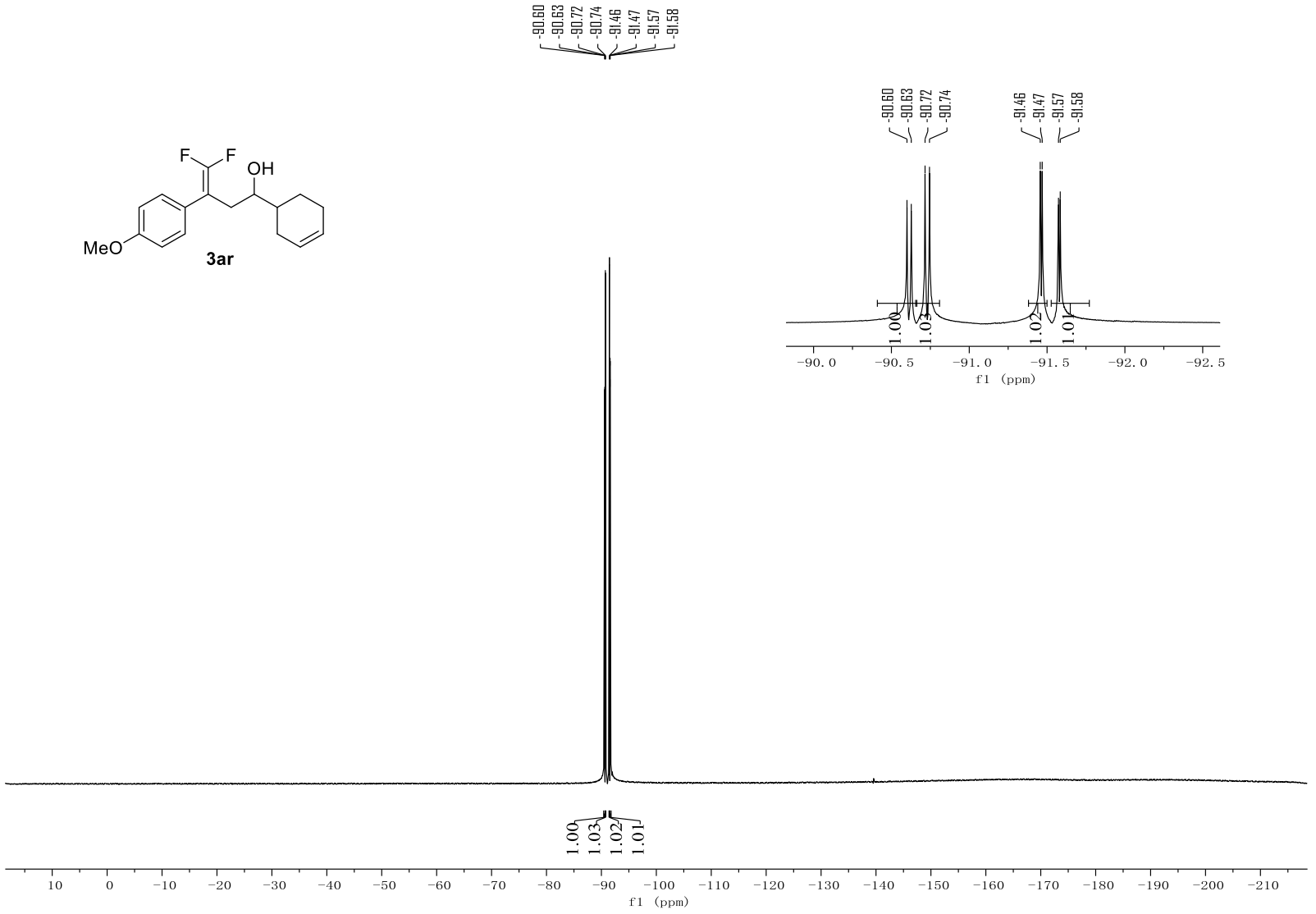

7.26
7.26
7.25
7.23
7.23
6.91
6.90
6.89
6.89
3.81
3.40
3.39
3.39
3.37
3.36
3.35
2.64
2.62
2.61
2.60
2.59
2.57
2.56
2.55
2.54
2.51
2.51
2.49
2.49
2.48
2.46
1.78
1.78
1.77
1.75
1.74
1.74
1.73
1.60
1.59
1.59
1.58
1.56
1.56
1.55
1.54
1.44
1.30
1.28
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.19
F
F
OH
MeO
N
Boc
3aq
2.07
2.00
3.02
1.00
2.05
2.09
1.09
2.05
9.02
4.15
f1 (ppm)

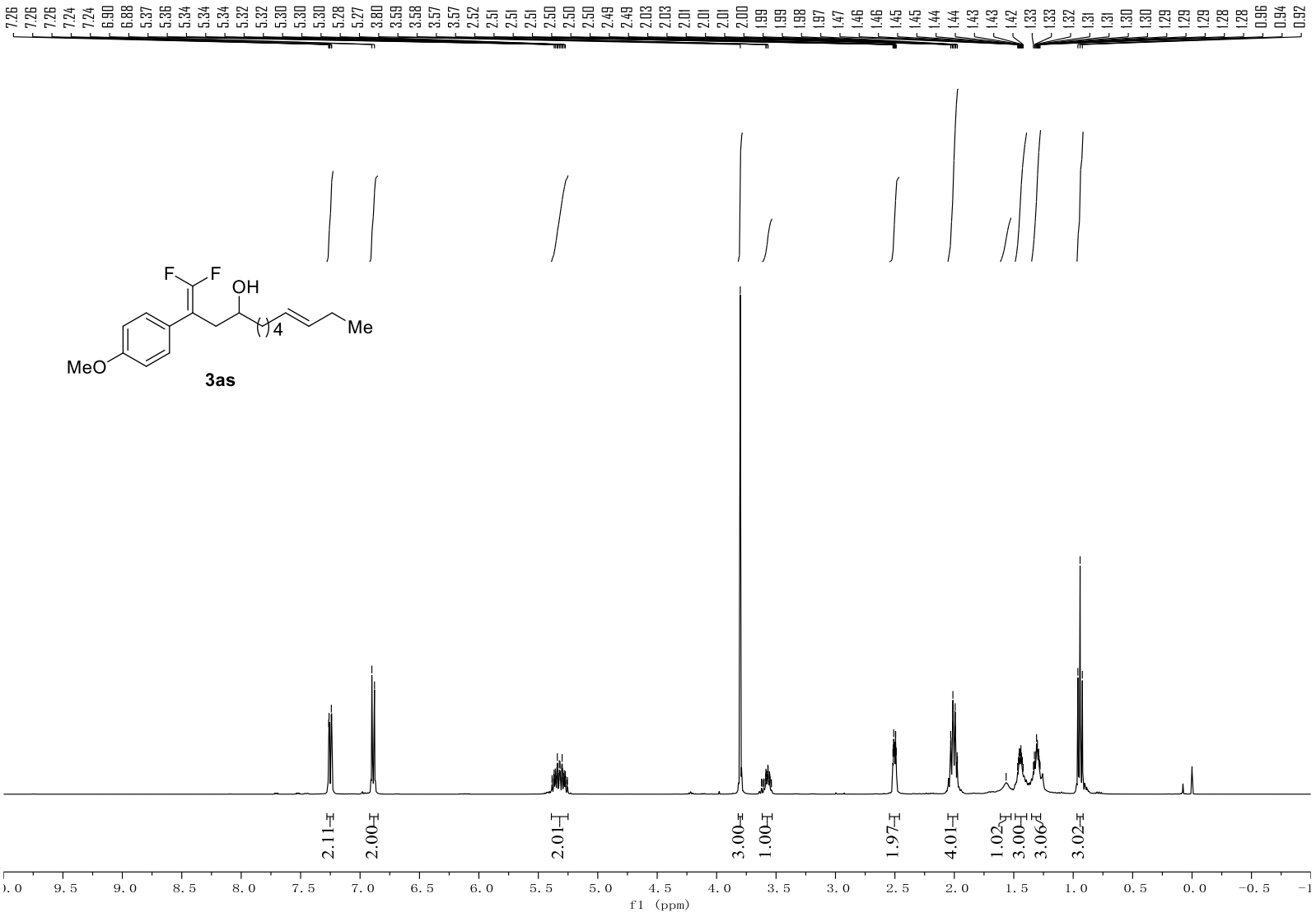

203.01
158.85
157.08
154.75
154.23
154.19
151.34
129.44
129.41
129.38
125.25
125.22
125.21
125.18
114.07
89.41
89.27
89.20
89.06
79.34
72.80
72.77
72.75
55.24
47.98
41.69
32.99
28.44
28.40
28.29
26.94
F
F
OH
MeO
N
Boc
3aq
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

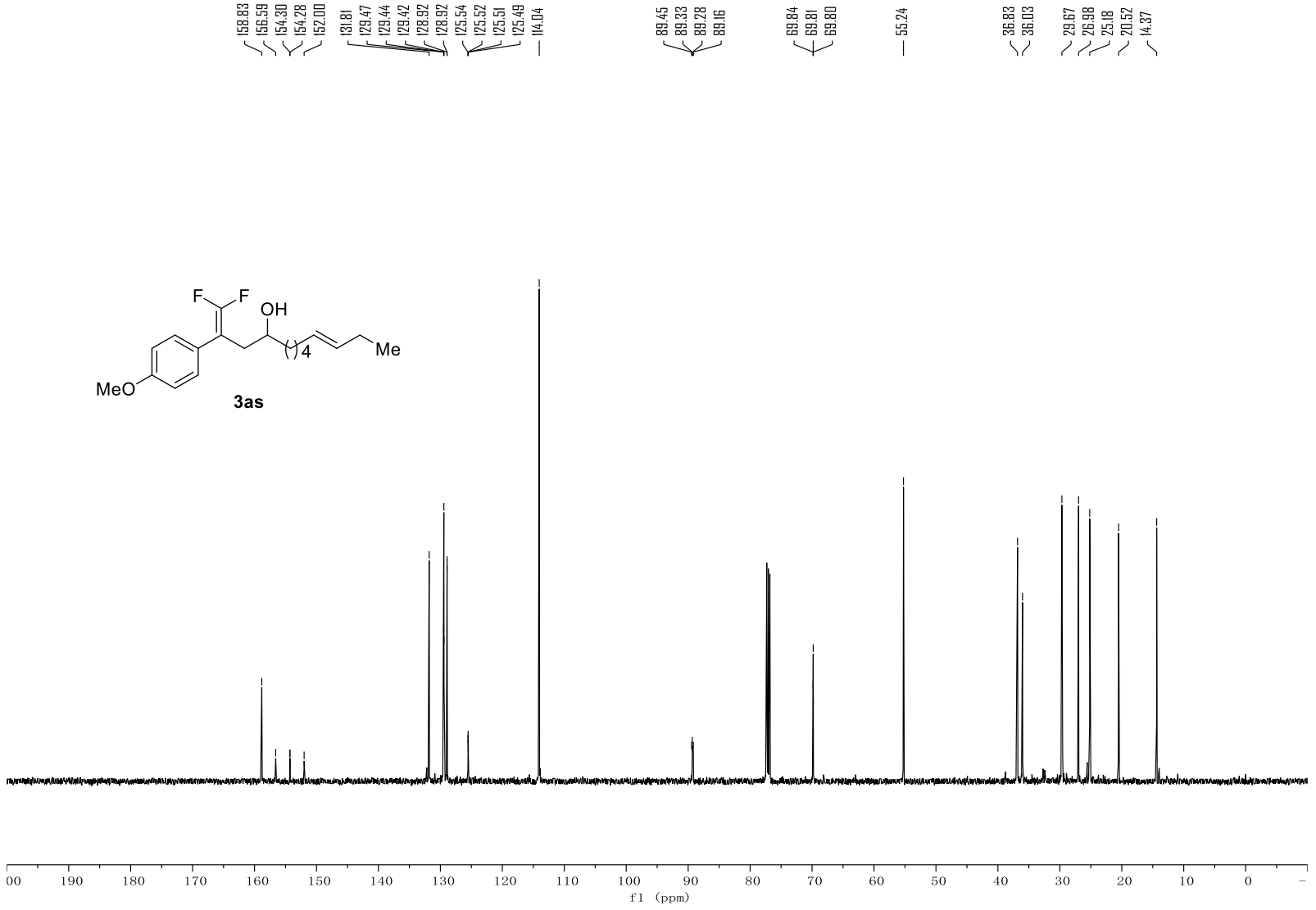

-90.28
-90.39
-91.22
-91.34
F
F
OH
MeO
N
Boc
3aq
1.00
1.00
1.00
1.00
f1 (ppm)
f1 (ppm)


7.27 7.27 7.26 7.25 7.25 6.91 6.89 5.70 5.69 5.68 5.67 5.67 5.66 5.66 5.65 5.65 5.64 5.63 3.81 3.50 3.49 3.49 3.48 3.48 3.47 3.46 3.46 3.45 3.41 3.40 3.40 3.39 3.38 2.63 2.62 2.60 2.56 2.55 2.54 2.53 2.53 2.51 2.49 2.47 2.47 2.12 2.10 2.09 2.08 2.07 2.05 2.04 2.03 2.01 1.97 1.94 1.91 1.90 1.86 1.84 1.69 1.66 1.66 1.63 1.61 1.59 1.53 1.48
F
F
OH
MeO
3ar
2.67
2.02
2.02
3.02
1.00
2.02
1.00
4.01
2.03
1.03
f1 (ppm)


158.83
157.10
157.06
154.25
154.22
151.37
129.49
129.46
129.42
127.31
126.85
126.23
125.95
125.42
125.39
125.38
125.35
114.05
89.61
89.59
89.47
89.45
89.40
89.38
89.25
89.23
77.36
77.04
76.72
73.19
73.17
73.14
73.12
55.25
39.37
39.11
33.13
33.12
33.09
28.12
25.96
25.51
25.25
23.74
F
F
OH
MeO
3ar
f1 (ppm)


-90.60
-90.63
-90.72
-90.74
-91.46
-91.47
-91.57
-91.58
F
F
OH
MeO
3ar
1.00
1.03
1.02
1.01
f1 (ppm)


F
F
OH
4
Me
MeO
3as
2.11
2.00
2.01
3.00
1.00
1.97
4.01
1.02
3.00
3.06
3.02
f1 (ppm)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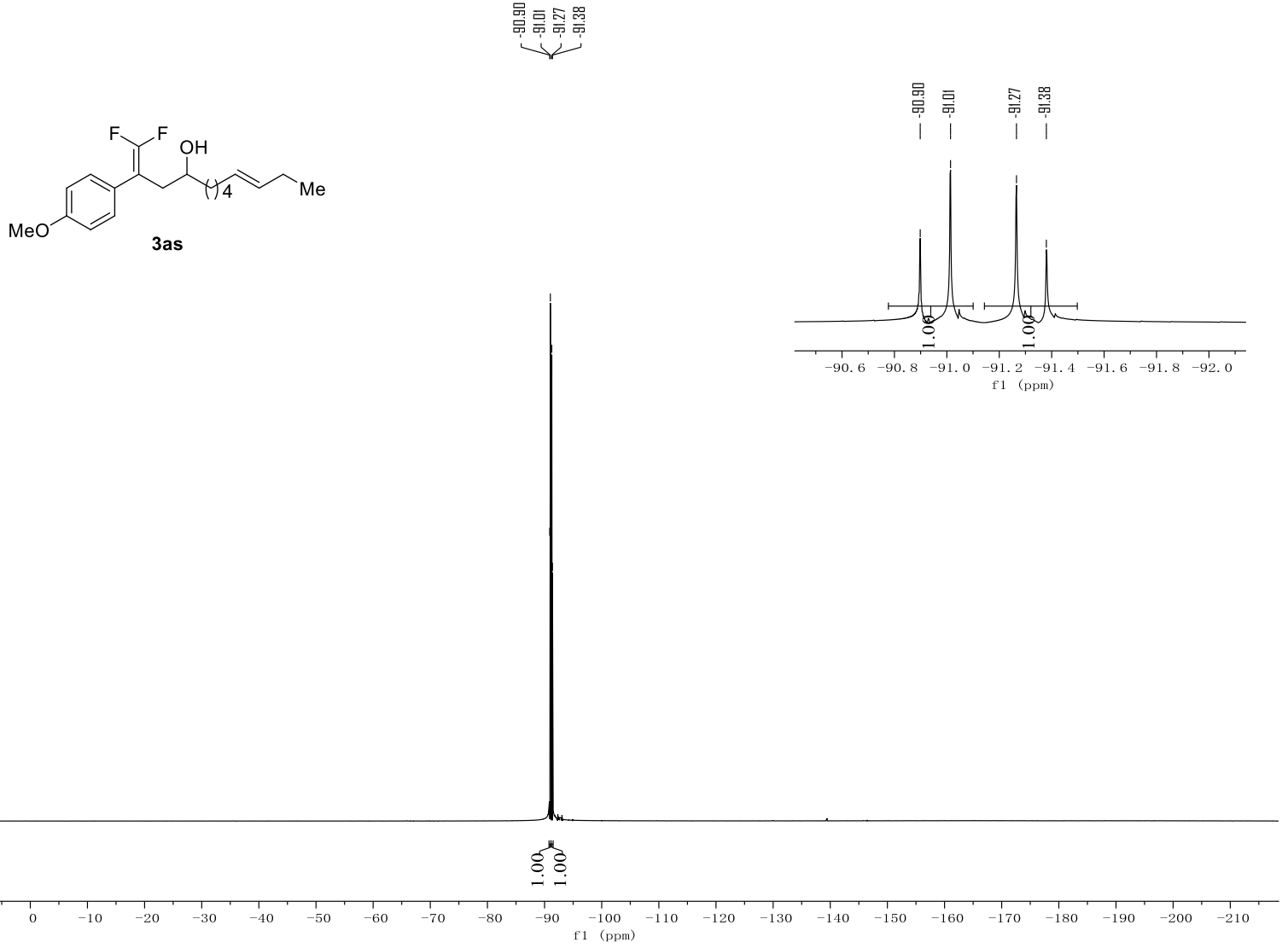
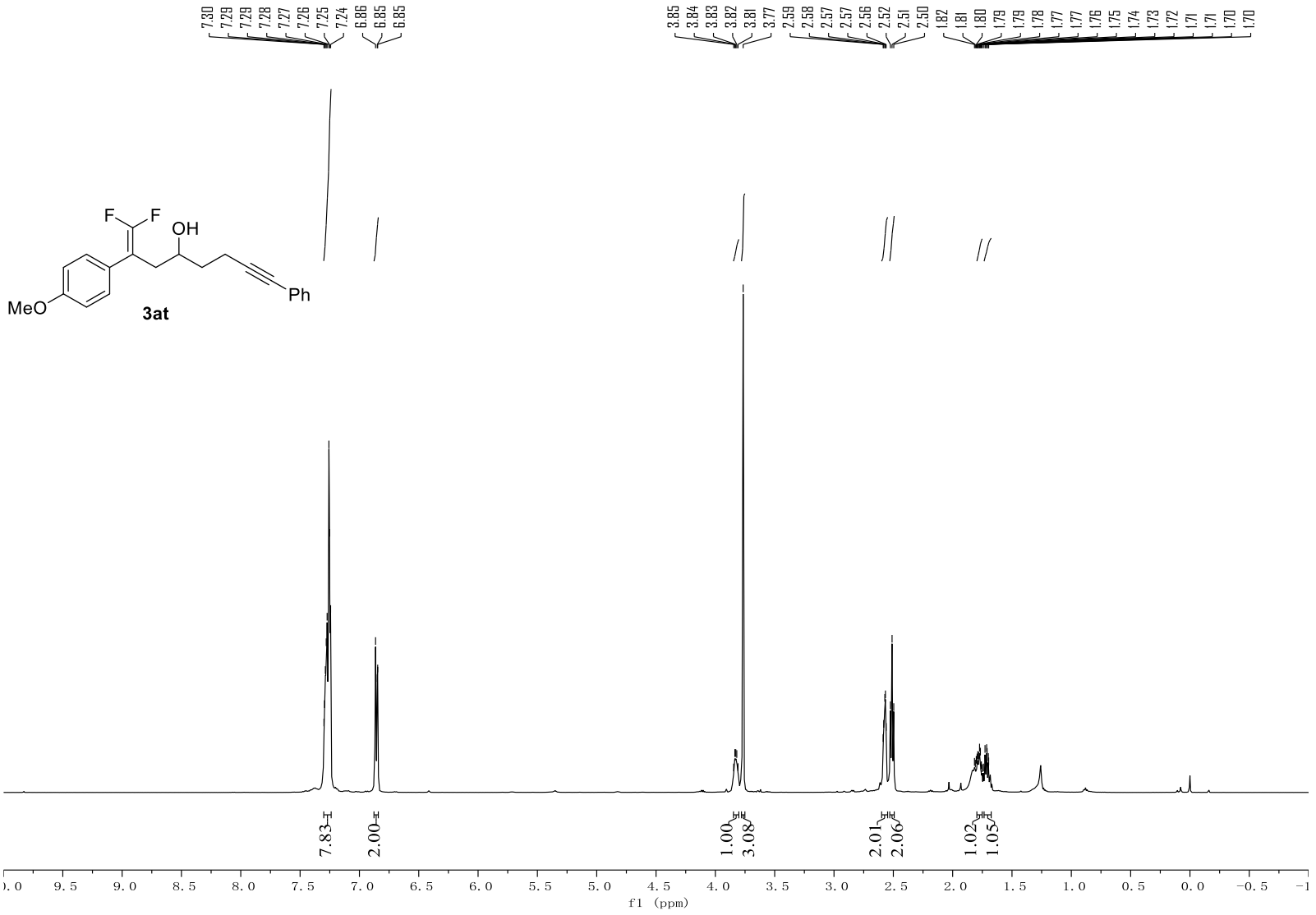
156.59
154.30
154.28
152.00
131.81
129.47
129.44
129.42
128.92
128.92
125.54
125.52
125.51
125.49
114.04
89.45
89.33
89.28
89.16
69.84
69.81
69.80
55.24
36.83
36.03
29.67
26.98
25.18
20.52
14.37
F
F
OH
4
Me
MeO
3as
f1 (ppm)


F
F
OH
4
Me
MeO
3as
-90.90
-91.01
-91.27
-91.38
1.00
1.00
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)
-90.90
-91.01
-91.27
-91.38
1.06
1.00
−90.6 −90.8 −91.0 −91.2 −91.4 −91.6 −91.8 −92.0
f1 (ppm)


7.30
7.29
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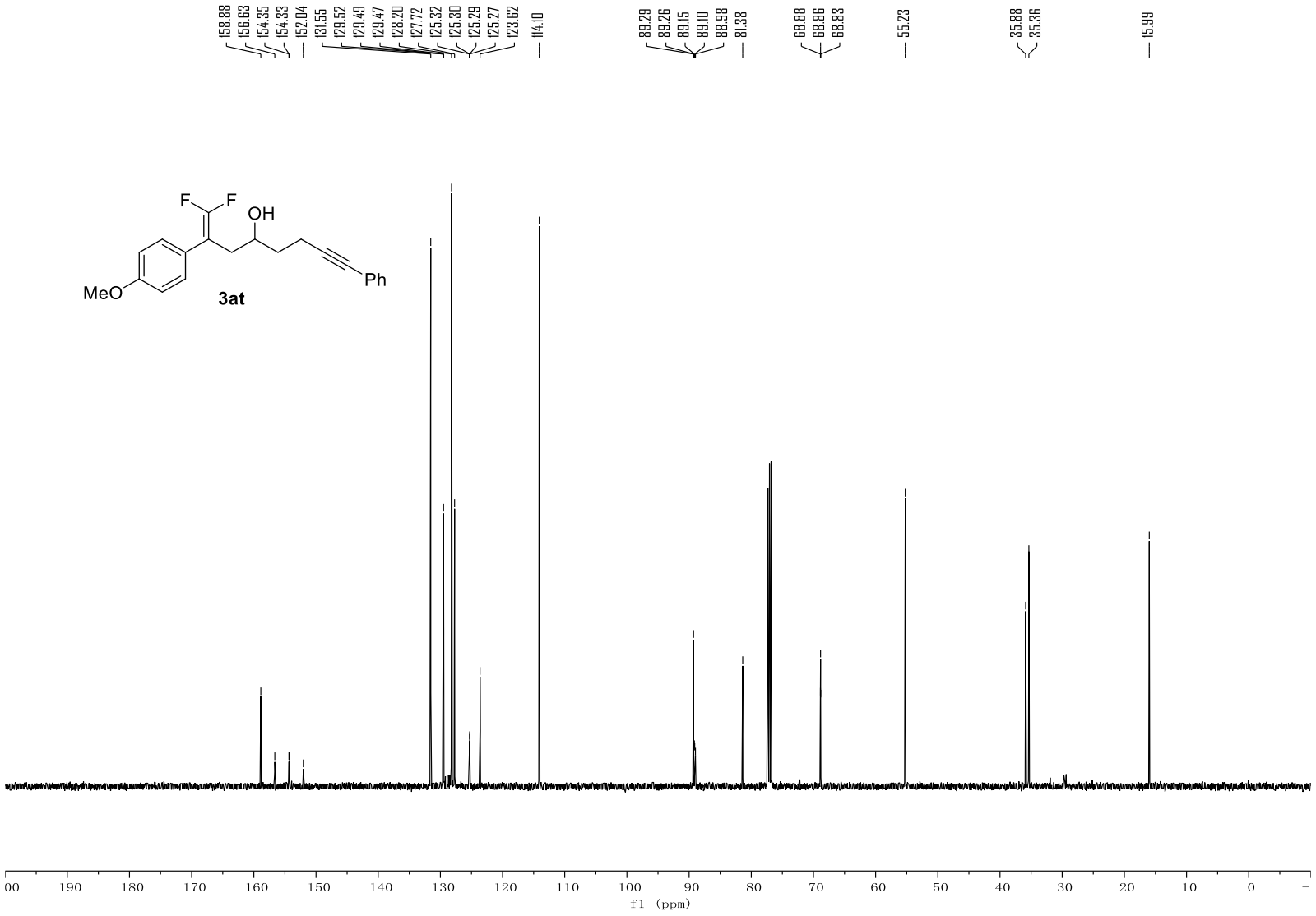
7.27
7.26
7.25
7.24
6.86
6.85
6.85
3.85
3.84
3.83
3.82
3.81
3.77
2.59
2.58
2.57
2.57
2.56
2.52
2.51
2.50
1.82
1.81
1.80
1.79
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.71
1.70
1.70
F
F
OH
MeO
Ph
3at
7.83
2.00
1.00
3.08
2.01
2.06
1.02
1.05
f1 (ppm)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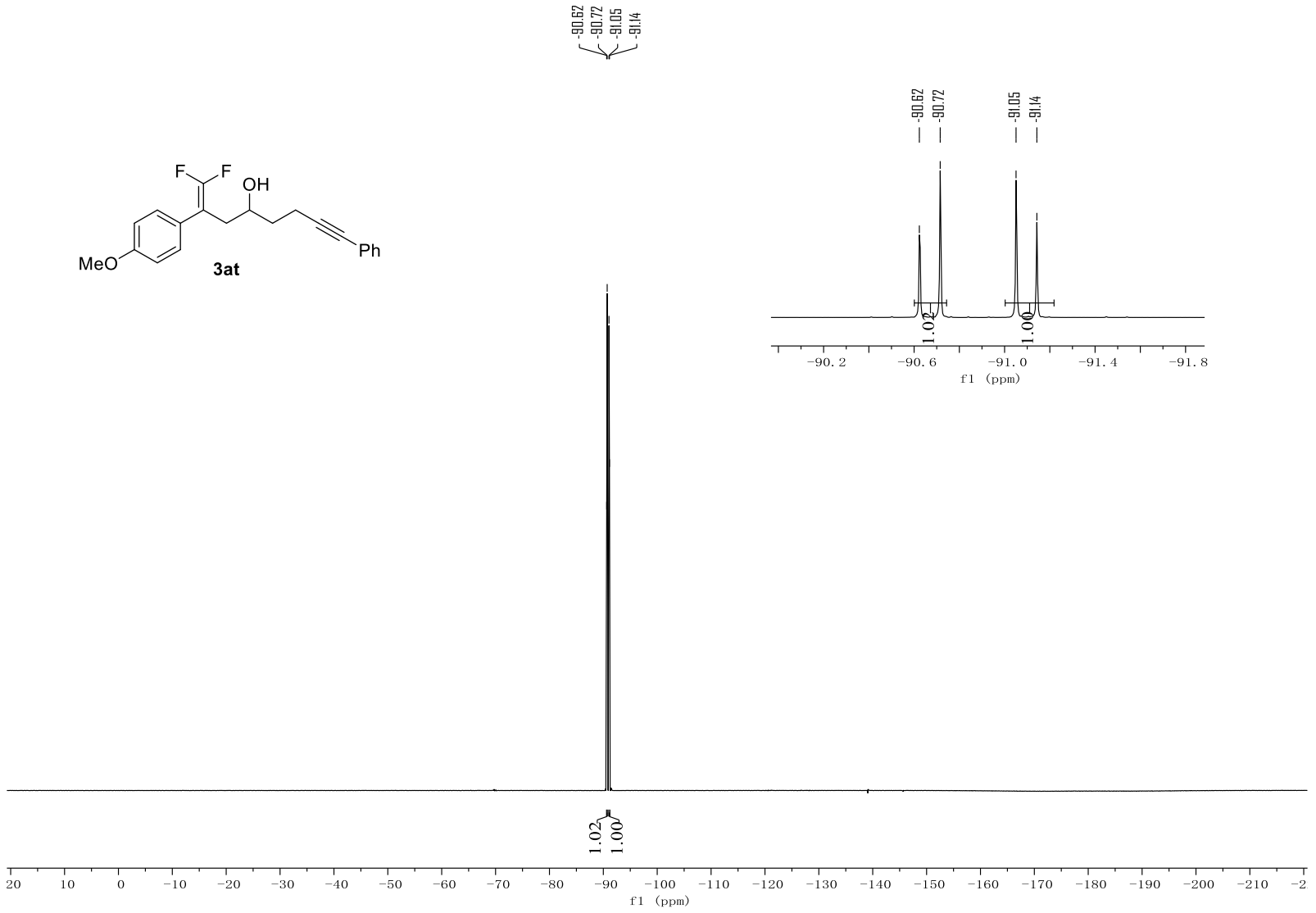
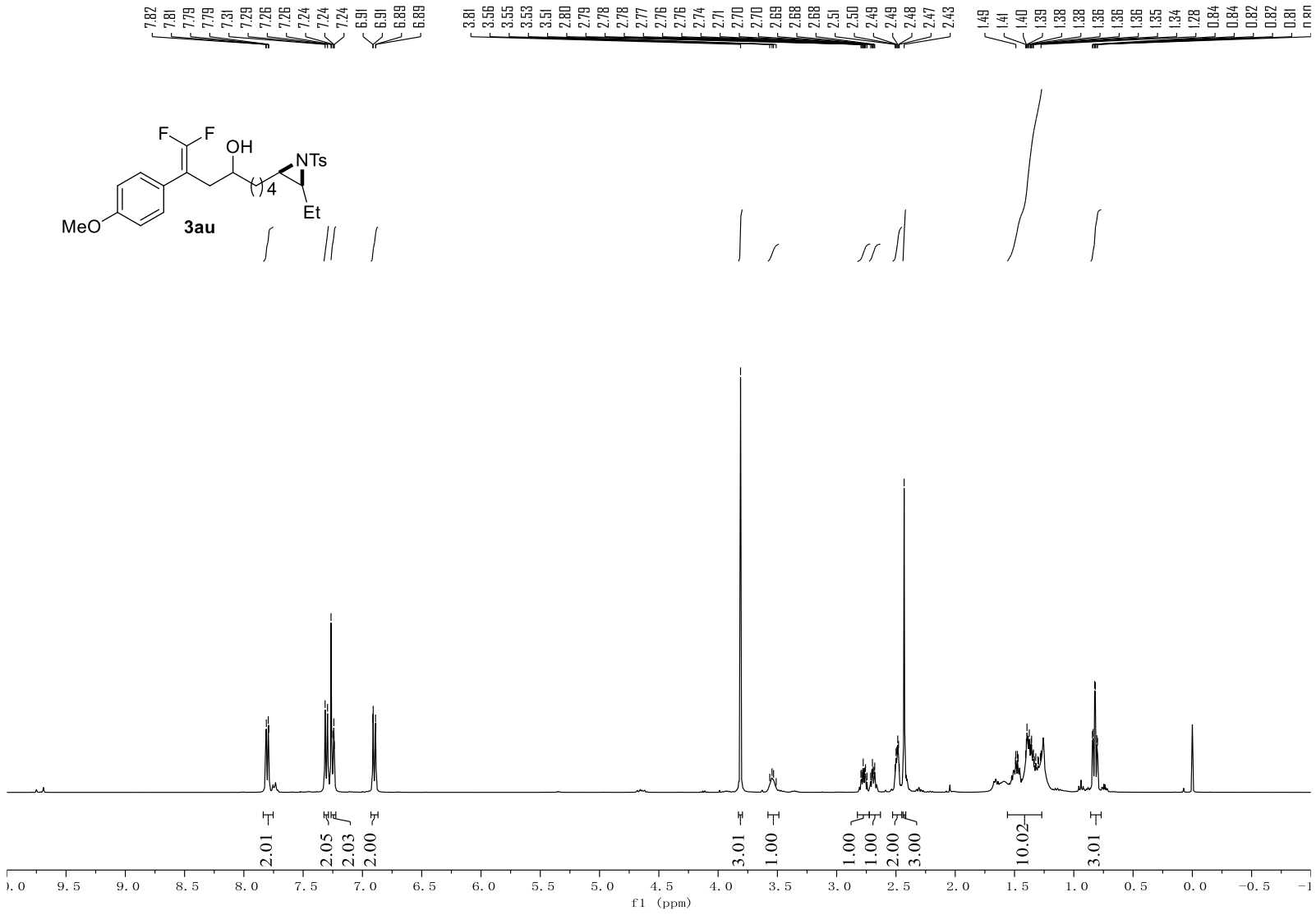
154.33
152.04
131.55
129.52
129.49
129.47
128.20
127.72
125.32
125.30
125.29
125.27
123.62
114.10
89.29
89.26
89.15
89.10
88.98
81.38
68.88
68.86
68.83
55.23
35.88
35.36
15.99
F
F
OH
MeO
Ph
3at
f1 (ppm)


-90.62
-90.72
-91.05
-91.14
F
F
OH
MeO
Ph
3at
1.02
1.00
-90.2
-90.6
-91.0
-91.4
-91.8
f1 (ppm)
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)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7.81
7.79
7.79
7.31
7.29
7.26
7.26
7.24
7.24
7.24
6.91
6.91
6.89
6.89
3.81
3.56
3.55
3.53
3.51
2.80
2.79
2.78
2.78
2.77
2.76
2.76
2.74
2.71
2.70
2.70
2.69
2.68
2.68
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2.49
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2.48
2.47
2.43
1.49
1.41
1.40
1.39
1.38
1.38
1.36
1.36
1.36
1.35
1.34
1.28
0.84
0.84
0.82
0.82
0.81
F
F
OH
NTs
4
Et
MeO
3au
2.01
2.05
2.03
2.00
3.01
1.00
1.00
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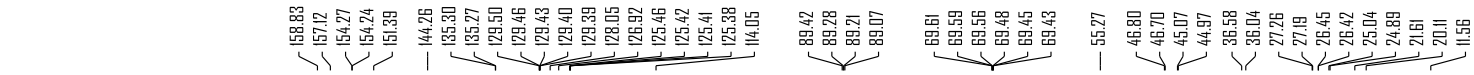
2.00
3.00
10.02
3.01
f1 (ppm)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144.26
135.30
135.27
129.50
129.46
129.43
129.40
129.39
128.05
126.92
125.46
125.42
125.41
125.38
114.05
89.42
89.28
89.21
89.07
69.61
69.59
69.56
69.48
69.45
69.43
55.27
46.80
46.70
45.07
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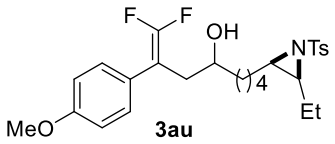
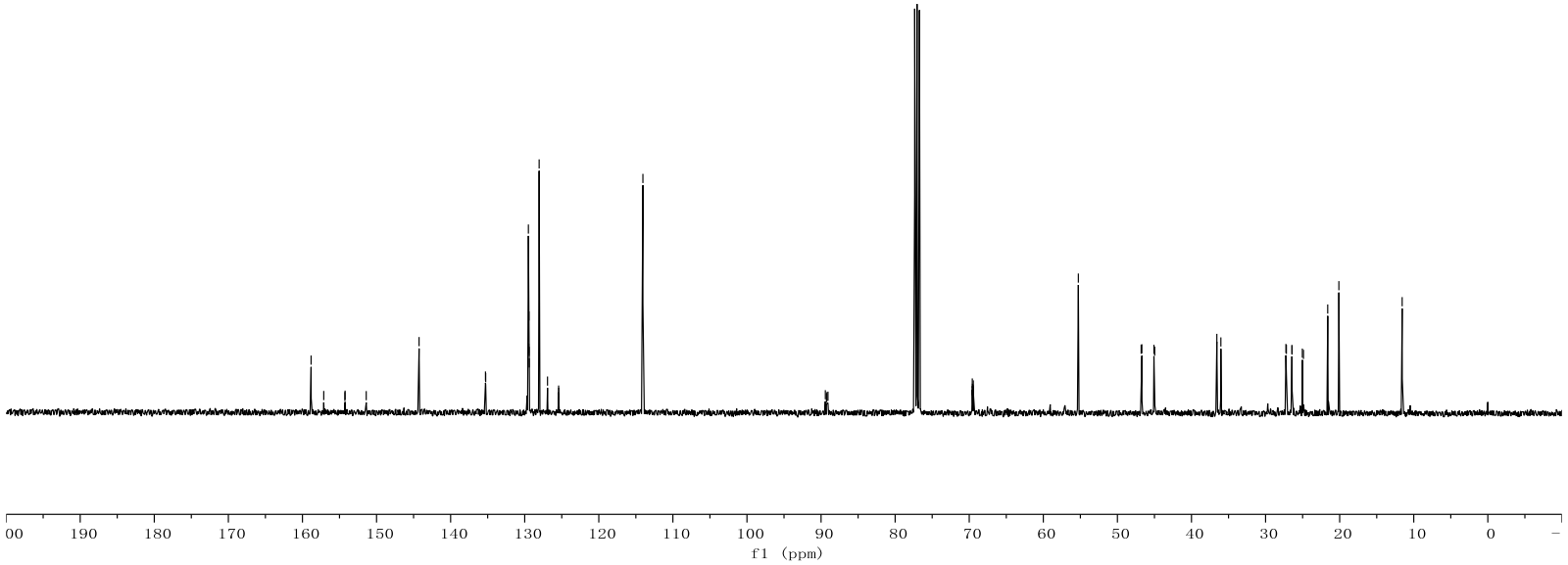
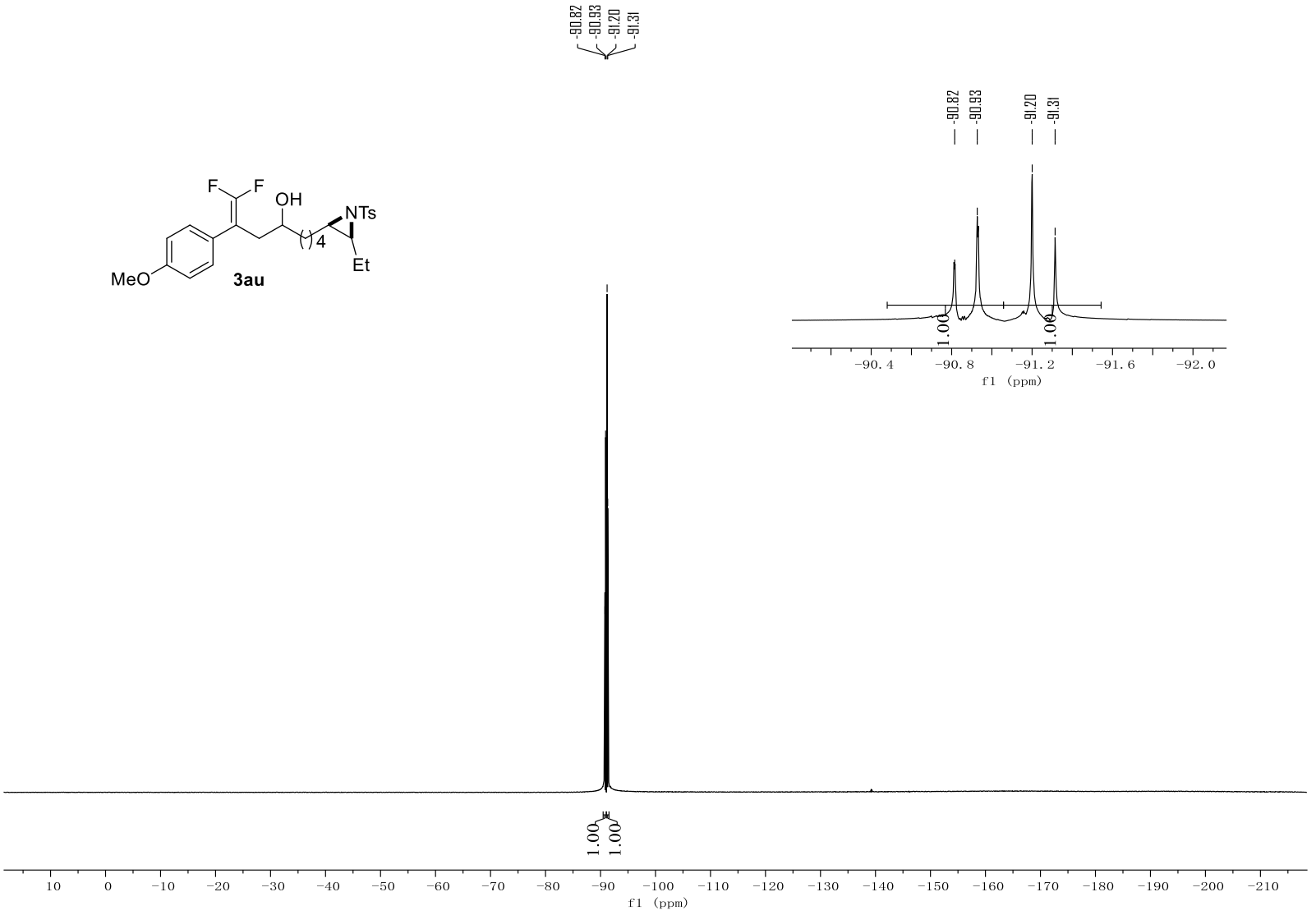
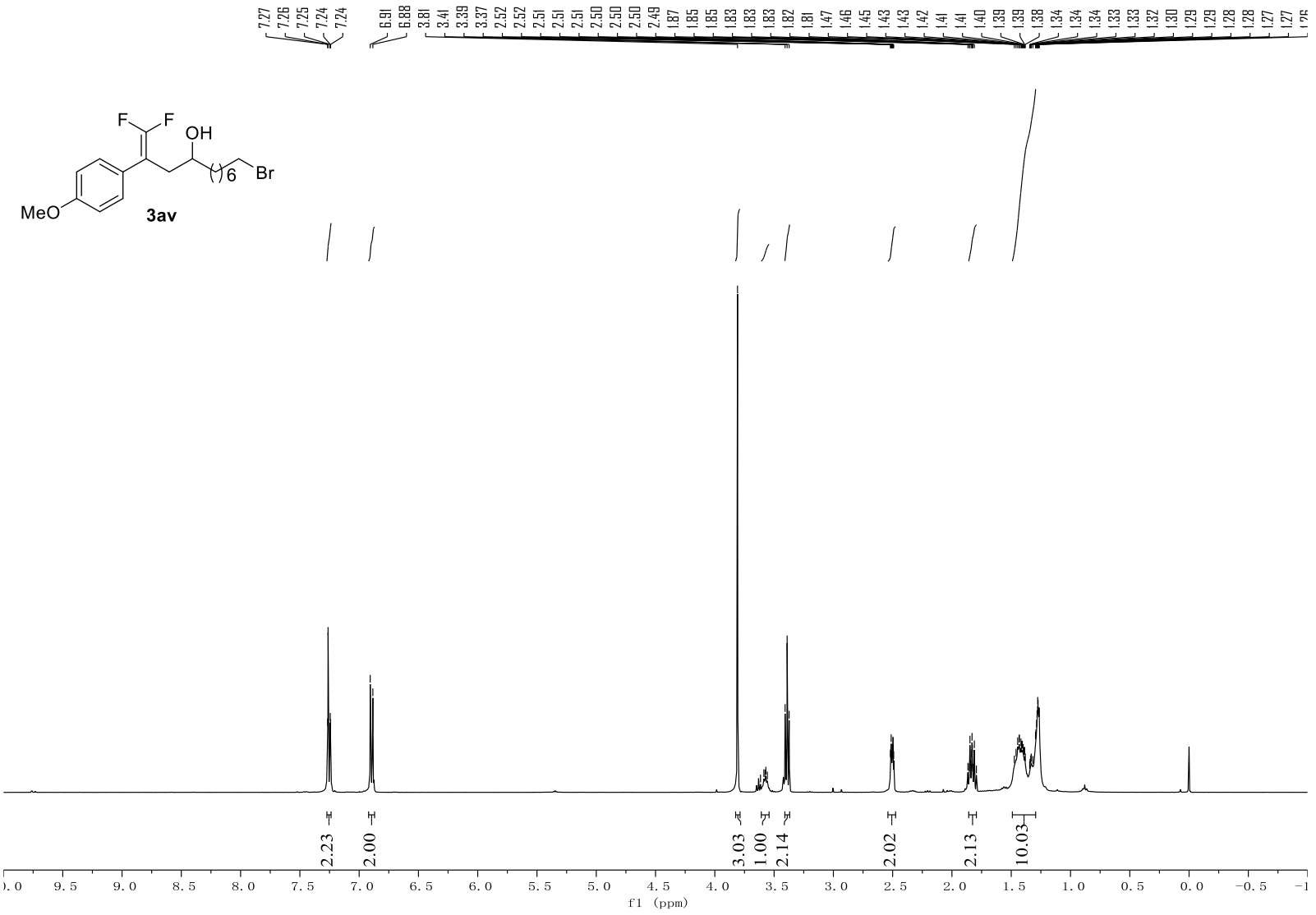
26.42
25.04
24.89
21.61
20.11
11.56

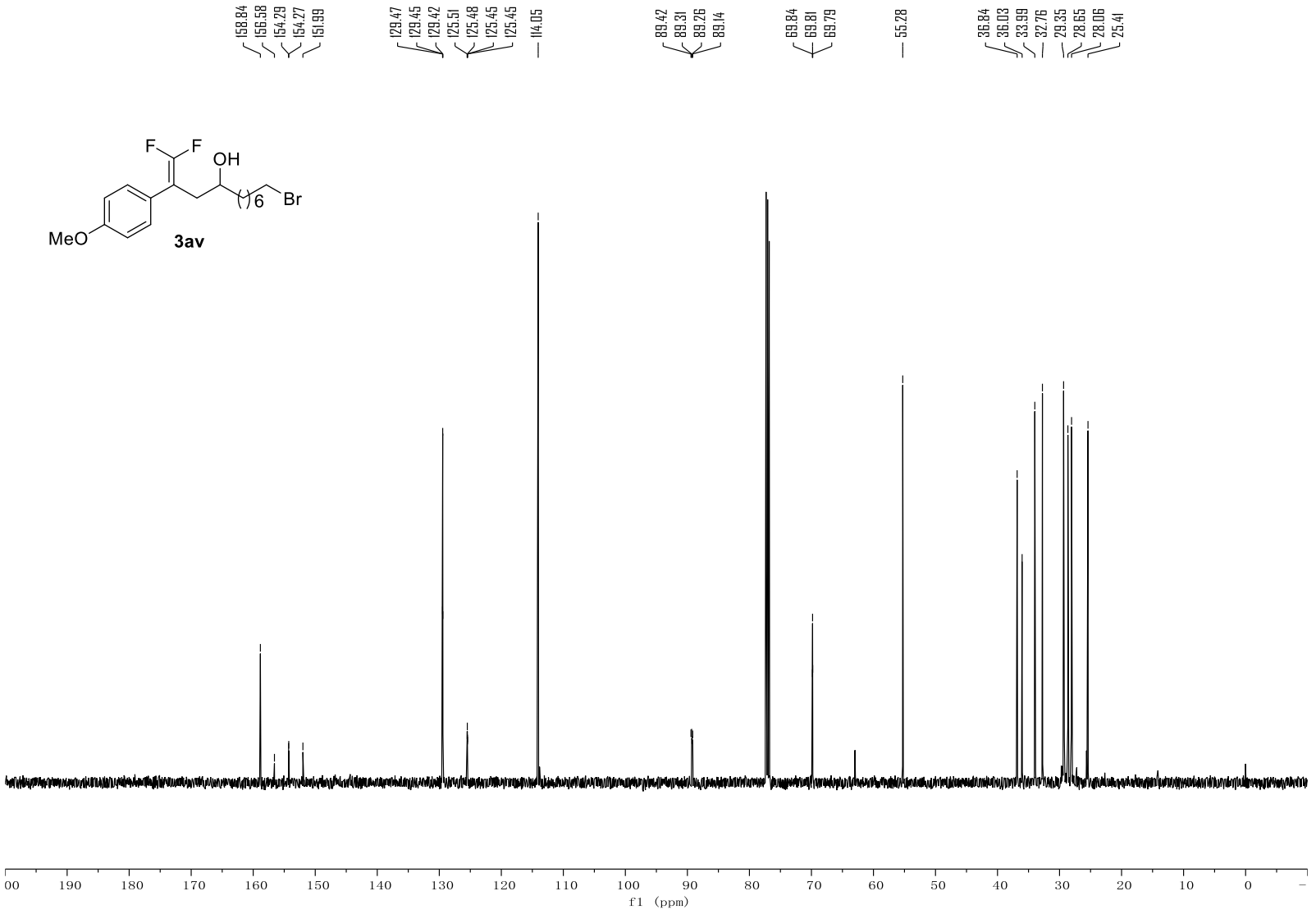

F
F
OH
NTs
4
Et
MeO

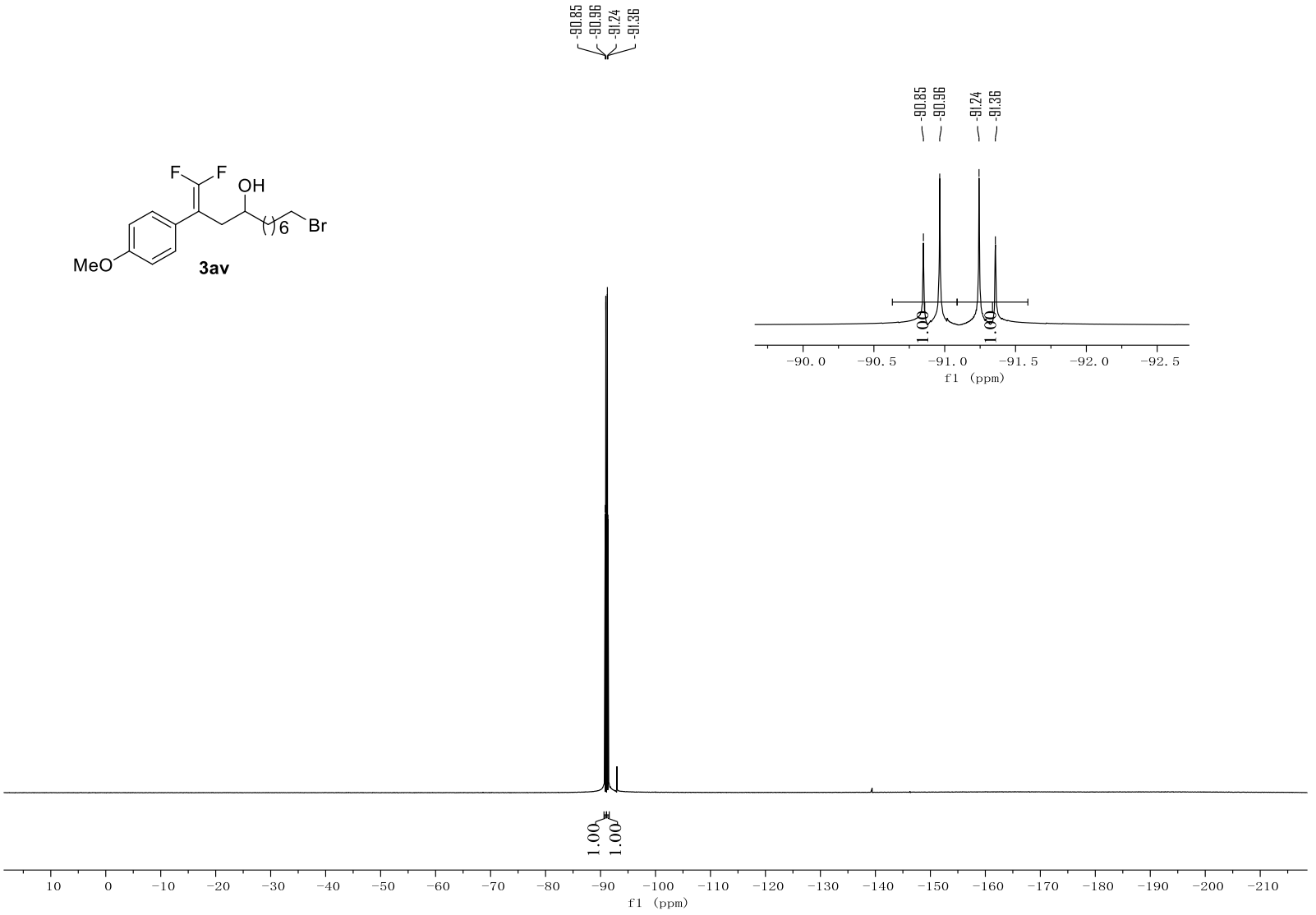
3au

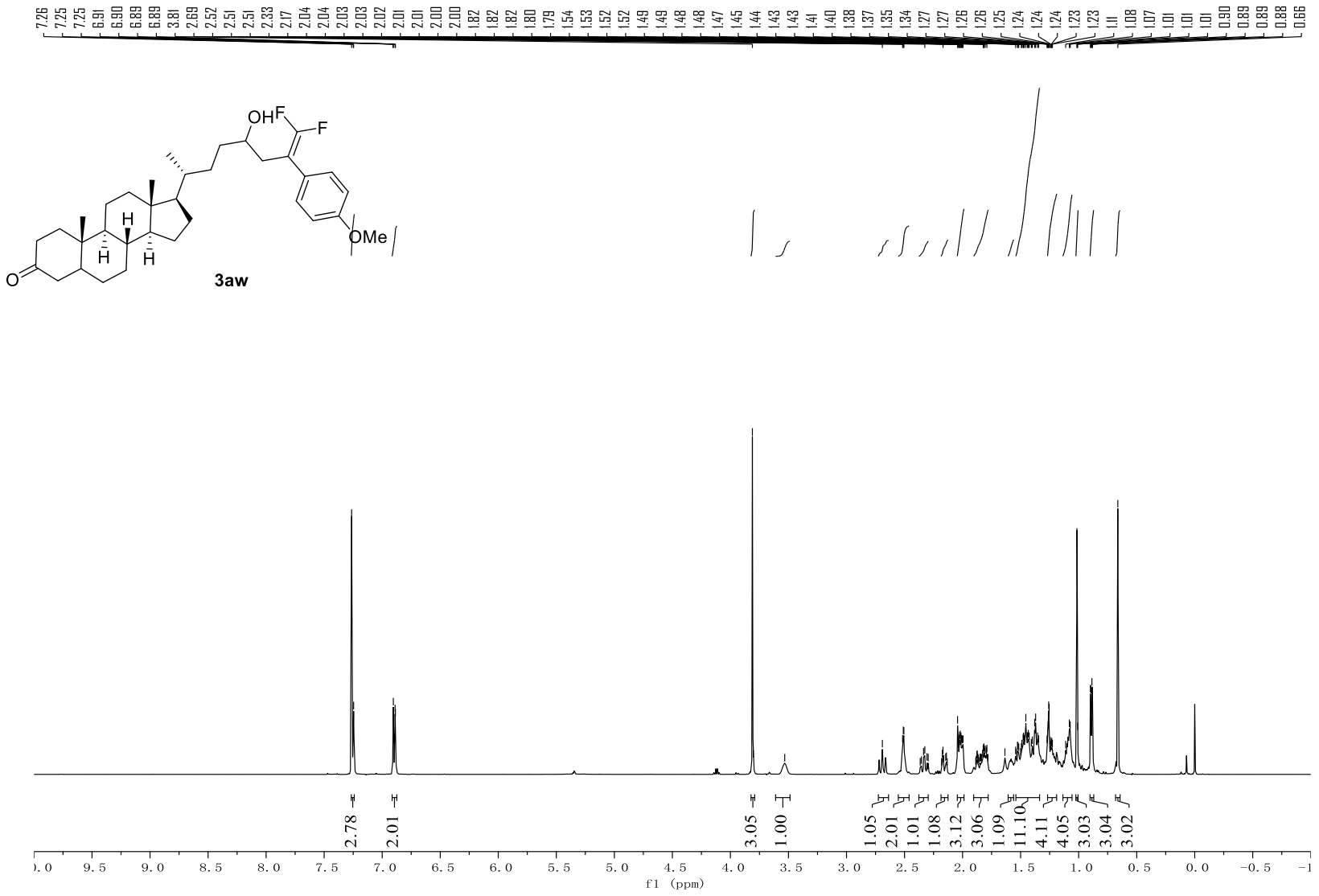

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

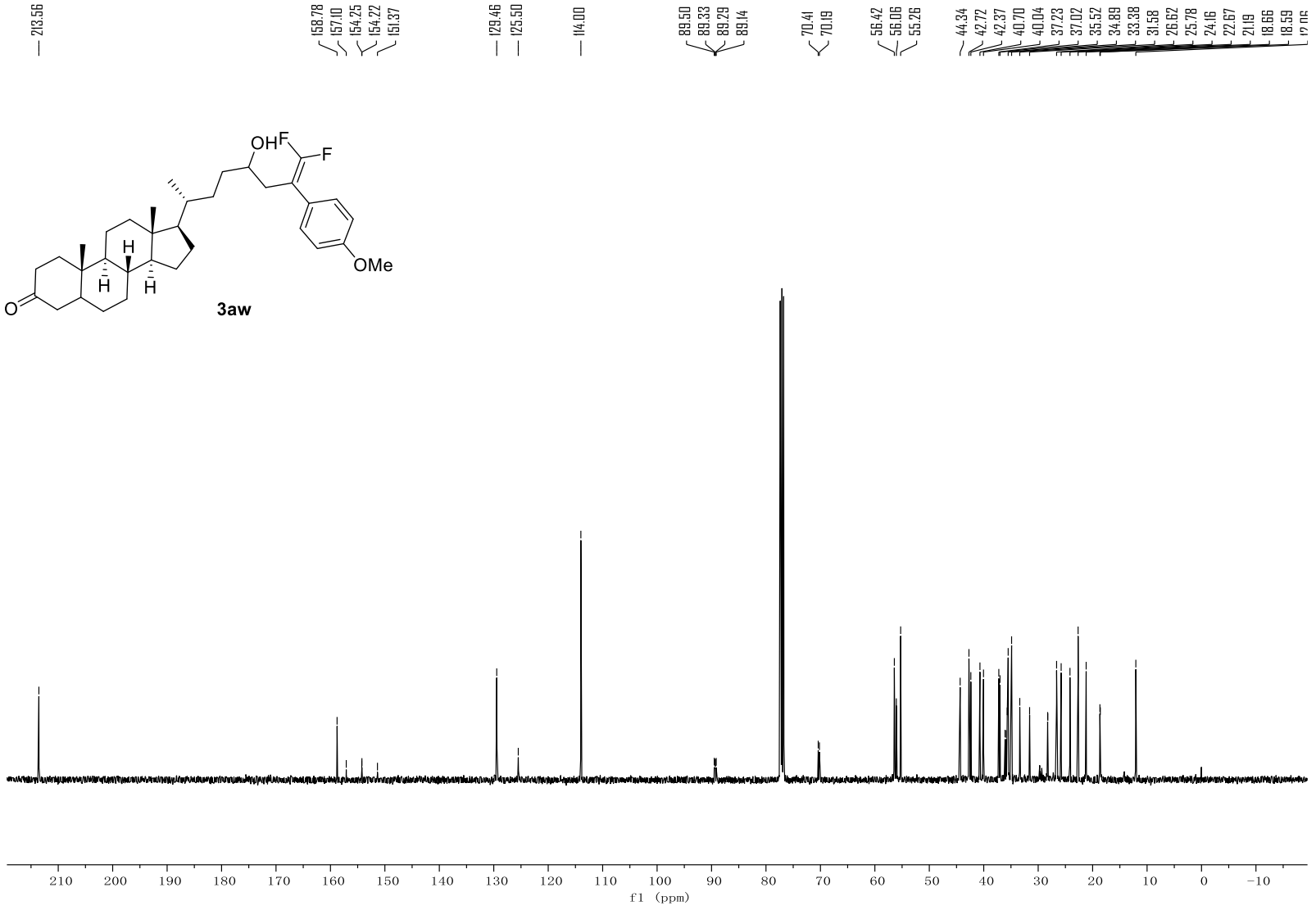

-90.82
-90.93
-91.20
-91.31
F
F
OH
NTs
4
Et
MeO
3au
1.00
1.00
-90.4
-90.8
-91.2
-91.6
-92.0
f1 (ppm)
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

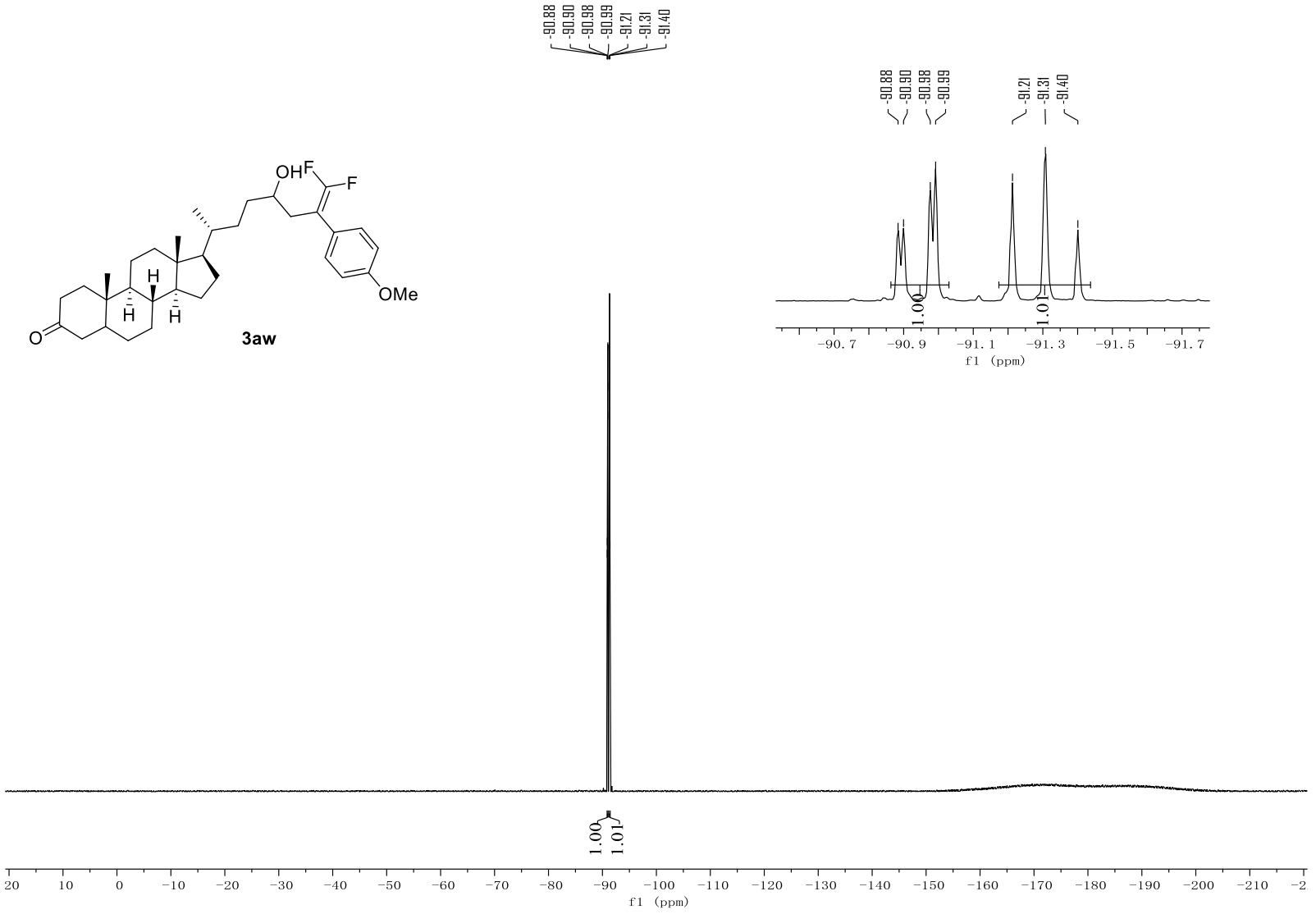

F
F
OH
6
Br
MeO
3av
7.27 7.26 7.25 7.24 7.24 6.91 6.88 3.81 3.41 3.39 3.37 2.52 2.52 2.51 2.51 2.51 2.50 2.50 2.50 2.50 2.49 1.87 1.85 1.85 1.83 1.83 1.83 1.82 1.81 1.47 1.46 1.45 1.43 1.43 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.34 1.34 1.34 1.33 1.33 1.32 1.30 1.29 1.29 1.28 1.28 1.27 1.27
2.23
2.00
3.03
1.00
2.14
2.02
2.13
10.03
f1 (ppm)

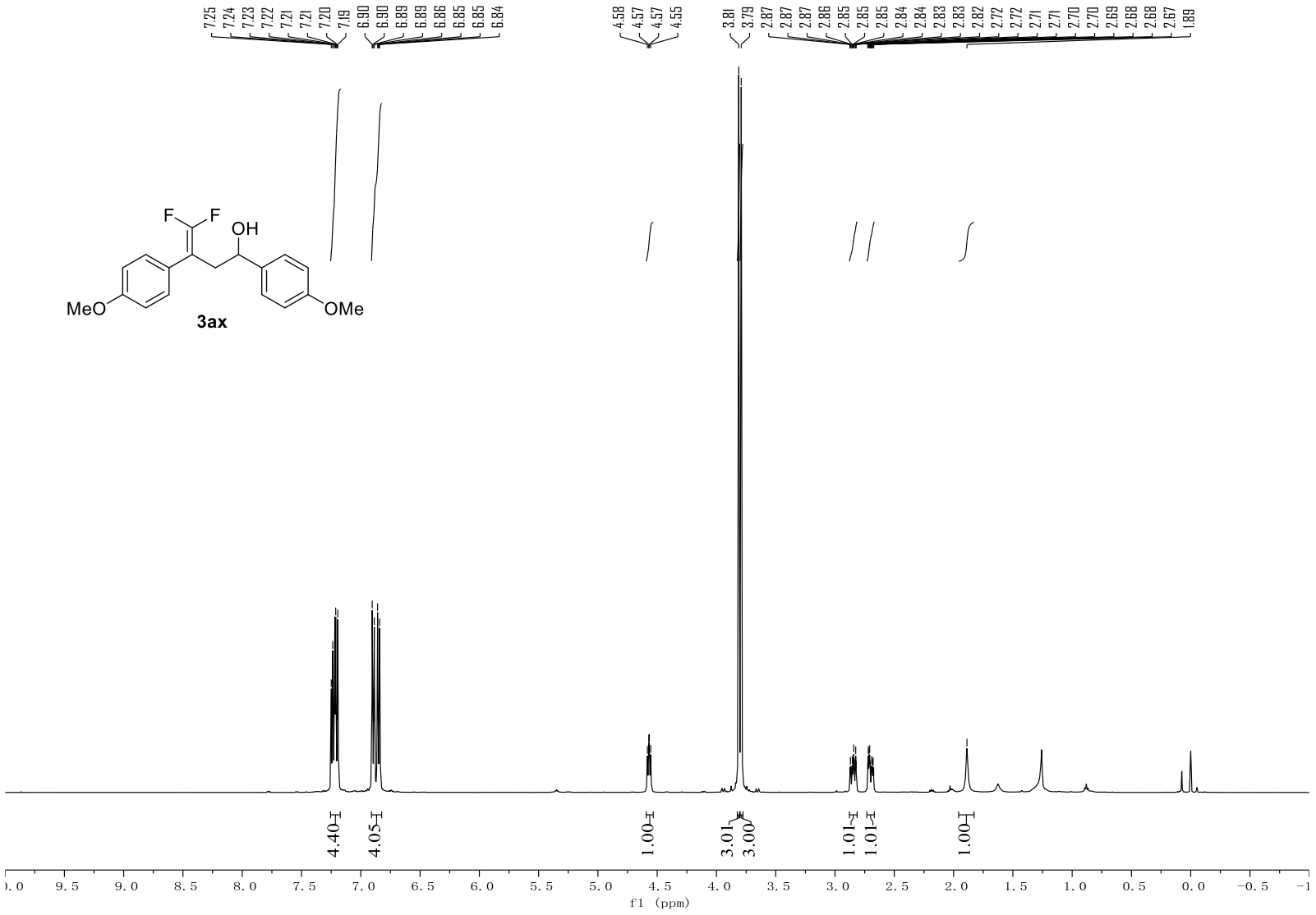

158.84
156.58
154.29
154.27
151.99
129.47
129.45
129.42
125.51
125.48
125.45
125.45
114.05
89.42
89.31
89.26
89.14
69.84
69.81
69.79
55.28
36.84
36.03
33.99
32.76
29.35
28.85
28.06
25.41
F
F
OH
6
Br
MeO
3av
f1 (ppm)

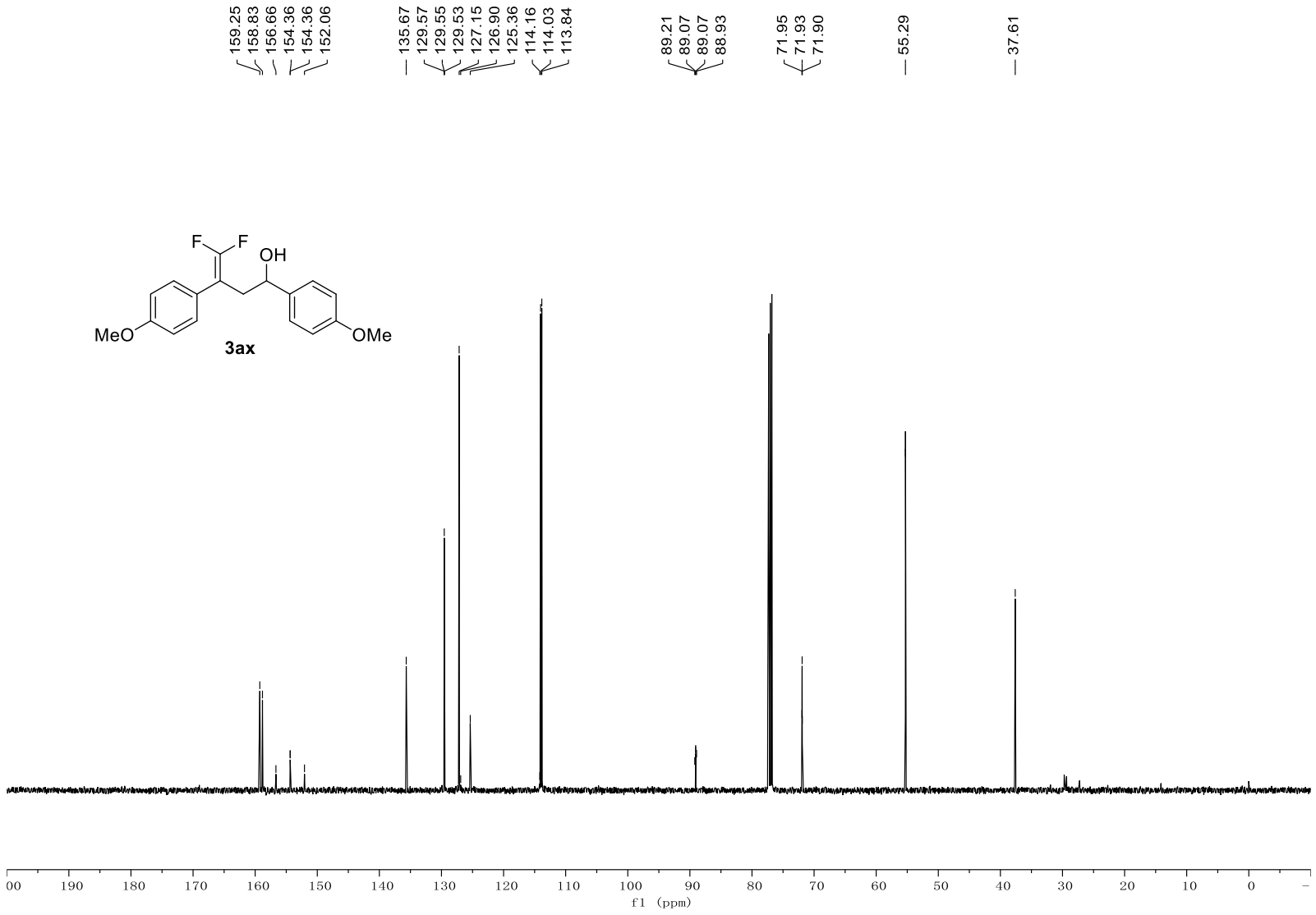

-90.85
-90.96
-91.24
-91.36
F
F
OH
6
Br
MeO
3av
1.00
1.00
-90.0
-90.5
-91.0
-91.5
-92.0
-92.5
f1 (ppm)
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

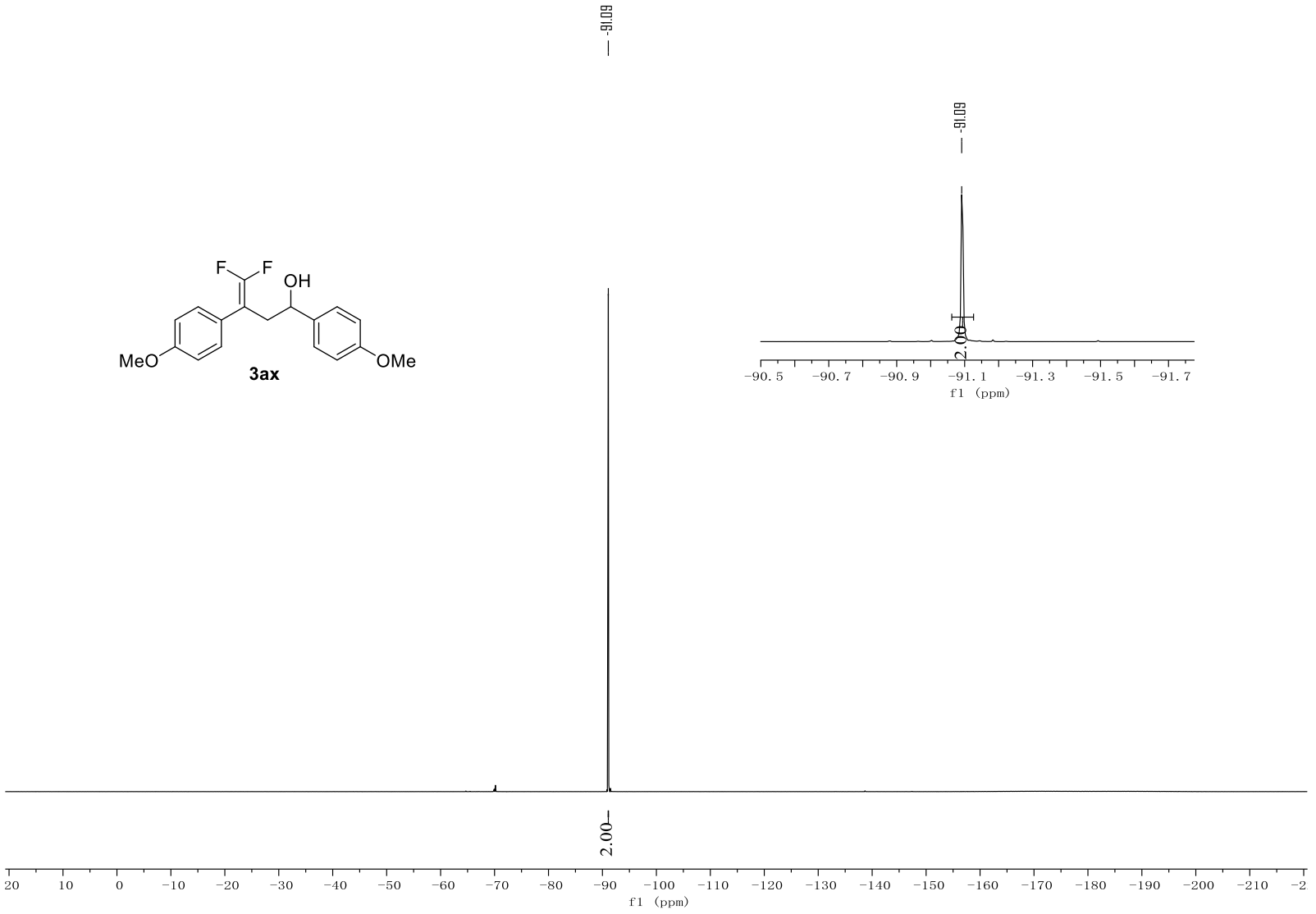

7.26 7.25 7.25 6.91 6.90 6.88 6.88 3.81 2.69 2.52 2.51 2.51 2.33 2.17 2.04 2.04 2.03 2.03 2.02 2.01 2.01 2.00 2.00 1.82 1.82 1.80 1.79 1.54 1.53 1.52 1.52 1.49 1.49 1.48 1.48 1.47 1.45 1.44 1.43 1.43 1.41 1.40 1.38 1.37 1.35 1.34 1.27 1.27 1.26 1.26 1.25 1.24 1.24 1.24 1.23 1.23 1.11 1.08 1.07 1.01 1.01 1.01 0.90 0.89 0.89 0.88 0.66
OH
F
F
OMe
H
H
H
O
3aw
2.78
2.01
3.05
1.00
1.05
2.01
1.01
1.08
3.12
3.06
1.09
11.10
4.11
4.05
3.03
3.04
3.02
f1 (ppm)

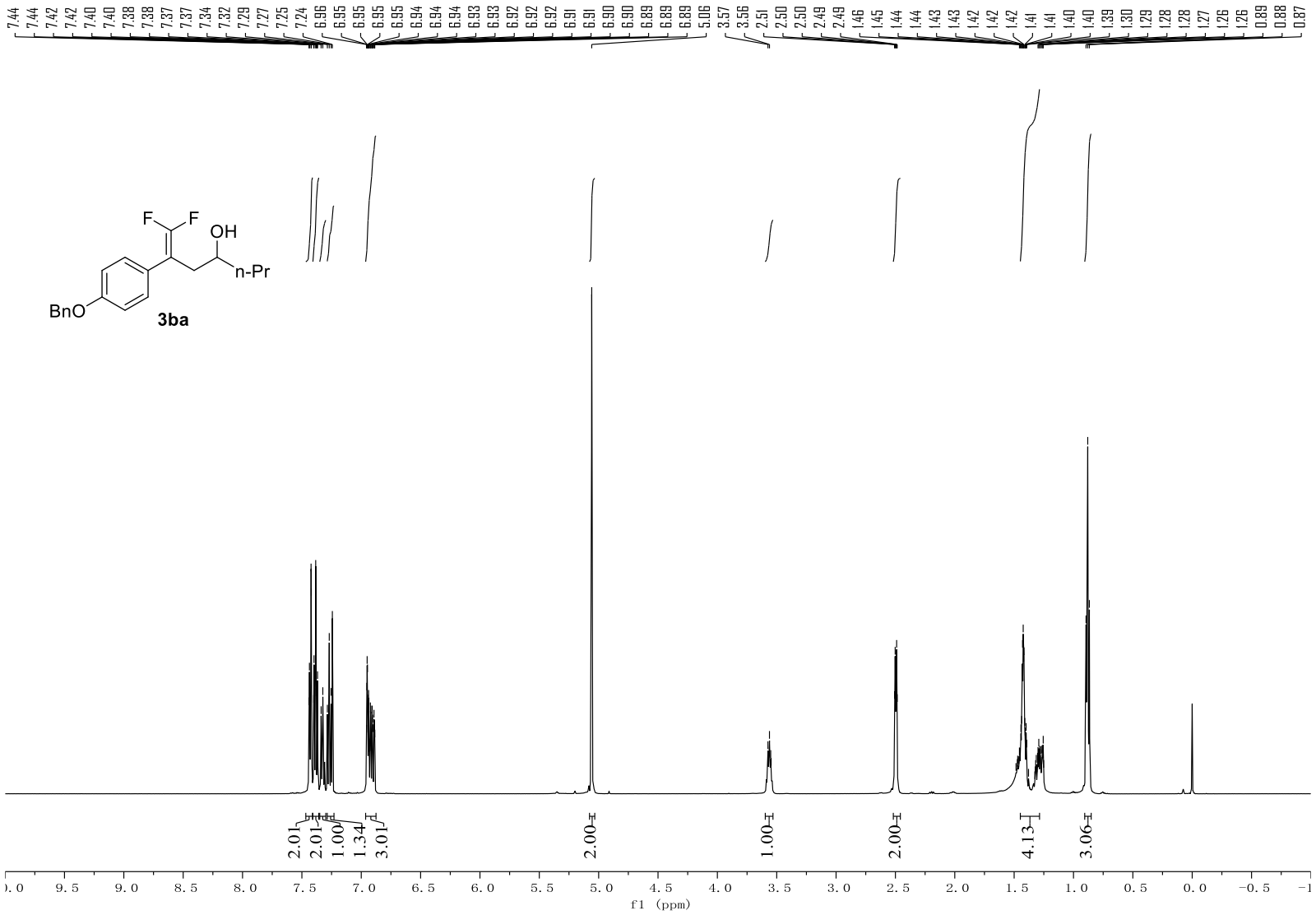

213.56
158.78
157.10
154.25
154.22
151.37
129.46
125.50
114.00
89.50
89.33
89.29
89.14
70.41
70.19
56.42
56.06
55.26
44.34
42.72
42.37
40.70
40.04
37.23
37.02
35.52
34.89
33.38
31.58
26.62
25.78
24.16
22.67
21.19
18.66
18.59
OH
F
F
OMe
H
H
H
O
3aw
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

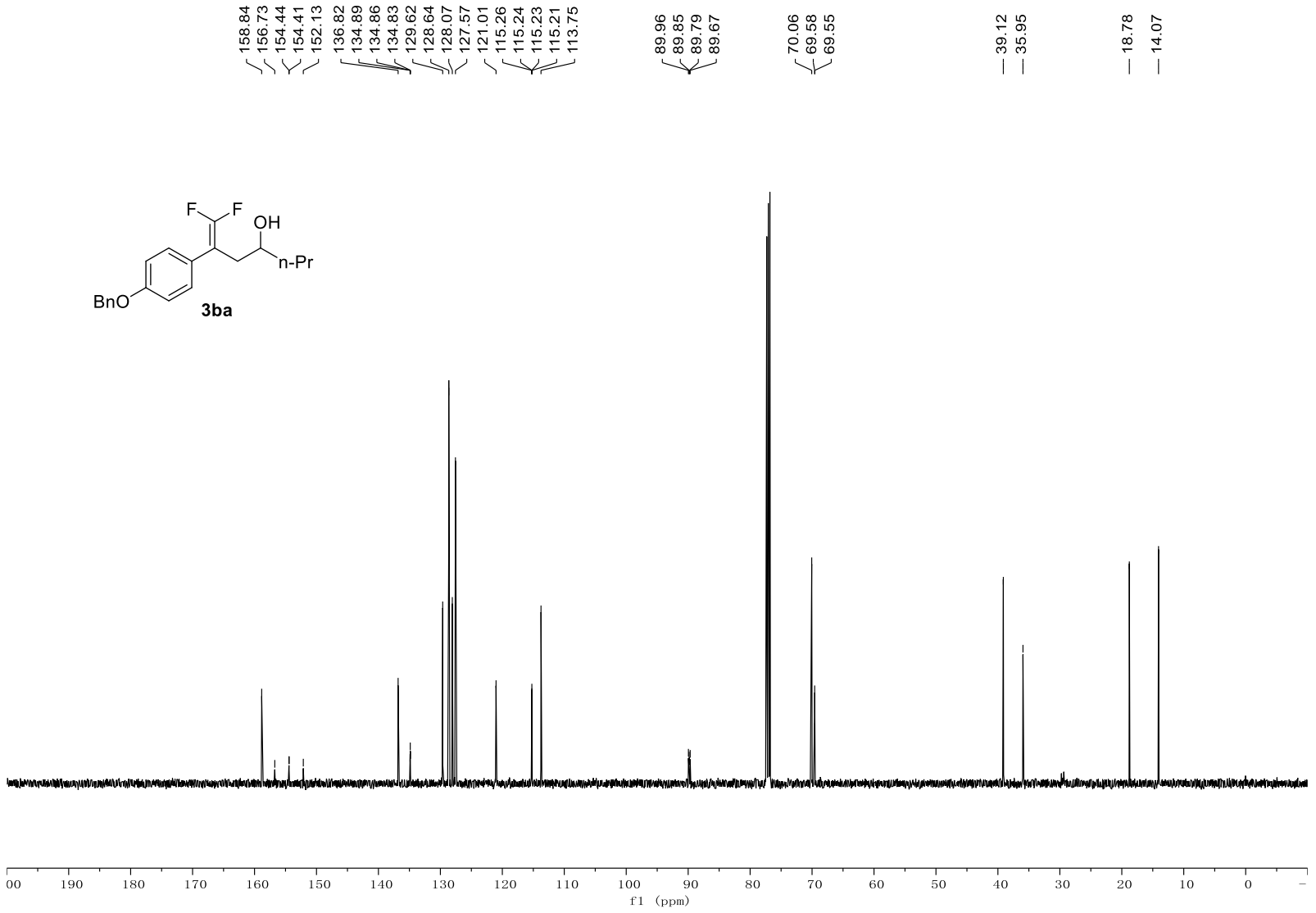

-90.88
-90.90
-90.98
-90.99
-91.21
-91.31
-91.40
OH
F
F
OMe
H
H
H
O
3aw
1.00
1.01
-90.7
-90.9
-91.1
-91.3
-91.5
-91.7
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

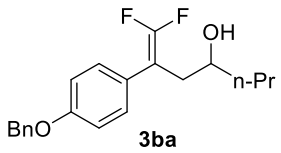

7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.19
6.90
6.90
6.89
6.89
6.86
6.85
6.85
6.84
4.58
4.57
4.57
4.55
3.81
3.79
2.87
2.87
2.87
2.86
2.85
2.85
2.84
2.84
2.83
2.83
2.82
2.72
2.72
2.71
2.71
2.70
2.70
2.69
2.68
2.68
2.67
1.89
F
F
OH
MeO
OMe
3ax
4.40
4.05
1.00
3.01
3.00
1.01
1.01
1.00
f1 (ppm)


159.25
158.83
156.66
154.36
154.36
152.06
135.67
129.57
129.55
129.53
127.15
126.90
125.36
114.16
114.03
113.84
89.21
89.07
89.07
88.93
71.95
71.93
71.90
55.29
37.61
F
F
OH
MeO
OMe
3ax
f1 (ppm)


-91.08
F
F
OH
MeO
OMe
3ax
2.00
-90.5
-90.7
-90.9
-91.1
-91.3
-91.5
-91.7
f1 (ppm)
2.00
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)


7.44 7.44 7.42 7.42 7.40 7.40 7.38 7.37 7.37 7.34 7.32 7.29 7.27 7.25 7.24 6.96 6.95 6.95 6.95 6.94 6.94 6.94 6.93 6.93 6.92 6.92 6.92 6.91 6.91 6.90 6.90 6.89 6.89 6.89 5.06 3.57 3.56 2.51 2.50 2.50 2.49 2.49 1.46 1.45 1.44 1.44 1.43 1.43 1.42 1.42 1.42 1.41 1.41 1.40 1.40 1.39 1.30 1.29 1.28 1.28 1.27 1.26 1.26 0.89 0.88 0.87
F
F
OH
n-Pr
BnO
3ba
2.01
2.01
1.00
1.34
3.01
2.00
1.00
2.00
4.13
3.06
f1 (ppm)

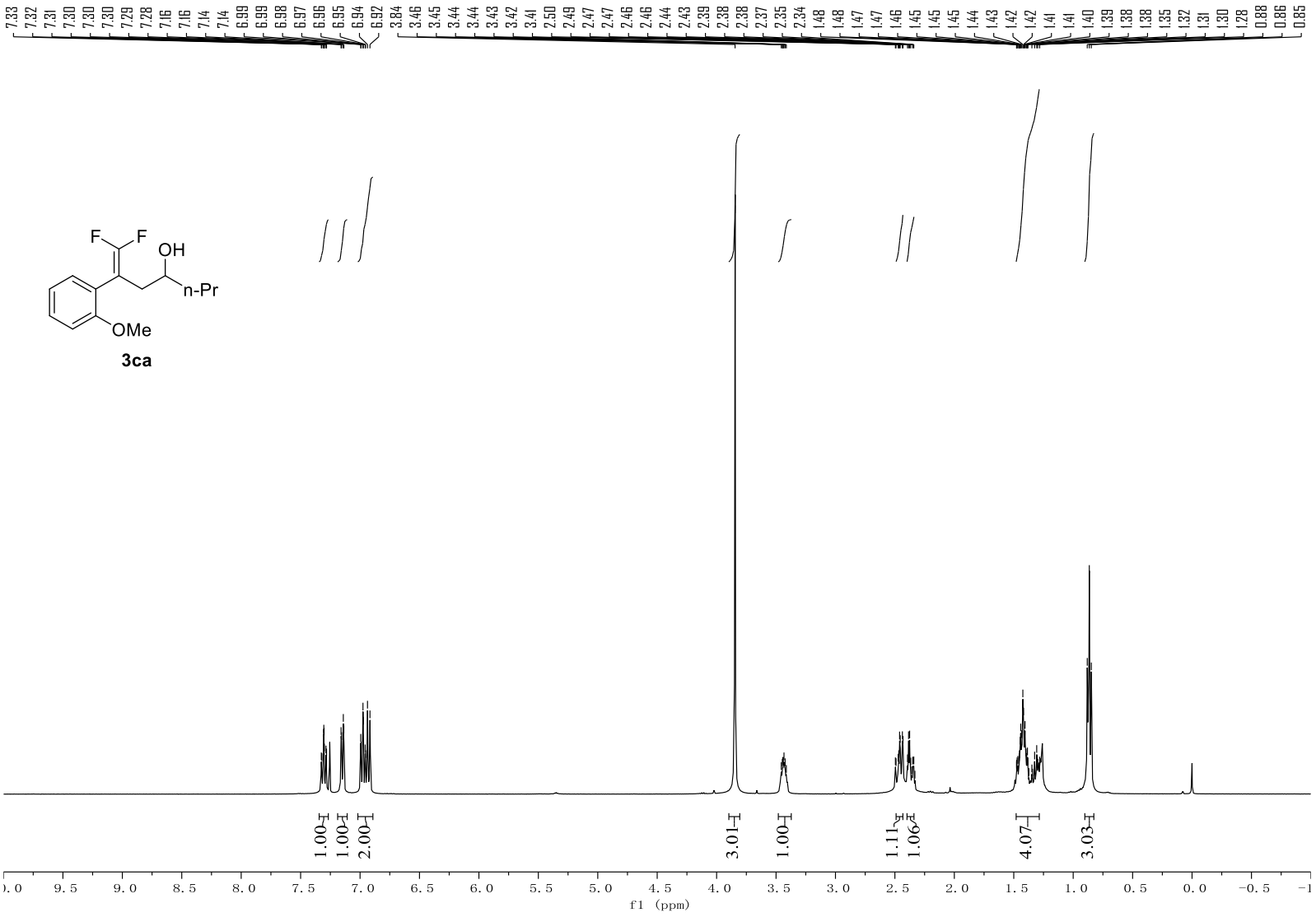

158.84
156.73
154.44
154.41
152.13
136.82
134.89
134.86
134.83
129.62
128.64
128.07
127.57
121.01
115.26
115.24
115.23
115.21
113.75
89.96
89.85
89.79
89.67
70.06
69.58
69.55
39.12
35.95
18.78
14.07
F
F
OH
n-Pr
BnO
3ba
f1 (ppm)

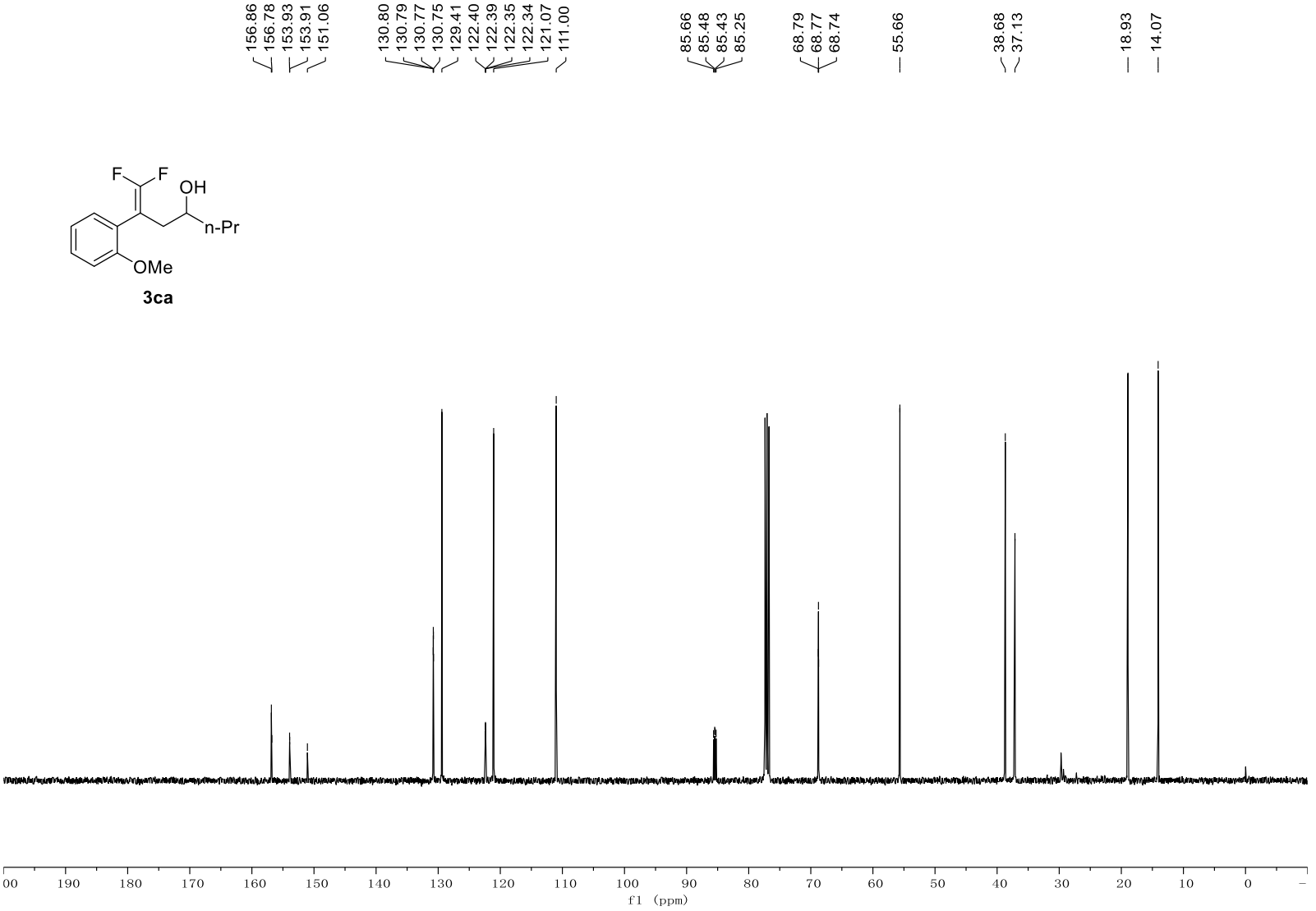

F
F
OH
n-Pr
BnO

3ba

-89.27
-89.35
-90.05
-90.13
1.00
1.01
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)

-89.27
-89.35
-90.05
-90.13
1.00
1.01
−89.0 −89.5 −90.0 −90.5 −91.0
f1 (ppm)


F
F
OH
n-Pr
OMe
3ca
f1 (ppm)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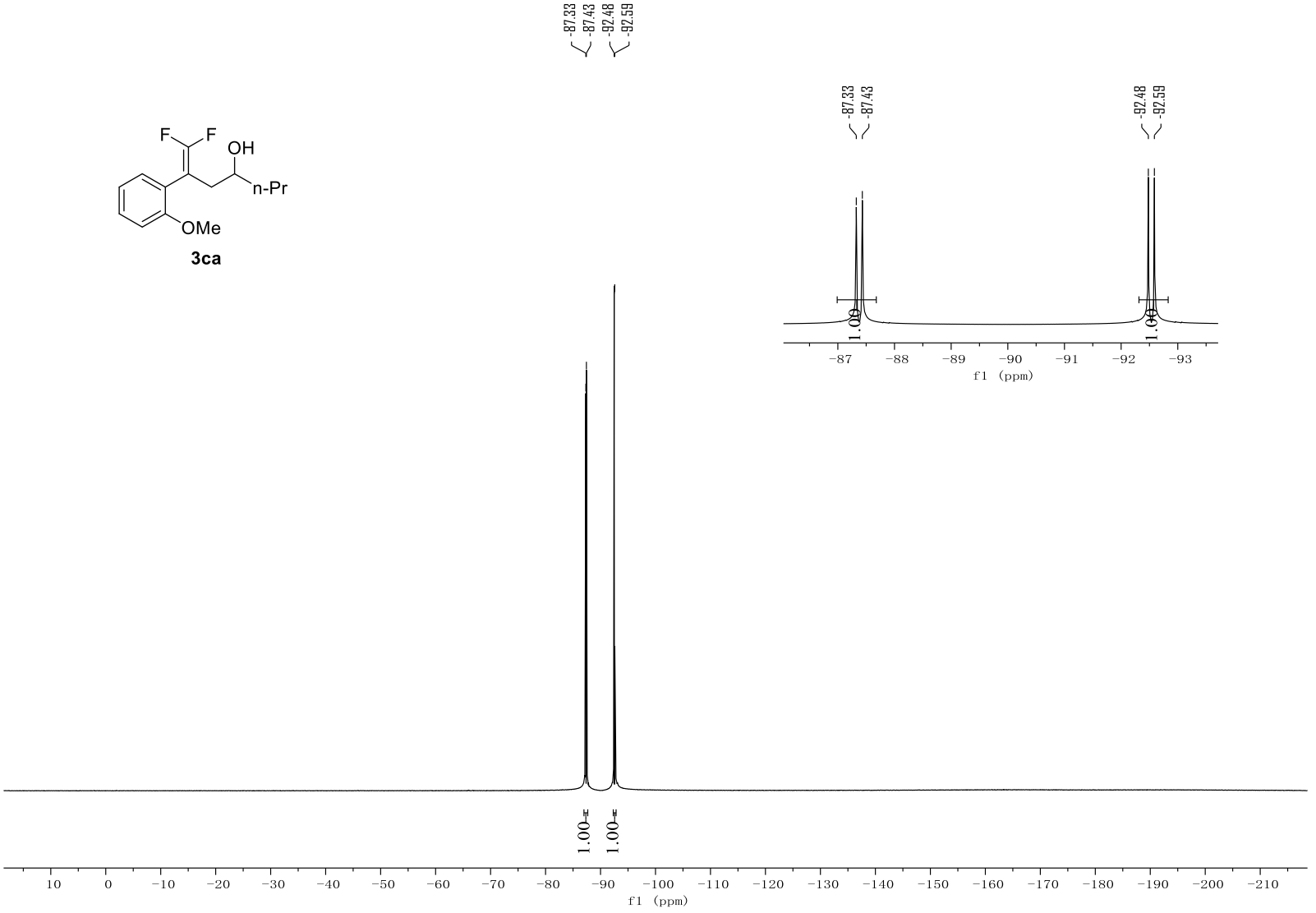
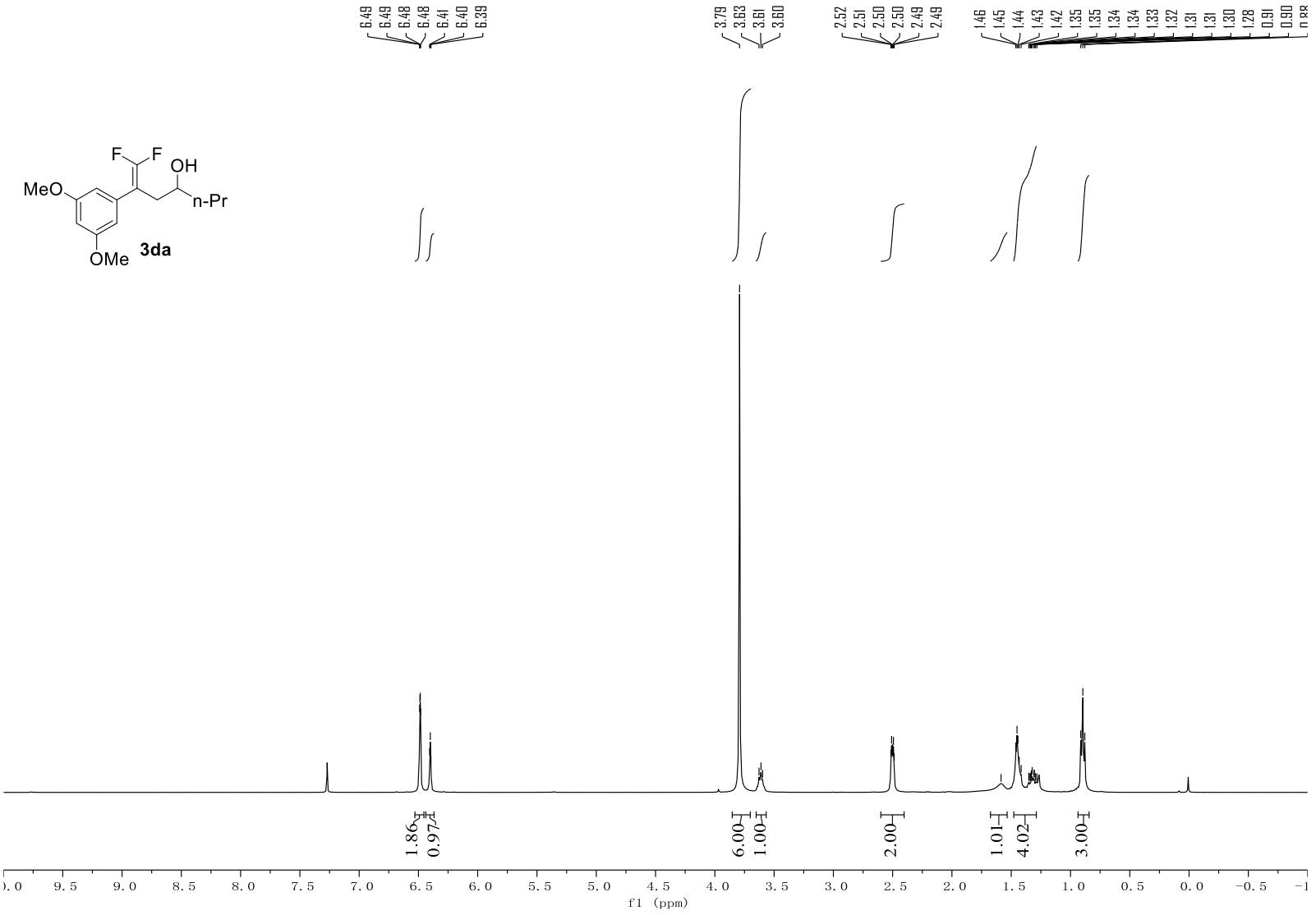
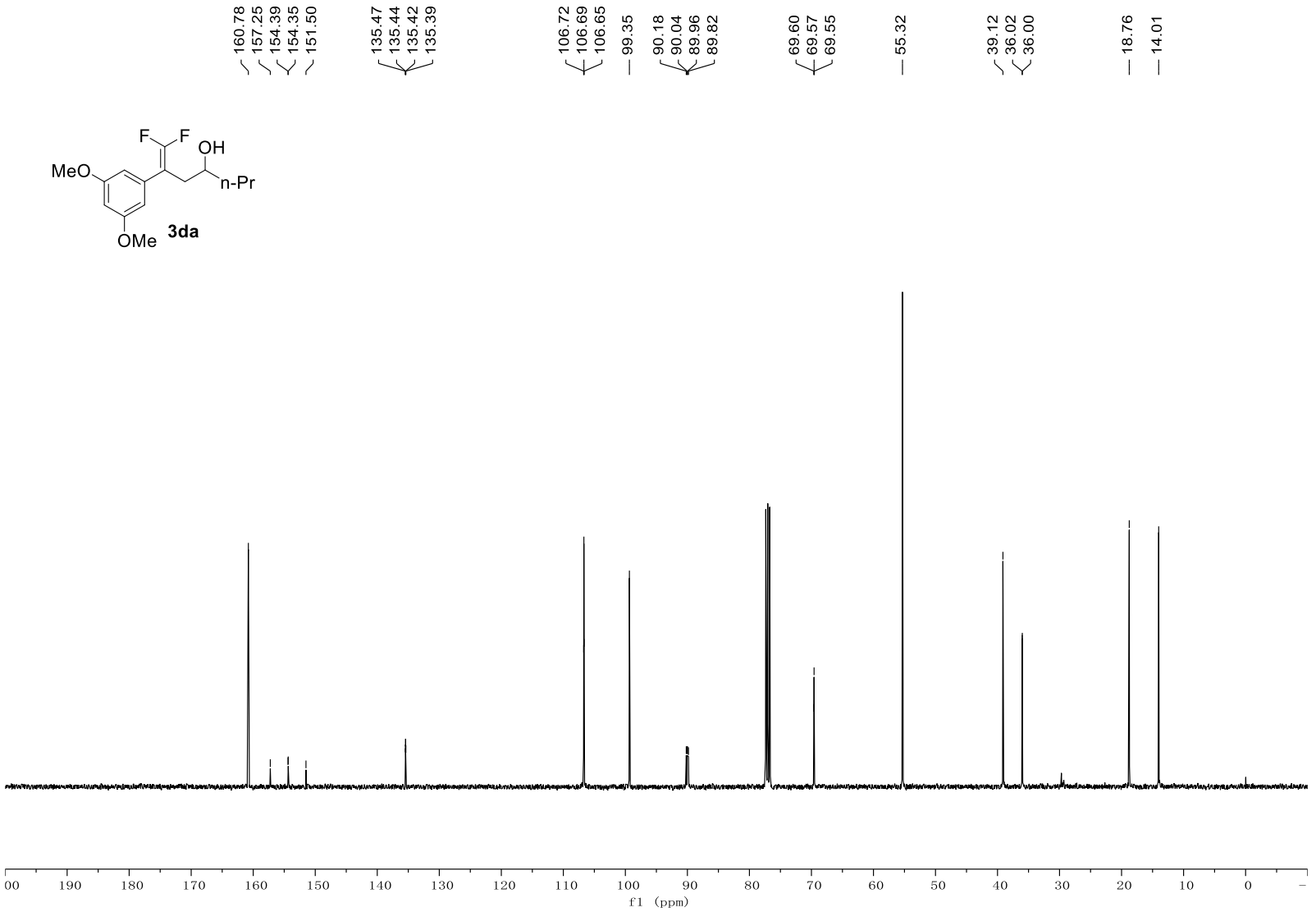
156.78
153.93
153.91
151.06
130.80
130.79
130.77
130.75
129.41
122.40
122.39
122.35
122.34
121.07
111.00
85.66
85.48
85.43
85.25
68.79
68.77
68.74
55.66
38.68
37.13
18.93
14.07
F
F
OH
n-Pr
OMe
3ca
f1 (ppm)


F
F
OH
n-Pr
OMe
3ca
-87.33
-87.43
-92.48
-92.59
1.00
1.00
f1 (ppm)
f1 (ppm)


6.49
6.49
6.48
6.48
6.41
6.40
6.39
3.79
3.63
3.61
3.60
2.52
2.51
2.50
2.50
2.49
2.49
1.46
1.45
1.44
1.43
1.42
1.35
1.35
1.34
1.34
1.33
1.32
1.31
1.31
1.30
1.28
0.91
0.90
F
F
OH
MeO
n-Pr
OMe
3da
1.86
0.97
6.00
1.00
2.00
1.01
4.02
3.00
f1 (ppm)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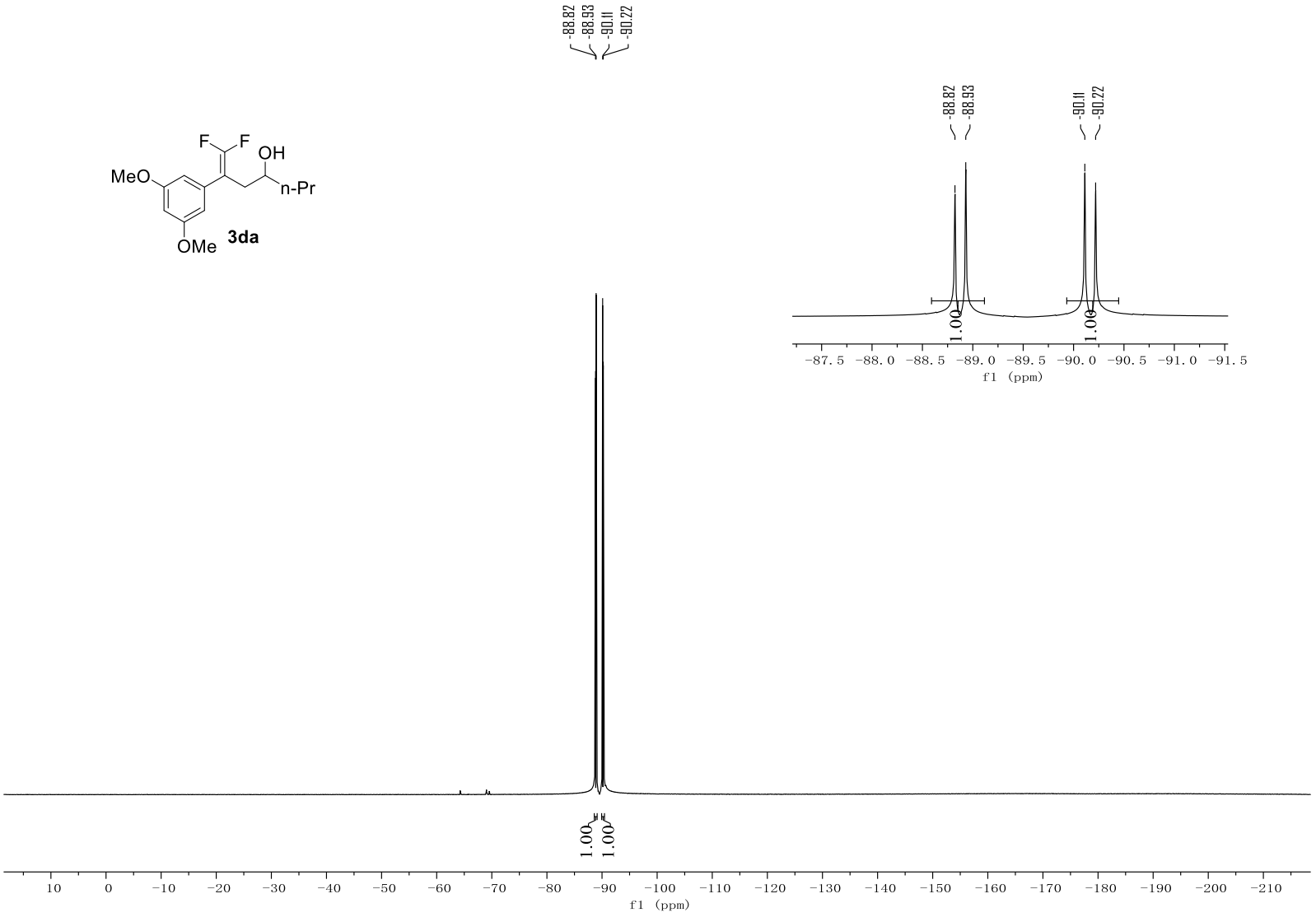
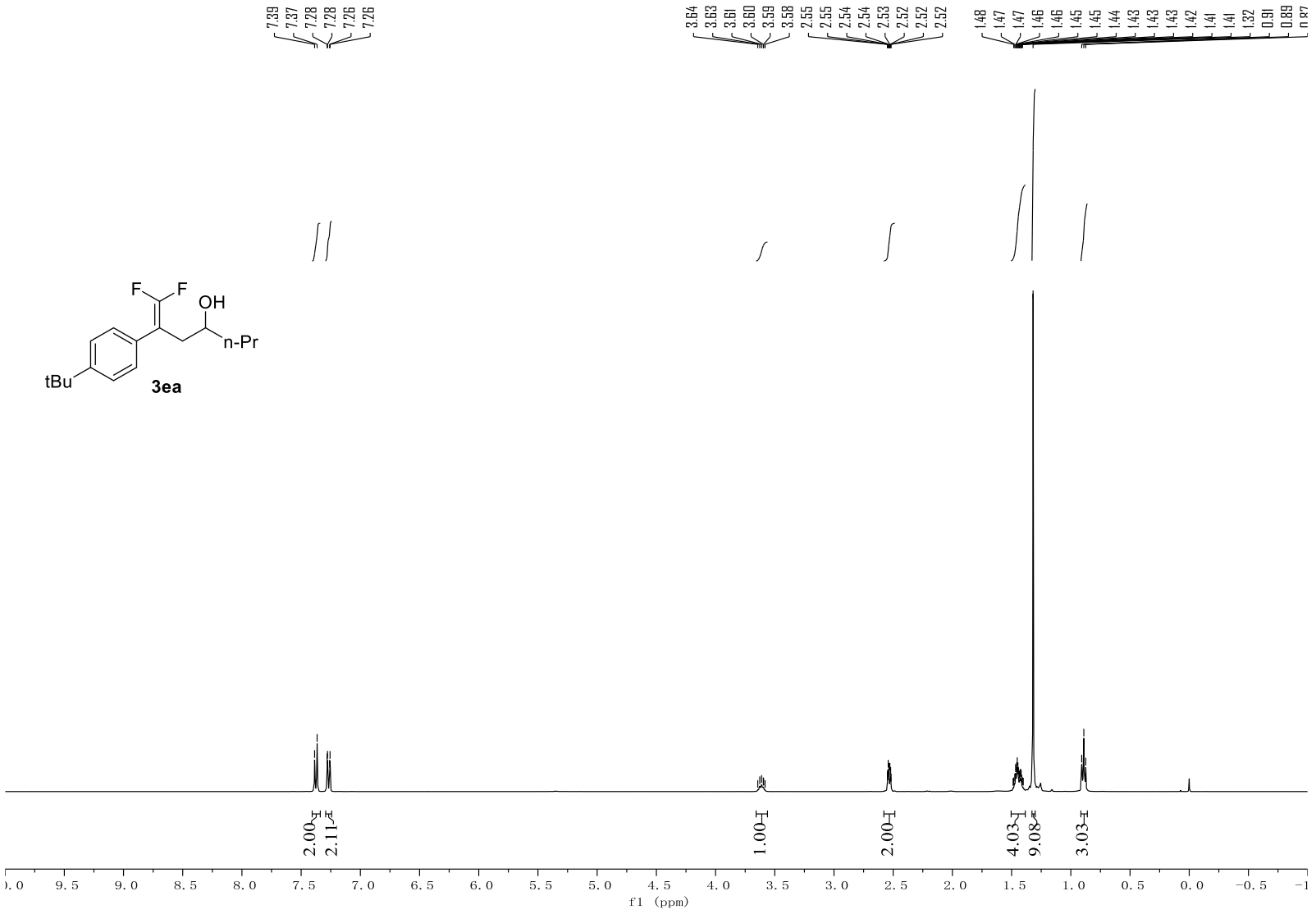
157.25
154.39
154.35
151.50
135.47
135.44
135.42
135.39
106.72
106.69
106.65
99.35
90.18
90.04
89.96
89.82
69.60
69.57
69.55
55.32
39.12
36.02
36.00
18.76
14.01
F
F
OH
MeO
n-Pr
OMe
3da
f1 (ppm)


-88.82
-88.93
-90.11
-90.22
F
F
OH
MeO
n-Pr
OMe
3da
1.00
1.00
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)
-88.82
-88.93
-90.11
-90.22
1.00
1.00
−87.5 −88.0 −88.5 −89.0 −89.5 −90.0 −90.5 −91.0 −91.5
f1 (ppm)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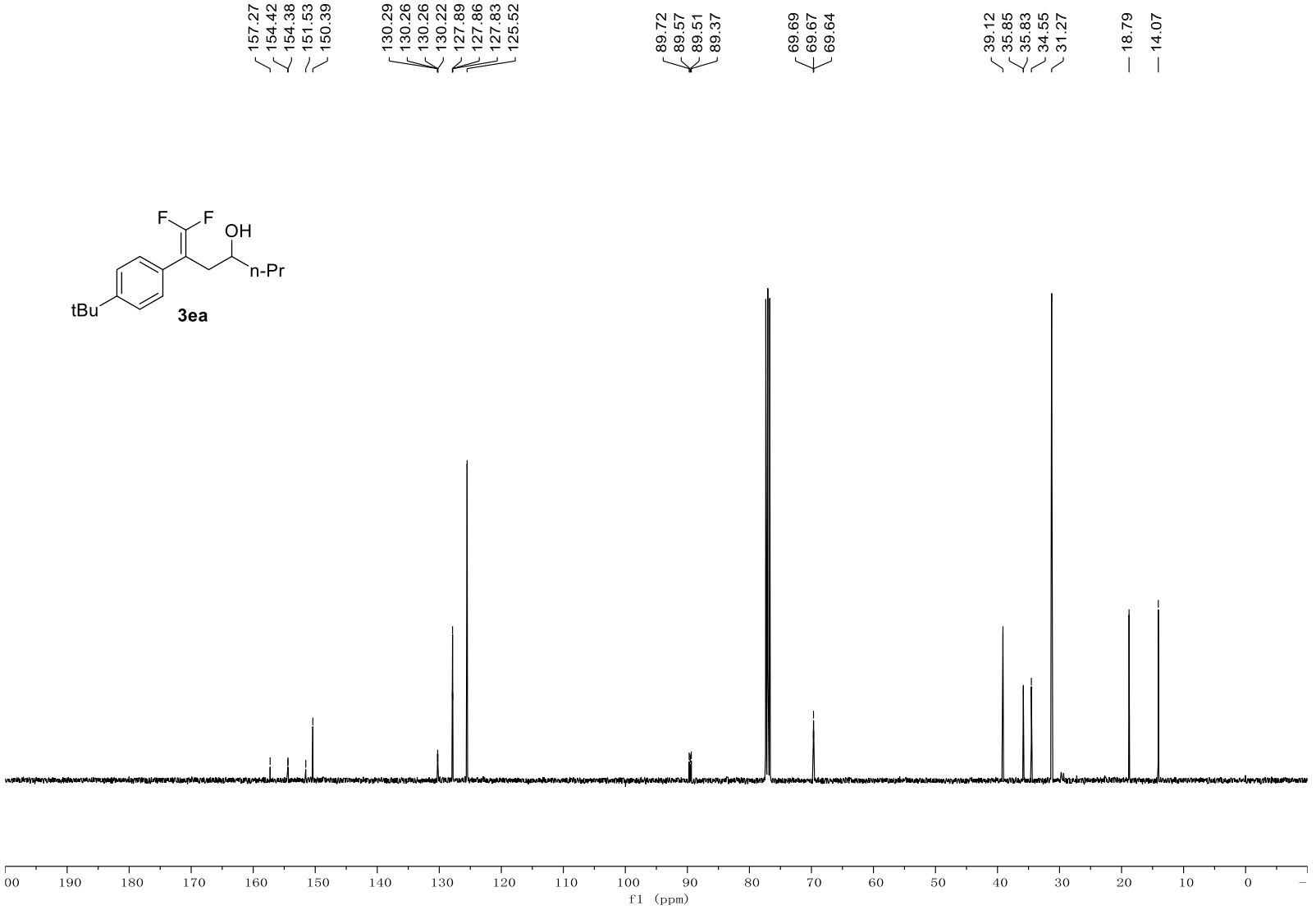
7.37
7.28
7.28
7.26
7.26
3.64
3.63
3.61
3.60
3.59
3.58
2.55
2.55
2.54
2.54
2.53
2.52
2.52
2.52
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.43
1.43
1.42
1.41
1.41
1.32
0.91
0.89
F
F
OH
n-Pr
tBu
3ea
2.00
2.11
1.00
2.00
4.03
9.08
3.03
f1 (ppm)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154.42
154.38
151.53
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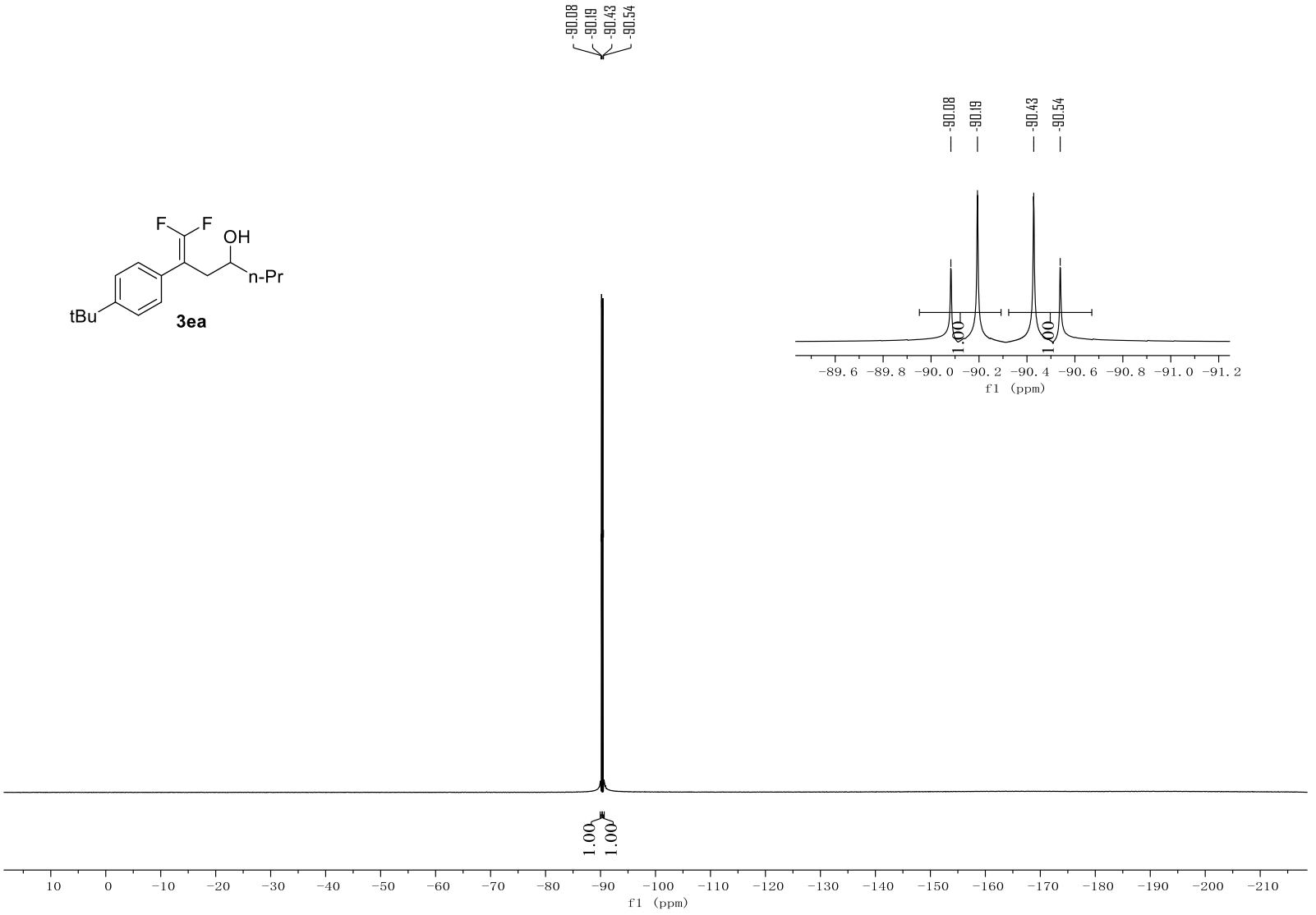
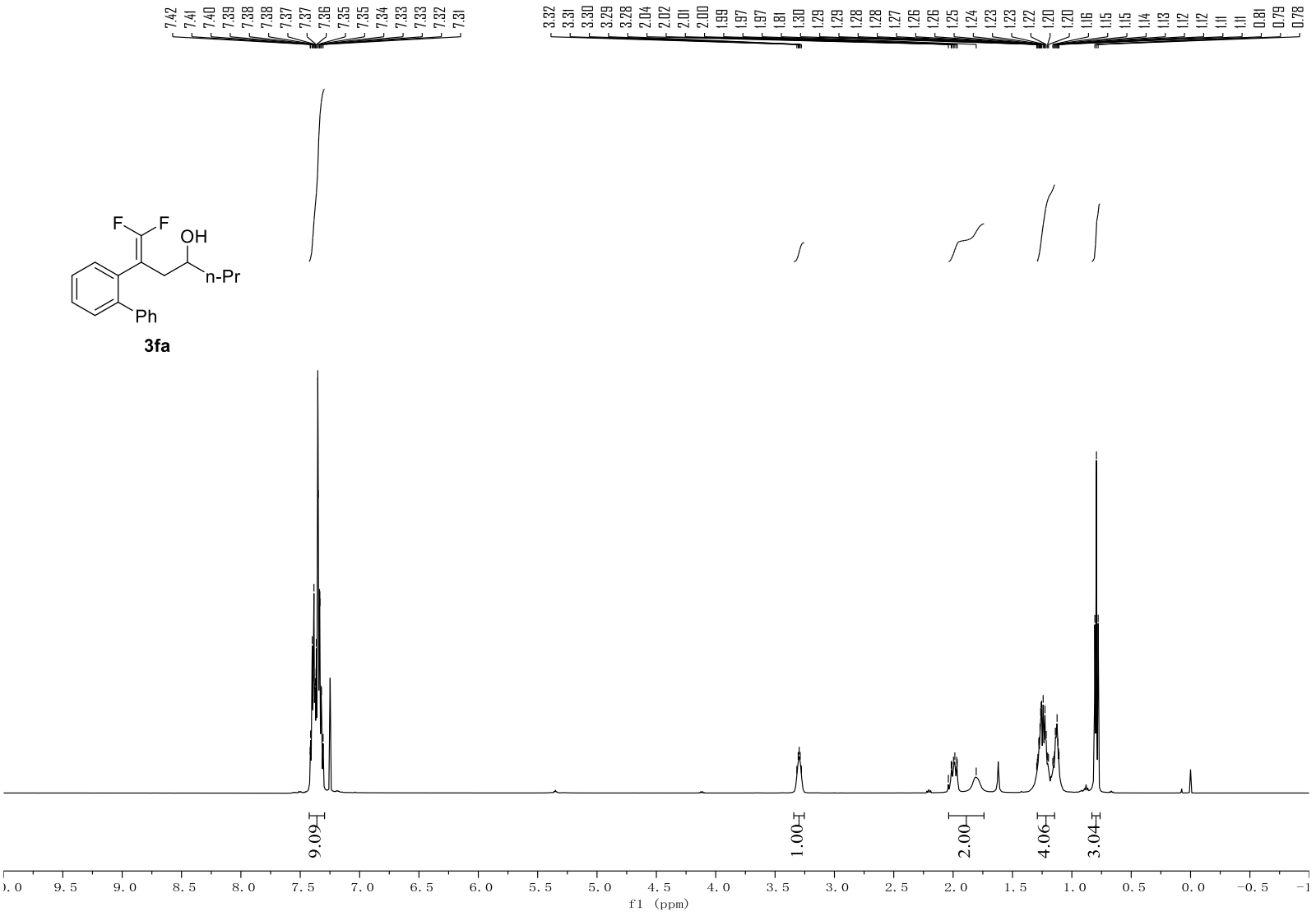
130.29
130.26
130.26
130.22
127.89
127.86
127.83
125.52
89.72
89.57
89.51
89.37
69.69
69.67
69.64
39.12
35.85
35.83
34.55
31.27
18.79
14.07
F
F
OH
n-Pr
tBu
3ea
f1 (ppm)


-90.08
-90.19
-90.43
-90.54
F
F
OH
n-Pr
tBu
3ea
1.00
1.00
1.00
1.00
-89.6 -89.8 -90.0 -90.2 -90.4 -90.6 -90.8 -91.0 -91.2
f1 (ppm)
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)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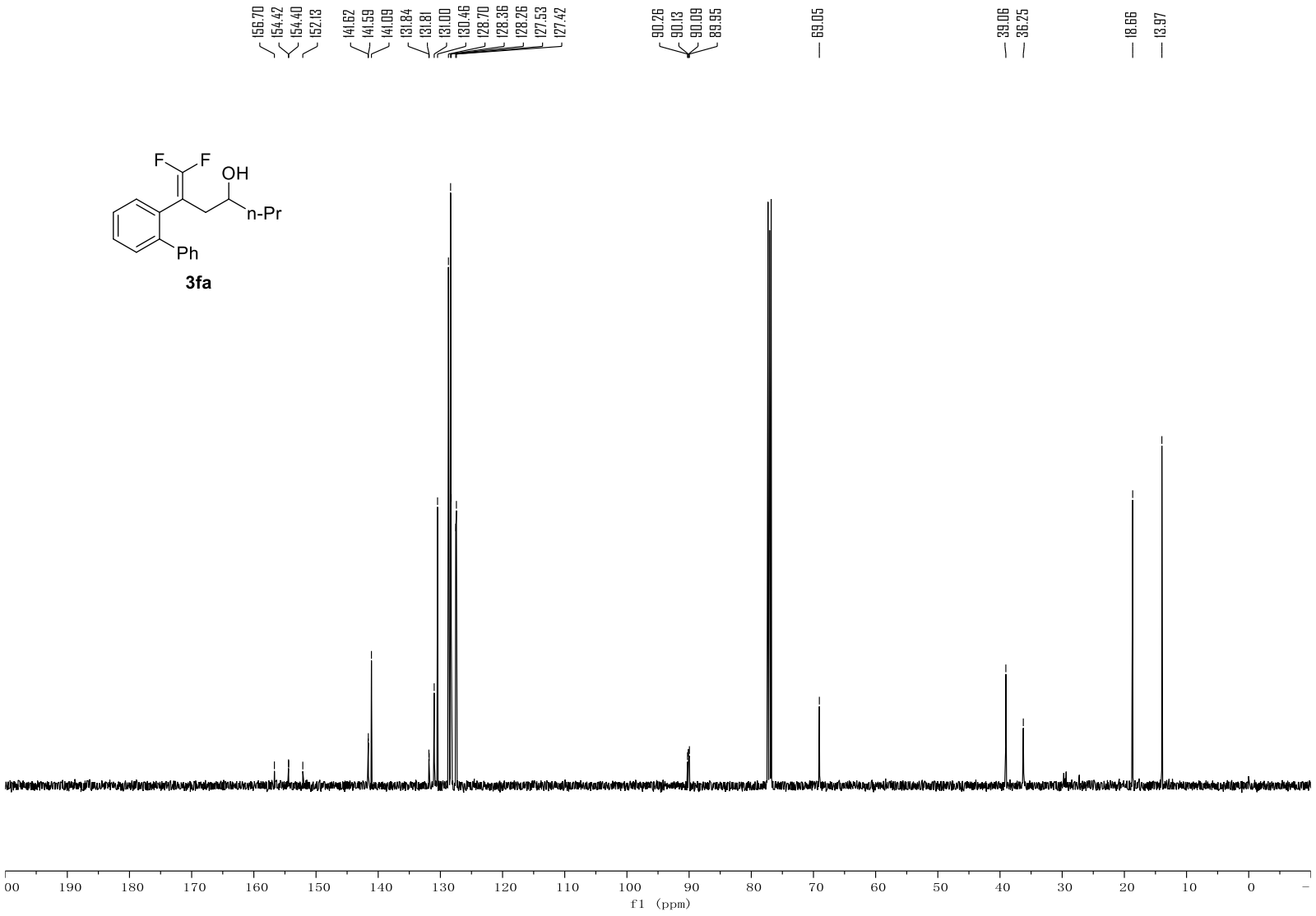
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
3.32
3.31
3.30
3.29
3.28
2.04
2.02
2.01
2.00
1.99
1.97
1.97
1.81
1.30
1.29
1.29
1.28
1.28
1.27
1.26
1.26
1.25
1.24
1.23
1.23
1.22
1.20
1.20
1.16
1.15
1.15
1.14
1.13
1.12
1.12
1.11
1.11
0.81
0.79
0.78
F
F
OH
n-Pr
Ph
3fa
9.09
1.00
2.00
4.06
3.04
f1 (ppm)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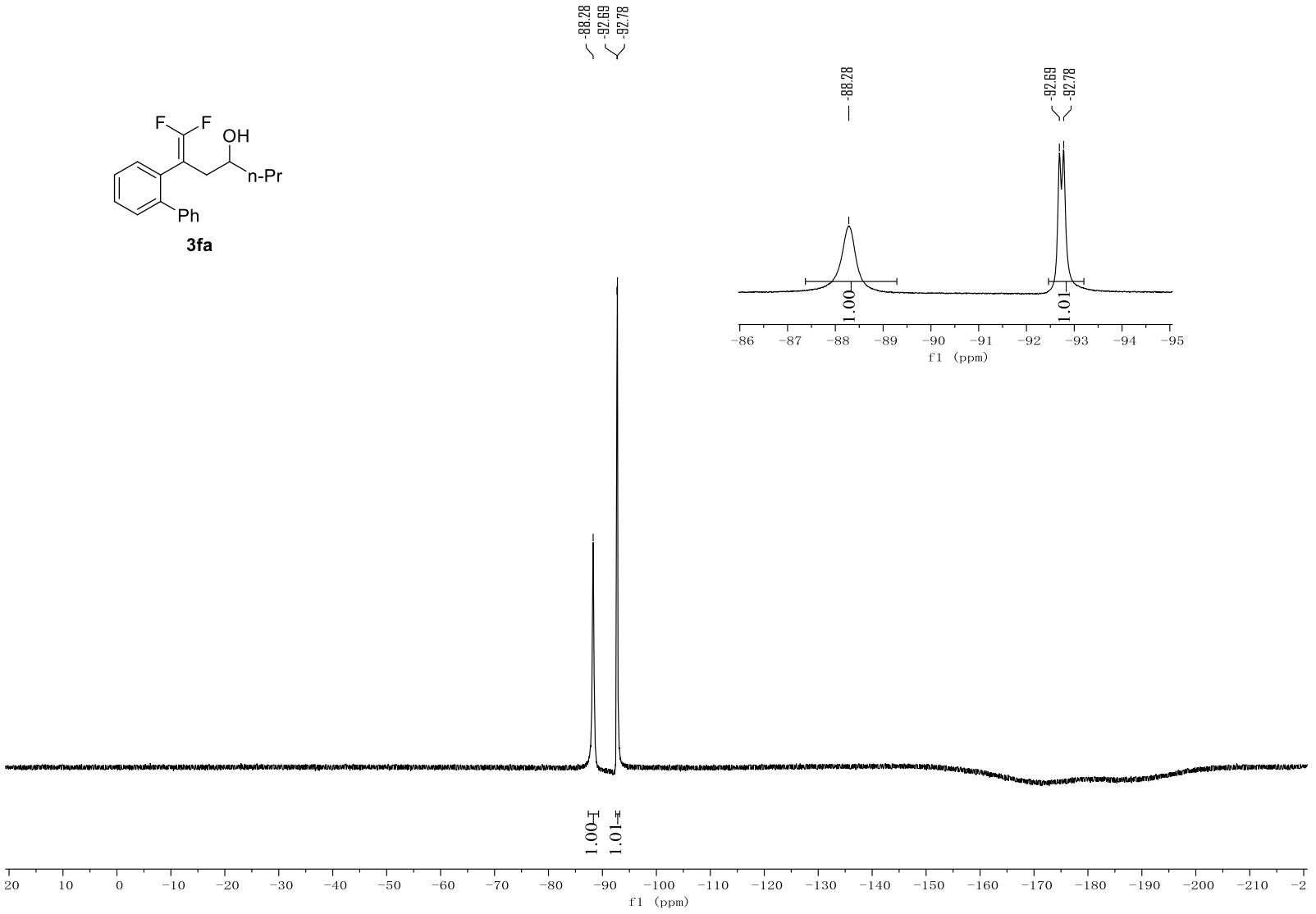
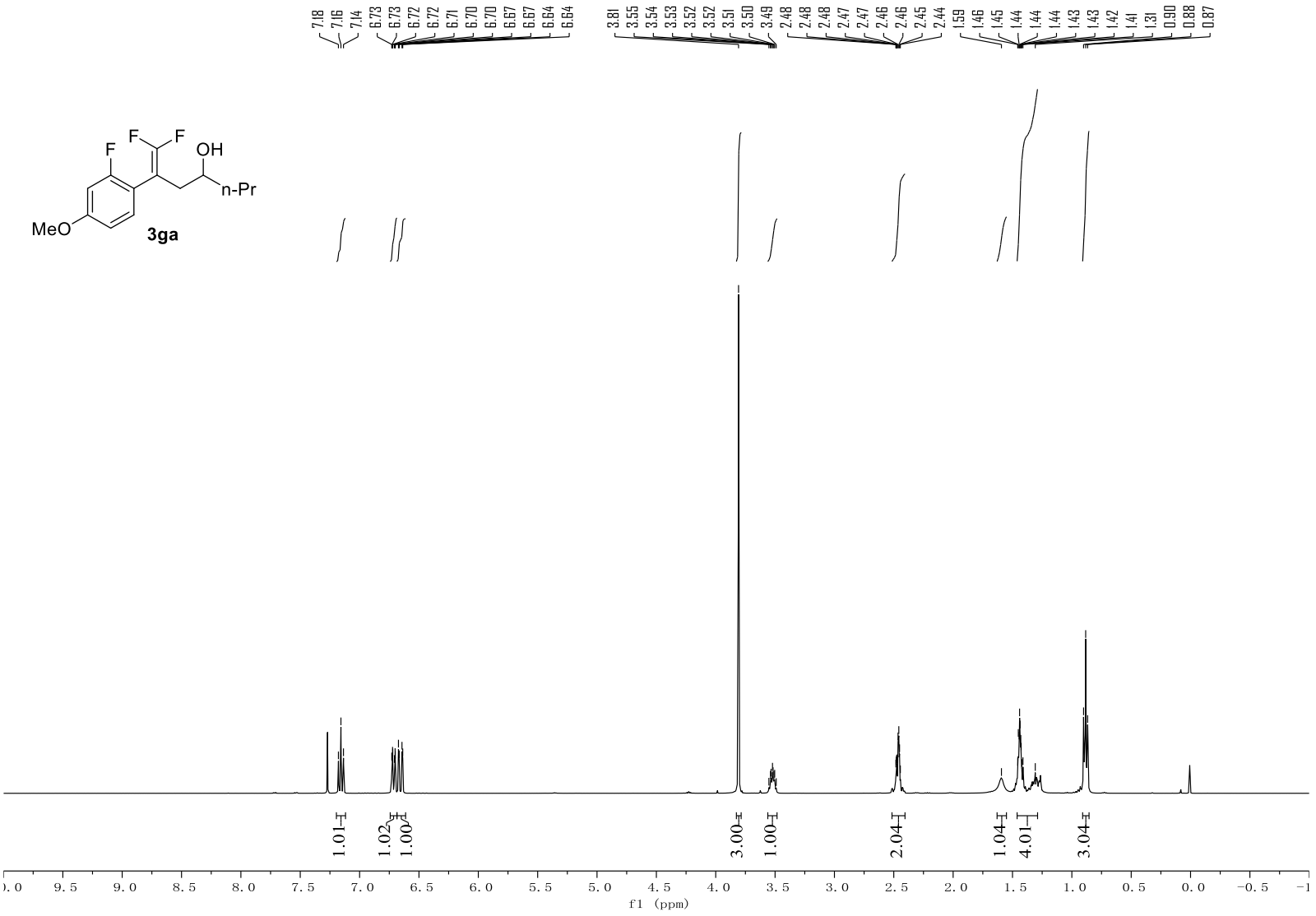
141.59
141.09
131.84
131.81
131.00
130.46
128.70
128.36
128.26
127.53
127.42
90.26
90.13
90.09
89.95
69.05
39.06
36.25
18.66
13.97
F
F
OH
n-Pr
Ph
3fa
f1 (ppm)


F
F
OH
n-Pr
Ph
3fa
-88.28
-92.69
-92.78
1.00
1.01
f1 (ppm)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7.14
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6.72
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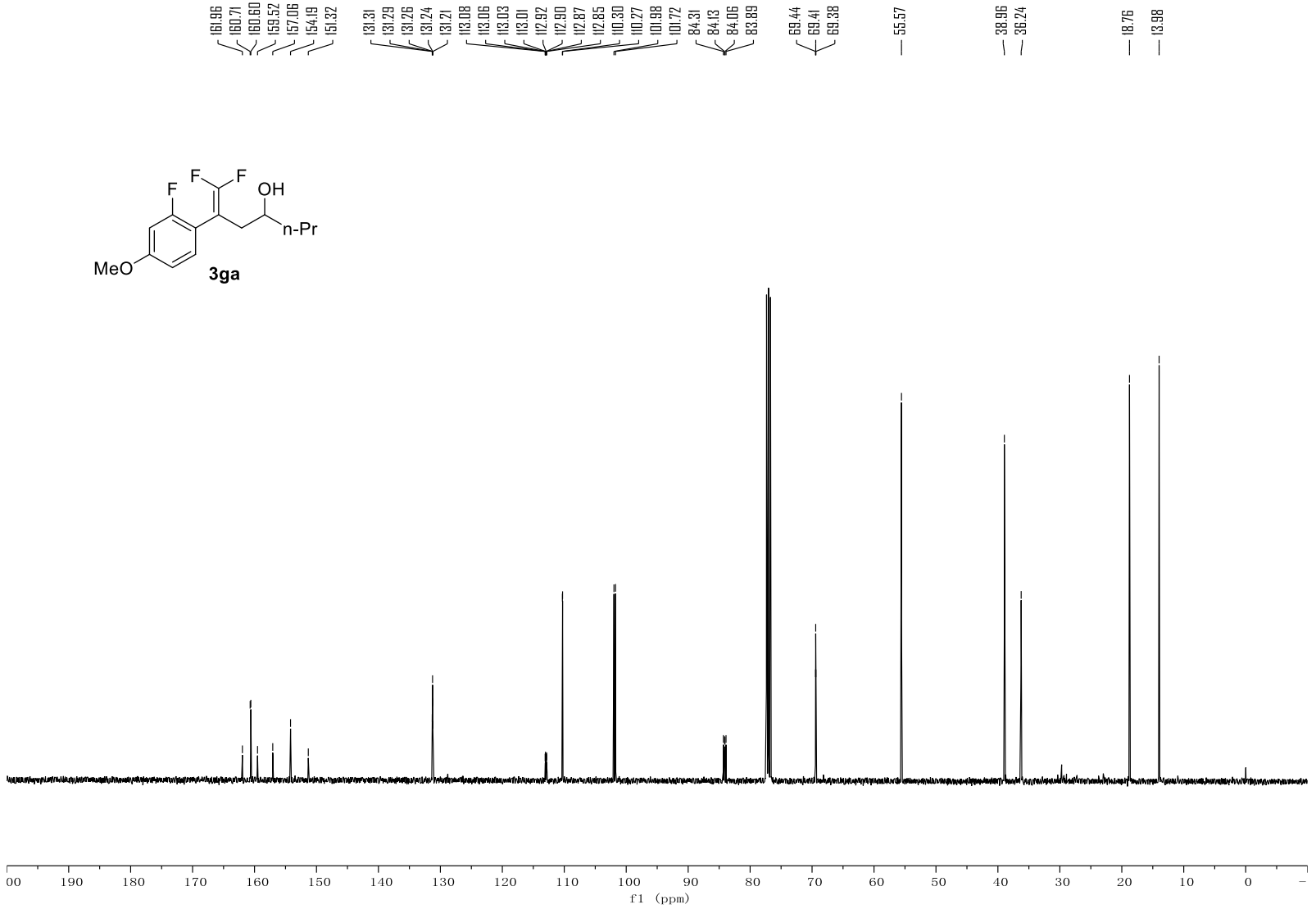
6.71
6.70
6.70
6.67
6.67
6.64
6.64
3.81
3.55
3.54
3.53
3.52
3.52
3.51
3.50
3.49
2.48
2.48
2.48
2.47
2.47
2.46
2.46
2.45
2.44
1.59
1.46
1.45
1.44
1.44
1.44
1.43
1.43
1.42
1.41
1.31
0.90
0.88
0.87
F
F
F
OH
n-Pr
MeO
3ga
1.01
1.02
1.00
3.00
1.00
2.04
1.04
4.01
3.04
f1 (ppm)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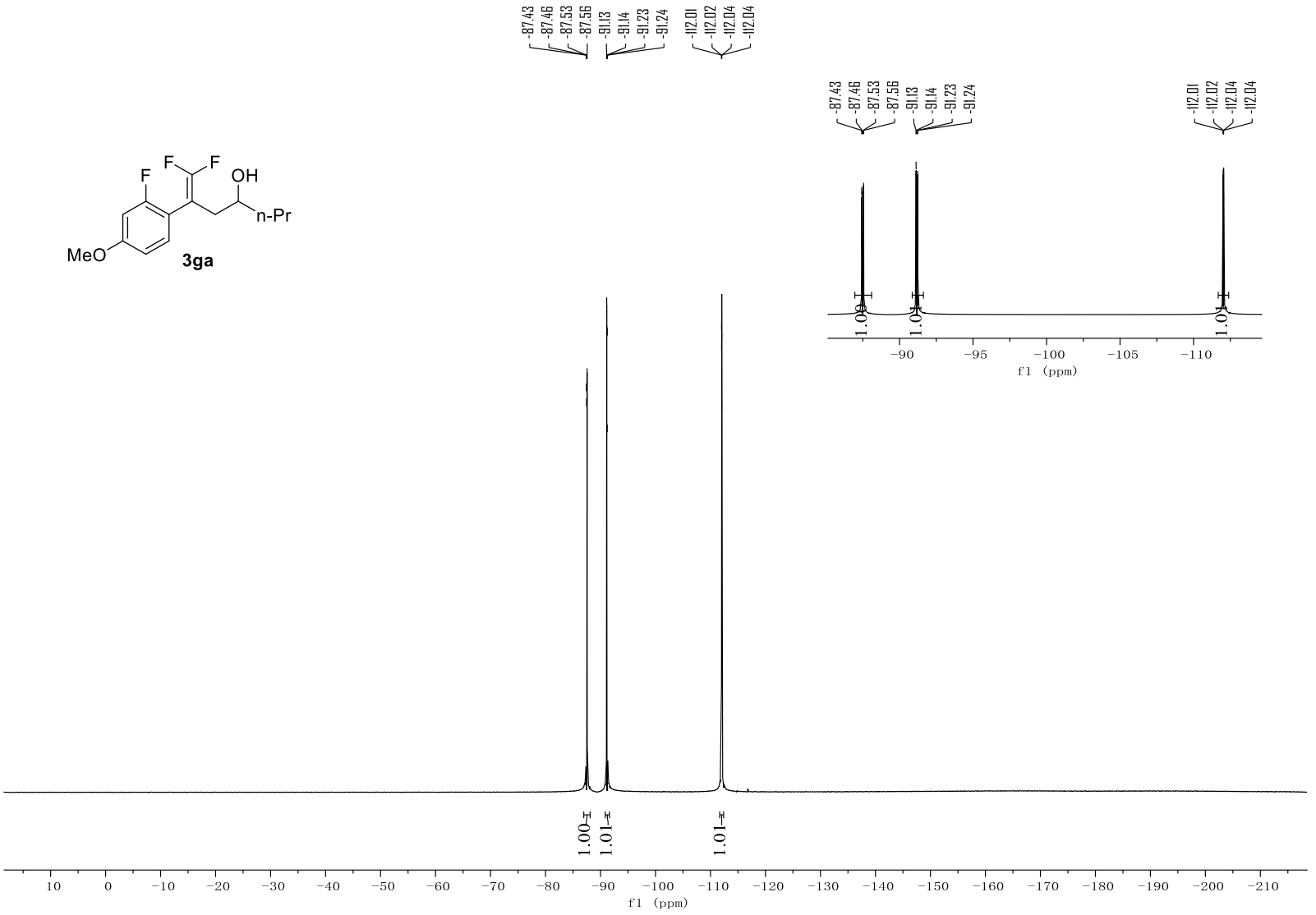
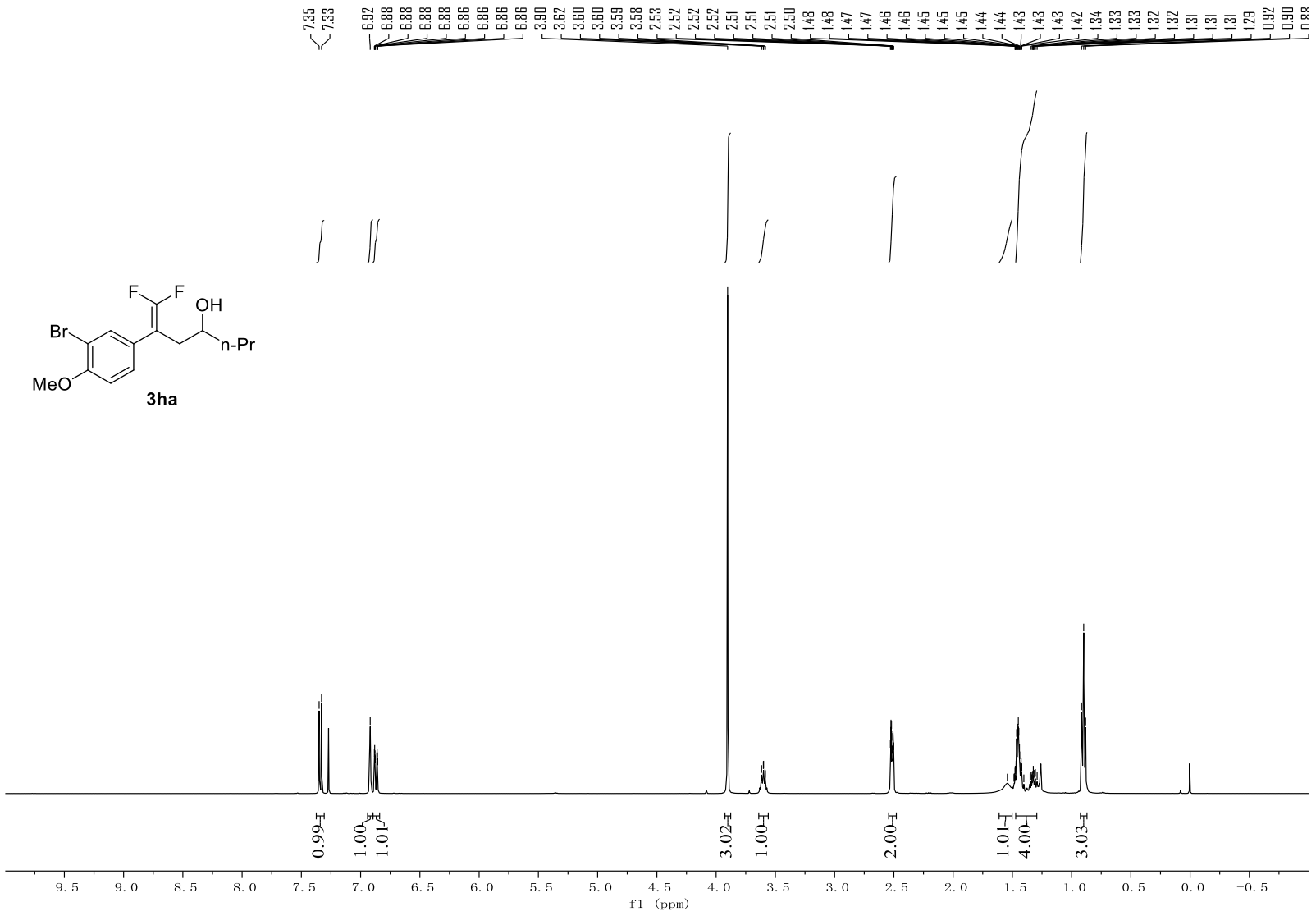
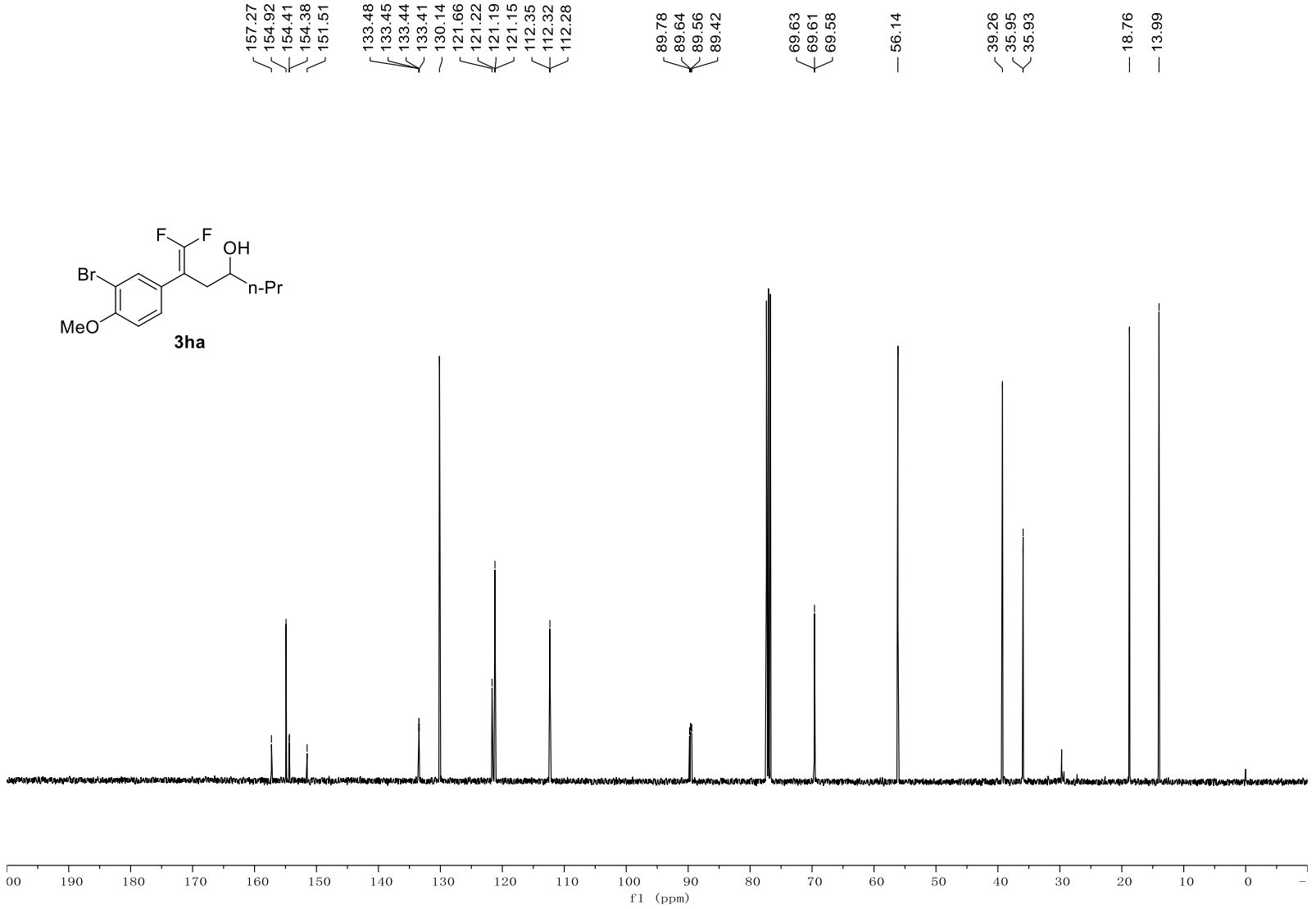
113.06
113.03
113.01
112.92
112.90
112.87
112.85
110.30
110.27
101.98
101.72
84.31
84.13
84.06
83.89
69.44
69.41
69.38
55.57
38.96
36.24
18.76
13.98
F
F
F
OH
n-Pr
MeO
3ga
f1 (ppm)


-87.43
-87.46
-87.53
-87.56
-91.13
-91.14
-91.23
-91.24
-112.01
-112.02
-112.04
-112.04
F
F
F
OH
n-Pr
MeO
3ga
1.00
1.01
1.01
f1 (ppm)


F
F
OH
Br
n-Pr
MeO
3ha
7.35
7.33
6.92
6.88
6.88
6.88
6.86
6.86
6.86
6.86
3.90
3.62
3.60
3.60
3.59
3.58
2.53
2.52
2.52
2.52
2.51
2.51
2.50
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.45
1.44
1.44
1.43
1.43
1.43
1.42
1.34
1.33
1.33
1.32
1.32
1.31
1.31
1.31
1.29
0.92
0.90
0.99
1.00
1.01
3.02
1.00
2.00
1.01
4.00
3.03
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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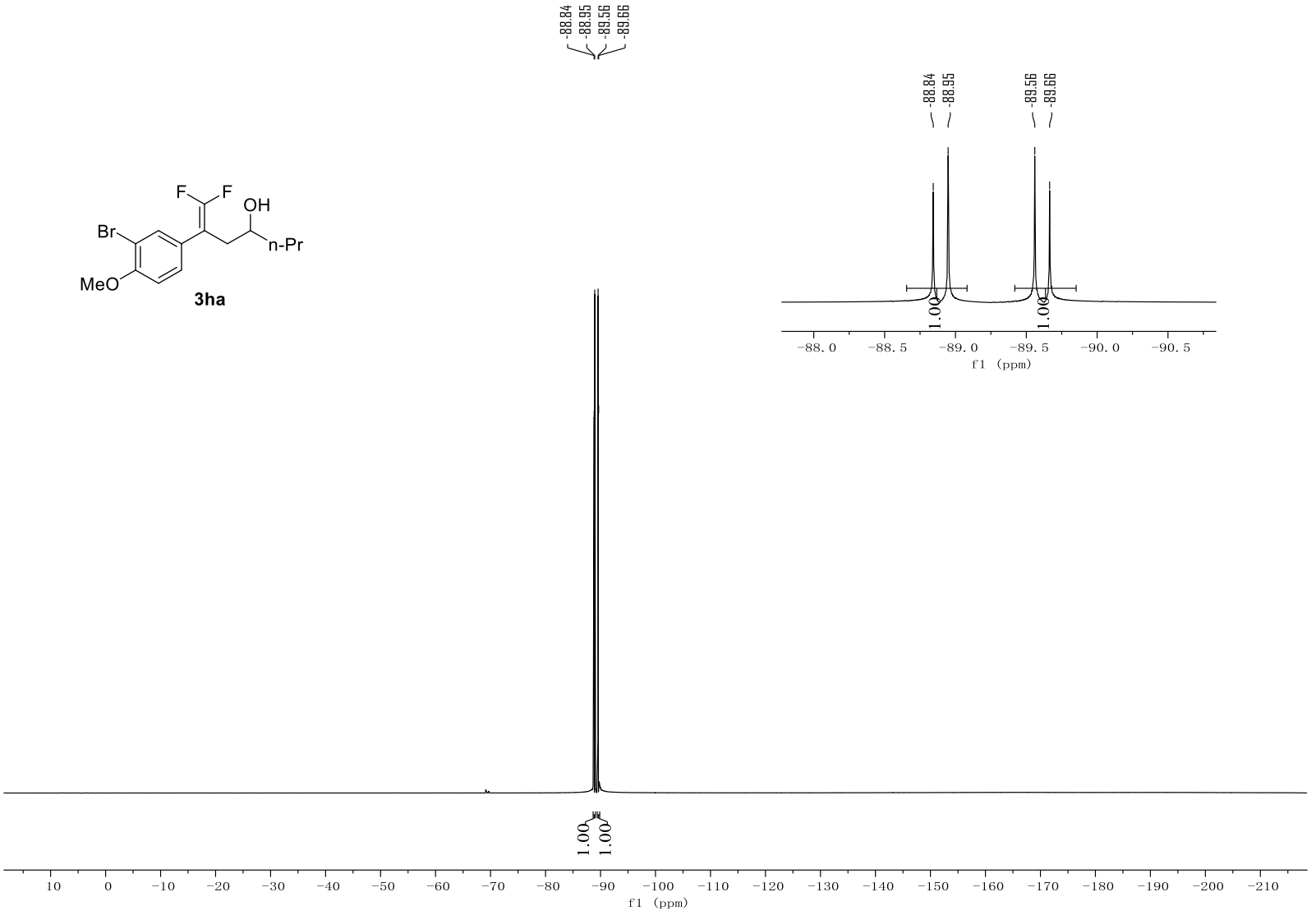
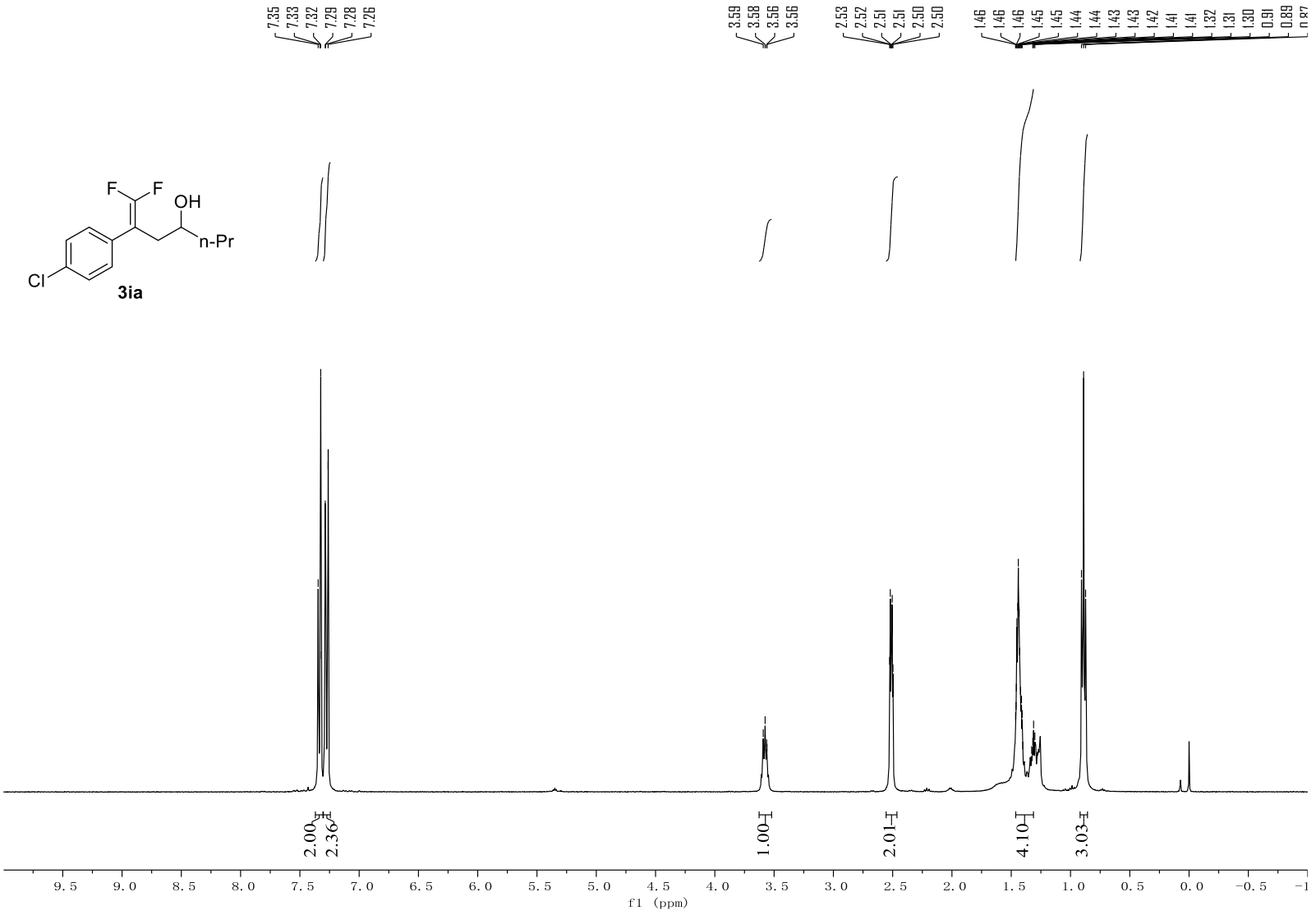
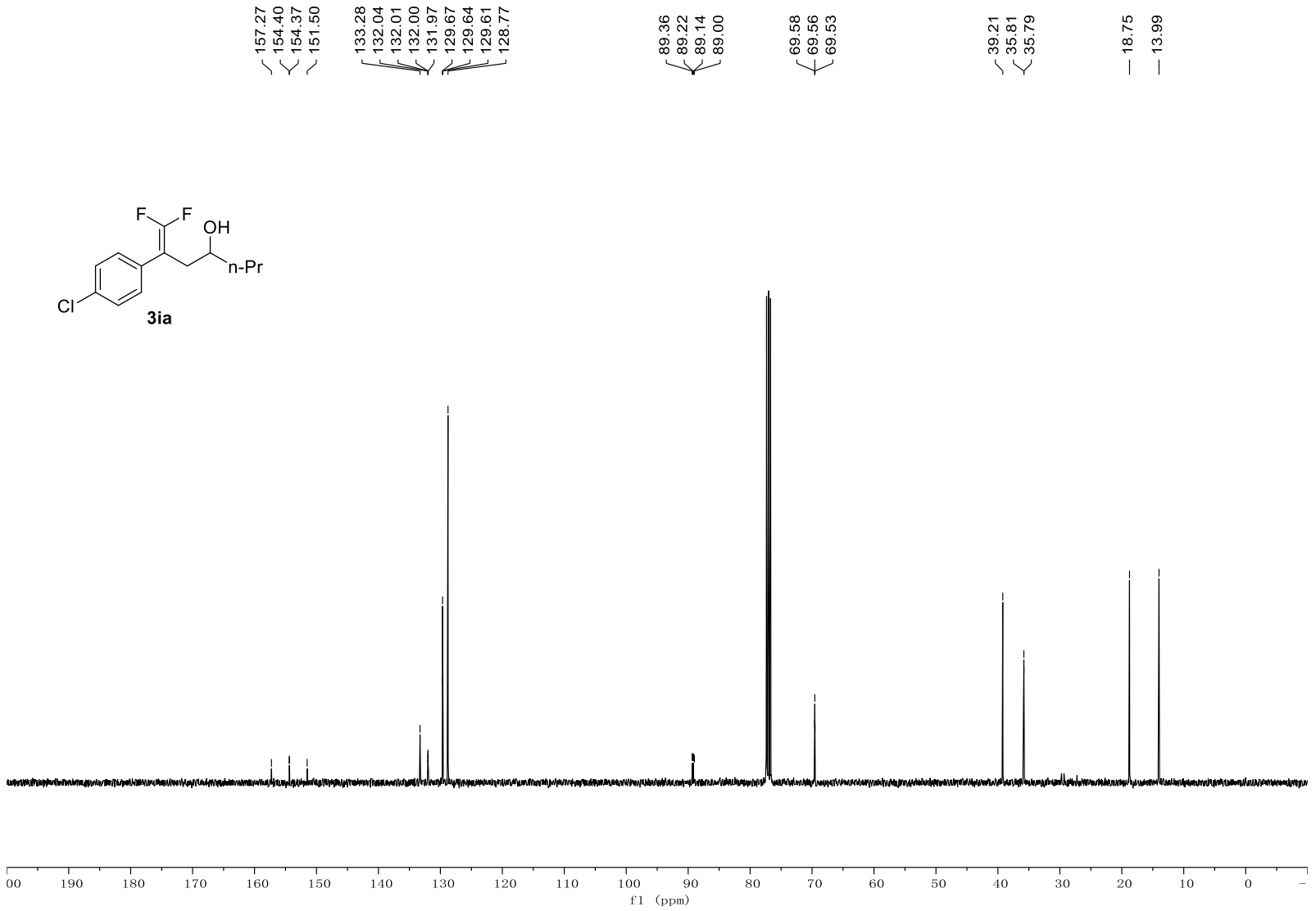
151.51
133.48
133.45
133.44
133.41
130.14
121.66
121.22
121.19
121.15
112.35
112.32
112.28
89.78
89.64
89.56
89.42
69.63
69.61
69.58
56.14
39.26
35.95
35.93
18.76
13.99
F
F
OH
Br
n-Pr
MeO
3ha
f1 (ppm)


F
F
OH
Br
n-Pr
MeO
3ha
-88.84
-88.95
-89.56
-89.66
1.00
1.00
-88.84
-88.95
-89.56
-89.66
1.00
1.00
-88.0
-88.5
-89.0
-89.5
-90.0
-90.5
f1 (ppm)
1.00
1.00
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)


7.35
7.33
7.32
7.29
7.28
7.26
3.59
3.58
3.56
3.56
2.53
2.52
2.51
2.51
2.50
2.50
1.46
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.42
1.41
1.41
1.32
1.31
1.30
0.91
0.89
F
F
OH
n-Pr
Cl
3ia
2.00
2.36
1.00
2.01
4.10
3.03
f1 (ppm)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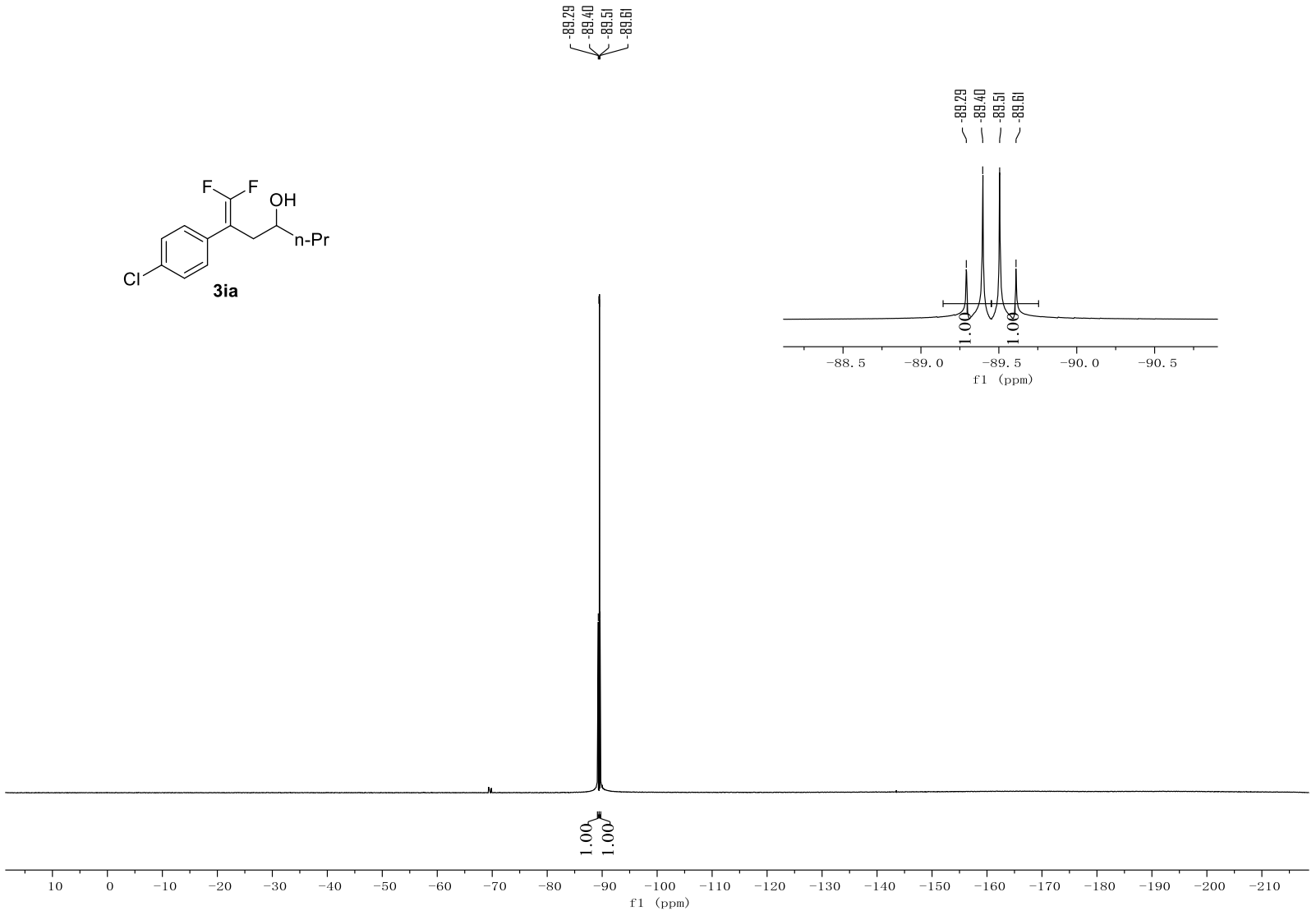
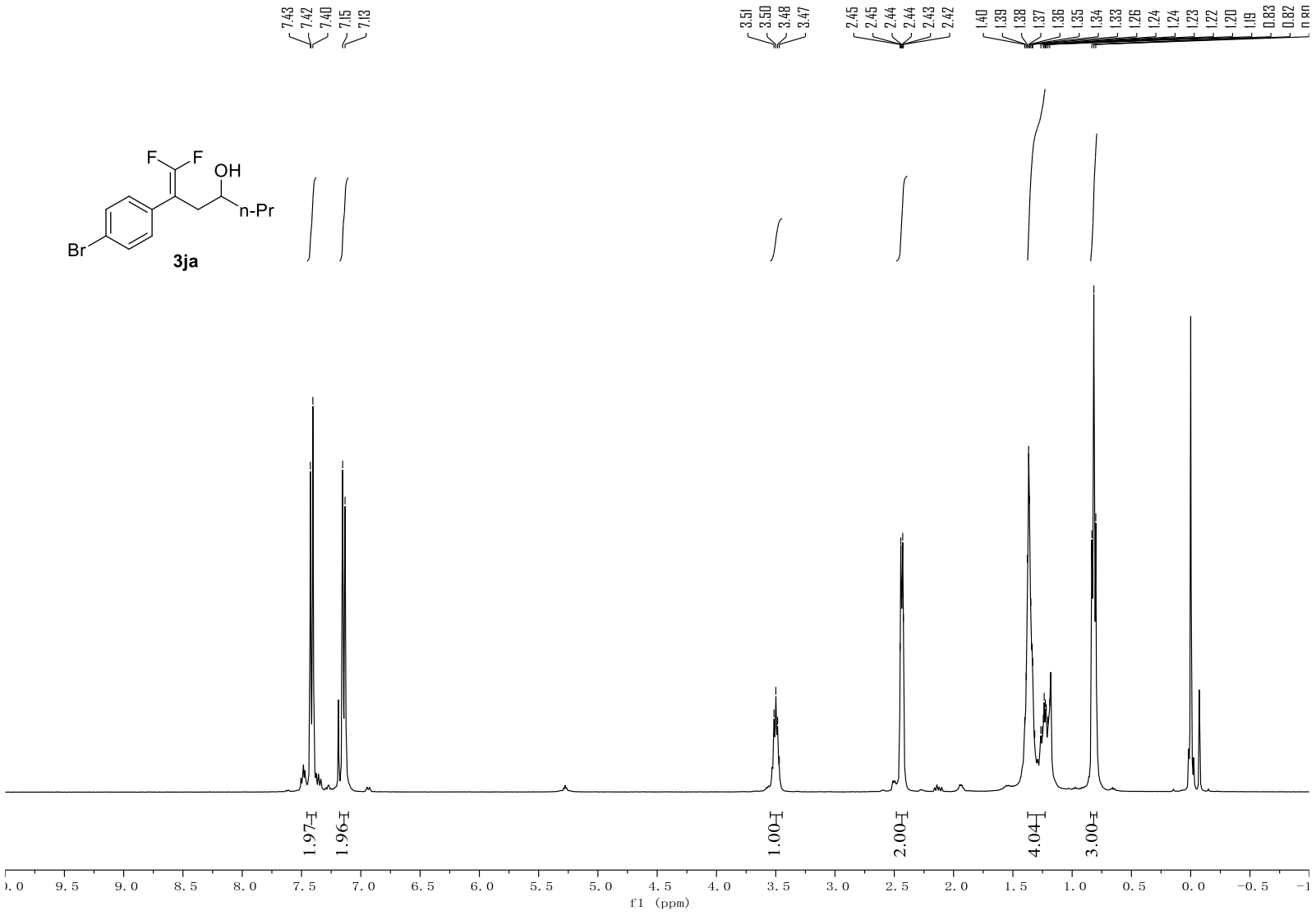
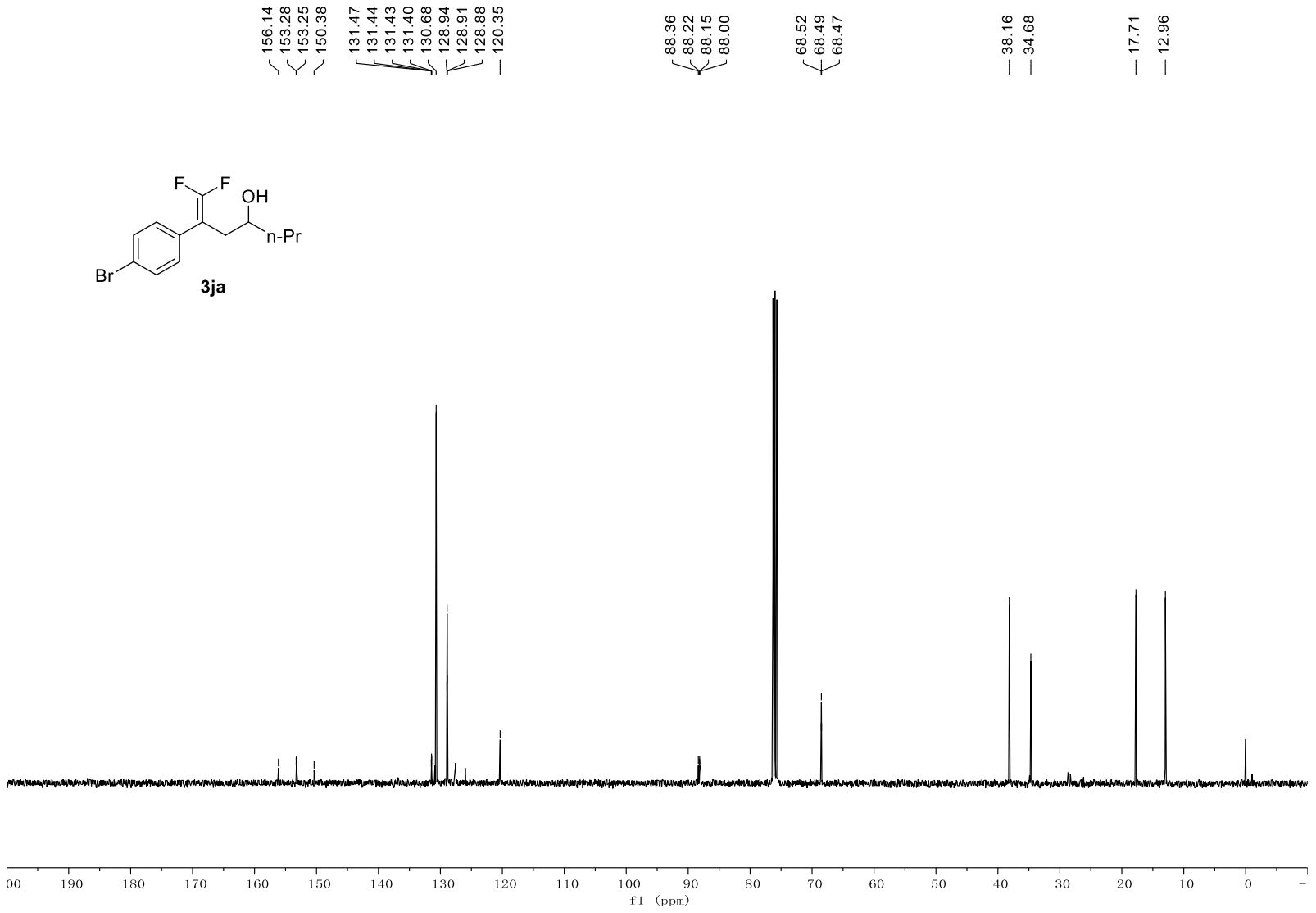
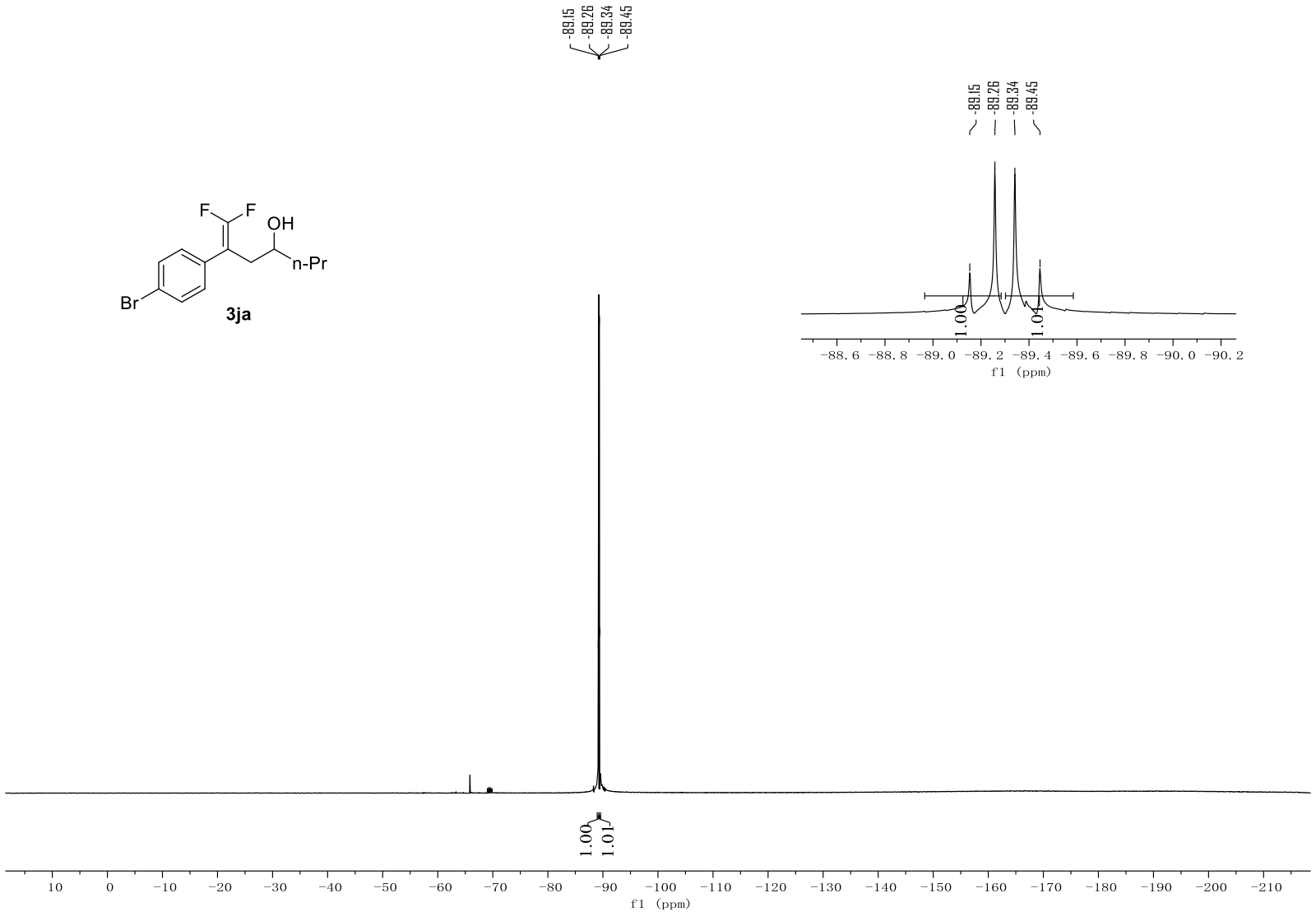
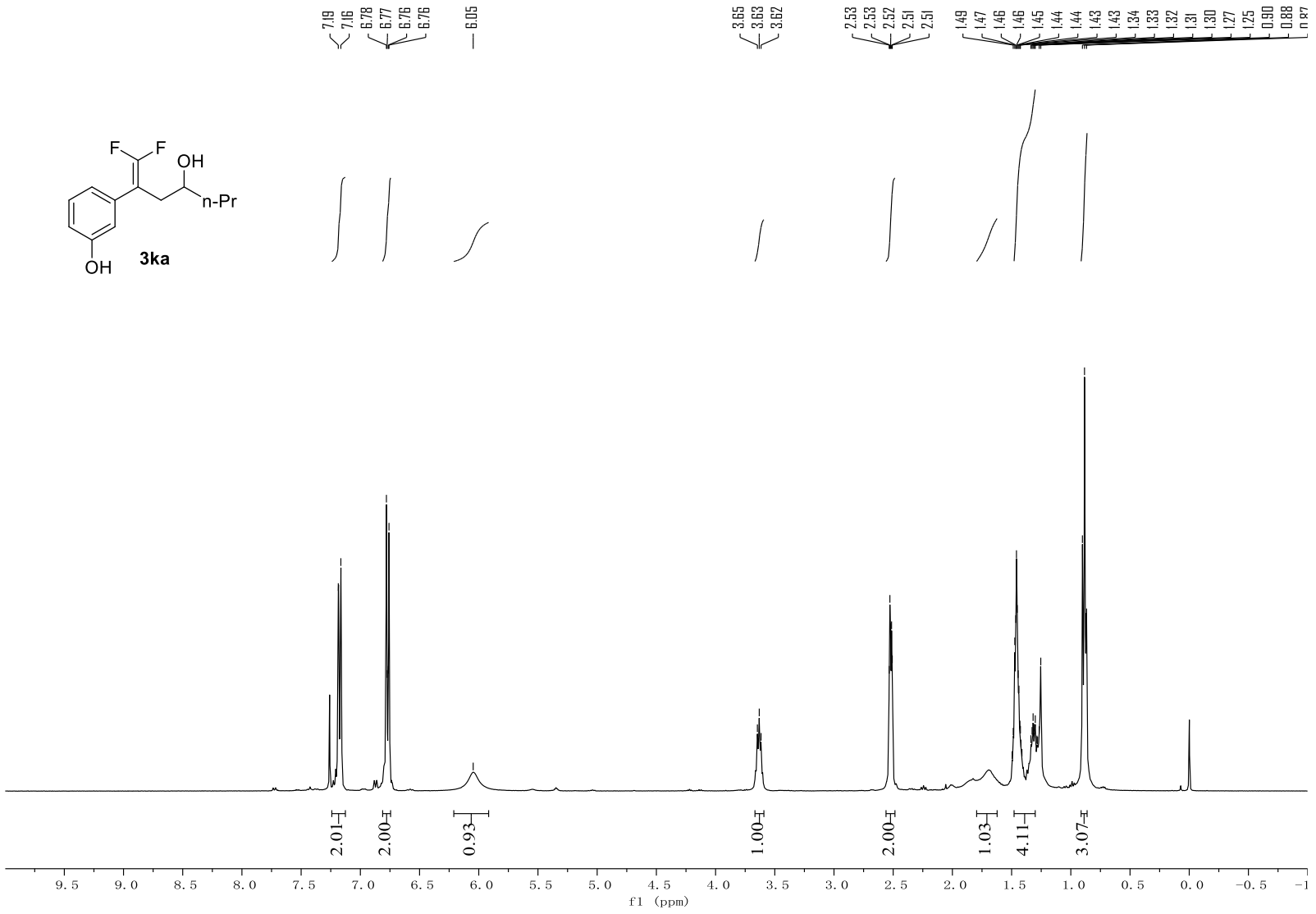
154.37
151.50
133.28
132.04
132.01
132.00
131.97
129.67
129.64
129.61
128.77
89.36
89.22
89.14
89.00
69.58
69.56
69.53
39.21
35.81
35.79
18.75
13.99
F
F
OH
n-Pr
Cl
3ia
f1 (ppm)

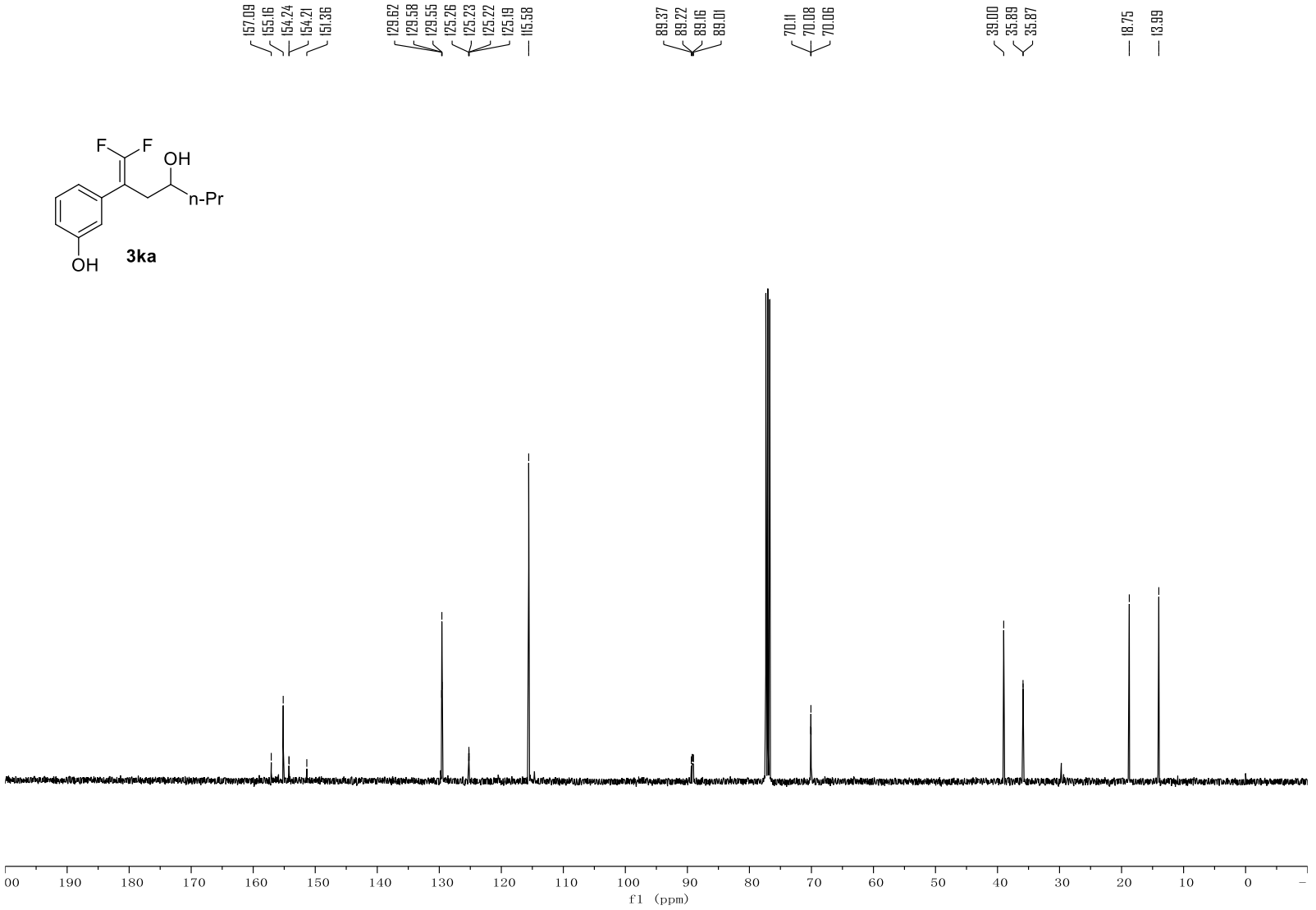

-89.29
-89.40
-89.51
-89.61
F
F
OH
n-Pr
Cl
3ia
1.00
1.00
-88.5
-89.0
-89.5
-90.0
-90.5
f1 (ppm)
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

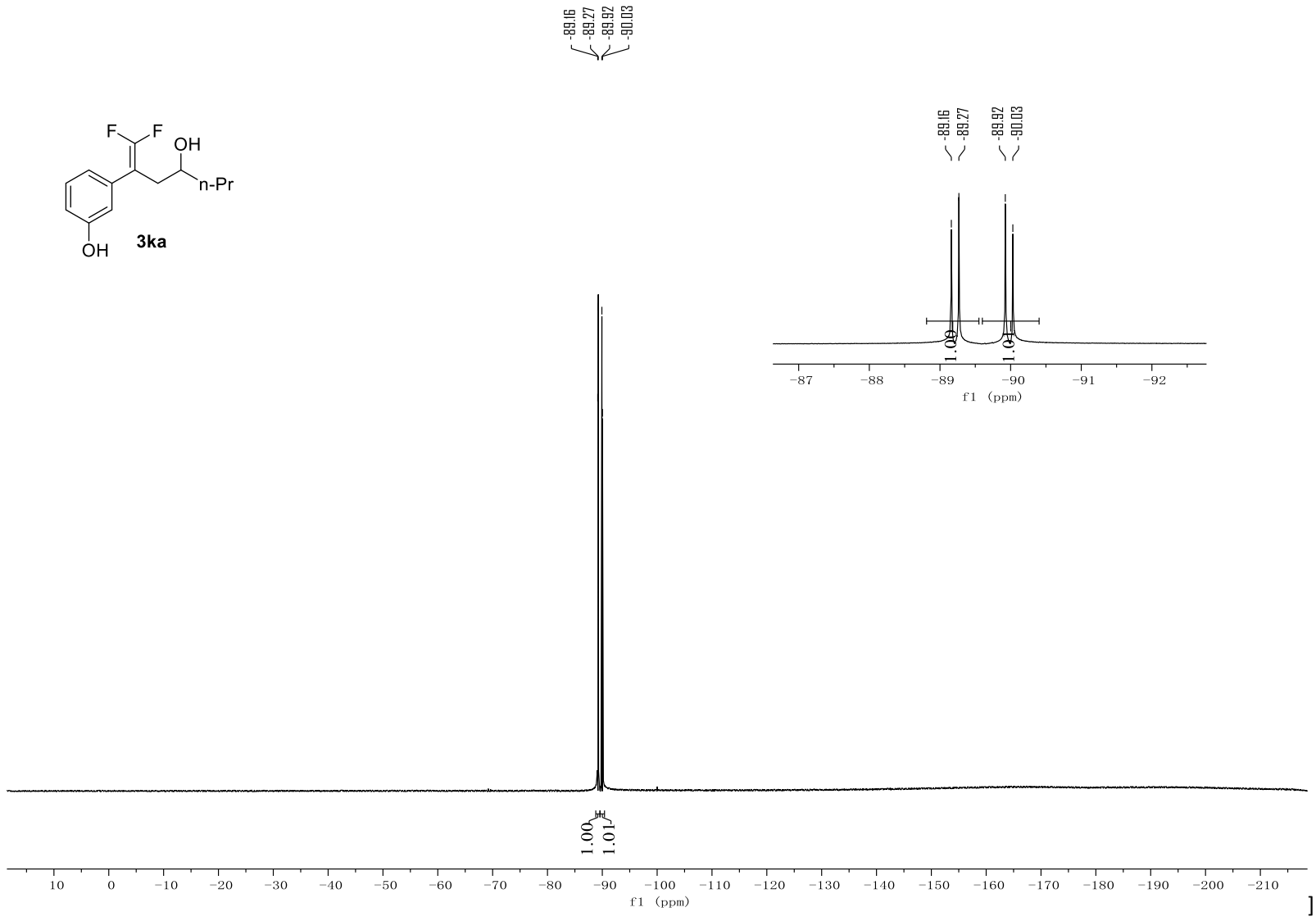

7.43
7.42
7.40
7.15
7.13
3.51
3.50
3.48
3.47
2.45
2.45
2.44
2.44
2.43
2.42
1.40
1.39
1.38
1.37
1.36
1.35
1.34
1.33
1.26
1.24
1.24
1.23
1.22
1.20
1.19
0.83
0.82
F
F
OH
n-Pr
Br
3ja
1.97
1.96
1.00
2.00
4.04
3.00
f1 (ppm)


156.14
153.28
153.25
150.38
131.47
131.44
131.43
131.40
130.68
128.94
128.91
128.88
120.35
88.36
88.22
88.15
88.00
68.52
68.49
68.47
38.16
34.68
17.71
12.96
F
F
OH
n-Pr
Br
3ja
f1 (ppm)

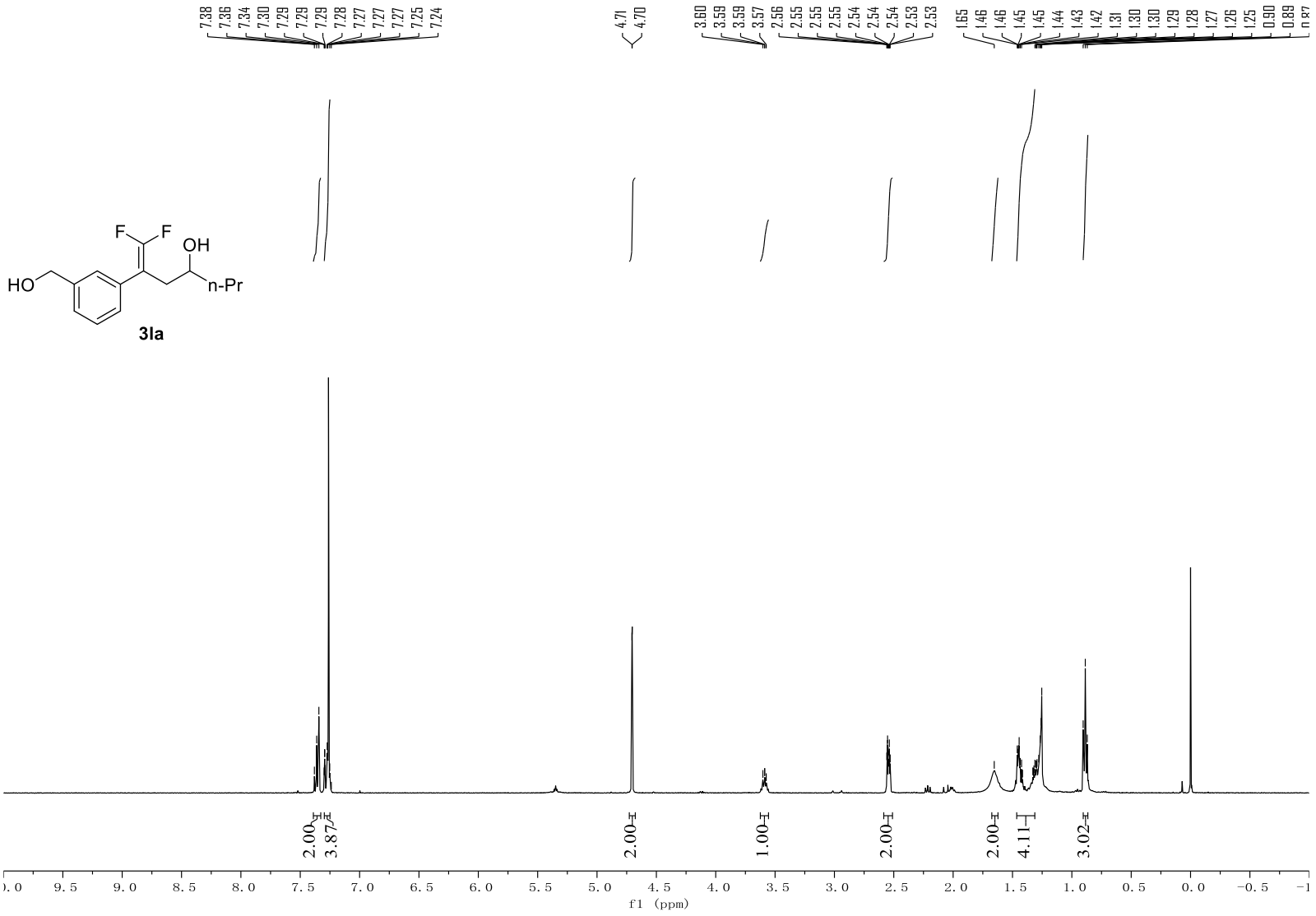

-89.15
-89.26
-89.34
-89.45
F
F
OH
n-Pr
Br
3ja
1.00
1.01
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)
-89.15
-89.26
-89.34
-89.45
1.00
1.04
−88.6 −88.8 −89.0 −89.2 −89.4 −89.6 −89.8 −90.0 −90.2
f1 (ppm)

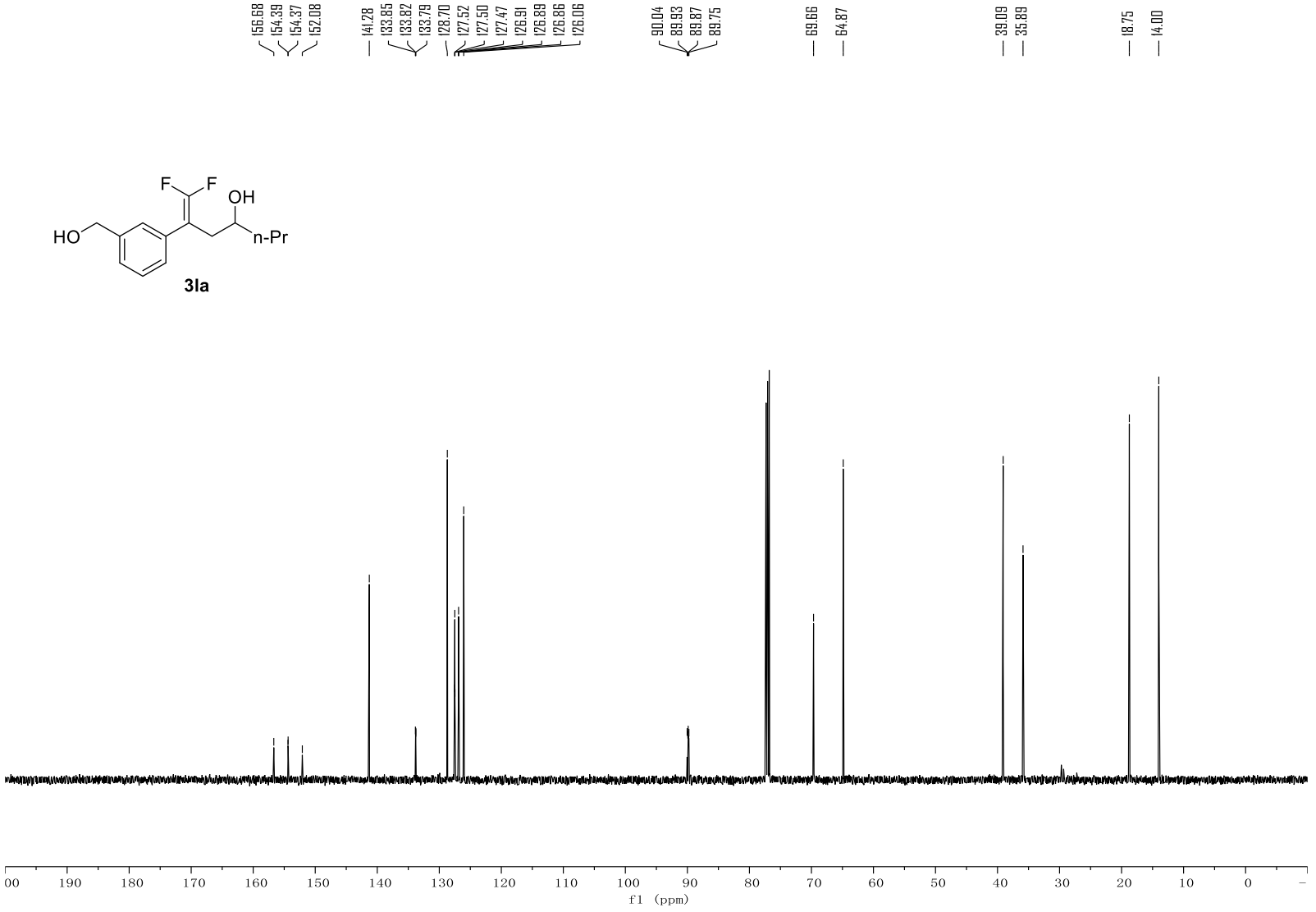

F
F
OH
n-Pr
OH
3ka
7.19
7.16
6.78
6.77
6.76
6.76
6.05
3.65
3.63
3.62
2.53
2.53
2.52
2.51
2.51
1.49
1.47
1.46
1.46
1.45
1.44
1.44
1.43
1.43
1.34
1.33
1.32
1.31
1.30
1.27
1.25
0.90
0.88
2.01
2.00
0.93
1.00
2.00
1.03
4.11
3.07
f1 (ppm)


157.09
155.16
154.24
154.21
151.36
129.62
129.58
129.55
125.26
125.23
125.22
125.19
116.58
89.37
89.22
89.16
89.01
70.11
70.08
70.06
39.00
35.89
35.87
18.75
13.99
F
F
OH
n-Pr
OH
3ka
f1 (ppm)


-89.16
-89.27
-89.92
-90.03
F
F
OH
n-Pr
OH
3ka
1.00
1.01
f1 (ppm)
1.06
1.04
f1 (ppm)

]


7.38
7.38
7.34
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.27
7.25
7.24
4.71
4.70
3.60
3.59
3.59
3.57
2.56
2.55
2.55
2.55
2.54
2.54
2.54
2.53
2.53
1.65
1.46
1.46
1.45
1.45
1.44
1.43
1.42
1.31
1.30
1.30
1.29
1.28
1.27
1.26
1.25
0.90
0.89
F
F
OH
HO
n-Pr
3Ia
2.00
3.87
2.00
1.00
2.00
2.00
4.11
3.02
f1 (ppm)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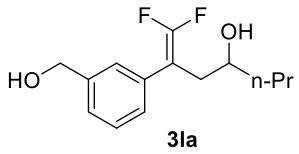
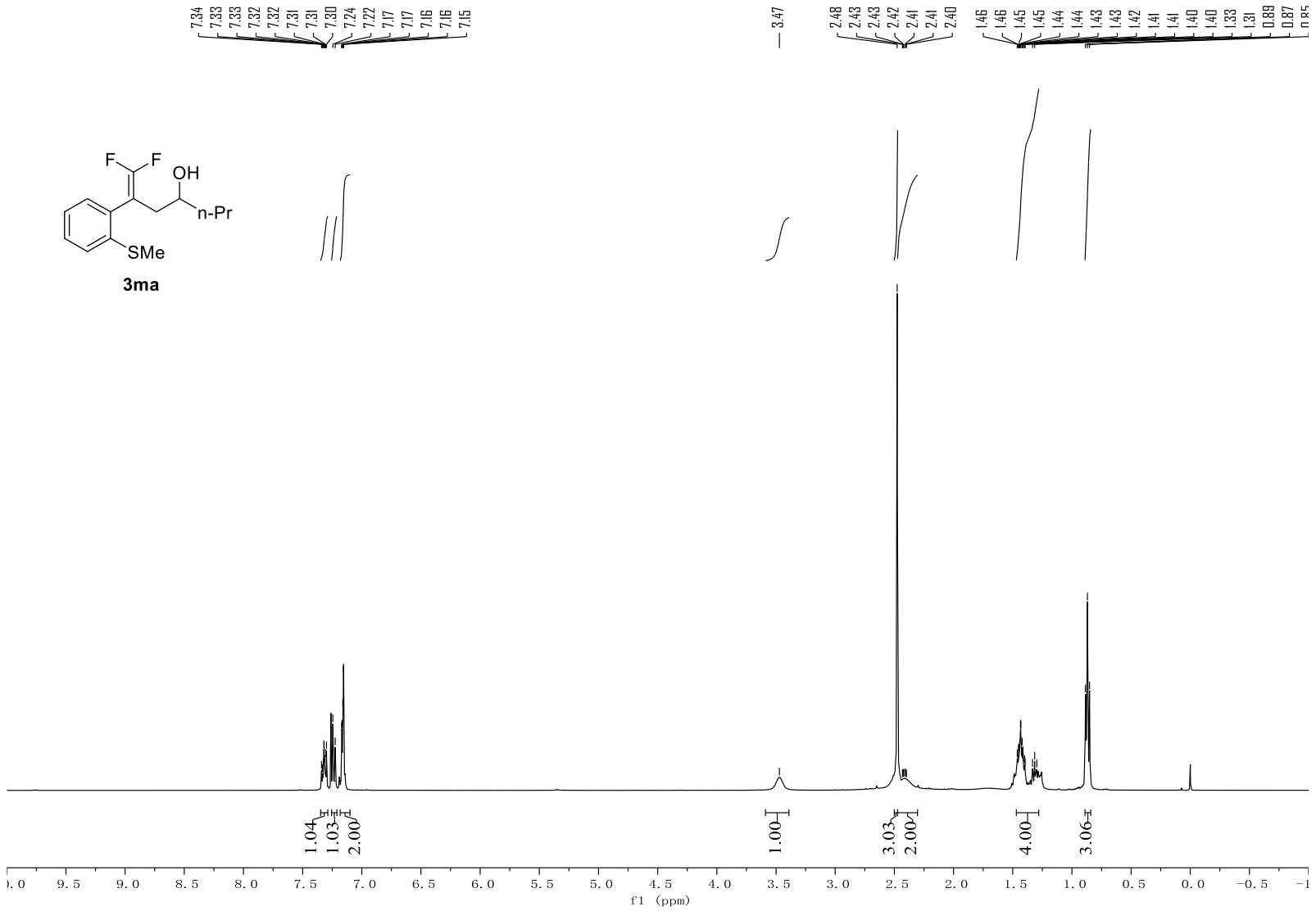
154.37
152.08
141.28
133.85
133.82
133.79
128.70
127.52
127.50
127.47
126.91
126.89
126.86
126.06
90.04
89.93
89.87
89.75
69.66
64.87
39.09
35.89
18.75
14.00
F
F
OH
HO
n-Pr
3la
f1 (ppm)


F
F
OH
HO
n-Pr

3la

-89.78
-89.89
-90.19
-90.29
1.00
1.01
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)

-89.78
-89.89
-90.19
-90.29
1.00
1.01
−88.5 −89.0 −89.5 −90.0 −90.5 −91.0 −91.5
f1 (ppm)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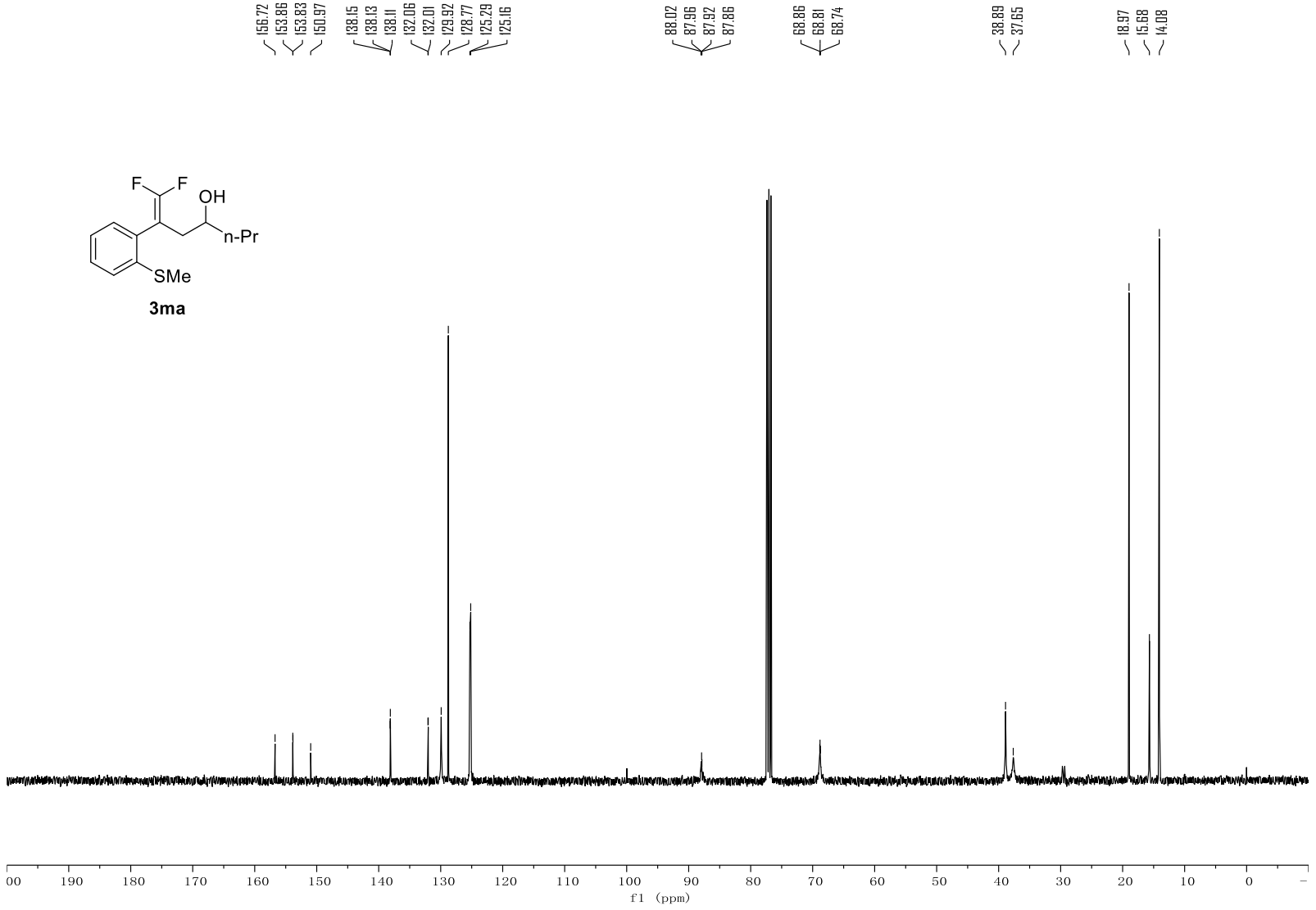
7.33
7.32
7.32
7.31
7.31
7.30
7.24
7.22
7.17
7.17
7.16
7.16
7.15
3.47
2.48
2.43
2.43
2.42
2.41
2.40
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.40
1.33
1.31
0.89
0.87
F
F
OH
n-Pr
SMe
3ma
1.04
1.03
2.00
1.00
3.03
2.00
4.00
3.06
f1 (ppm)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150.97
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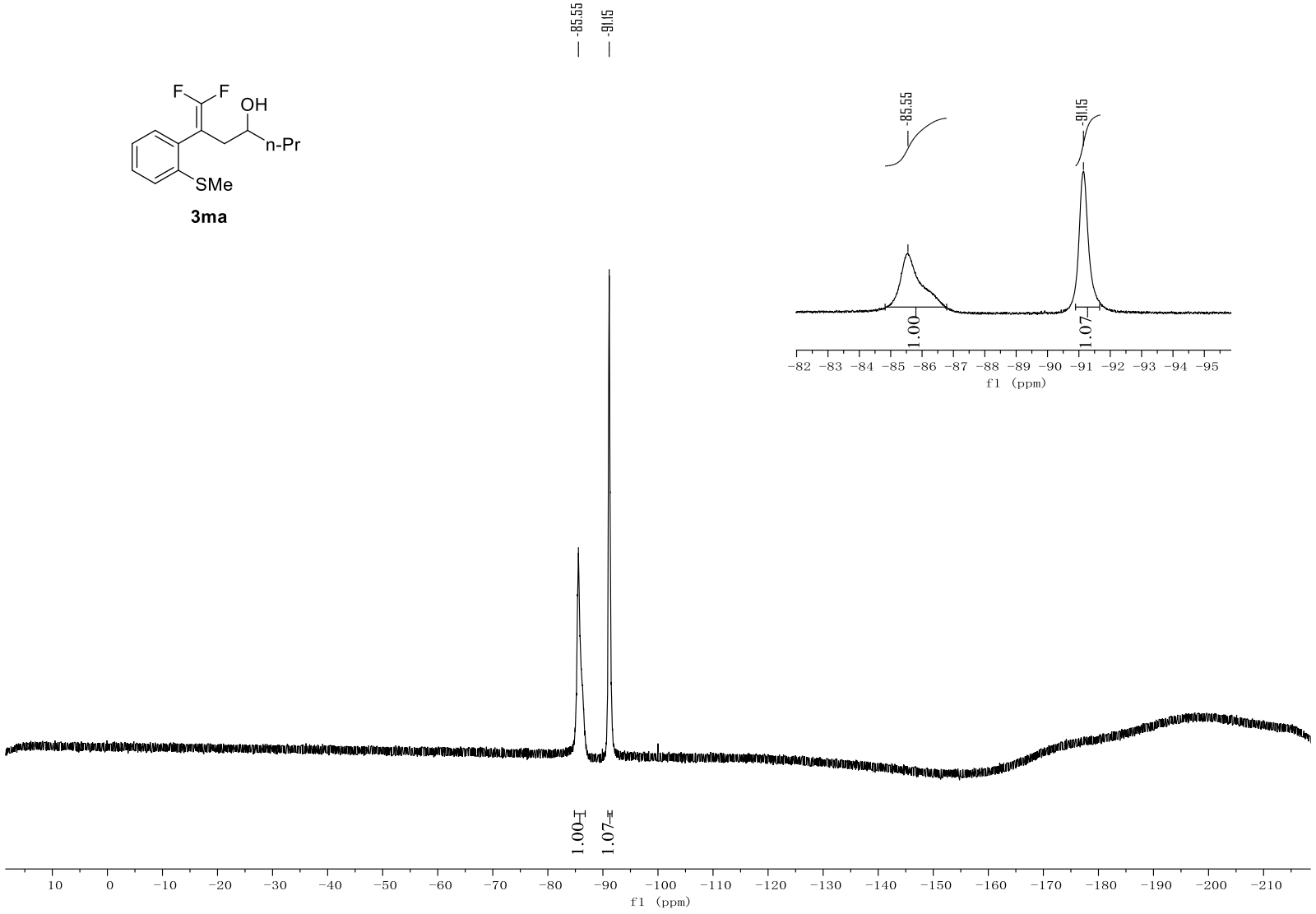
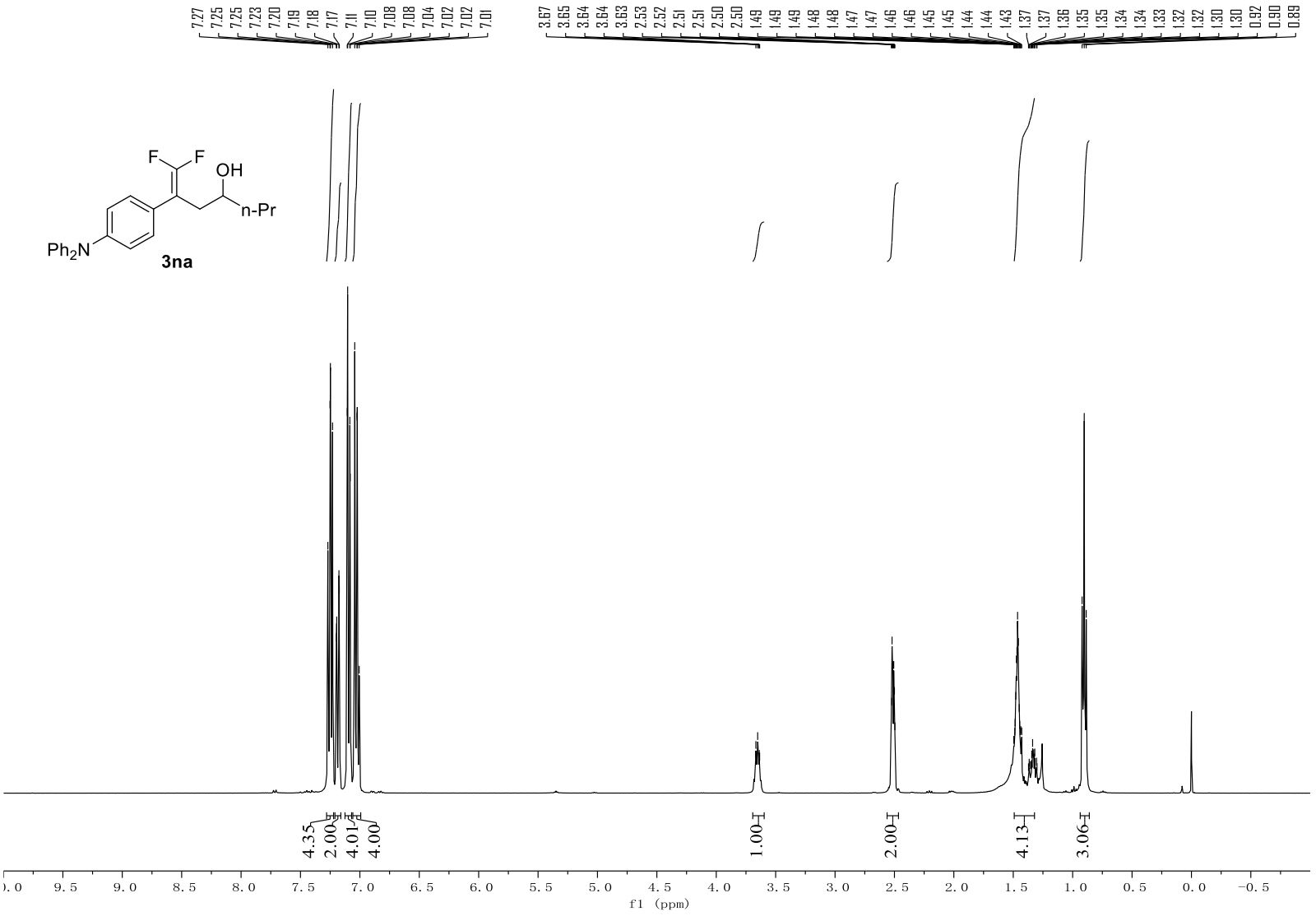
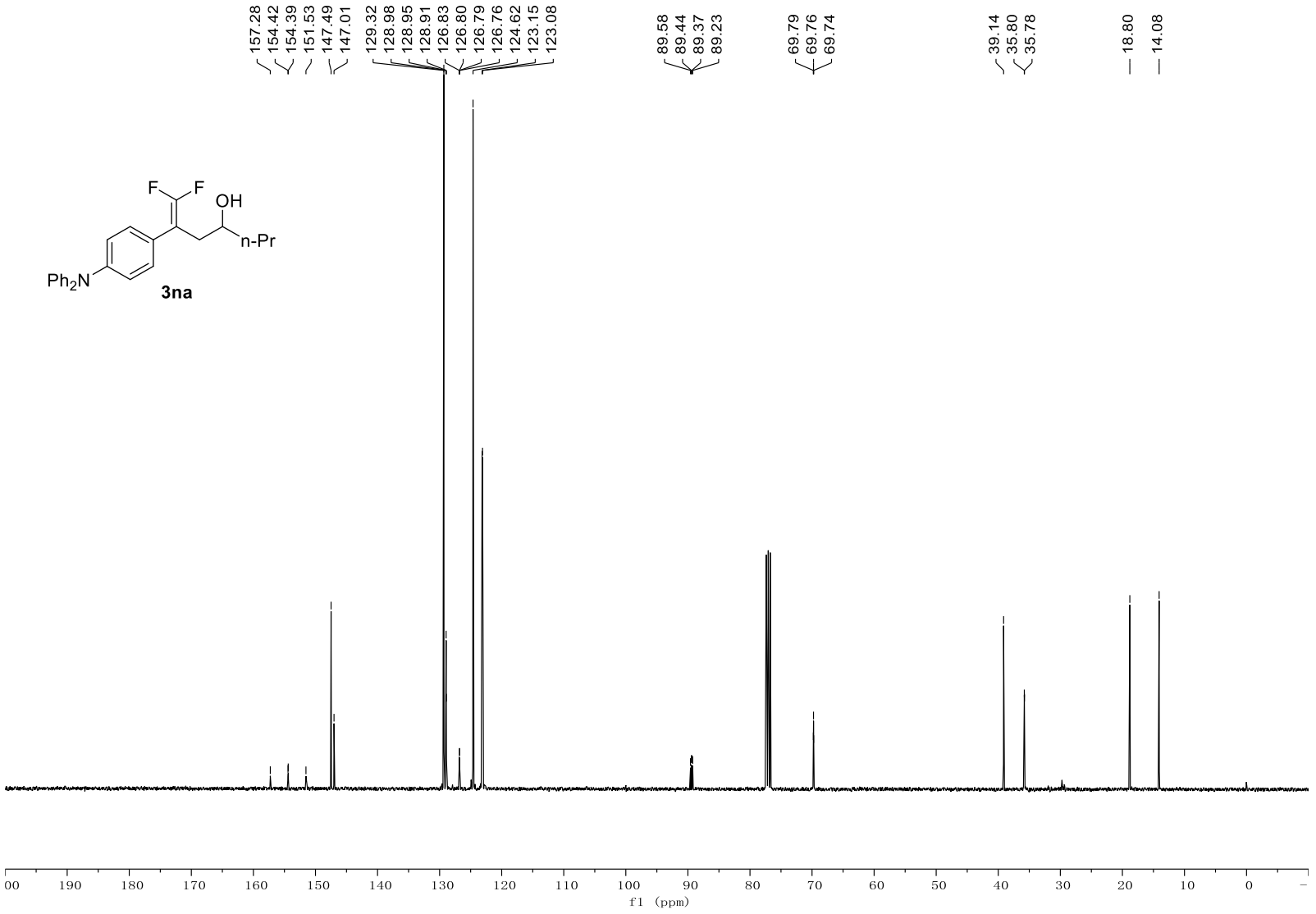
138.13
138.11
132.06
132.01
129.92
128.77
125.29
125.16
88.02
87.96
87.92
87.86
68.86
68.81
68.74
38.89
37.65
18.97
15.68
14.08
F
F
OH
n-Pr
SMe
3ma
f1 (ppm)


F
F
OH
n-Pr
SMe
3ma
-85.55
-91.15
1.00
1.07
f1 (ppm)


F
F
OH
n-Pr
Ph2N
3na
7.27 7.25 7.25 7.23 7.20 7.19 7.18 7.17 7.11 7.10 7.08 7.08 7.04 7.02 7.02 7.01
3.67 3.65 3.64 3.64 3.63 2.53 2.52 2.51 2.51 2.50 2.50 1.49 1.49 1.49 1.48 1.48 1.47 1.47 1.46 1.46 1.45 1.45 1.44 1.44 1.43 1.37 1.37 1.36 1.35 1.35 1.34 1.34 1.33 1.32 1.32 1.30 1.30 0.92 0.90 0.89
4.35
2.00
4.01
4.00
1.00
2.00
4.13
3.06
f1 (ppm)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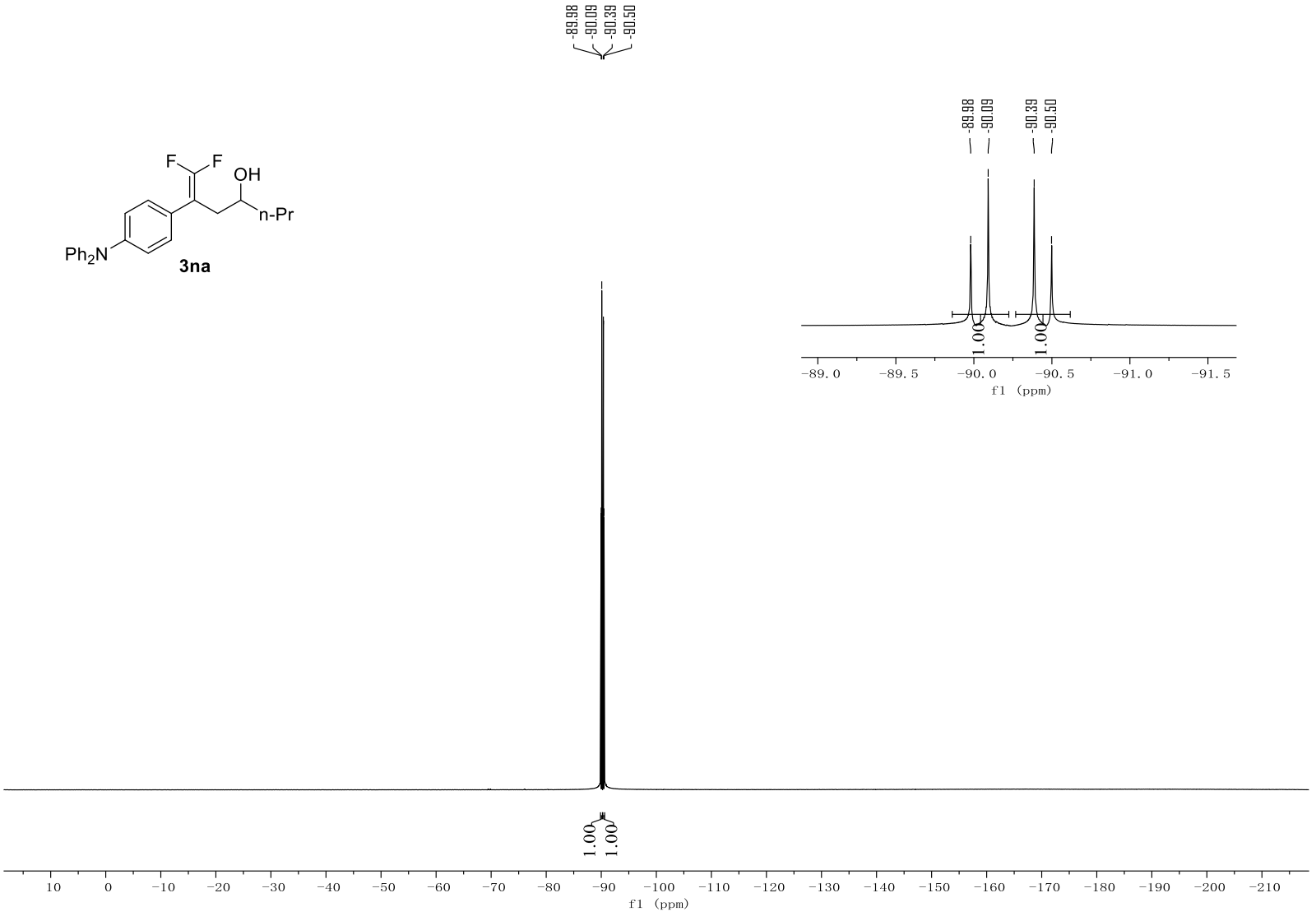
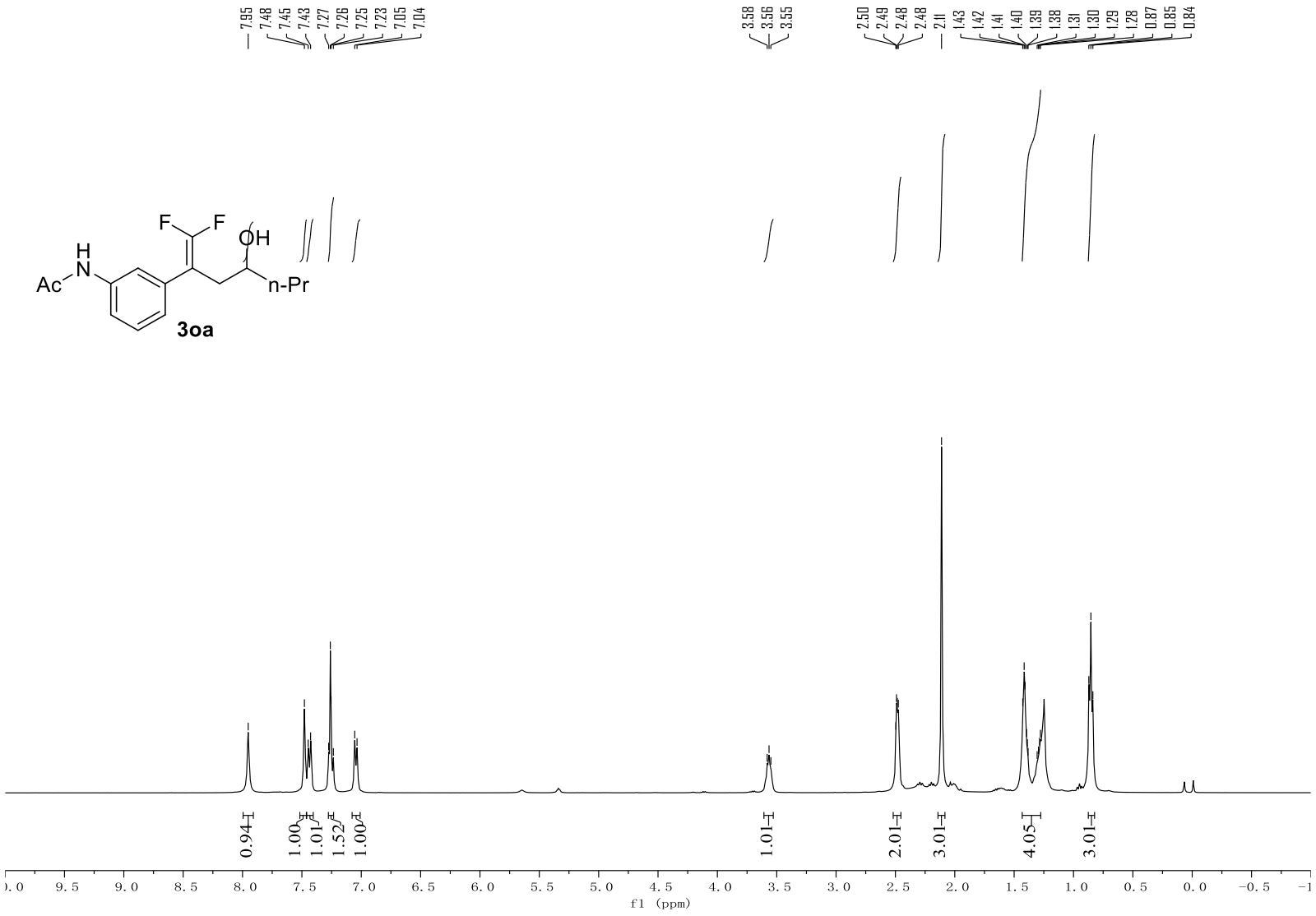
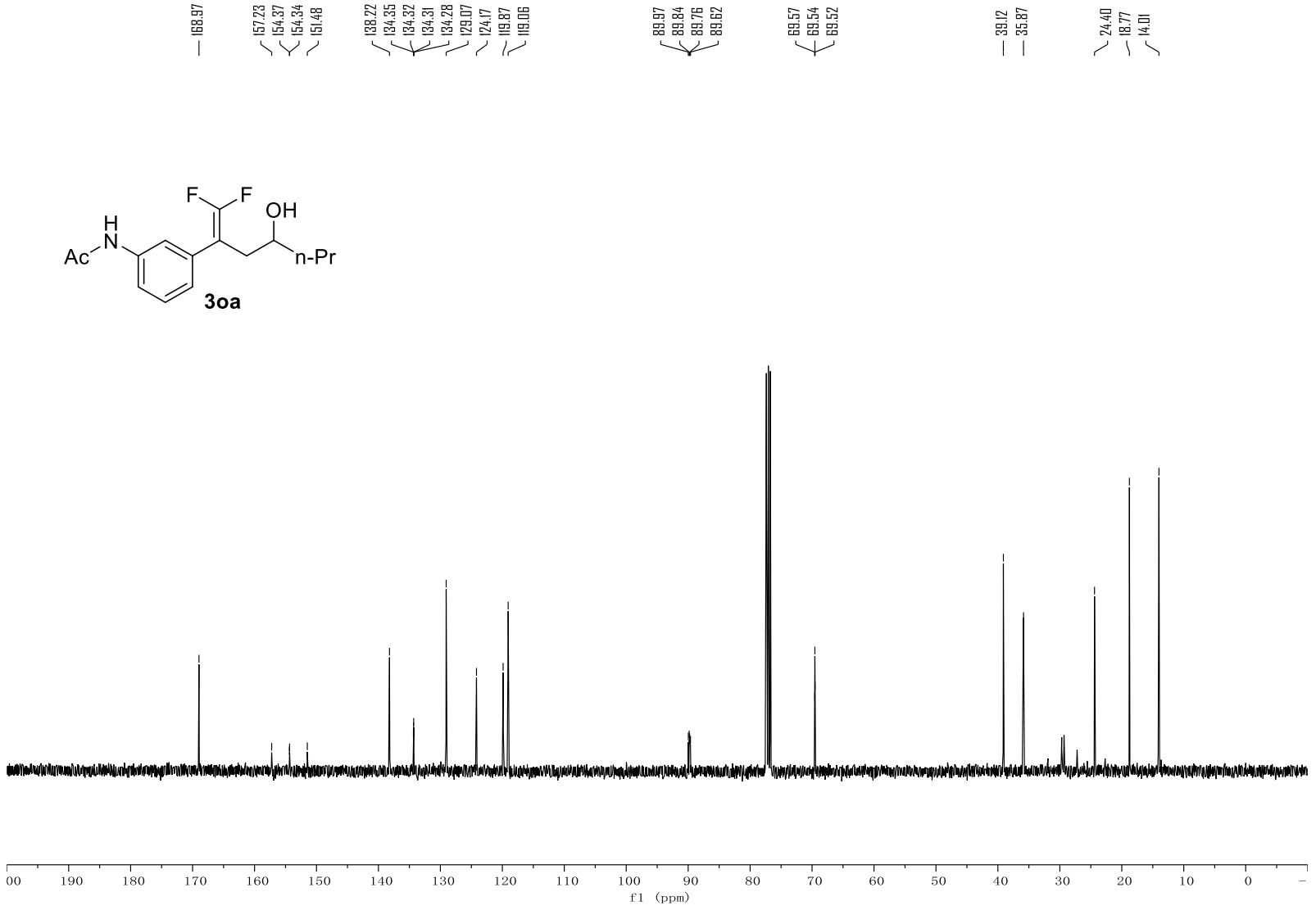
154.42
154.39
151.53
147.49
147.01
129.32
128.98
128.95
128.91
126.83
126.80
126.79
126.76
124.62
123.15
123.08
89.58
89.44
89.37
89.23
69.79
69.76
69.74
39.14
35.80
35.78
18.80
14.08
F
F
OH
n-Pr
Ph2N
3na
f1 (ppm)


-89.98
-90.09
-90.39
-90.50
F
F
OH
n-Pr
Ph2N
3na
-89.98
-90.09
-90.39
-90.50
1.00
1.00
-89.0
-89.5
-90.0
-90.5
-91.0
-91.5
f1 (ppm)
1.00
1.00
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)


7.95
7.48
7.45
7.43
7.27
7.26
7.25
7.23
7.05
7.04
3.58
3.56
3.55
2.50
2.49
2.48
2.48
2.11
1.43
1.42
1.41
1.40
1.39
1.38
1.31
1.30
1.29
1.28
0.87
0.85
0.84
F
F
OH
H
N
Ac
n-Pr
3oa
0.94
1.00
1.01
1.52
1.00
1.01
2.01
3.01
4.05
3.01
f1 (ppm)


168.97
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154.34
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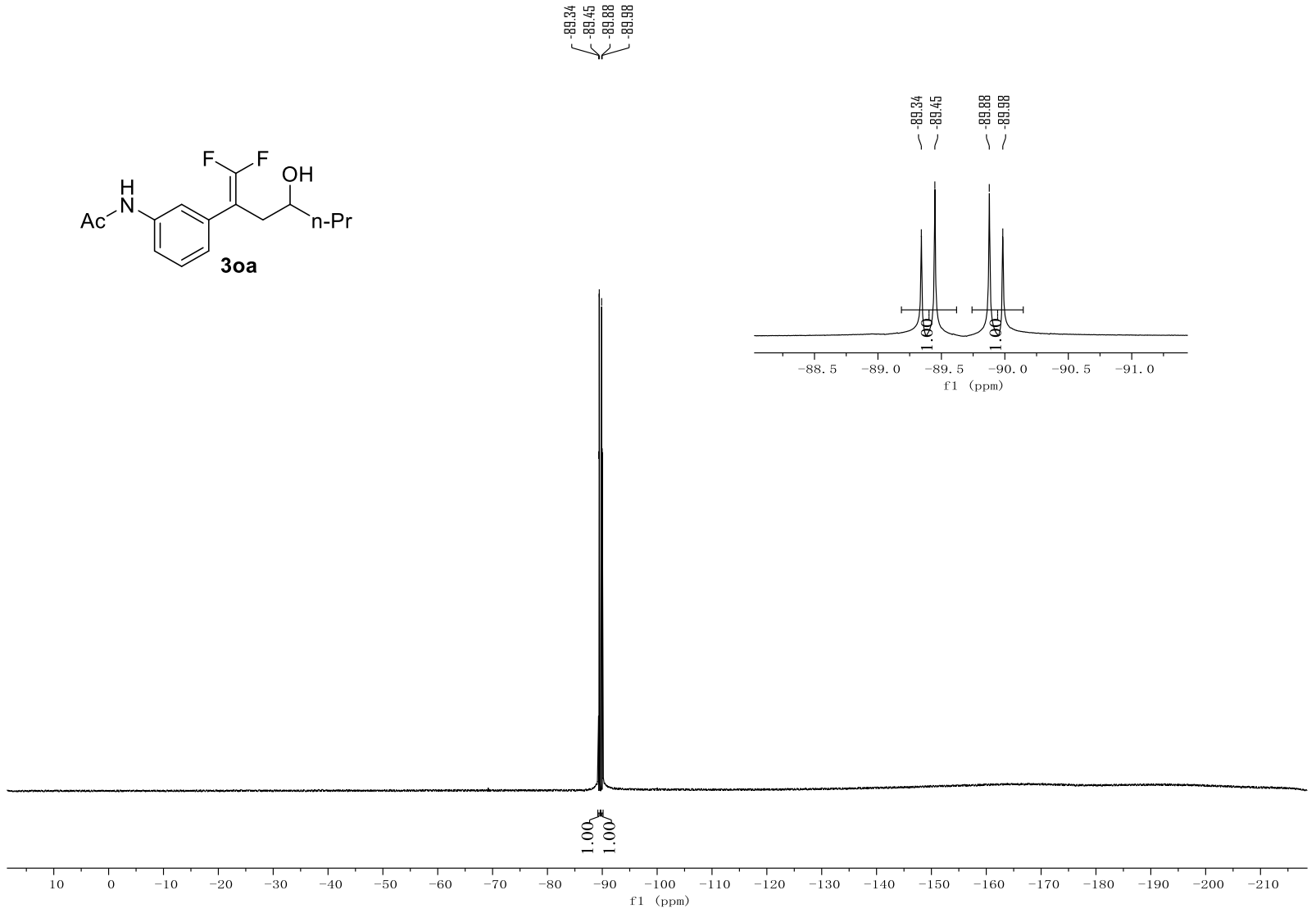
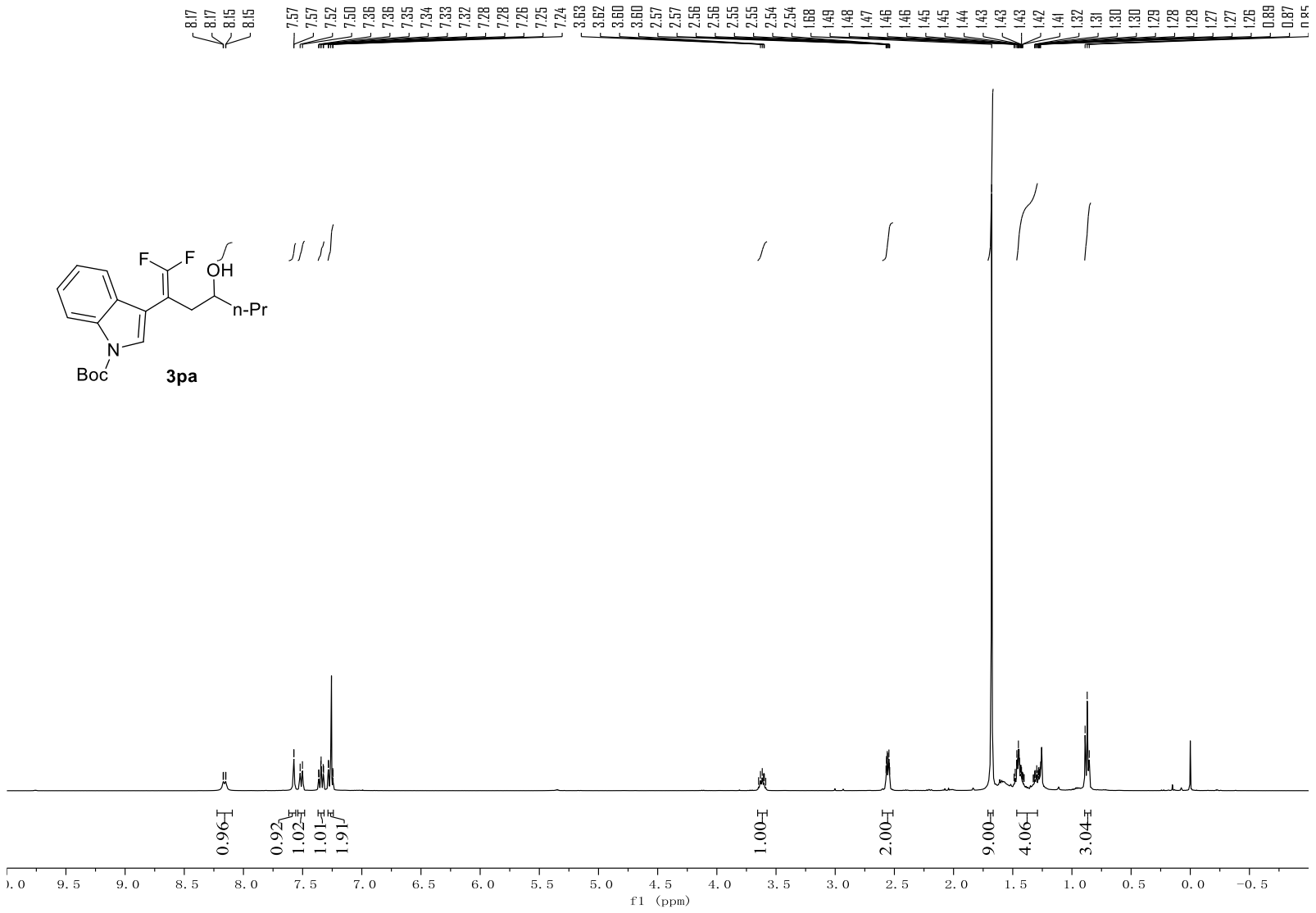
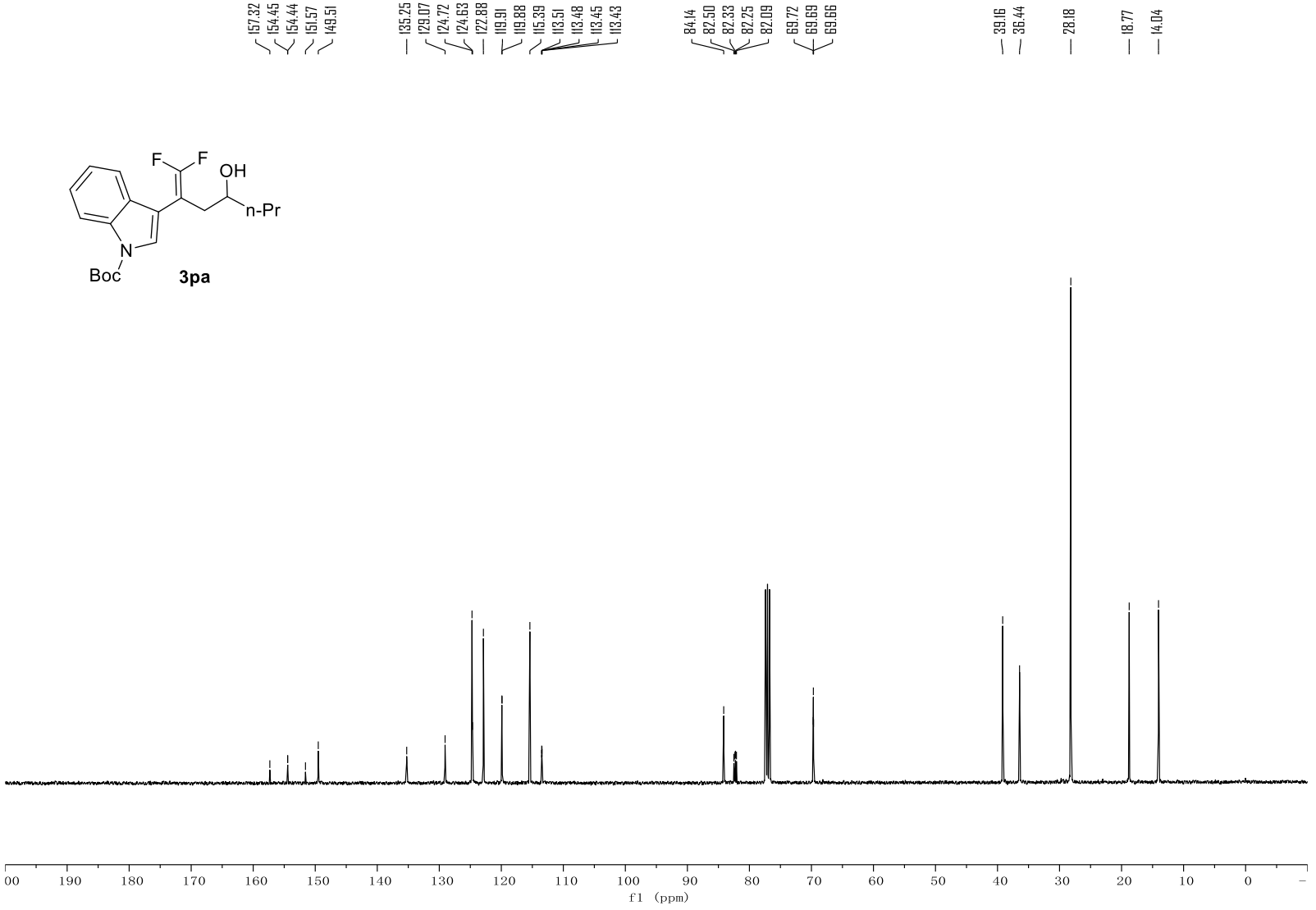
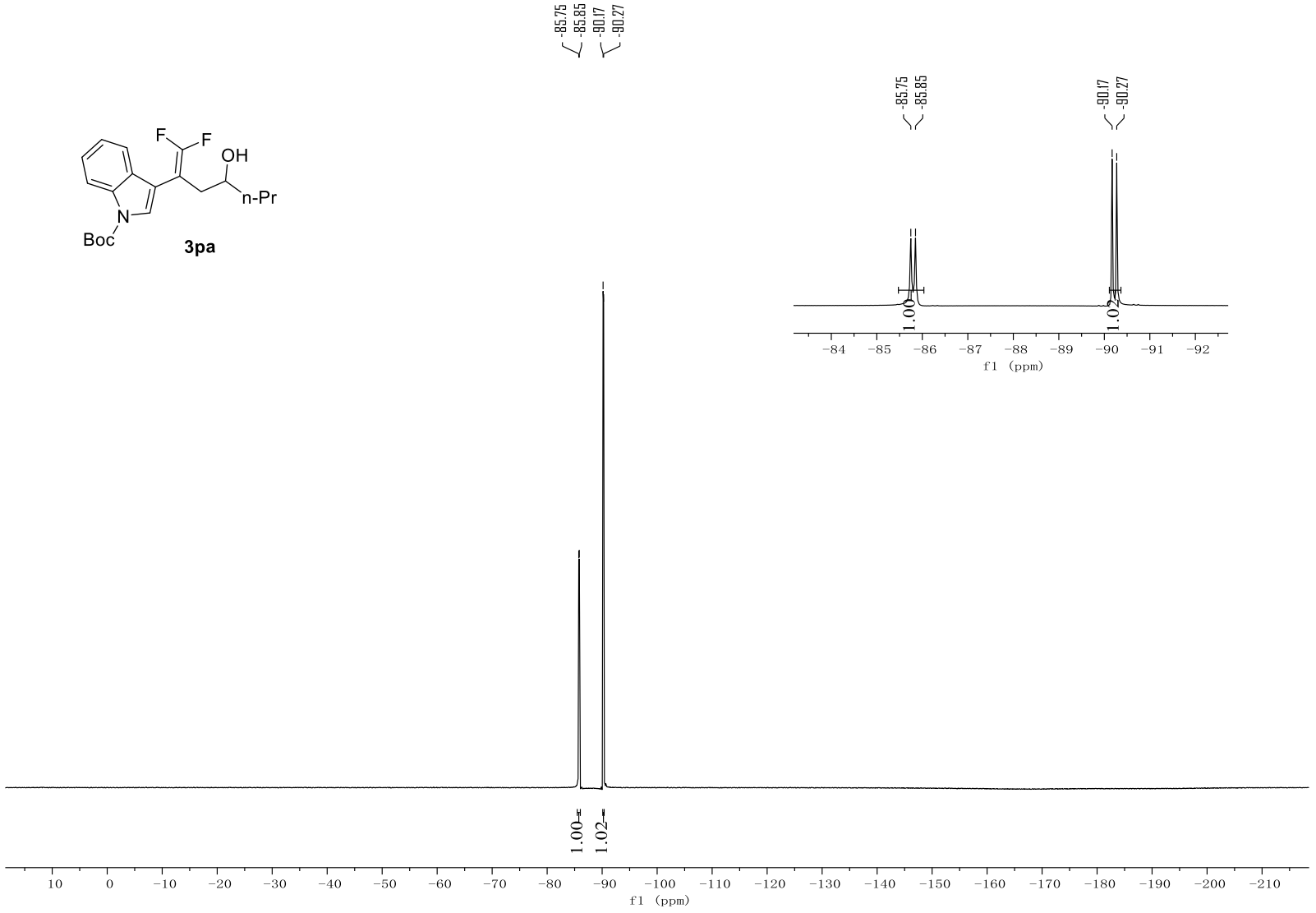
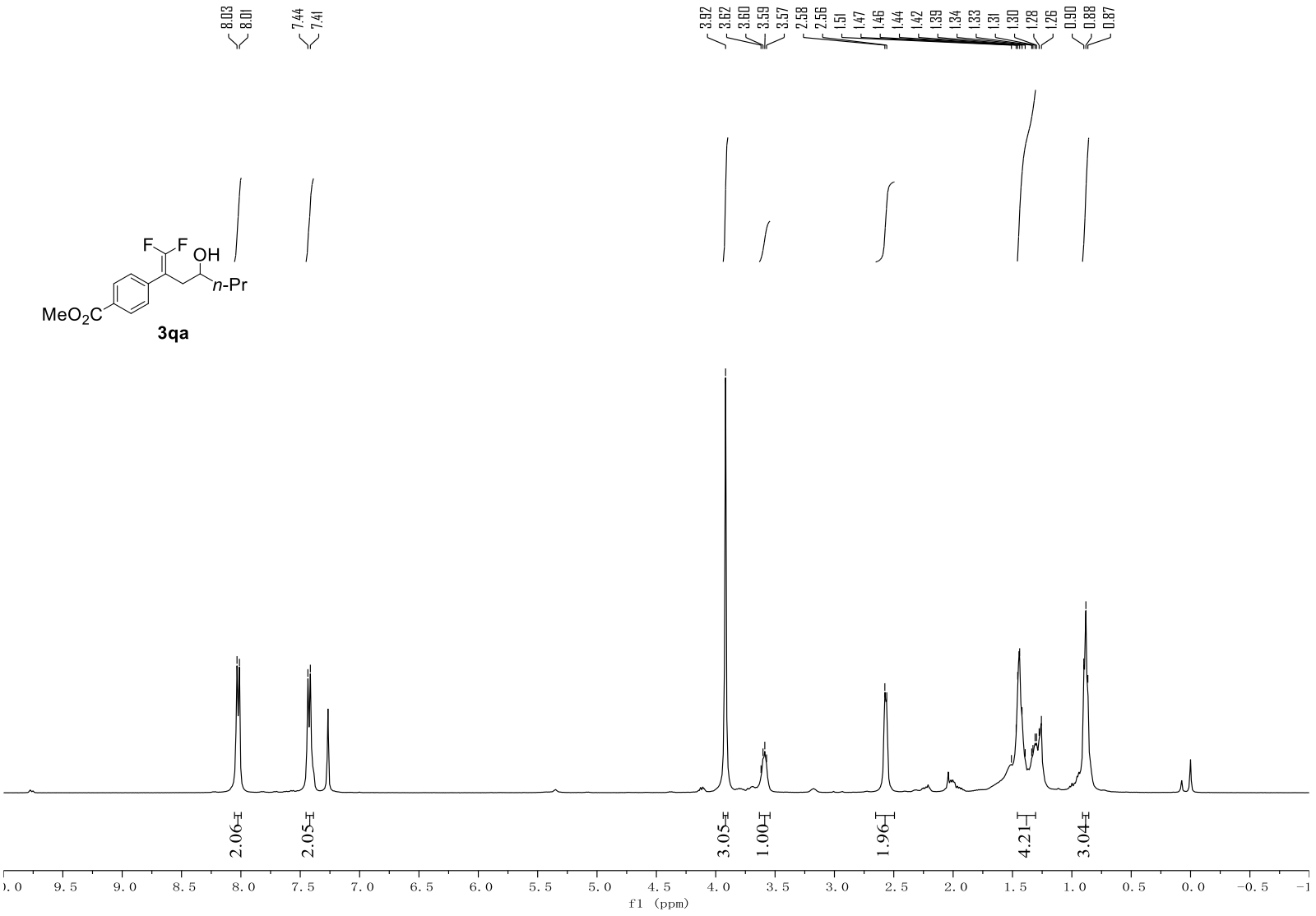
138.22
134.35
134.32
134.31
134.28
129.07
124.17
119.87
119.06
89.97
89.84
89.76
89.62
69.57
69.54
69.52
39.12
35.87
24.40
18.77
14.01
F
F
OH
H
N
Ac
n-Pr
3oa
f1 (ppm)

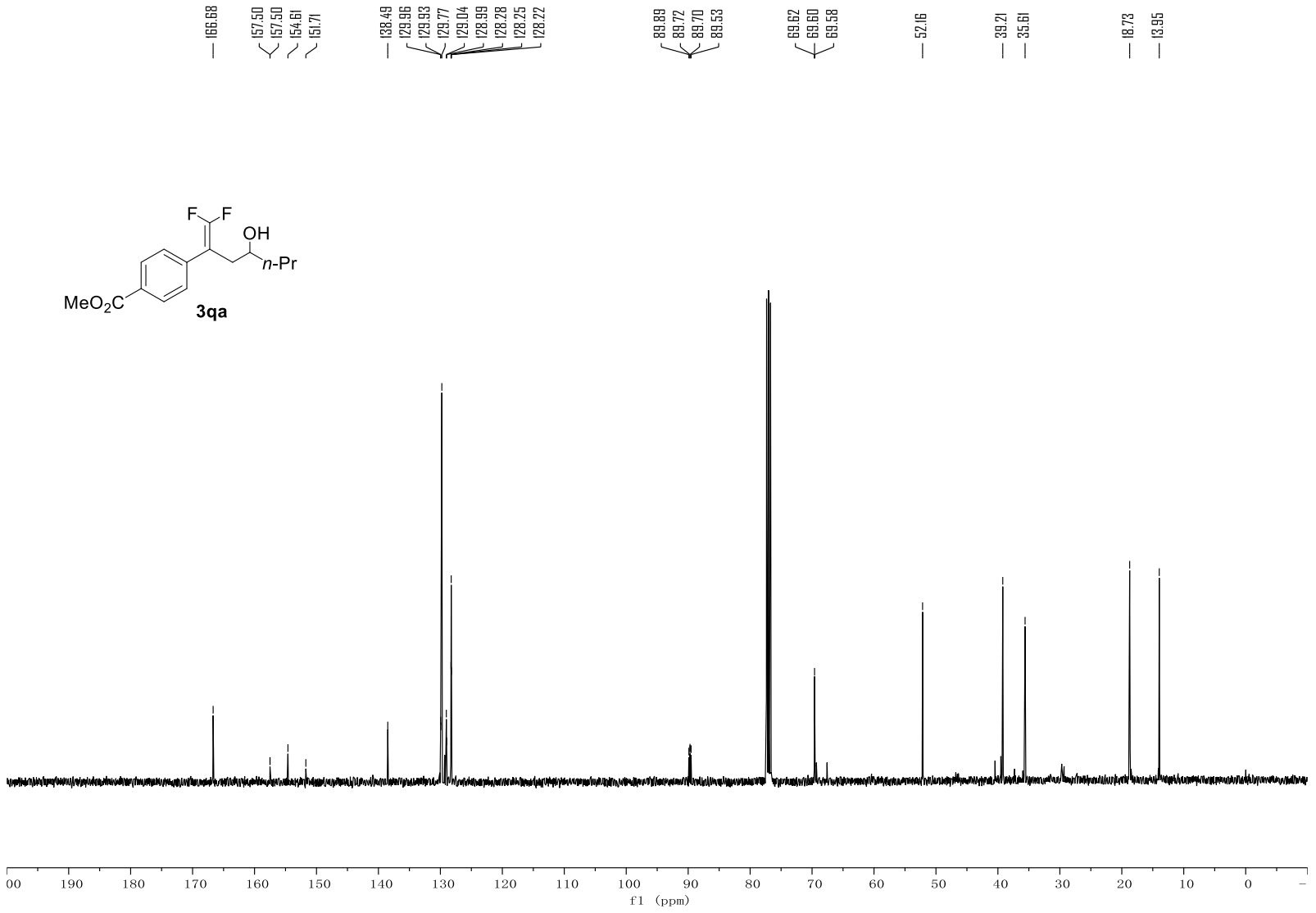

-89.34
-89.45
-89.88
-89.98
F
F
OH
H
N
Ac
n-Pr
3oa
1.00
1.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)
-89.34
-89.45
-89.88
-89.98
1.00
1.00
−88.5 −89.0 −89.5 −90.0 −90.5 −91.0
f1 (ppm)

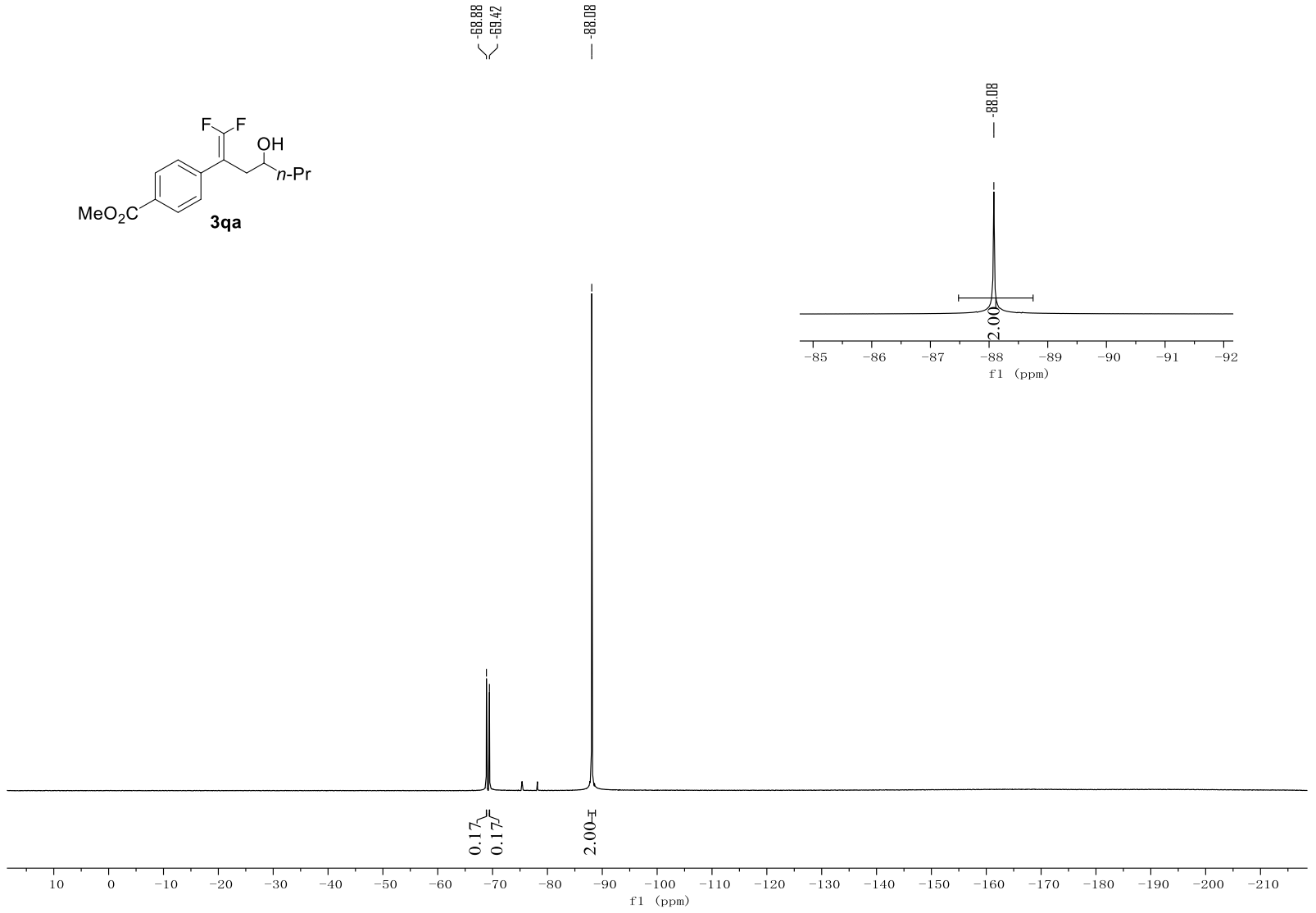

F
F
OH
n-Pr
N
Boc
3pa
f1 (ppm)

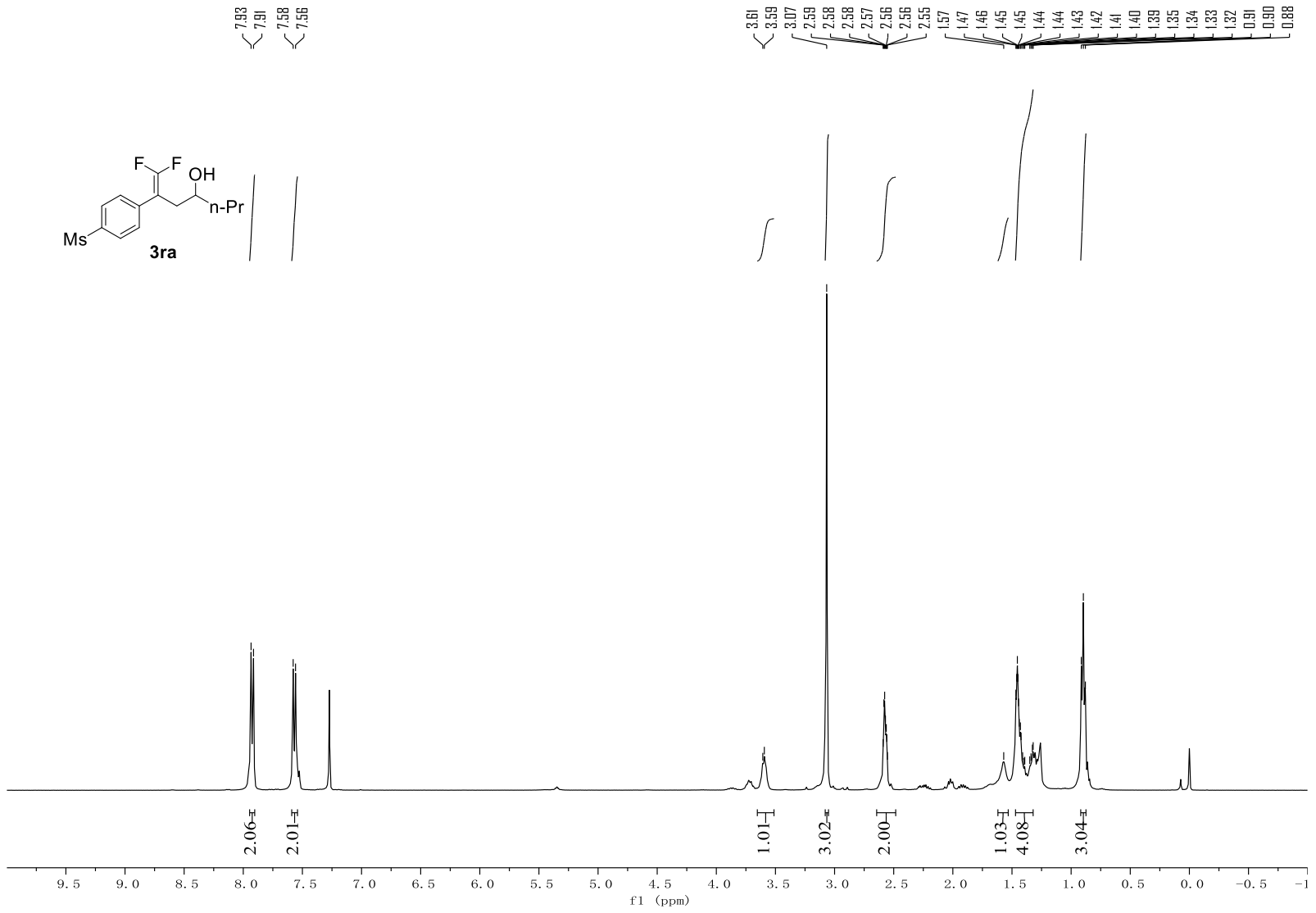

157.32
154.45
154.44
151.57
149.51
135.25
129.07
124.72
124.63
122.88
119.91
119.88
115.39
113.51
113.48
113.45
113.43
84.14
82.50
82.33
82.25
82.09
69.72
69.69
69.66
39.16
36.44
28.18
18.77
14.04
F
F
OH
n-Pr
N
Boc
3pa
f1 (ppm)

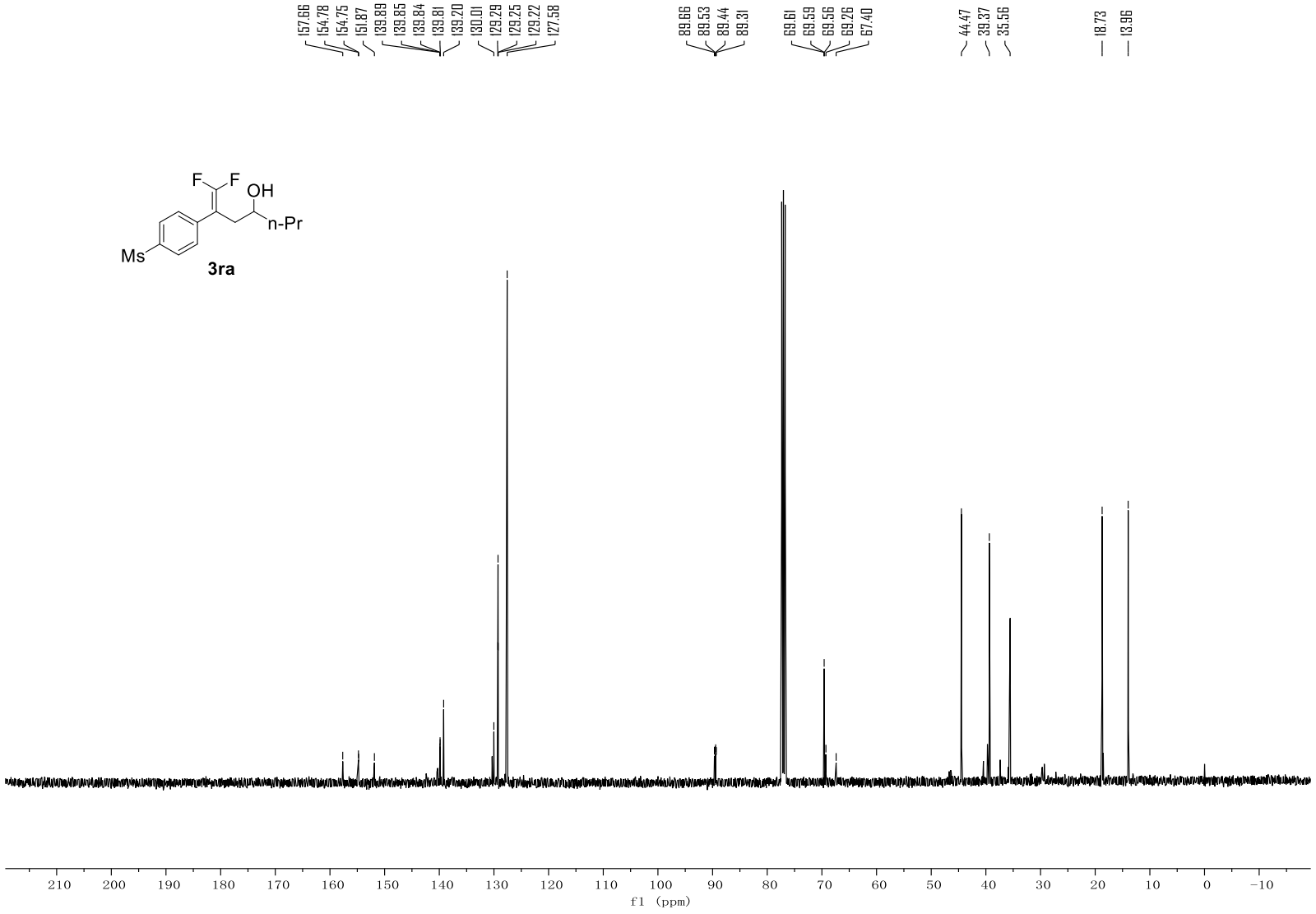

-85.75
-85.85
-90.17
-90.27
F
F
OH
n-Pr
N
Boc
3pa
1.00
1.02
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)
−84 −85 −86 −87 −88 −89 −90 −91 −92
f1 (ppm)

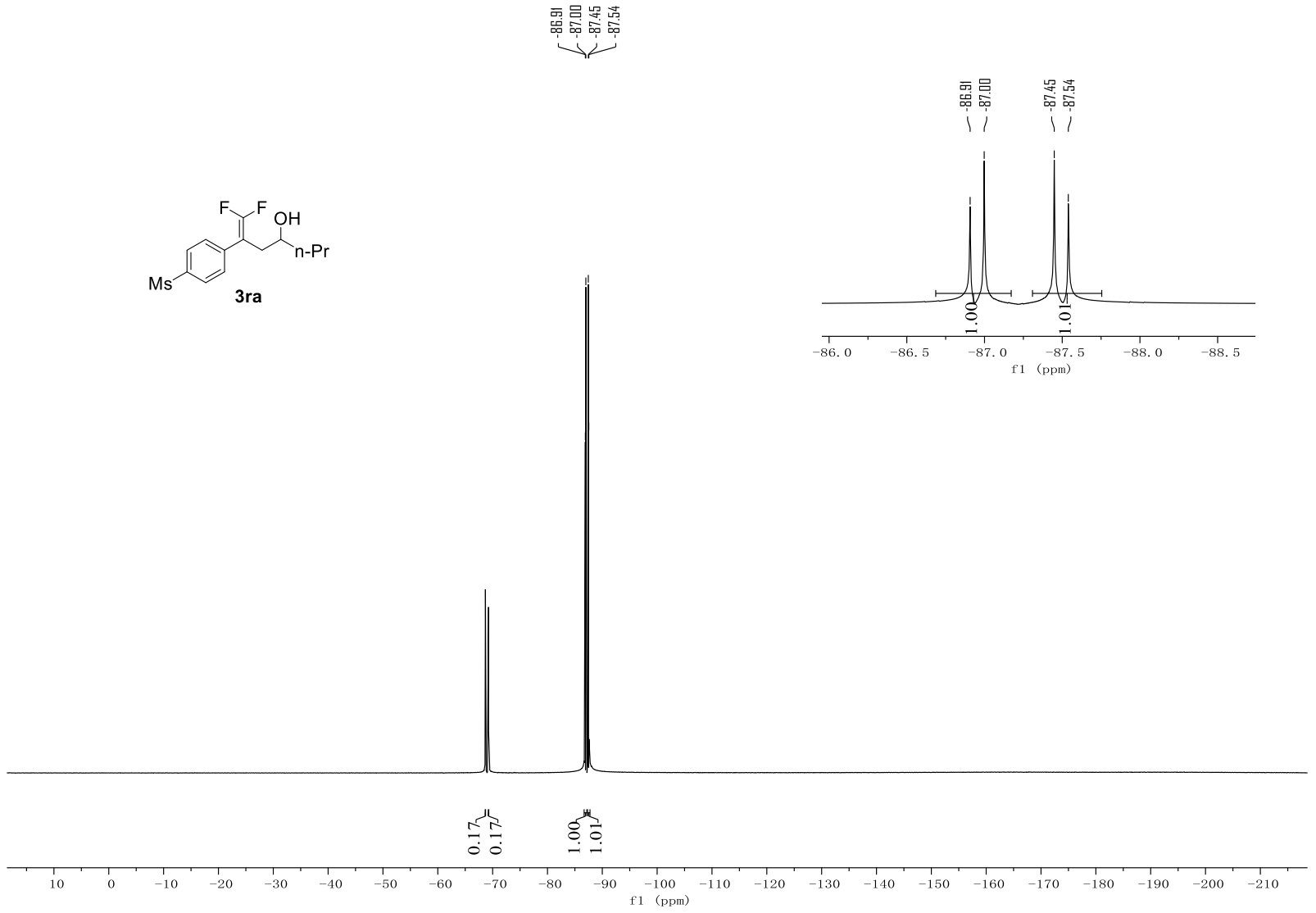

8.03
8.01
7.44
7.41
3.92
3.62
3.60
3.59
3.57
2.58
2.56
1.51
1.47
1.46
1.44
1.42
1.39
1.34
1.33
1.31
1.30
1.28
1.26
0.90
0.88
0.87
F
F
OH
n-Pr
MeO2C
3qa
2.06
2.05
3.05
1.00
1.96
4.21
3.04
f1 (ppm)

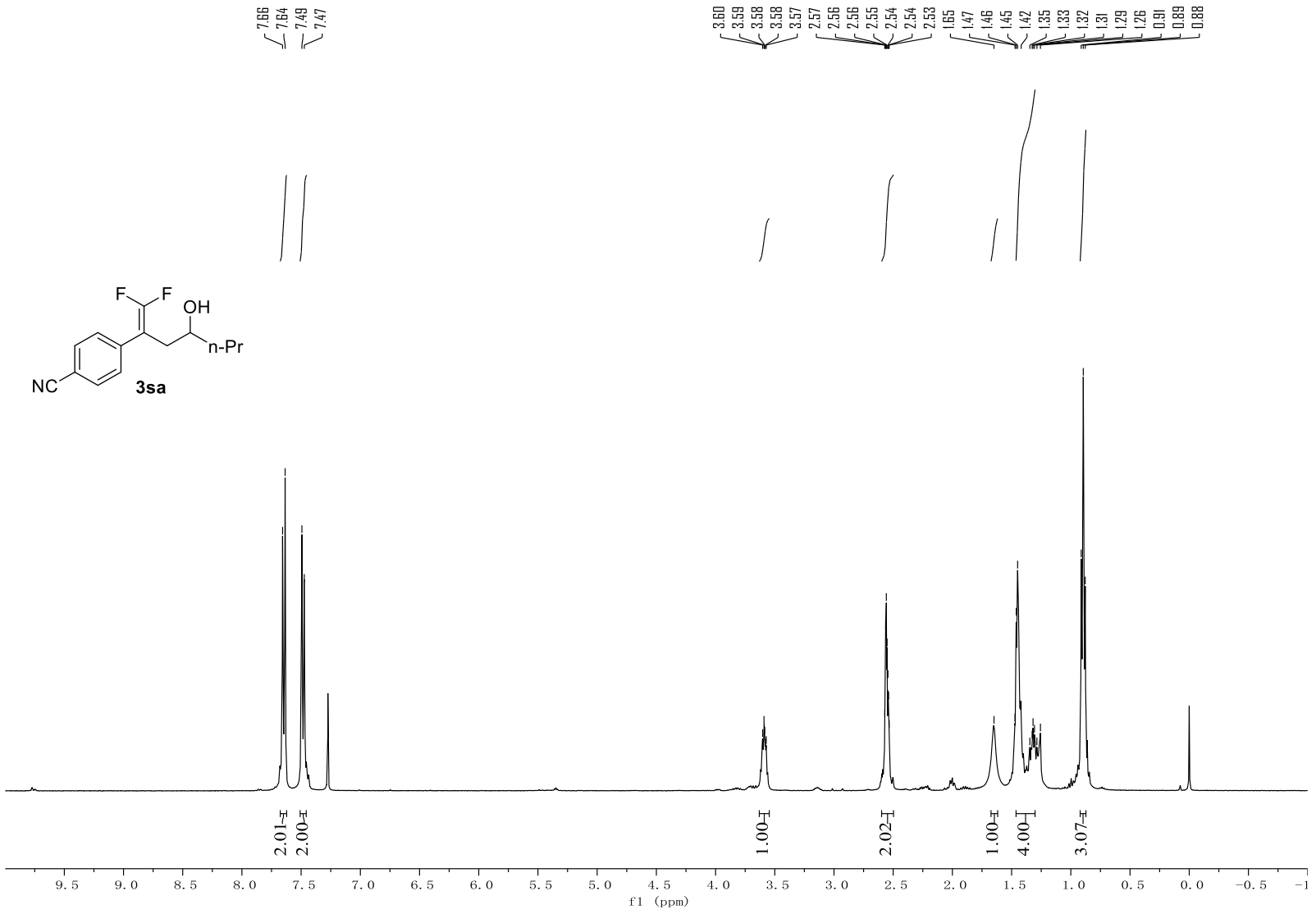

166.68
157.50
157.50
154.61
151.71
138.49
129.96
129.93
129.77
129.04
128.99
128.28
128.25
128.22
89.89
89.72
89.70
89.53
69.62
69.60
69.58
52.16
39.21
35.61
18.73
13.95
F
F
OH
n-Pr
MeO2C
3qa
f1 (ppm)

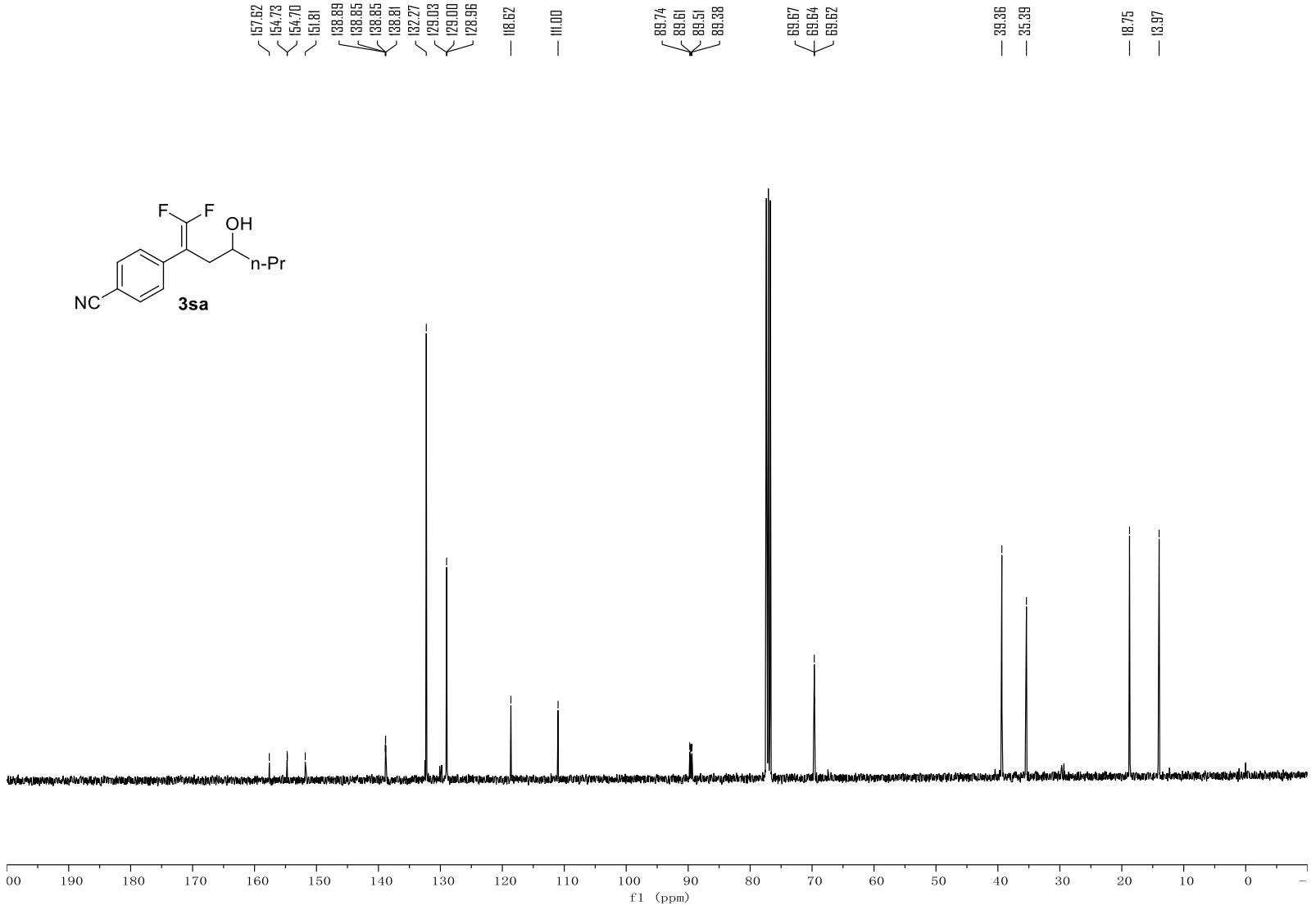

F
F
OH
n-Pr
MeO2C
3qa
-68.88
-69.42
-88.08
-88.08
2.00
0.17
0.17
2.00
f1 (ppm)
f1 (ppm)

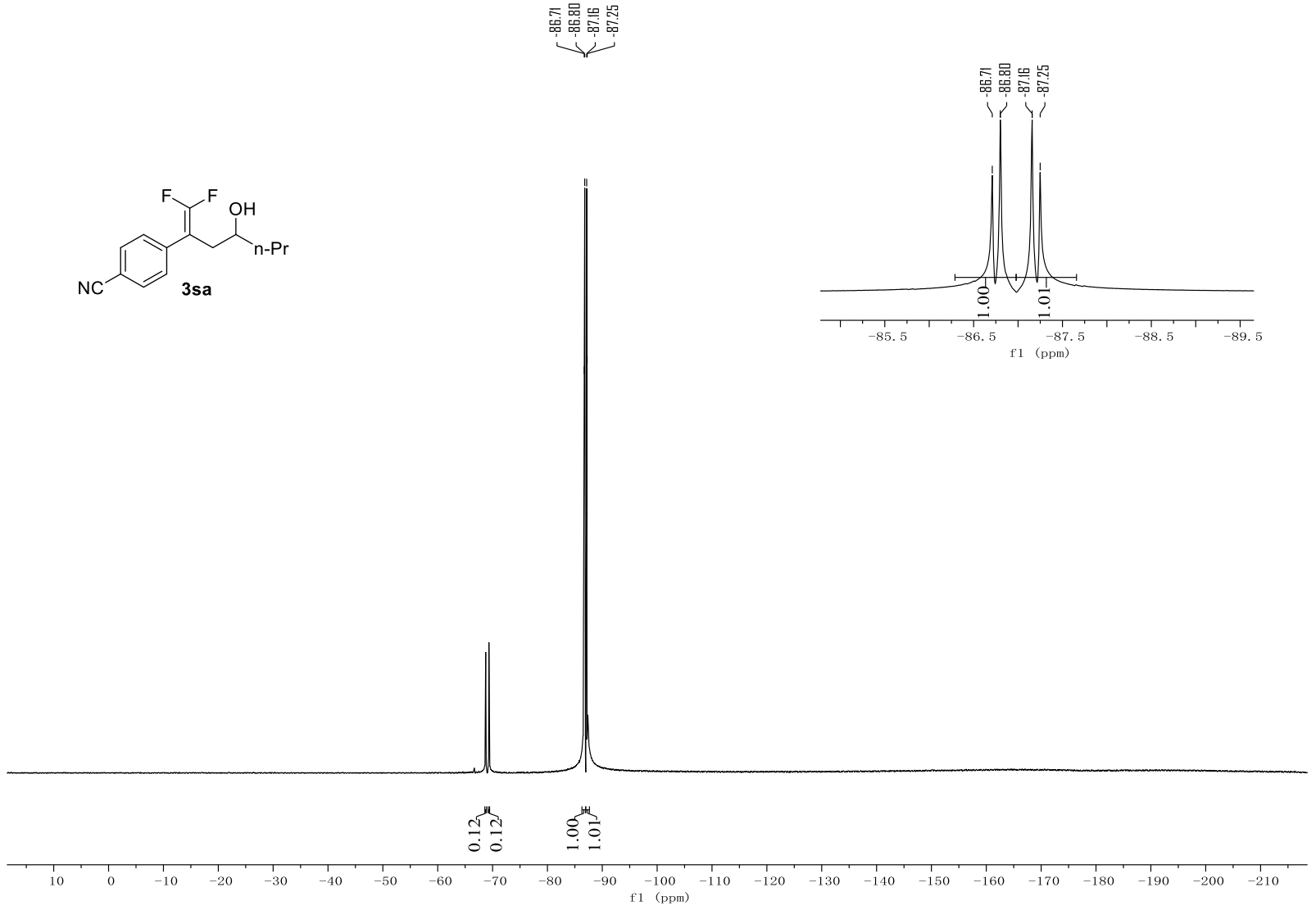

7.93
7.91
7.58
7.56
3.61
3.59
3.07
2.59
2.58
2.58
2.57
2.56
2.56
2.55
1.57
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.42
1.41
1.40
1.39
1.35
1.34
1.33
1.32
0.91
0.90
0.88
F
F
OH
n-Pr
Ms
3ra
2.06
2.01
1.01
3.02
2.00
1.03
4.08
3.04
f1 (ppm)

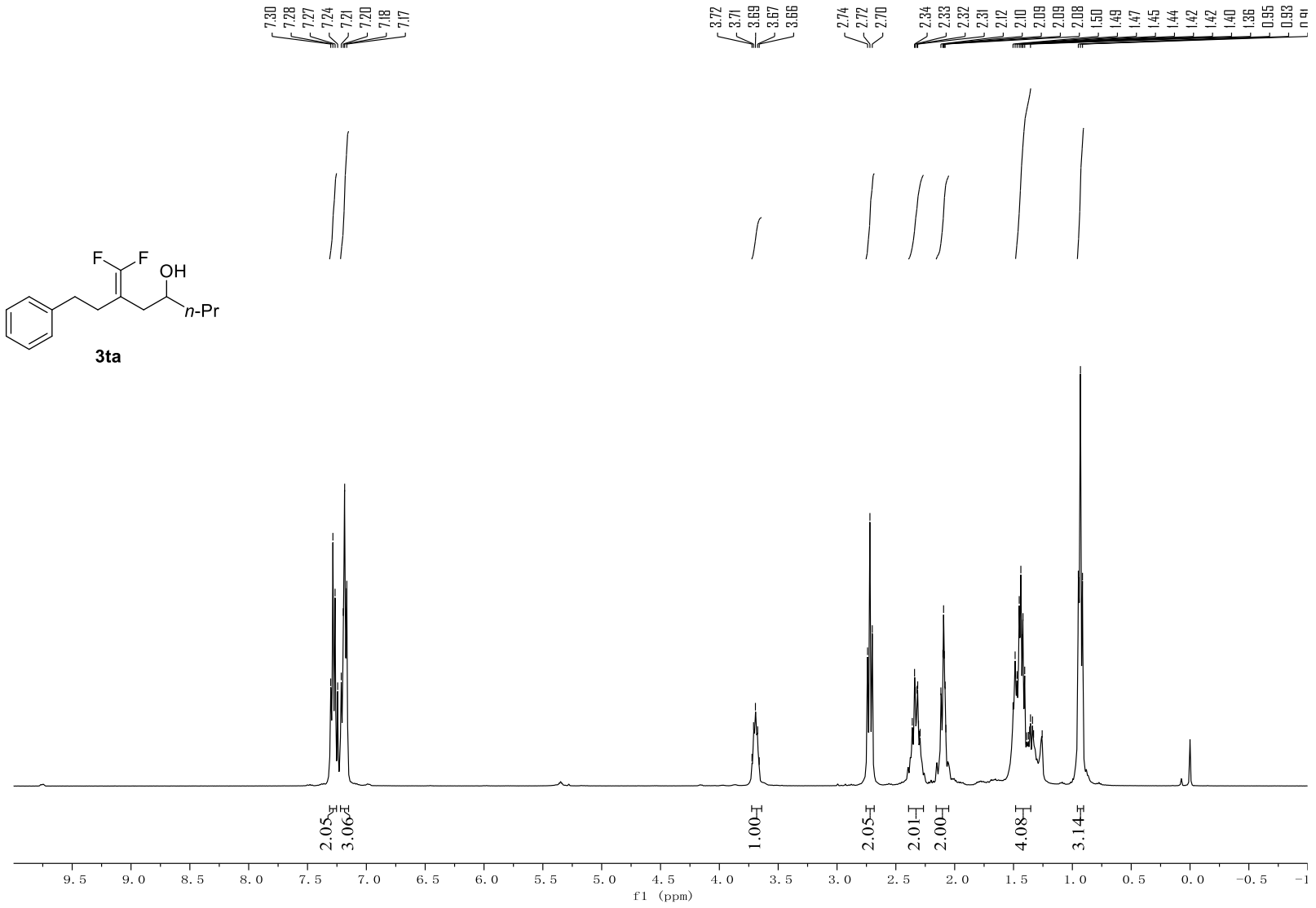

157.66
154.78
154.75
151.87
139.89
139.85
139.84
139.81
139.20
130.01
129.29
129.25
129.22
127.58
89.66
89.53
89.44
89.31
69.61
69.59
69.56
69.26
67.40
44.47
39.37
35.56
18.73
13.96
F
F
OH
n-Pr
Ms
3ra
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

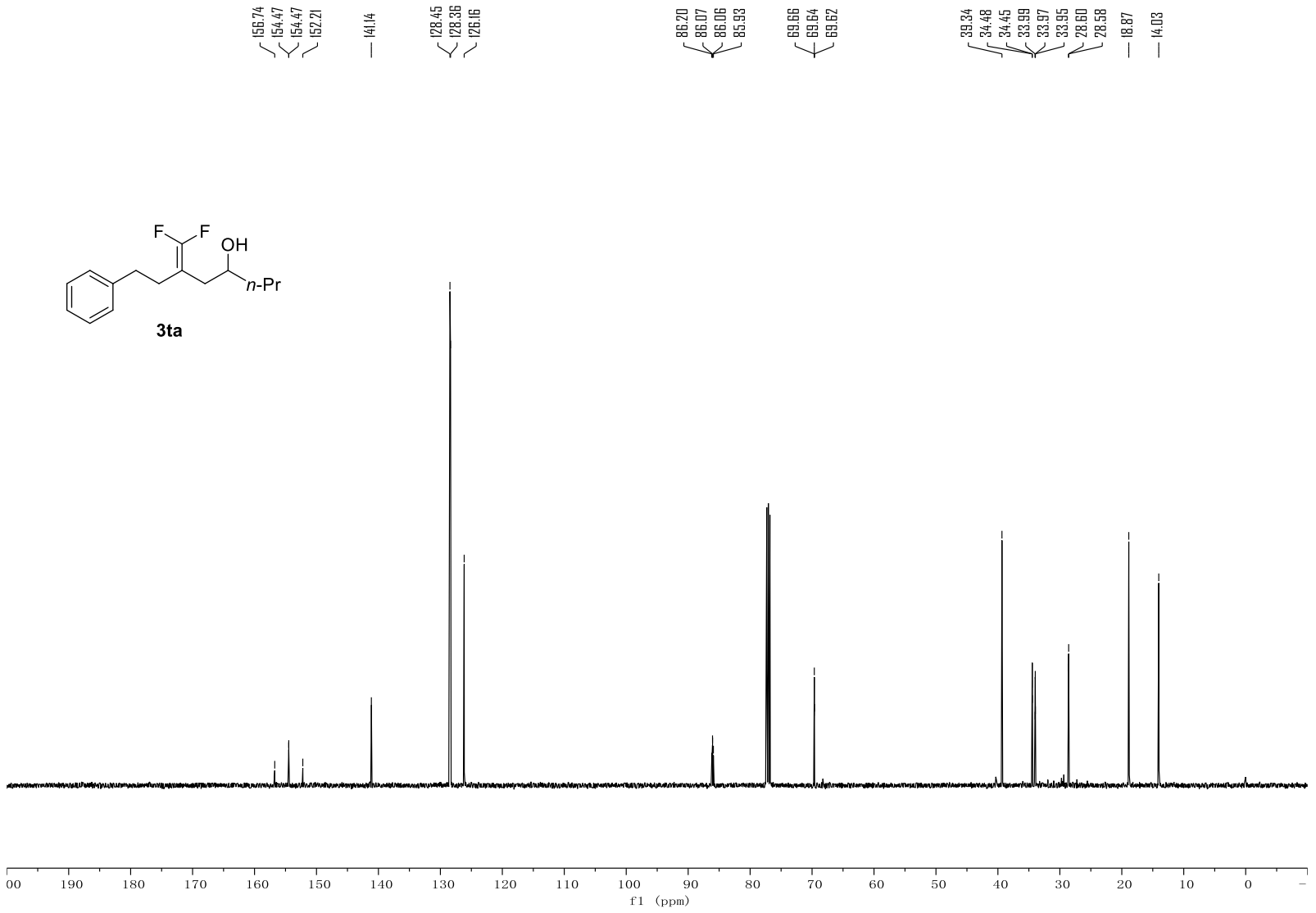

-86.91
-87.00
-87.45
-87.54
F
F
OH
n-Pr
Ms
3ra
1.00
1.01
f1 (ppm)
0.17
0.17
1.00
1.01
f1 (ppm)

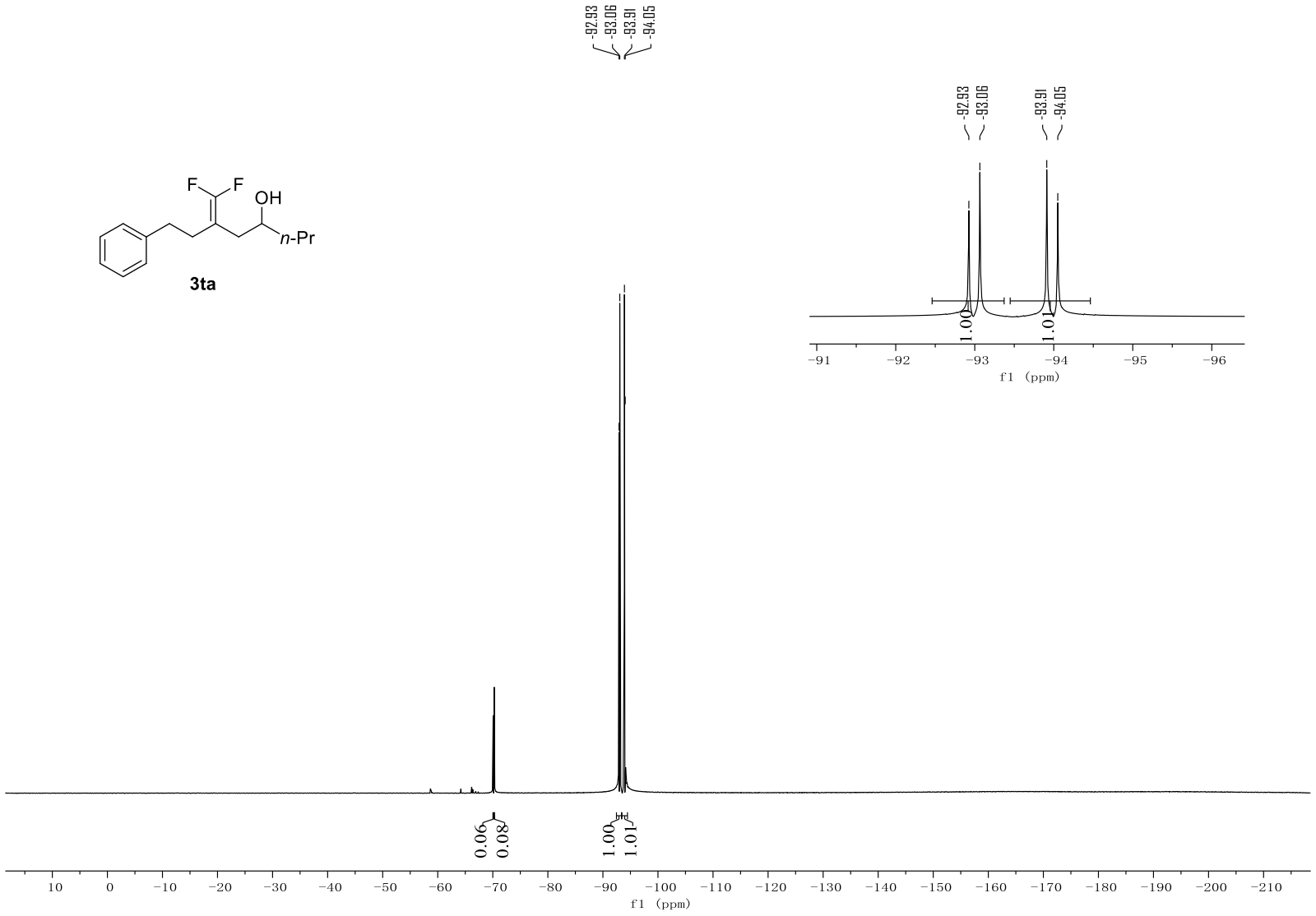

7.66
7.64
7.49
7.47
3.60
3.59
3.58
3.58
3.57
2.57
2.56
2.56
2.55
2.54
2.54
2.53
1.65
1.47
1.46
1.45
1.42
1.35
1.33
1.32
1.31
1.29
1.26
0.91
0.89
0.88
F
F
OH
n-Pr
NC
3sa
2.01
2.00
1.00
2.02
1.00
4.00
3.07
f1 (ppm)

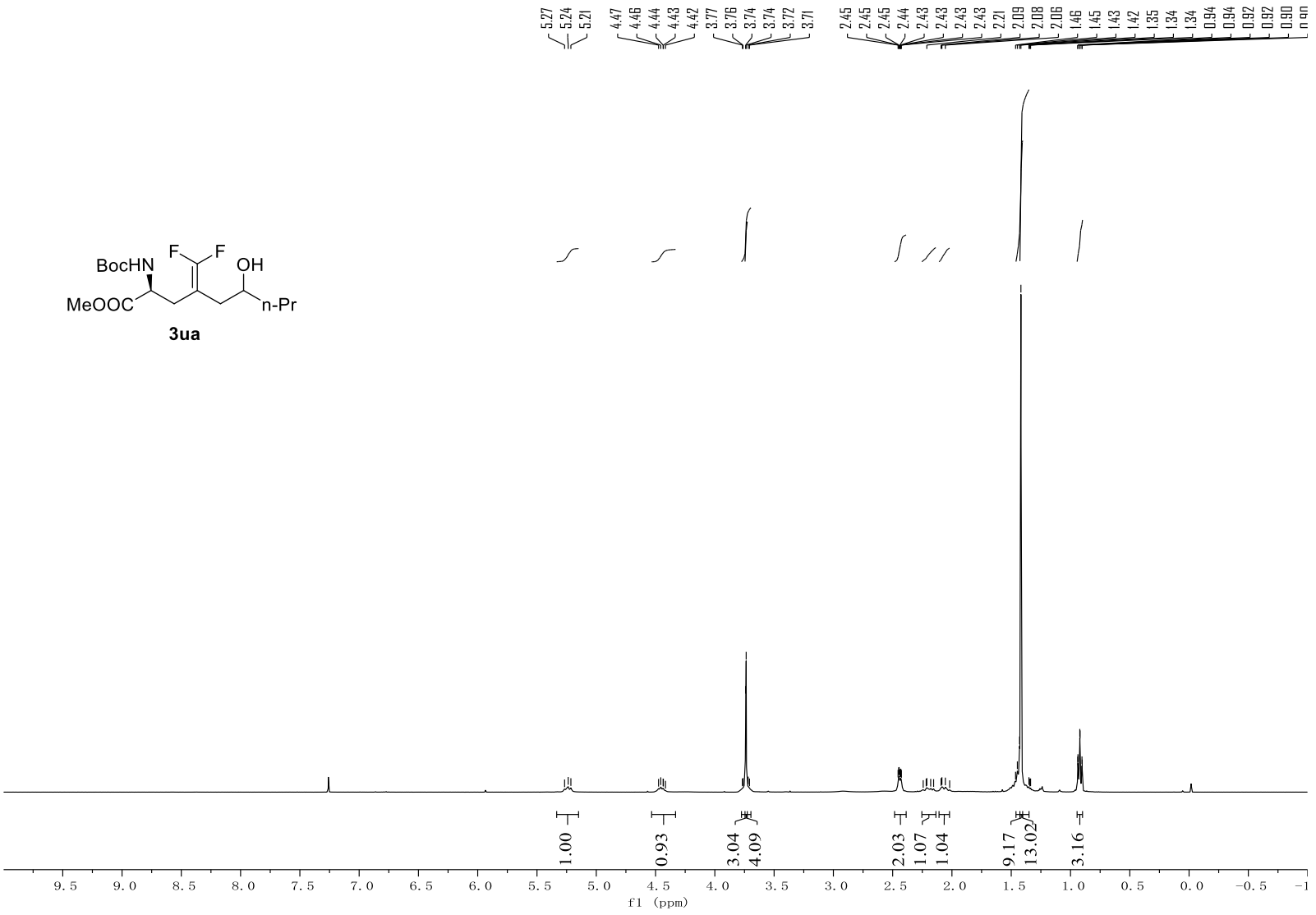

157.62
154.73
154.70
151.81
138.89
138.85
138.85
138.81
132.27
129.03
129.00
128.96
118.62
111.00
89.74
89.61
89.51
89.38
69.67
69.64
69.62
39.36
35.39
18.75
13.97
F
F
OH
n-Pr
NC
3sa
f1 (ppm)

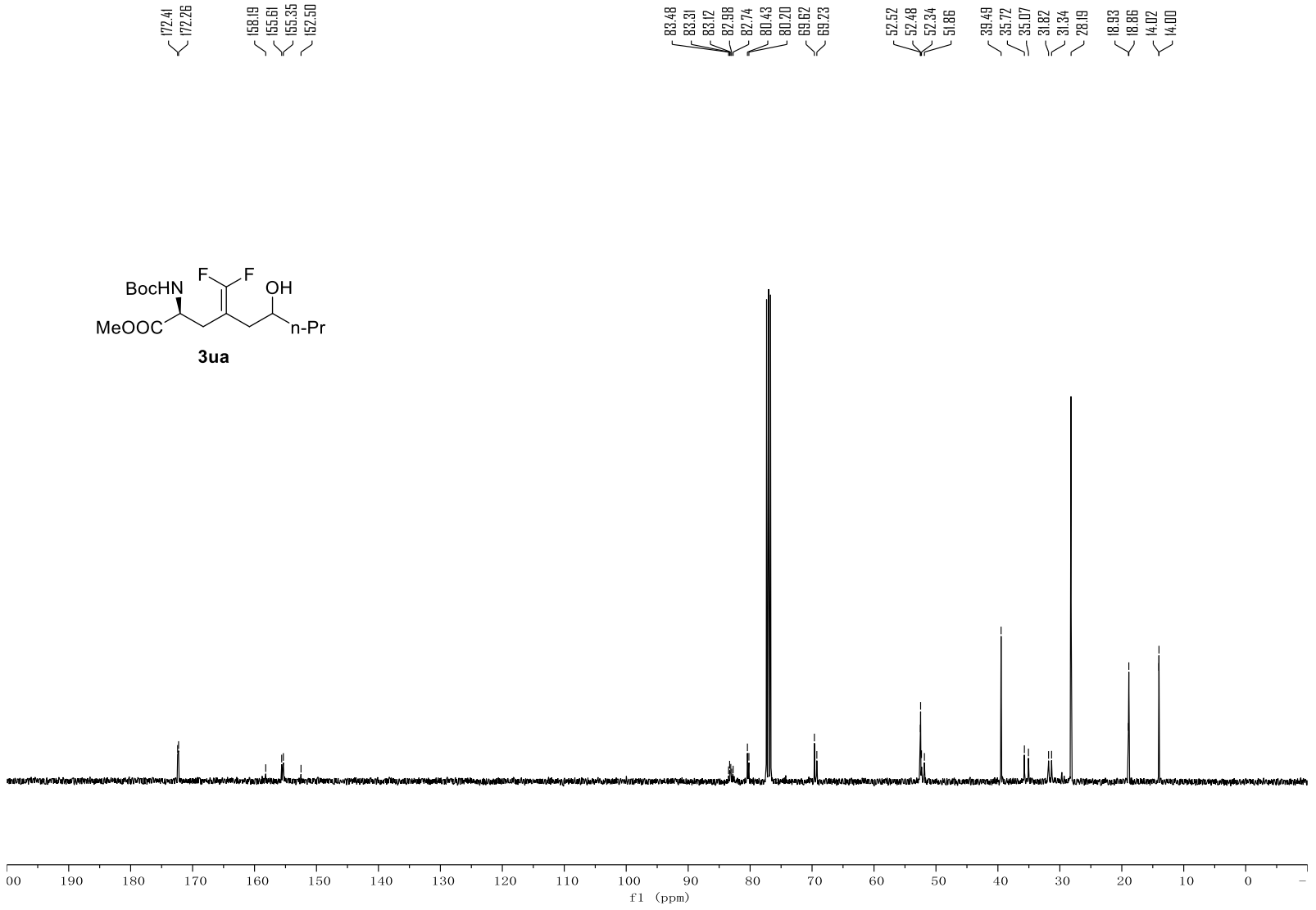

-86.71
-86.80
-87.16
-87.25
F
F
OH
n-Pr
NC
3sa
1.00
1.01
-85.5
-86.5
-87.5
-88.5
-89.5
f1 (ppm)
0.12
0.12
1.00
1.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

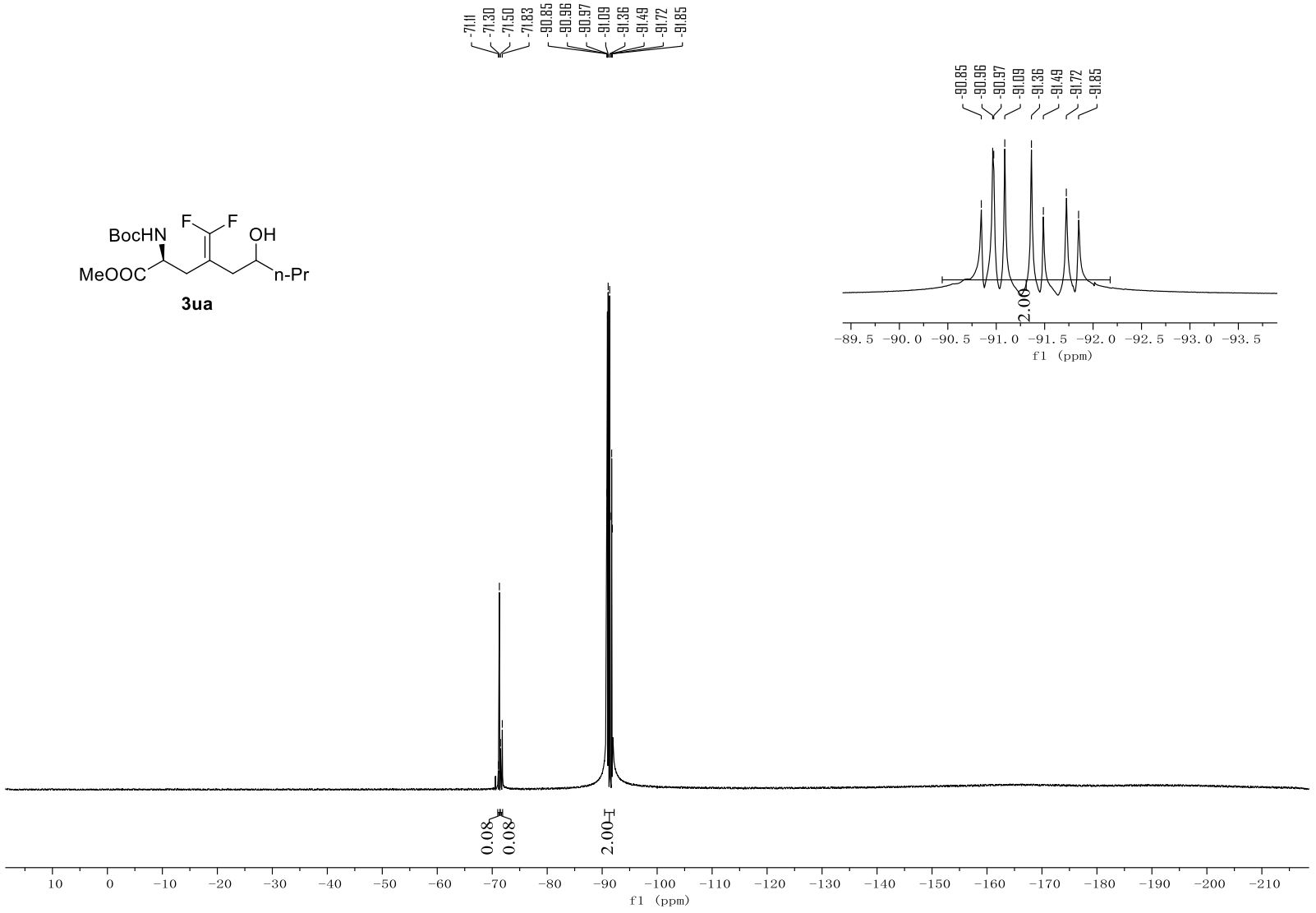

7.30
7.28
7.27
7.24
7.21
7.20
7.18
7.17
3.72
3.71
3.69
3.67
3.66
2.74
2.72
2.70
2.34
2.33
2.32
2.31
2.12
2.10
2.09
2.09
2.08
1.50
1.49
1.47
1.45
1.44
1.42
1.42
1.40
1.36
0.95
0.93
F
F
OH
n-Pr
3ta
2.05
3.06
1.00
2.05
2.01
2.00
4.08
3.14
f1 (ppm)

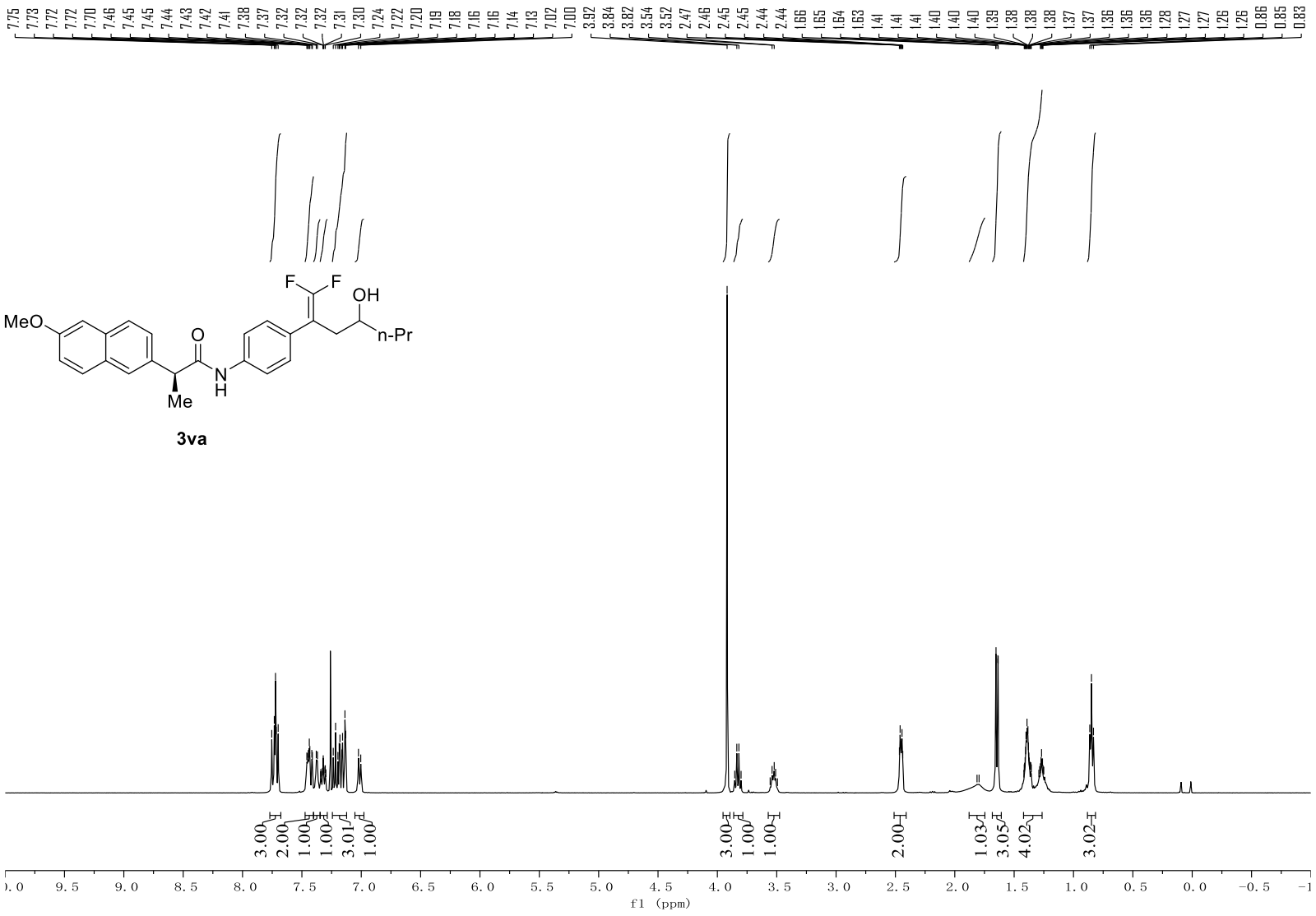

156.74
154.47
154.47
152.21
141.14
128.45
128.38
126.16
86.20
86.07
86.06
85.93
69.66
69.64
69.62
39.34
34.48
34.45
33.99
33.97
33.95
28.60
28.58
18.87
14.03
F
F
OH
n-Pr
3ta
f1 (ppm)

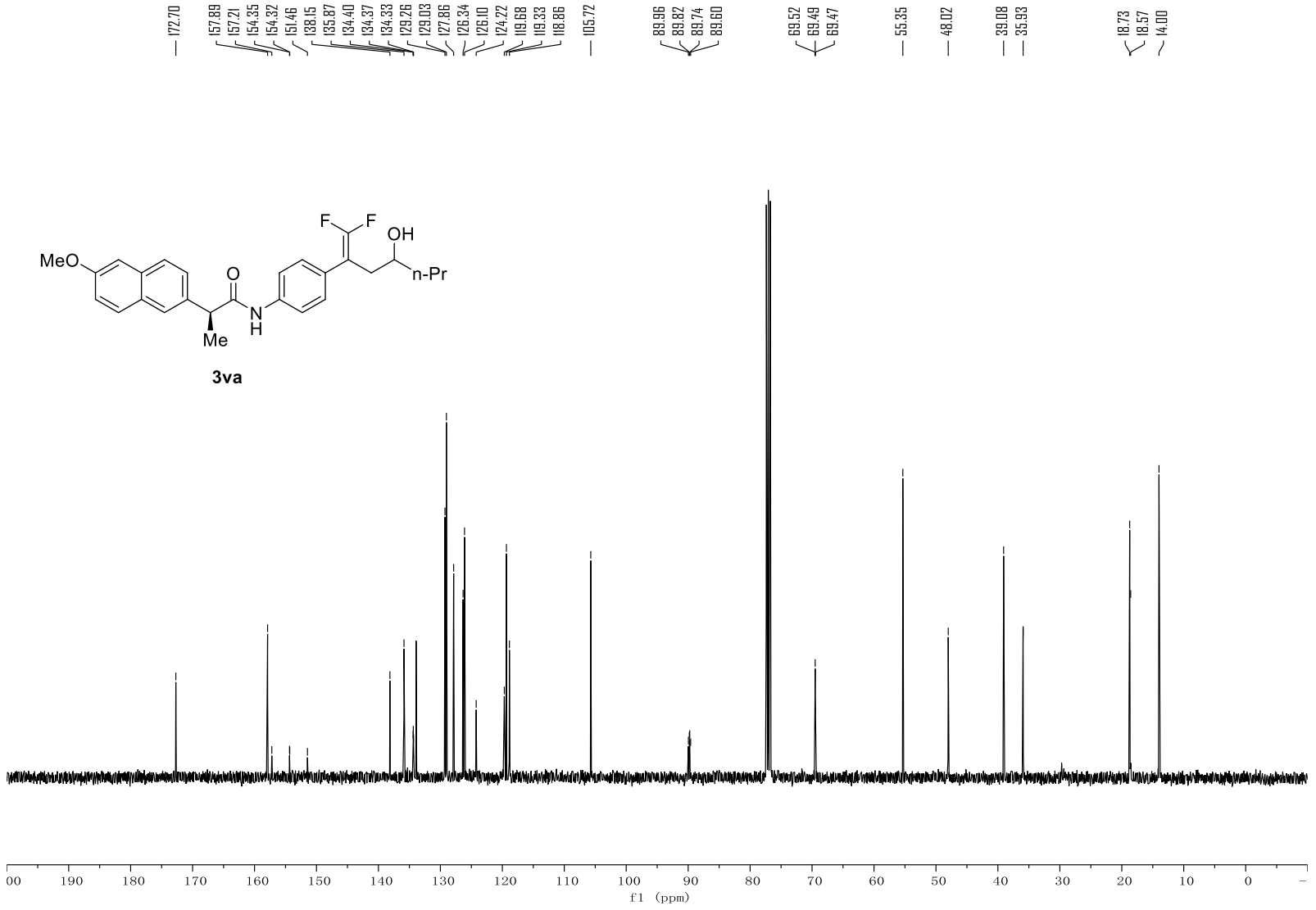

-92.93
-93.06
-93.91
-94.05
F
F
OH
n-Pr
3ta
1.00
1.01
f1 (ppm)
0.06
0.08
1.00
1.01
f1 (ppm)

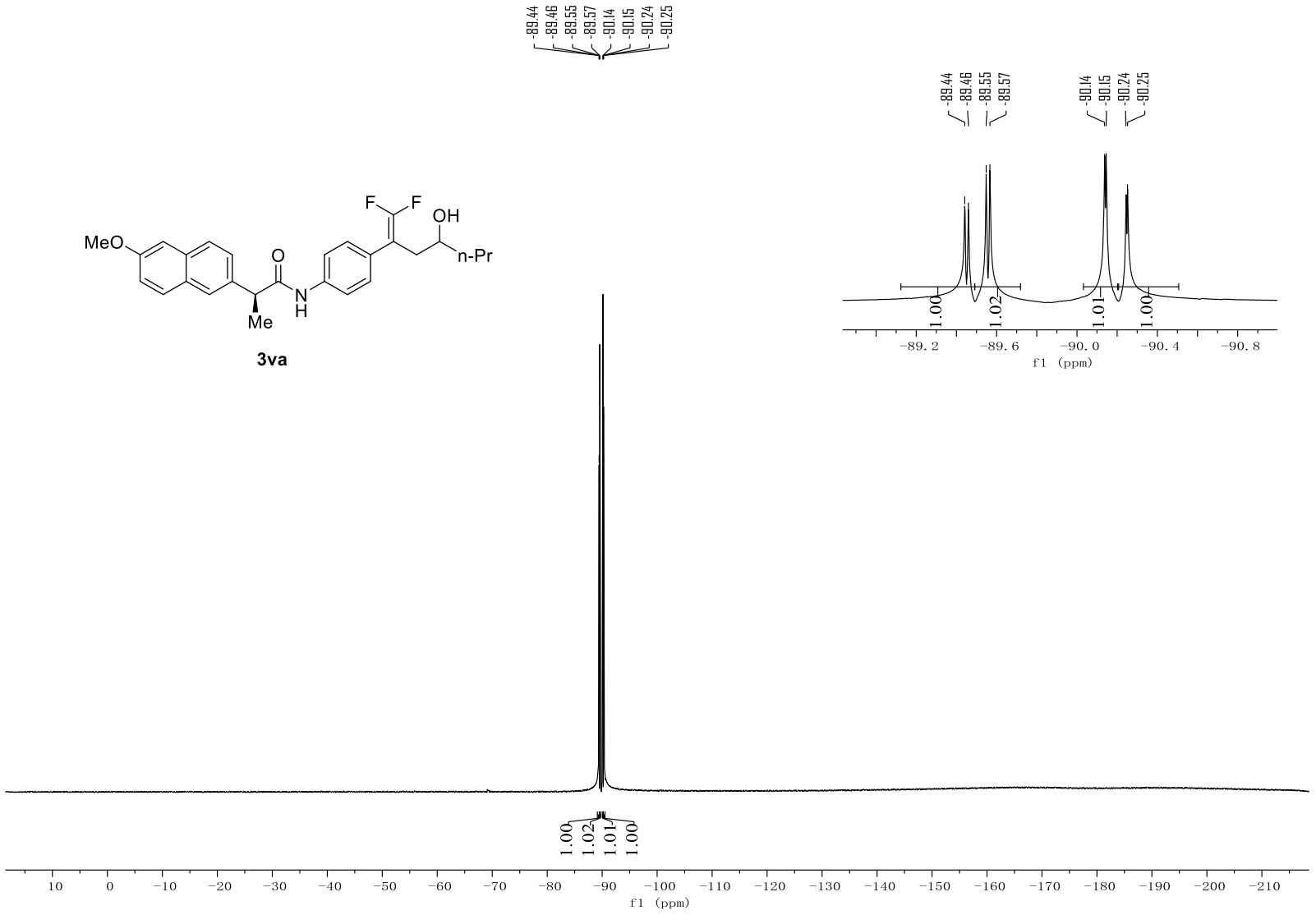

BocHN
F
F
OH
MeOOC
n-Pr
3ua
5.27
5.24
5.21
4.47
4.46
4.44
4.43
4.42
3.77
3.76
3.74
3.74
3.72
3.71
2.45
2.45
2.45
2.44
2.43
2.43
2.43
2.43
2.21
2.09
2.08
2.06
1.46
1.45
1.43
1.42
1.35
1.34
1.34
0.94
0.94
0.92
0.92
0.90
1.00
0.93
3.04
4.09
2.03
1.07
1.04
9.17
13.02
3.16
f1 (ppm)

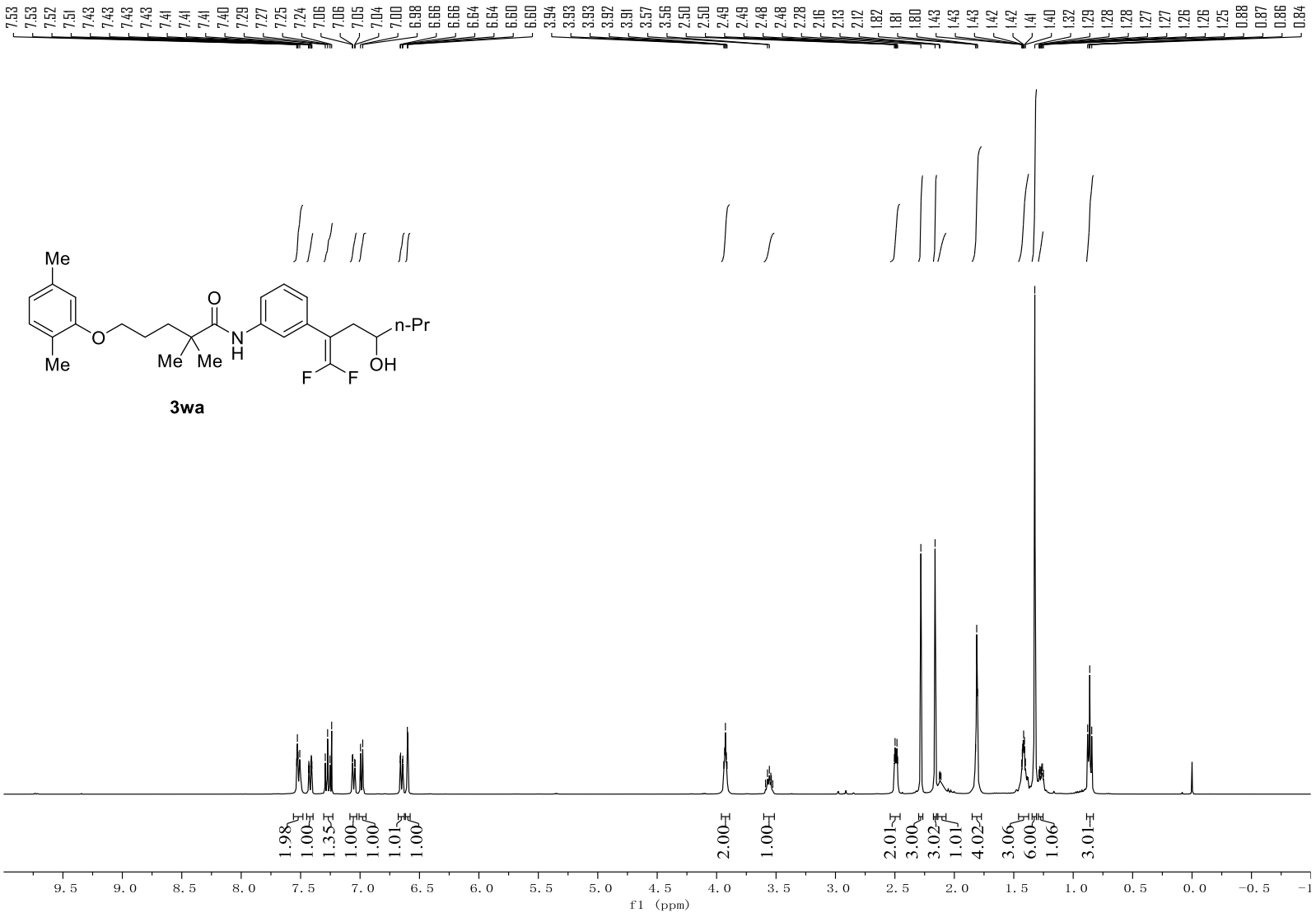

172.41
172.26
158.19
155.61
155.35
152.50
83.48
83.31
83.12
82.98
82.74
80.43
80.20
69.62
69.23
52.52
52.48
52.34
51.86
39.49
35.72
35.07
31.82
31.34
28.19
18.93
18.86
14.02
14.00
BocHN
F
F
OH
MeOOC
n-Pr
3ua
f1 (ppm)


-71.11
-71.30
-71.50
-71.83
-90.85
-90.96
-90.97
-91.09
-91.36
-91.49
-91.72
-91.85
BocHN
F
F
OH
MeOOC
n-Pr
3ua
2.00
f1 (ppm)
0.08
0.08
2.00
f1 (ppm)

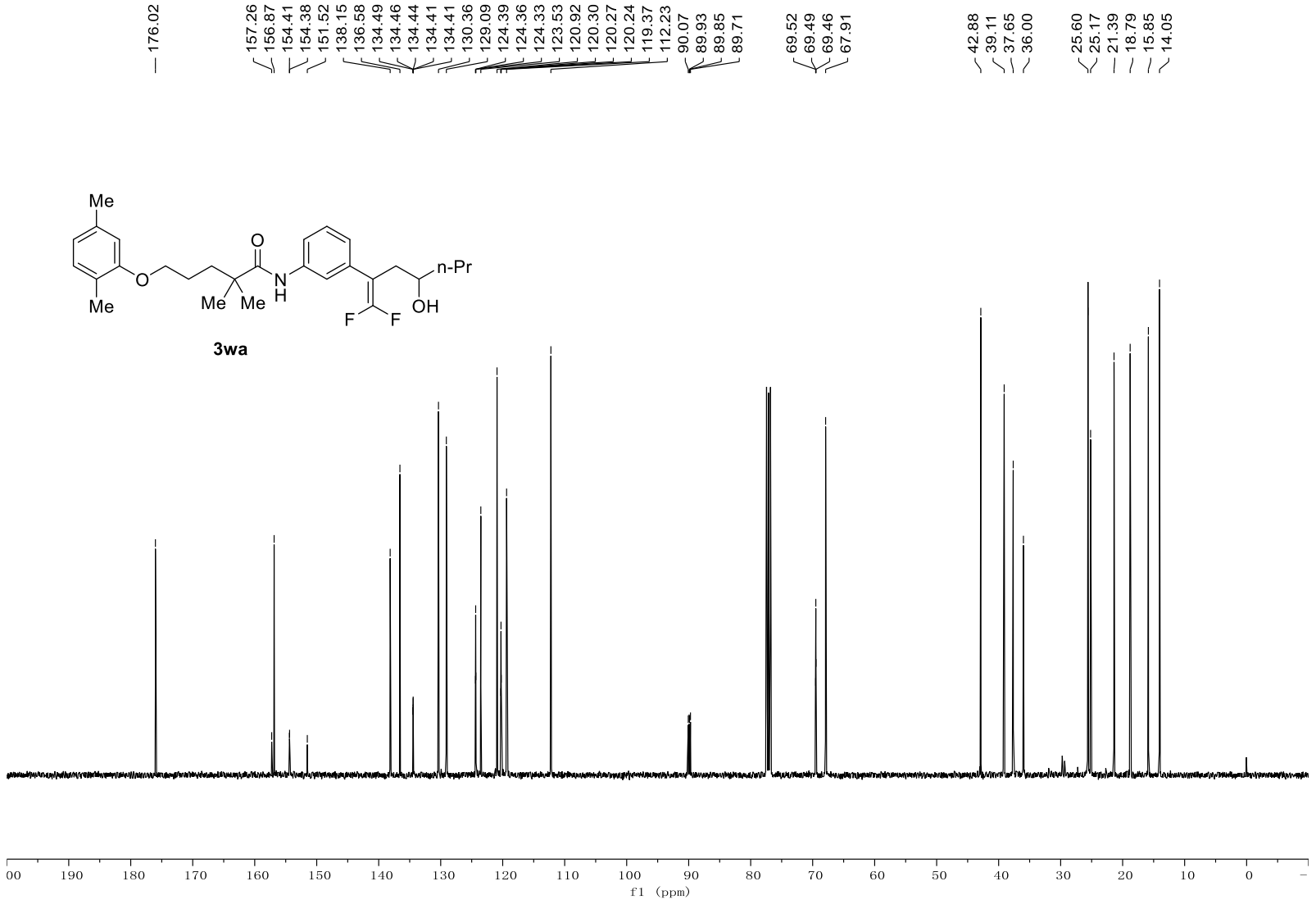

7.75 7.73 7.72 7.72 7.72 7.70 7.46 7.45 7.45 7.44 7.43 7.42 7.41 7.38 7.37 7.32 7.32 7.32 7.31 7.30 7.24 7.22 7.20 7.19 7.18 7.16 7.16 7.14 7.13 7.02 7.00
3.92 3.84 3.82 3.54 3.52 2.47 2.46 2.45 2.45 2.44 2.44 1.66 1.65 1.64 1.63 1.41 1.41 1.41 1.40 1.40 1.40 1.39 1.38 1.38 1.38 1.37 1.37 1.36 1.36 1.36 1.28 1.27 1.27 1.26 1.26 0.86 0.85 0.83
MeO
O
N
H
Me
F
F
OH
n-Pr
3va
3.00 2.00 1.00 1.00 3.01 1.00
3.00 1.00 1.00 2.00 1.03 3.05 4.02 3.02
f1 (ppm)

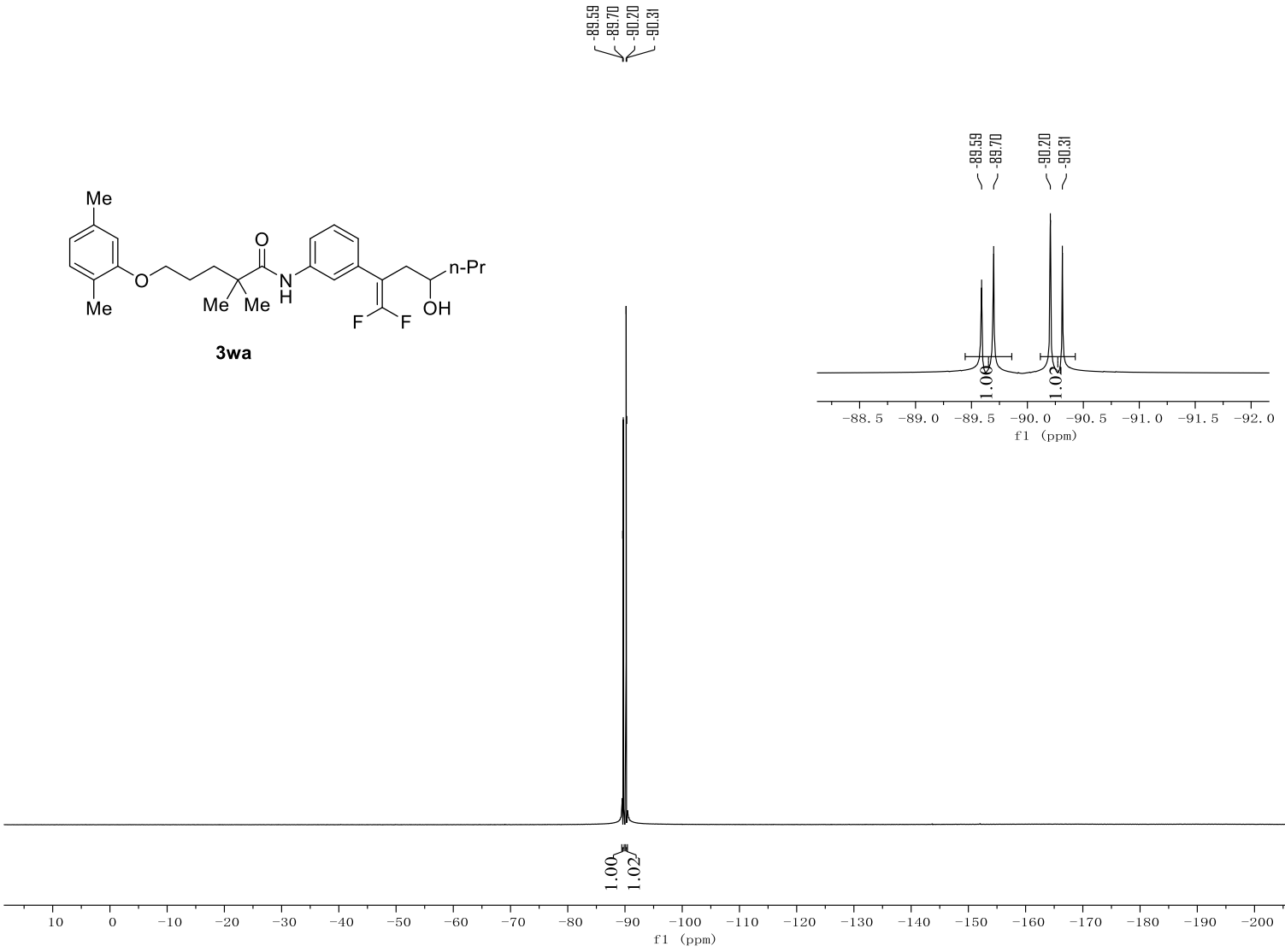

172.70
157.89
157.21
154.35
154.32
151.46
138.15
135.87
134.40
134.37
134.33
129.26
129.03
127.86
126.34
126.10
124.22
119.68
119.33
118.86
105.72
89.96
89.82
89.74
89.60
69.52
69.49
69.47
55.35
48.02
39.08
35.93
18.73
18.57
14.00
MeO
O
F
F
OH
n-Pr
N
H
Me
3va
f1 (ppm)

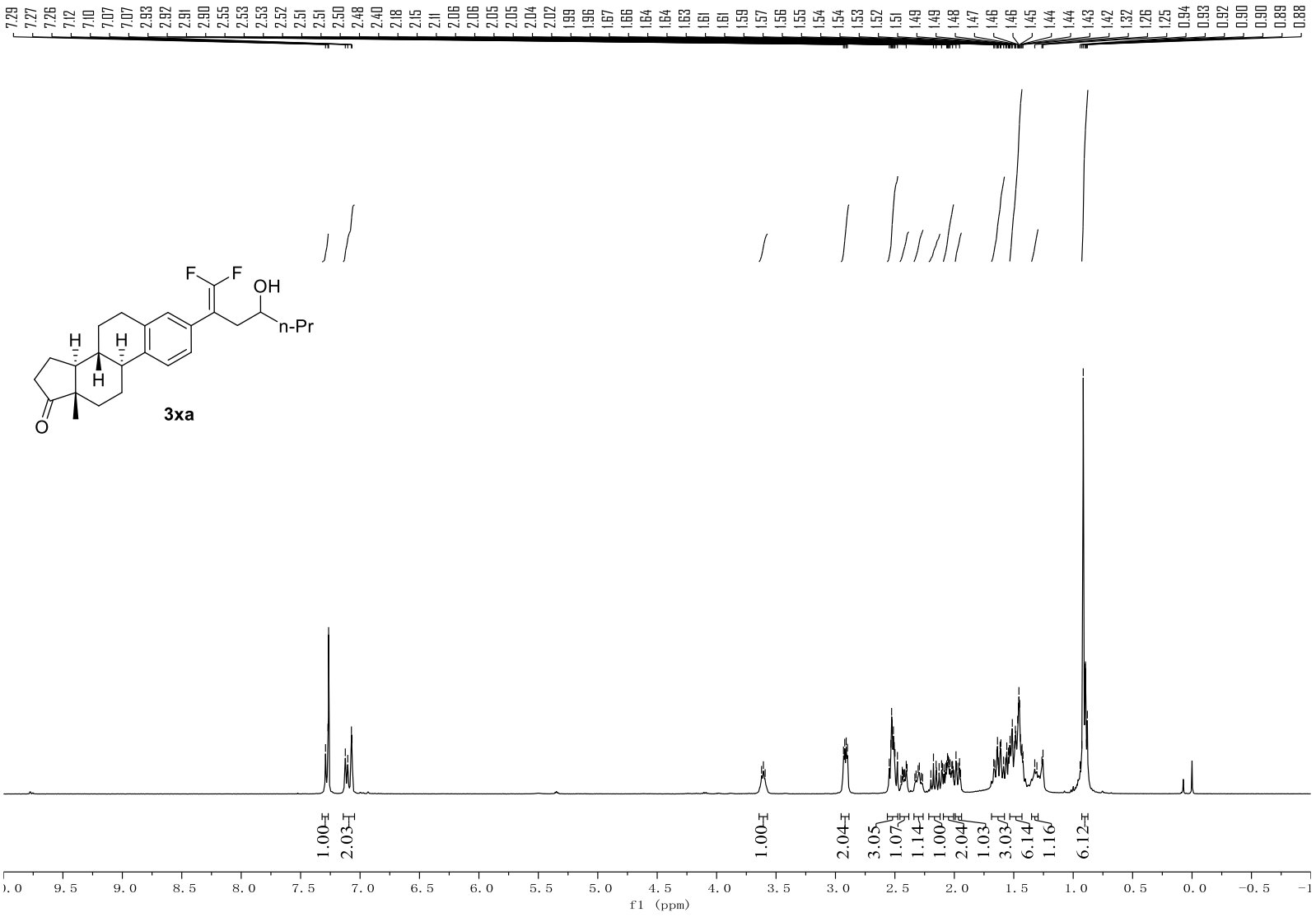

-89.44
-89.46
-89.55
-89.57
-90.14
-90.15
-90.24
-90.25
MeO
O
N
H
F
F
OH
n-Pr
Me
3va
1.00
1.02
1.01
1.00
f1 (ppm)

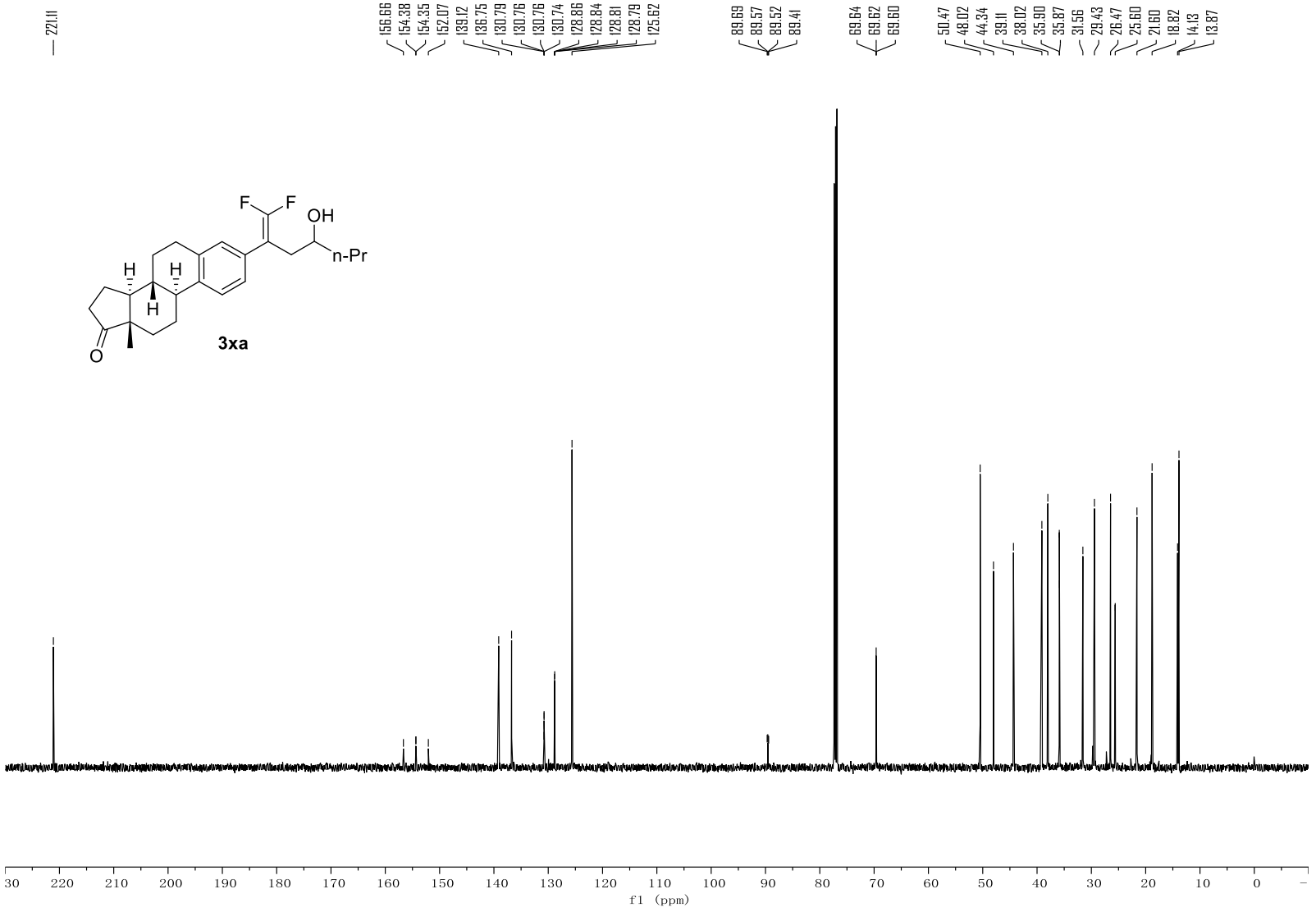

7.53 7.53 7.52 7.51 7.43 7.43 7.43 7.43 7.41 7.41 7.41 7.40 7.29 7.27 7.25 7.24 7.06 7.06 7.05 7.04 7.00 6.98 6.66 6.66 6.64 6.64 6.60 6.60
3.94 3.93 3.93 3.92 3.91 3.57 3.56 2.50 2.50 2.49 2.49 2.48 2.48 2.28 2.16 2.13 2.12 1.82 1.81 1.80 1.43 1.43 1.43 1.42 1.42 1.41 1.40 1.32 1.29 1.28 1.28 1.28 1.27 1.27 1.26 1.26 1.25 0.88 0.87 0.86 0.84
Me
Me
O
O
N
H
Me
Me
F
F
OH
n-Pr
1.98 1.00 1.35 1.00 1.00 1.01 1.00
2.00 1.00
2.01 3.00 3.02 1.01 4.02 3.06 6.00 1.06 3.01
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 −1
f1 (ppm)

3wa


176.02
157.26
156.87
154.41
154.38
151.52
138.15
136.58
134.49
134.46
134.44
134.41
134.41
130.36
129.09
124.39
124.36
124.33
123.53
120.92
120.30
120.27
120.24
119.37
112.23
90.07
89.93
89.85
89.71
69.52
69.49
69.46
67.91
42.88
39.11
37.65
36.00
25.60
25.17
21.39
18.79
15.85
14.05
Me
Me
O
Me
Me
O
N
H
n-Pr
F
F
OH
3wa
f1 (ppm)


-89.59
-89.70
-90.20
-90.31
Me
Me
O
N
H
Me
Me
O
n-Pr
OH
F
F
3wa
1.00
1.02
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)
-89.59
-89.70
-90.20
-90.31
1.06
1.02
−88.5 −89.0 −89.5 −90.0 −90.5 −91.0 −91.5 −92.0
f1 (ppm)


7.29 7.27 7.26 7.12 7.10 7.07 7.07 2.93 2.92 2.91 2.90 2.55 2.53 2.53 2.52 2.51 2.51 2.50 2.48 2.40 2.18 2.15 2.11 2.06 2.06 2.05 2.05 2.04 2.02 1.99 1.96 1.67 1.66 1.64 1.64 1.63 1.61 1.61 1.59 1.57 1.56 1.55 1.54 1.54 1.53 1.52 1.51 1.49 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.44 1.43 1.42 1.32 1.26 1.25 0.94 0.93 0.92 0.90 0.90 0.89 0.88
F
F
OH
n-Pr
H
H
H
O
3xa
1.00
2.03
1.00
2.04
3.05
1.07
1.14
1.00
2.04
1.03
3.03
6.14
1.16
6.12
f1 (ppm)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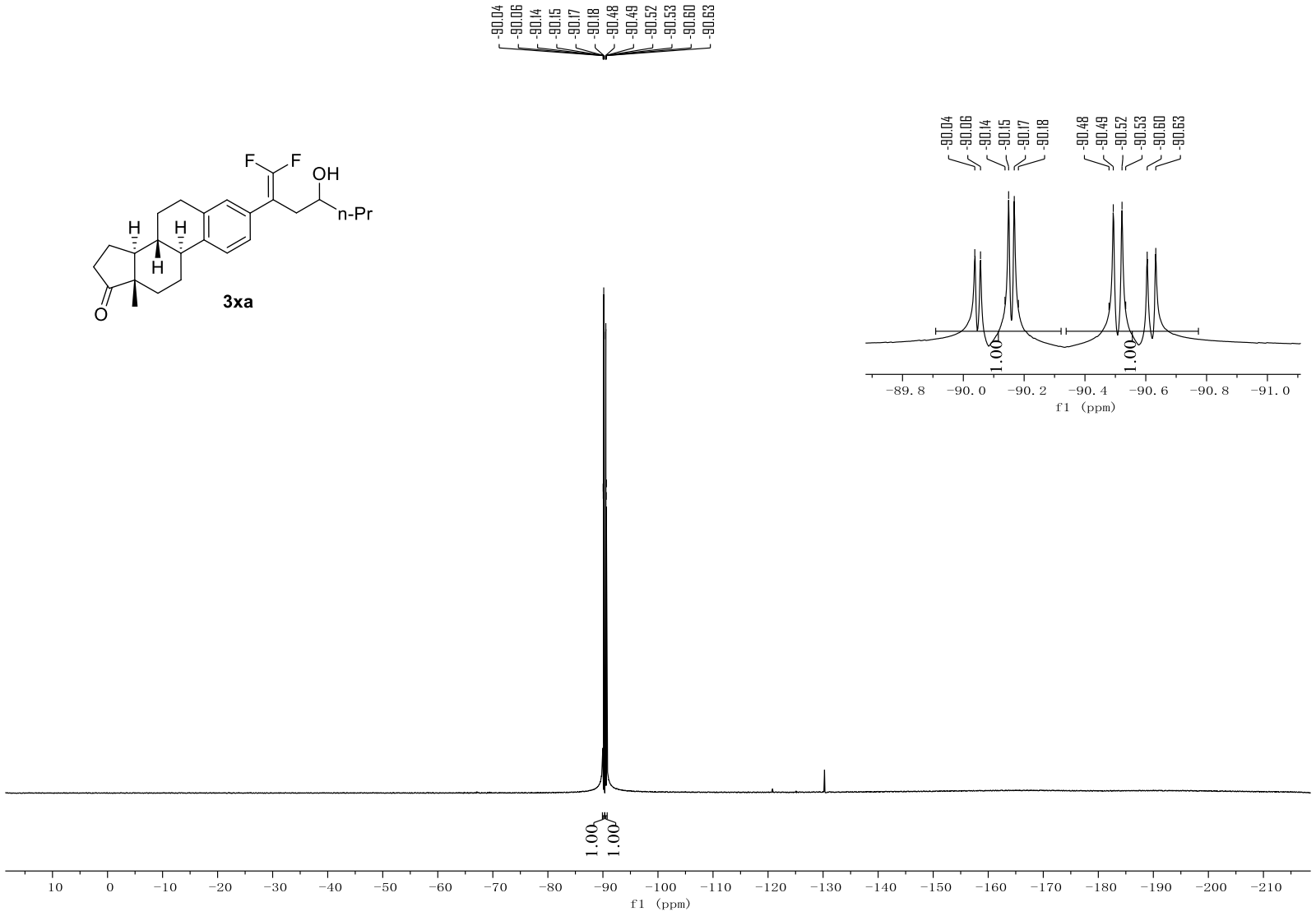
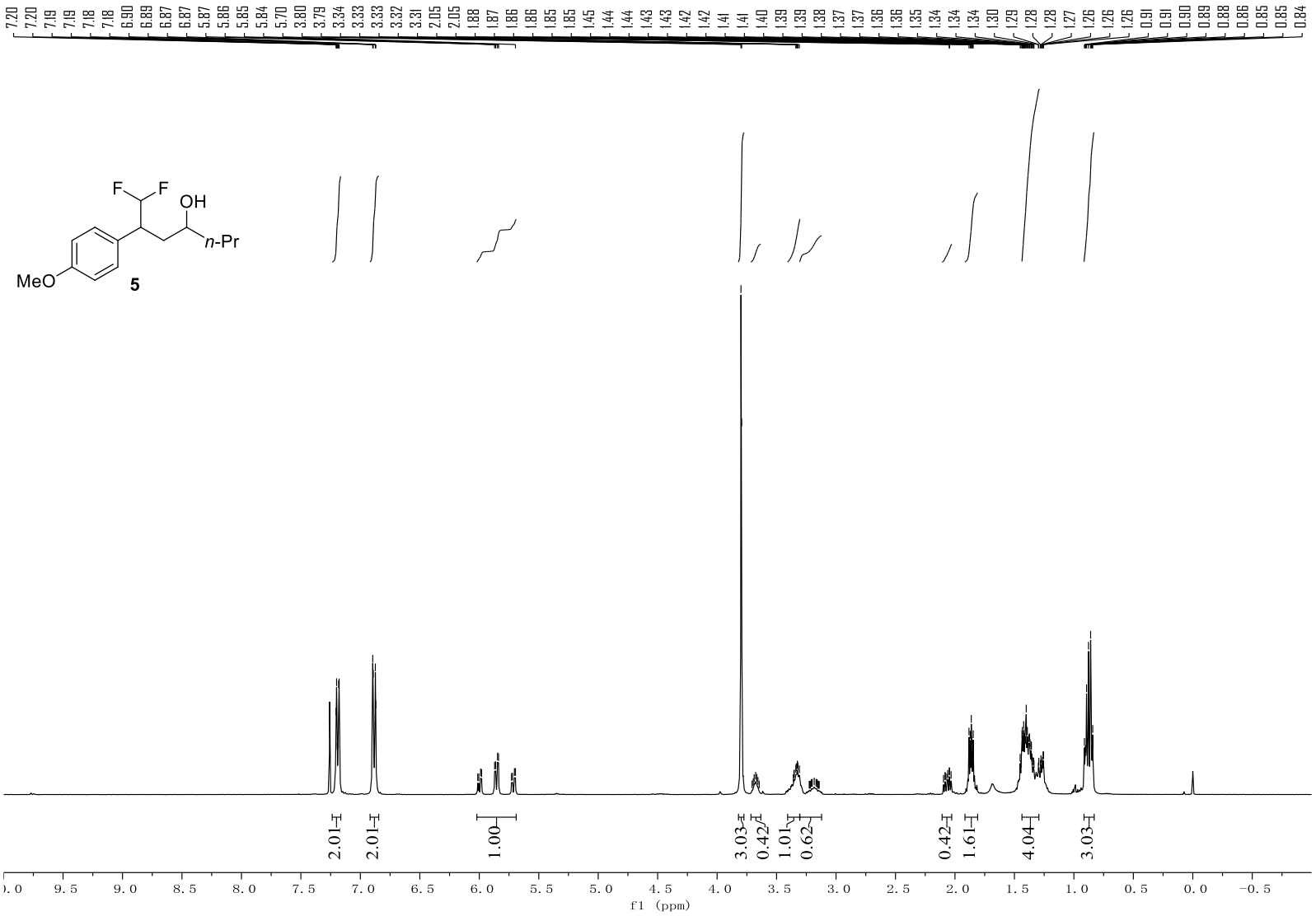
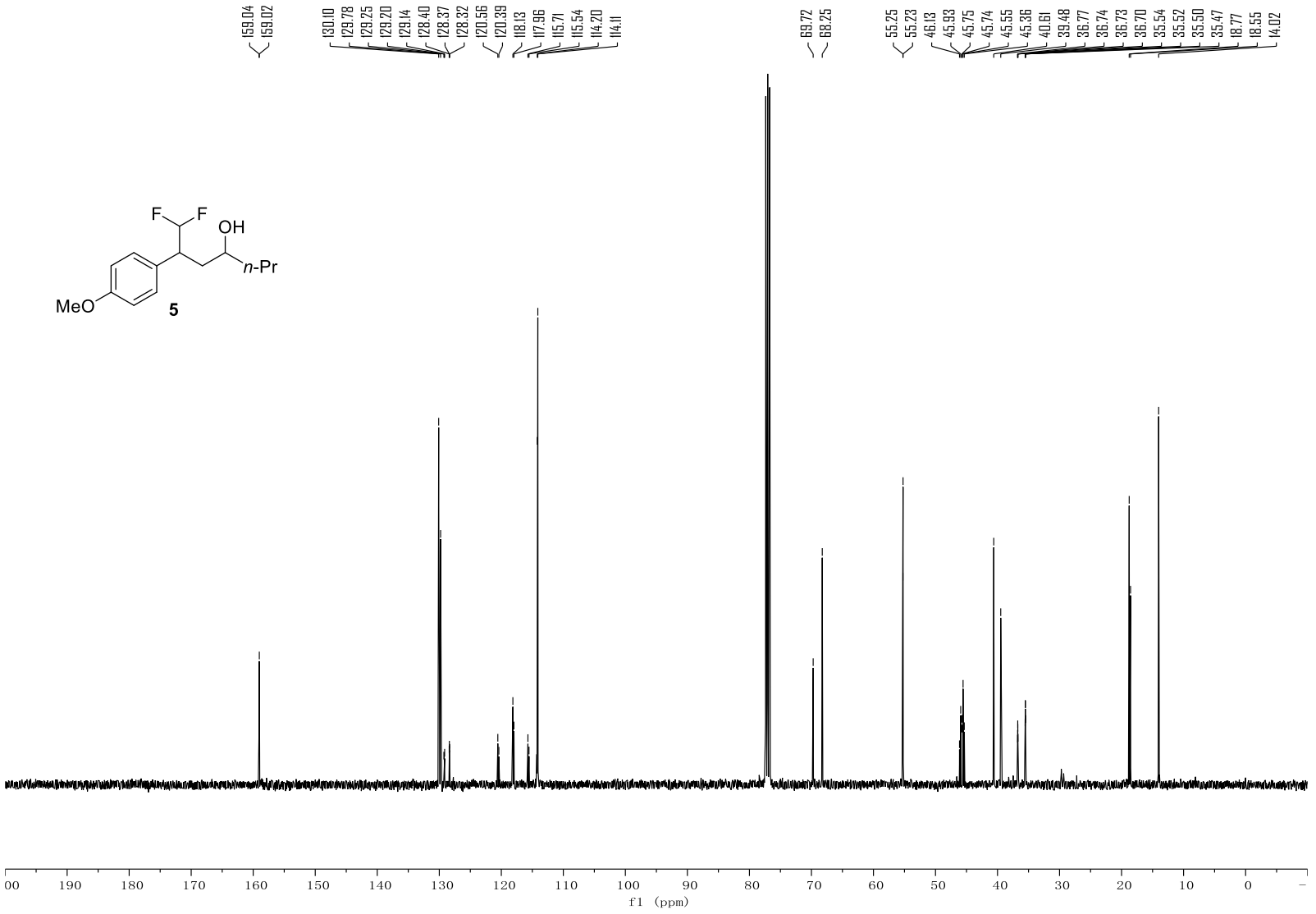
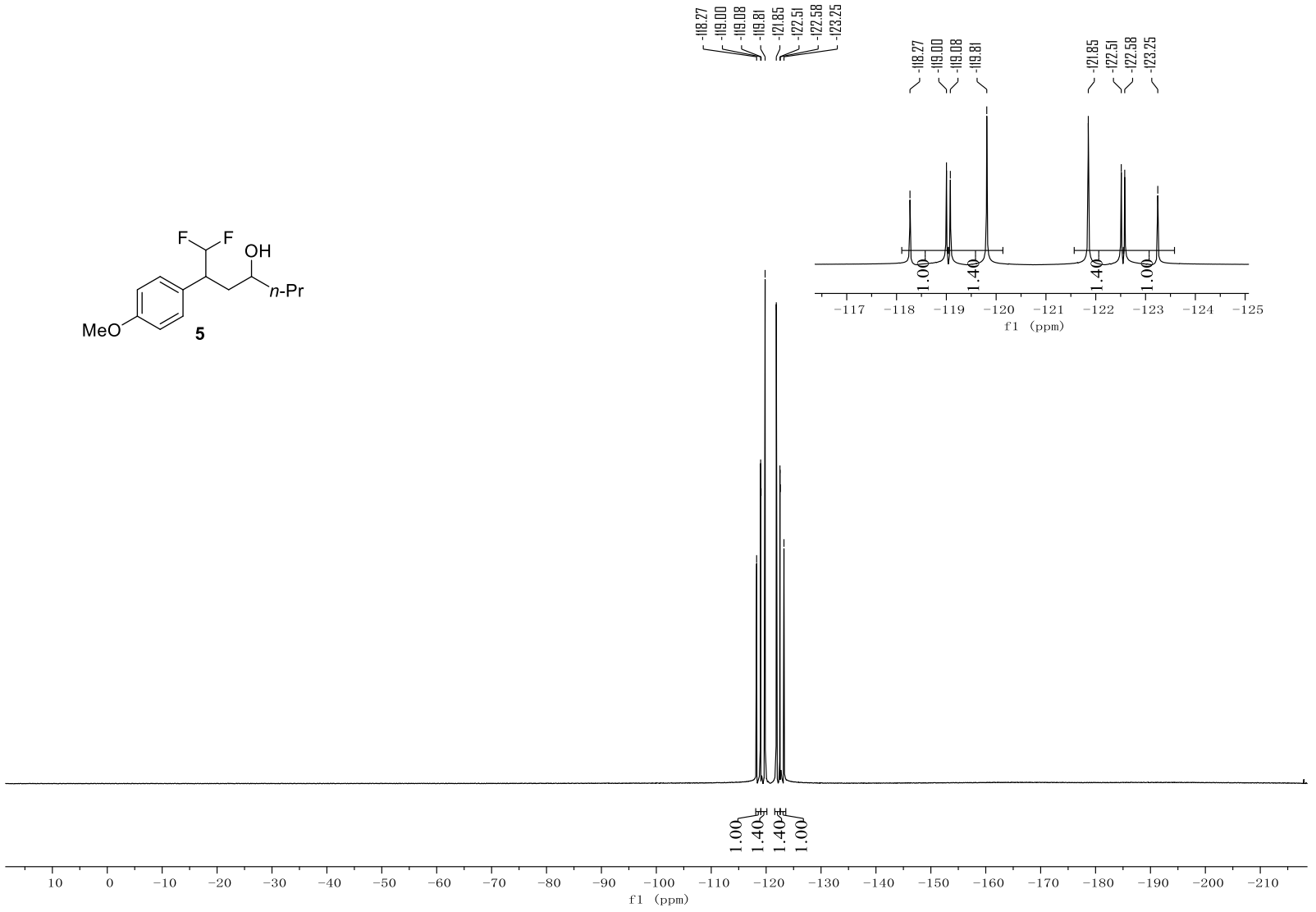
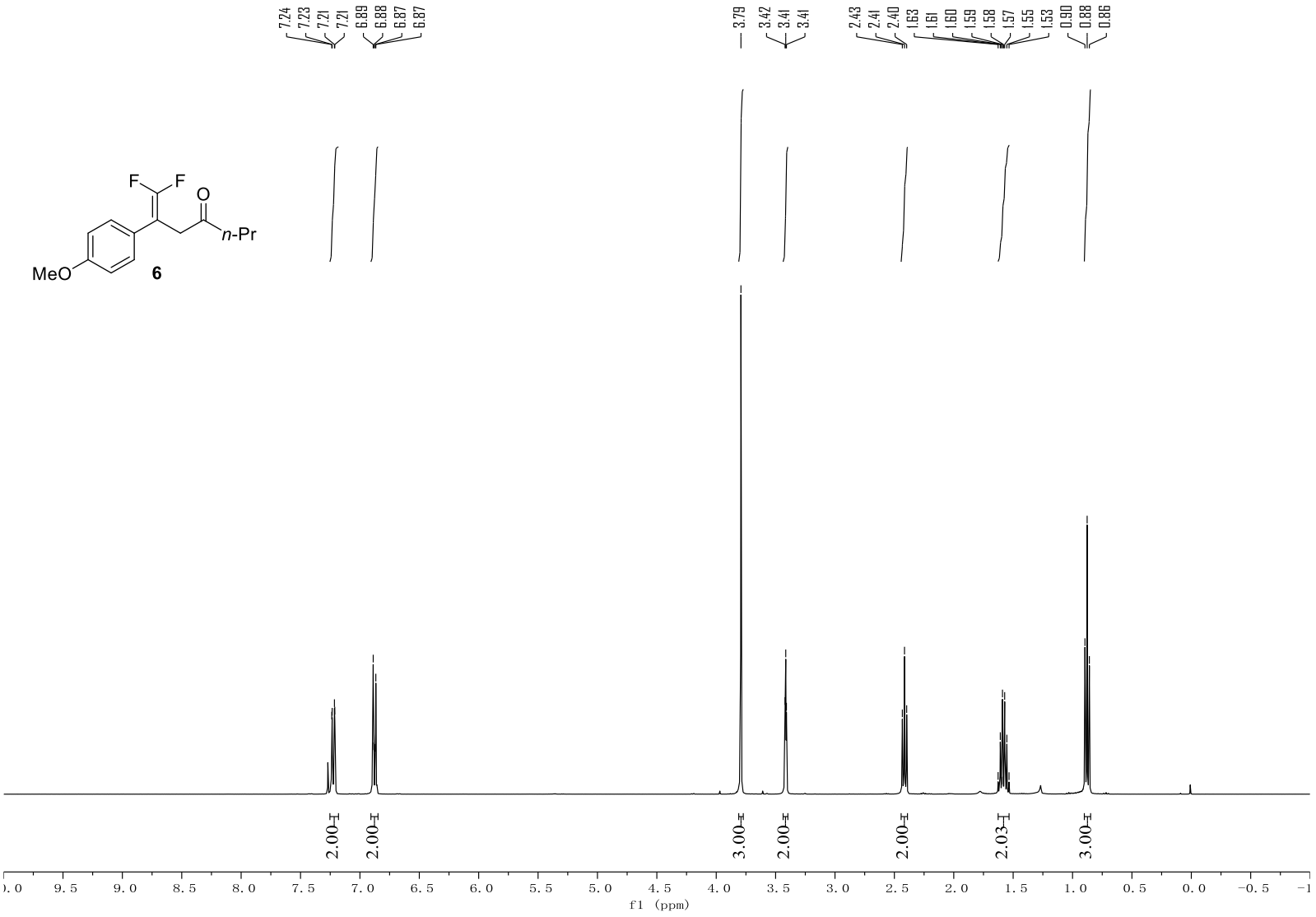
156.66
154.38
154.35
152.07
139.12
136.75
130.79
130.76
130.76
130.74
128.86
128.84
128.81
128.79
125.62
89.69
89.57
89.52
89.41
69.64
69.62
69.60
50.47
48.02
44.34
39.11
38.02
35.90
35.87
31.56
29.43
26.47
25.60
21.60
18.82
14.13
13.87
F
F
OH
n-Pr
H
H
H
O
3xa
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

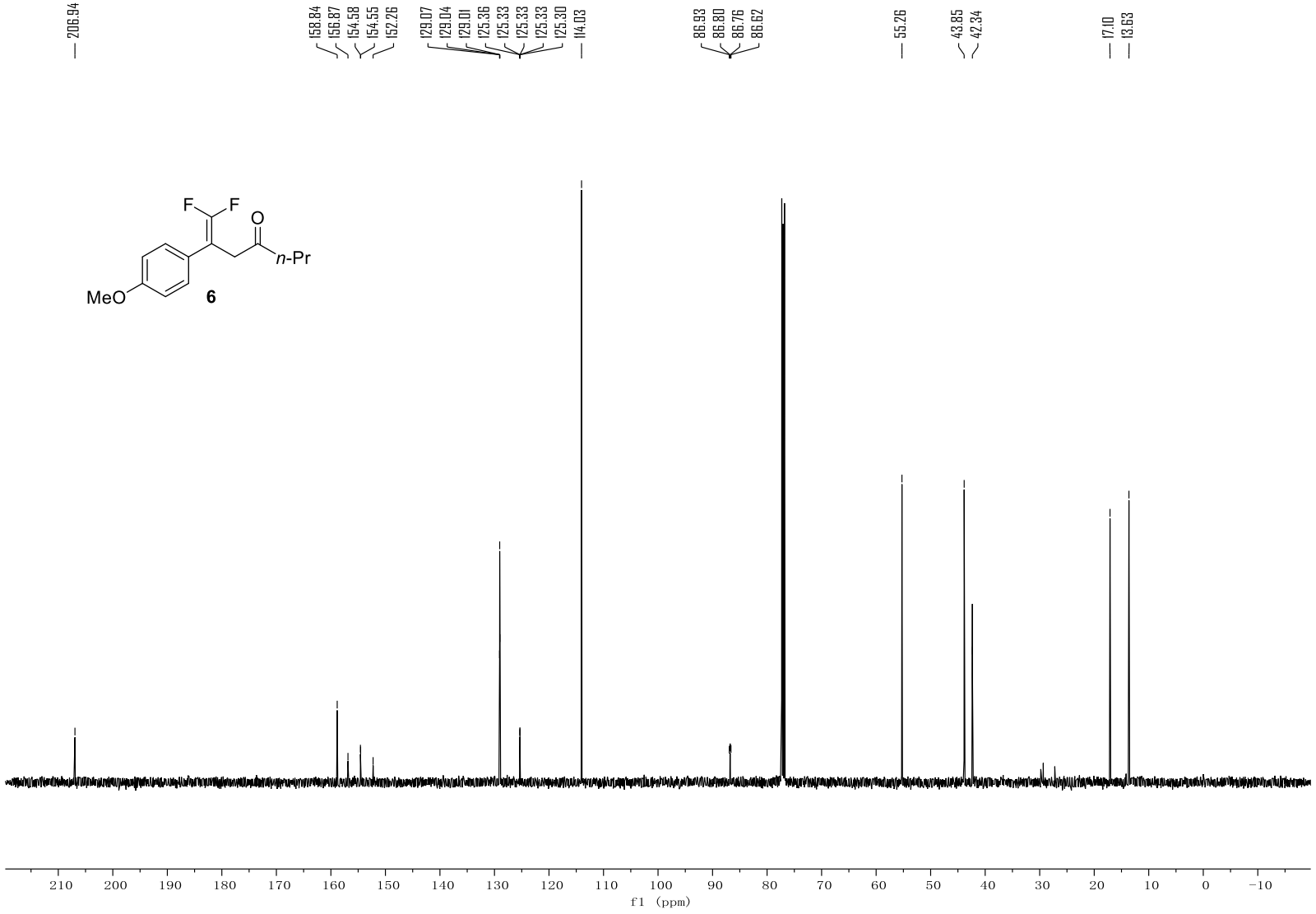

-90.04
-90.06
-90.14
-90.15
-90.17
-90.18
-90.48
-90.49
-90.52
-90.53
-90.60
-90.63
F
F
OH
n-Pr
H
H
H
O
3xa
1.00
1.00
-89.8
-90.0
-90.2
-90.4
-90.6
-90.8
-91.0
f1 (ppm)
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

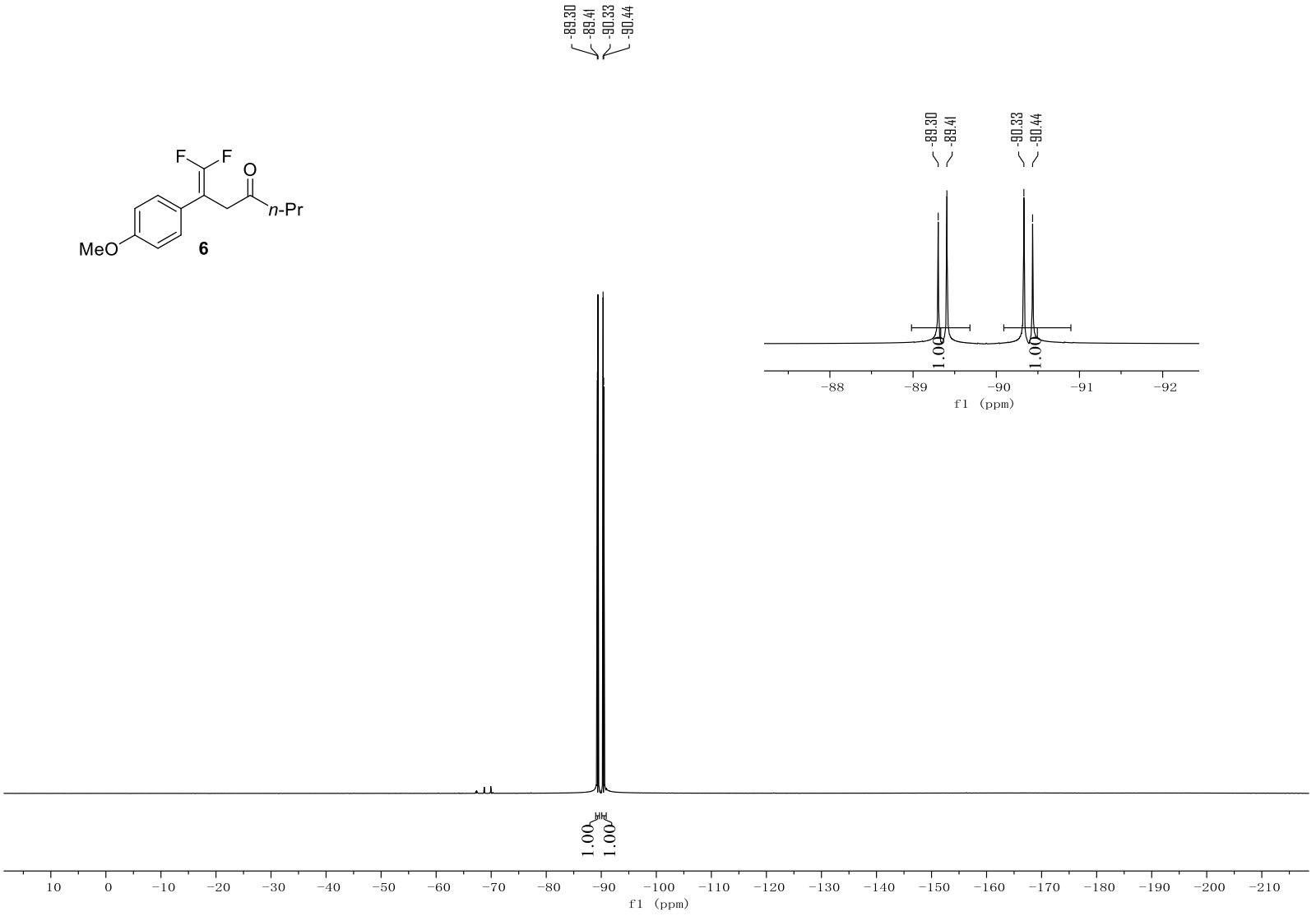

7.20 7.20 7.19 7.19 7.18 7.18 6.90 6.89 6.87 6.87 5.87 5.86 5.85 5.84 5.70 3.80 3.79 3.34 3.33 3.33 3.32 3.31 2.05 2.05 1.88 1.87 1.86 1.86 1.85 1.85 1.45 1.44 1.44 1.43 1.43 1.42 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.37 1.37 1.36 1.36 1.35 1.34 1.34 1.34 1.30 1.29 1.28 1.28 1.27 1.26 1.26 1.26 0.91 0.91 0.90 0.89 0.88 0.86 0.85 0.85 0.84
F
F
OH
n-Pr
MeO
5
2.01
2.01
1.00
3.03
0.42
1.01
0.62
0.42
1.61
4.04
3.03
f1 (ppm)

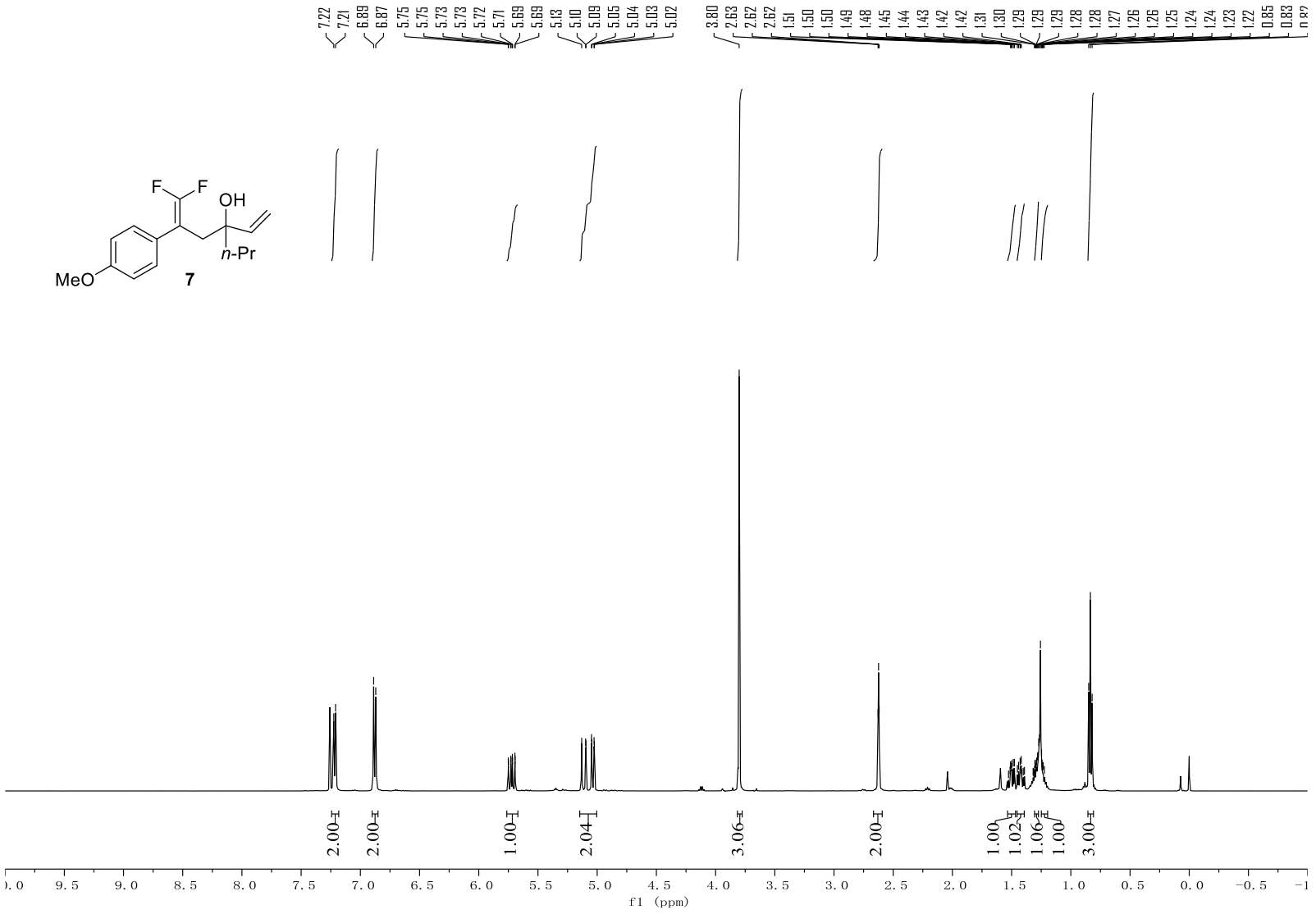

159.04
159.02
130.10
129.78
129.25
129.20
129.14
128.40
128.37
128.32
120.56
120.39
118.13
117.96
115.71
115.54
114.20
114.11
69.72
68.25
55.25
55.23
46.13
45.93
45.75
45.74
45.55
45.36
40.61
39.48
36.77
36.74
36.73
36.70
35.54
35.52
35.50
35.47
18.77
18.55
14.02
F
F
OH
n-Pr
MeO
5
f1 (ppm)

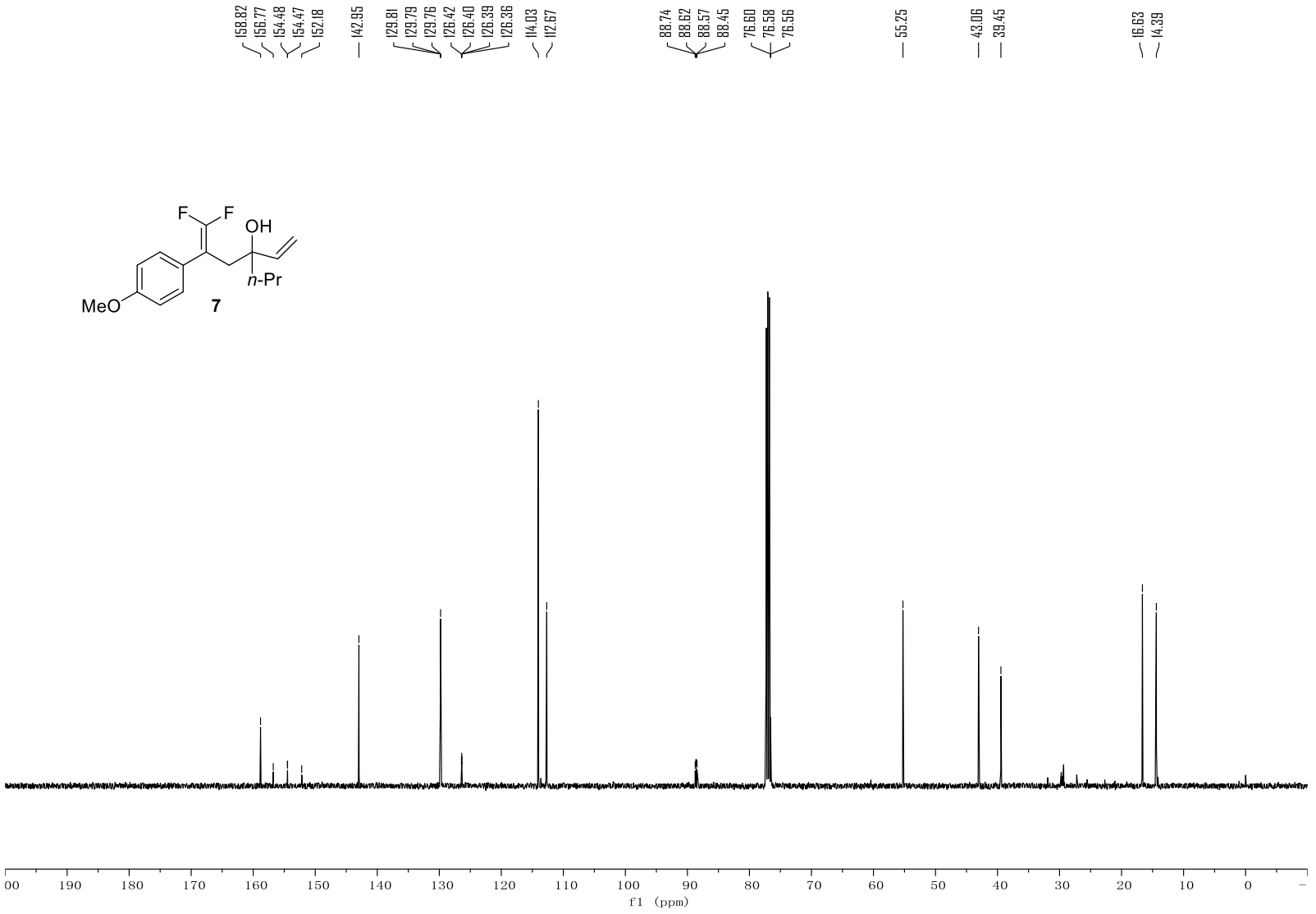

F
F
OH
n-Pr
MeO
5
-118.27
-119.00
-119.08
-119.81
-121.85
-122.51
-122.58
-123.25
1.00
1.40
1.40
1.00
f1 (ppm)

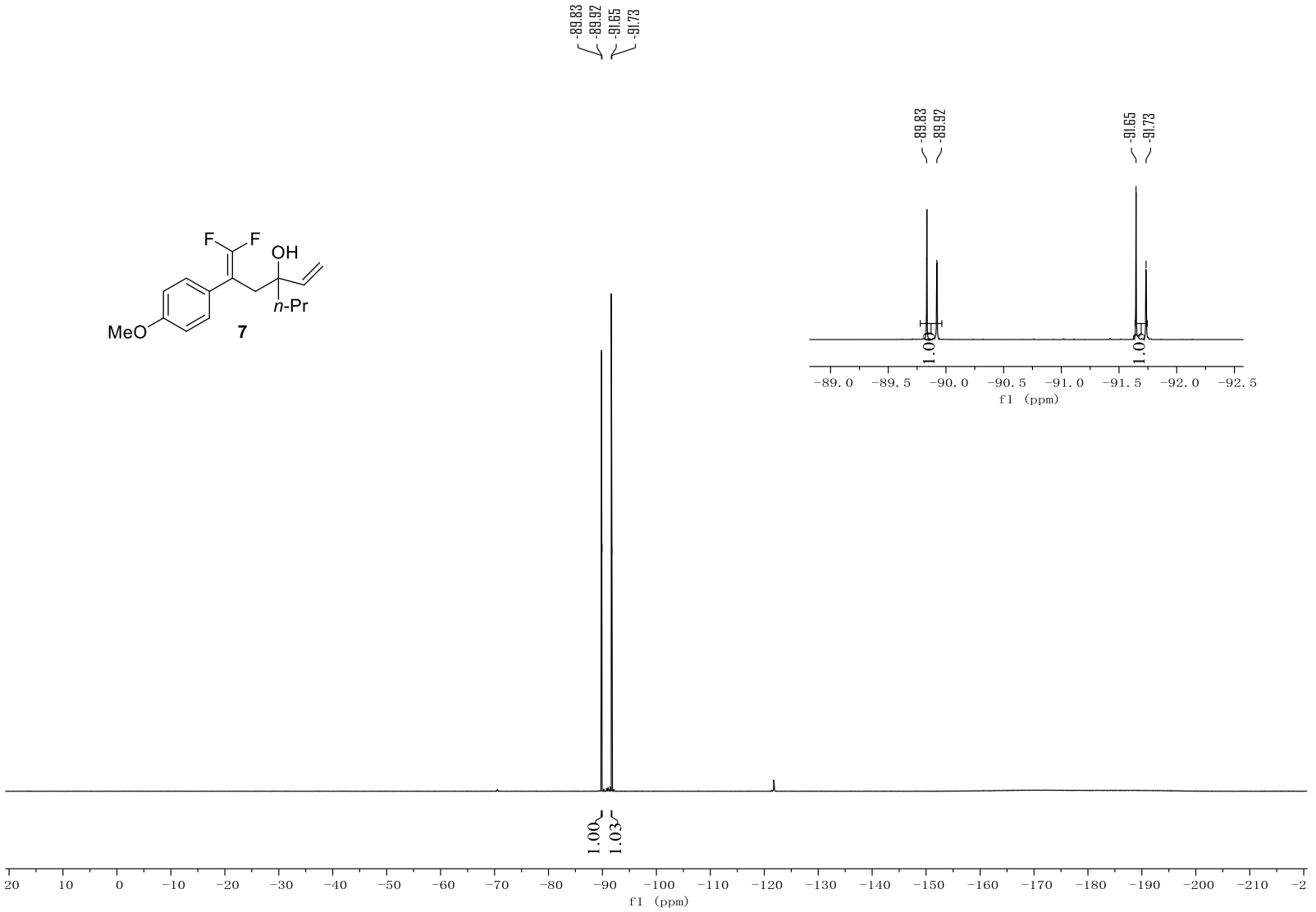

7.24
7.23
7.21
7.21
6.89
6.88
6.87
6.87
3.79
3.42
3.41
3.41
2.43
2.41
2.40
1.63
1.61
1.60
1.59
1.58
1.57
1.55
1.53
0.90
0.88
0.86
F
F
O
n-Pr
MeO
6
2.00
2.00
3.00
2.00
2.00
2.03
3.00
f1 (ppm)

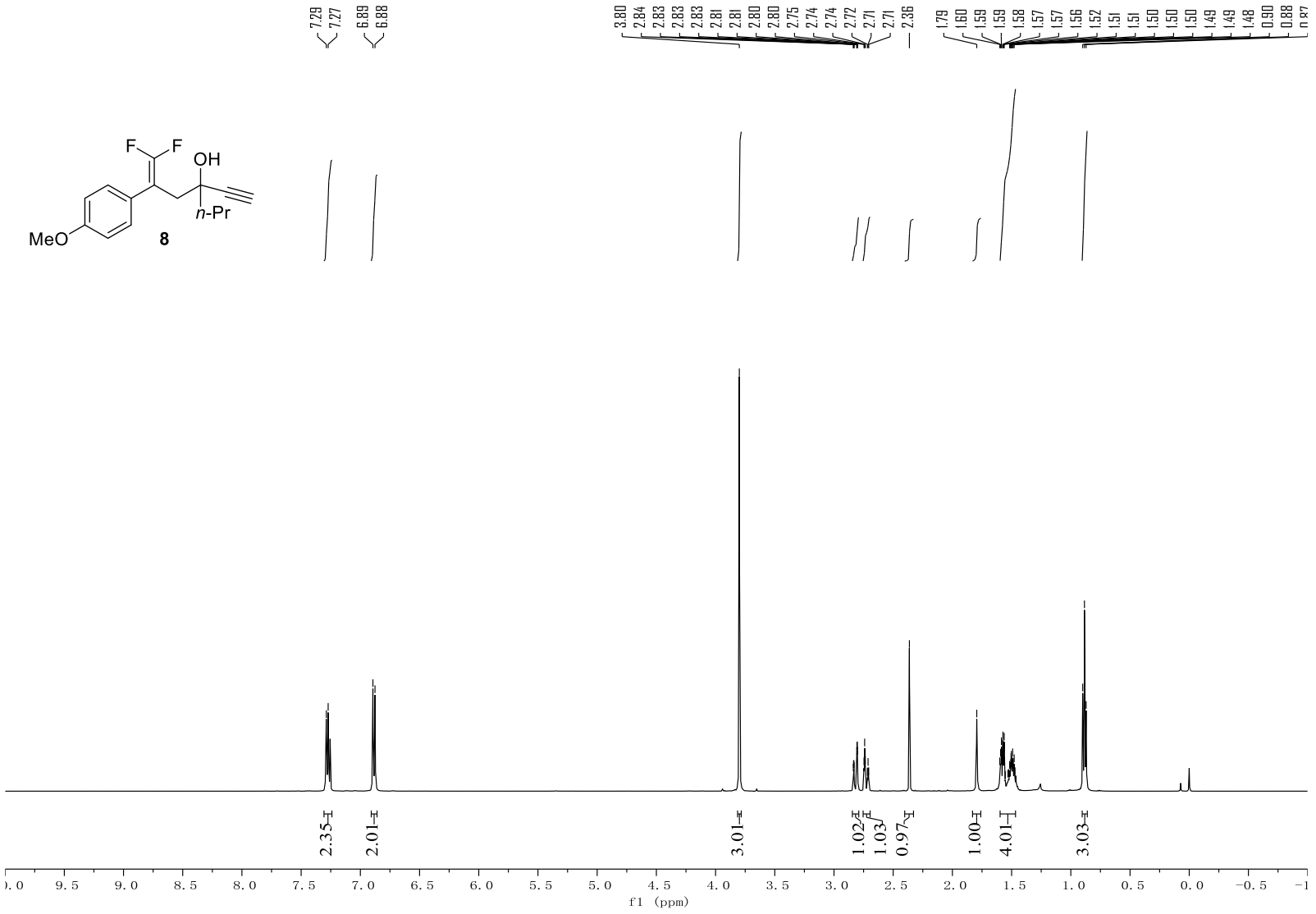

206.94
158.84
156.87
154.58
154.55
152.26
129.07
129.04
129.01
125.36
125.33
125.33
125.33
125.30
114.03
86.93
86.80
86.76
86.62
55.26
43.85
42.34
17.10
13.63
F
F
O
n-Pr
MeO
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

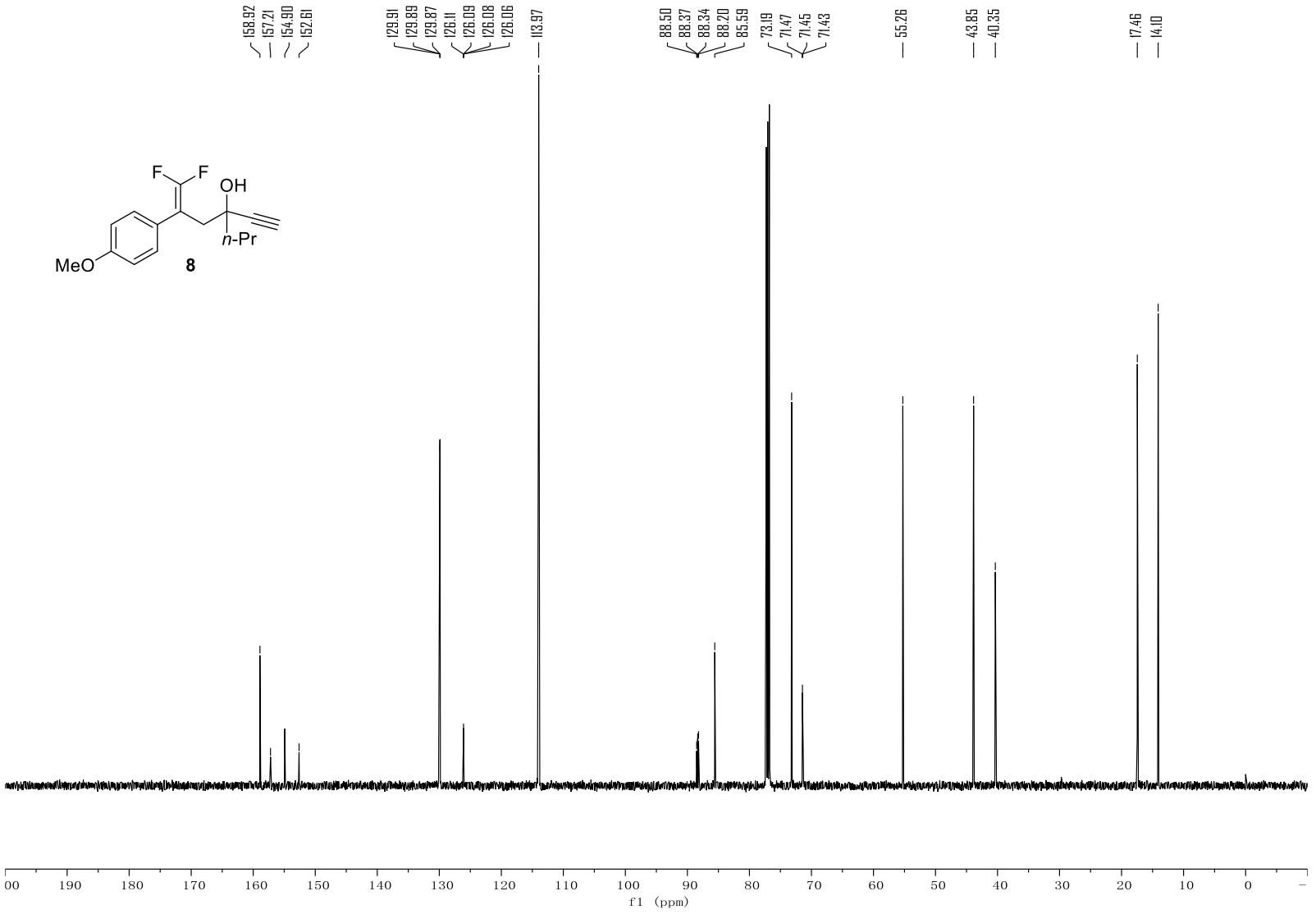

F
F
O
n-Pr
MeO
6
-89.30
-89.41
-90.33
-90.44
1.00
1.00
1.00
1.00
f1 (ppm)
f1 (ppm)

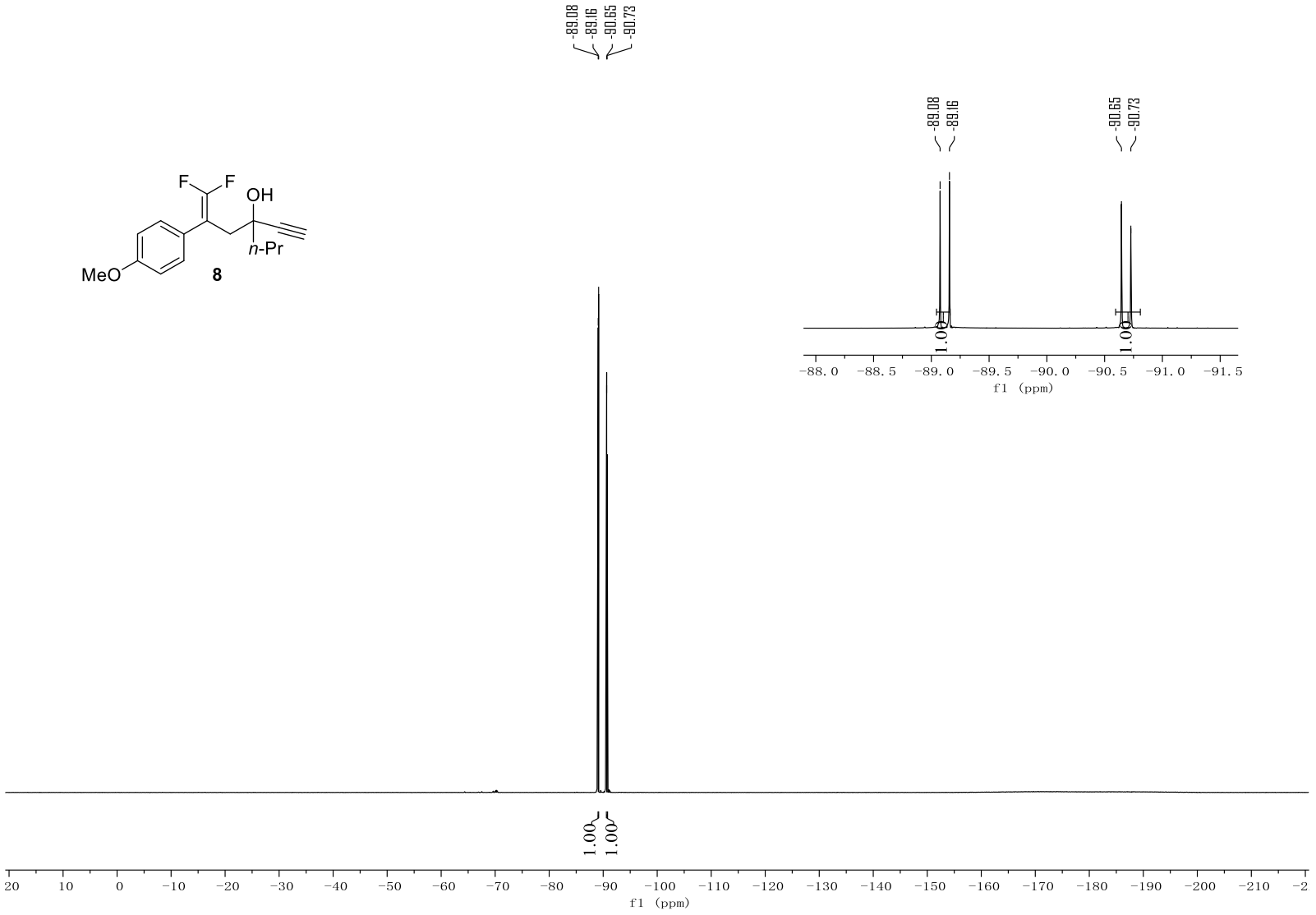

F
F
OH
n-Pr
MeO
7
7.22
7.21
6.89
6.87
5.75
5.75
5.73
5.73
5.72
5.71
5.69
5.69
5.13
5.10
5.09
5.05
5.04
5.03
5.02
3.80
2.63
2.62
2.62
1.51
1.50
1.50
1.49
1.48
1.45
1.44
1.43
1.42
1.42
1.31
1.30
1.29
1.29
1.29
1.28
1.28
1.27
1.26
1.26
1.25
1.24
1.24
1.23
1.22
0.85
0.83
2.00
2.00
1.00
2.04
3.06
2.00
1.00
1.02
1.06
1.00
3.00
f1 (ppm)

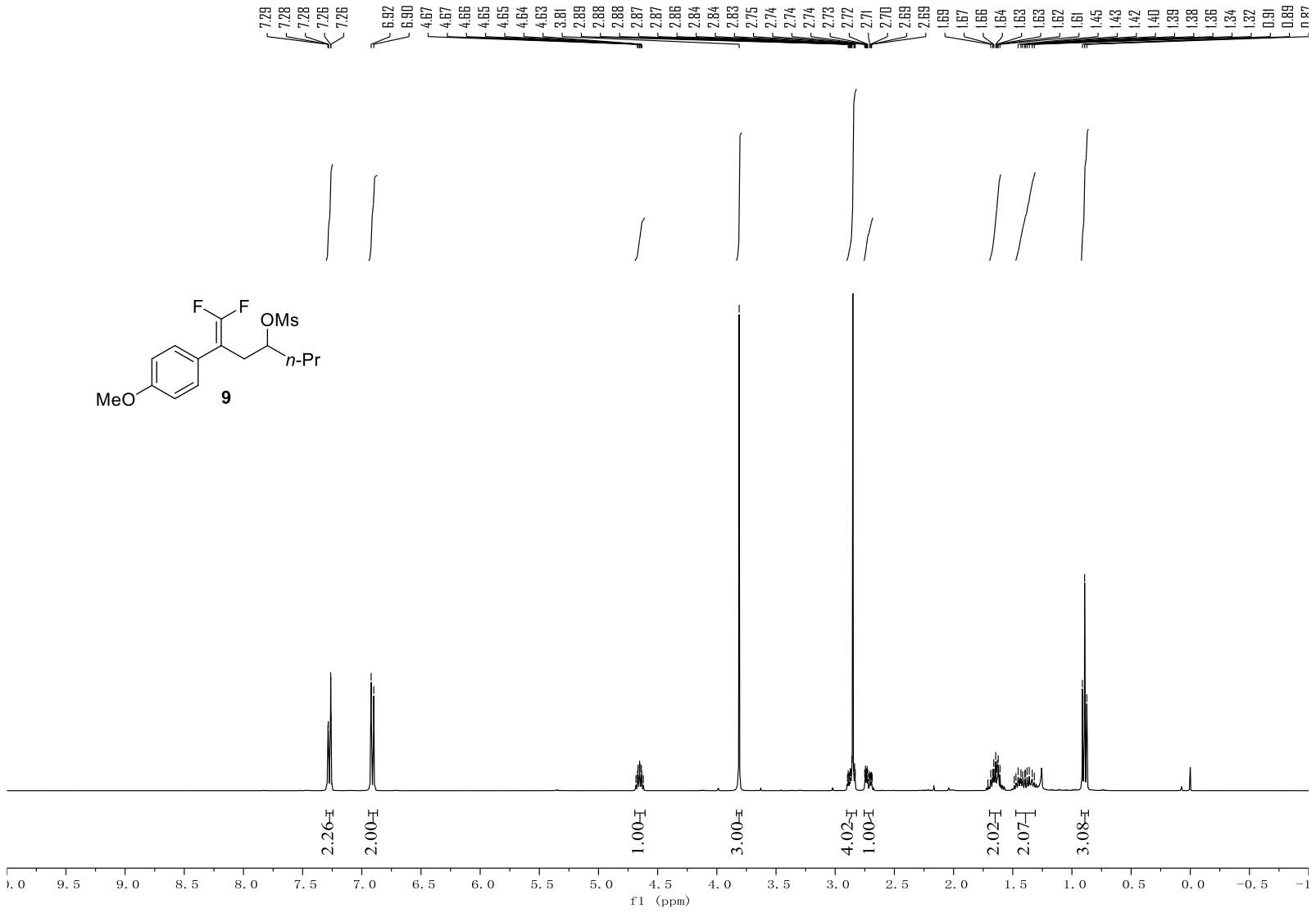

158.82
156.77
154.48
154.47
152.18
142.95
129.81
129.79
129.76
126.42
126.40
126.39
126.36
114.03
112.67
88.74
88.62
88.57
88.45
76.60
76.58
76.56
55.25
43.06
39.45
16.63
14.39
F
F
OH
n-Pr
MeO
7
f1 (ppm)

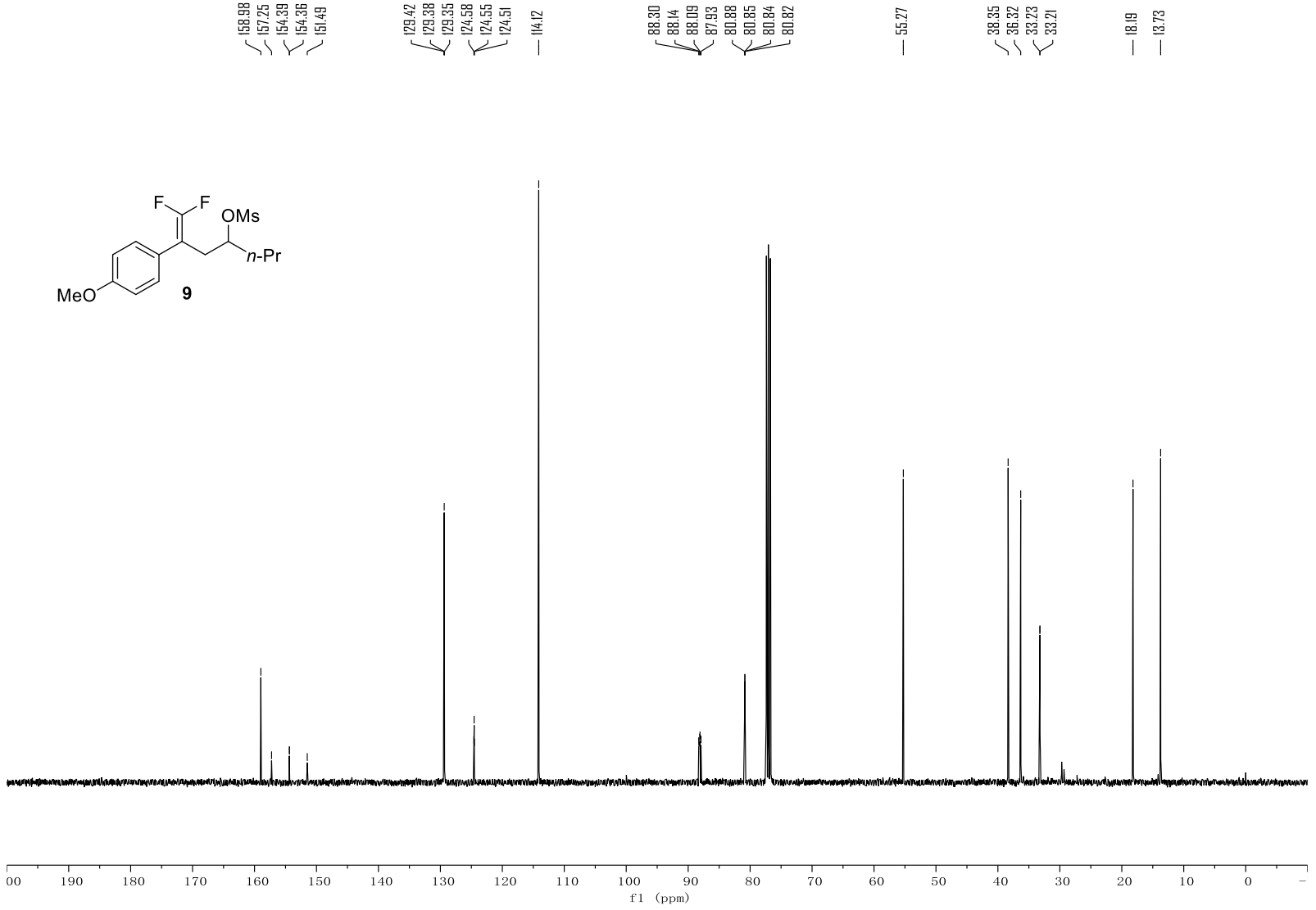

-89.83
-89.92
-91.65
-91.73
F
F
OH
n-Pr
MeO
7
1.00
1.03
f1 (ppm)


F
F
OH
n-Pr
MeO
8
7.29
7.27
6.89
6.88
3.80
2.84
2.83
2.83
2.83
2.81
2.81
2.80
2.80
2.75
2.74
2.74
2.72
2.71
2.71
2.38
1.79
1.60
1.59
1.59
1.58
1.57
1.57
1.56
1.52
1.51
1.51
1.50
1.50
1.50
1.49
1.49
1.48
0.90
0.88
2.35
2.01
3.01
1.02
1.03
0.97
1.00
4.01
3.03
f1 (ppm)


158.92
157.21
154.90
152.61
129.91
129.89
129.87
126.11
126.09
126.08
126.06
113.97
88.50
88.37
88.34
88.20
85.59
73.19
71.47
71.45
71.43
55.26
43.85
40.35
17.46
14.10
F
F
OH
n-Pr
MeO
8
f1 (ppm)


F
F
OH
n-Pr
MeO
8
-89.08
-89.16
-90.65
-90.73
1.00
1.00
1.00
1.00
f1 (ppm)
f1 (ppm)


7.29
7.28
7.28
7.26
7.26
6.92
6.90
4.67
4.67
4.66
4.65
4.65
4.64
4.63
3.81
2.89
2.88
2.88
2.87
2.87
2.86
2.84
2.84
2.83
2.75
2.74
2.74
2.74
2.73
2.72
2.71
2.70
2.69
2.69
1.69
1.67
1.66
1.64
1.63
1.63
1.62
1.61
1.45
1.43
1.42
1.40
1.39
1.38
1.36
1.34
1.32
0.91
0.89
F
F
OMs
n-Pr
MeO
9
2.26
2.00
1.00
3.00
4.02
1.00
2.02
2.07
3.08
f1 (ppm)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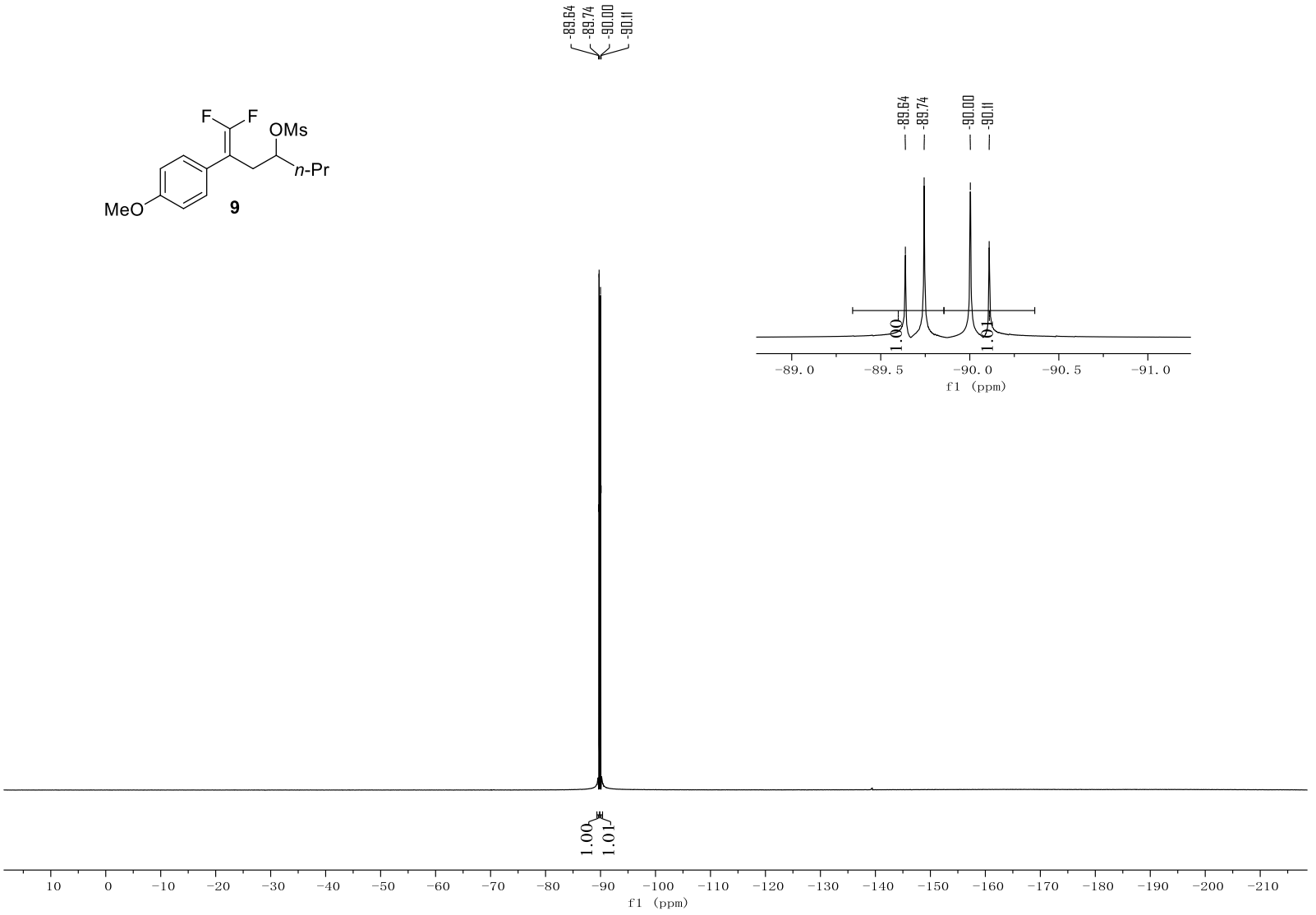
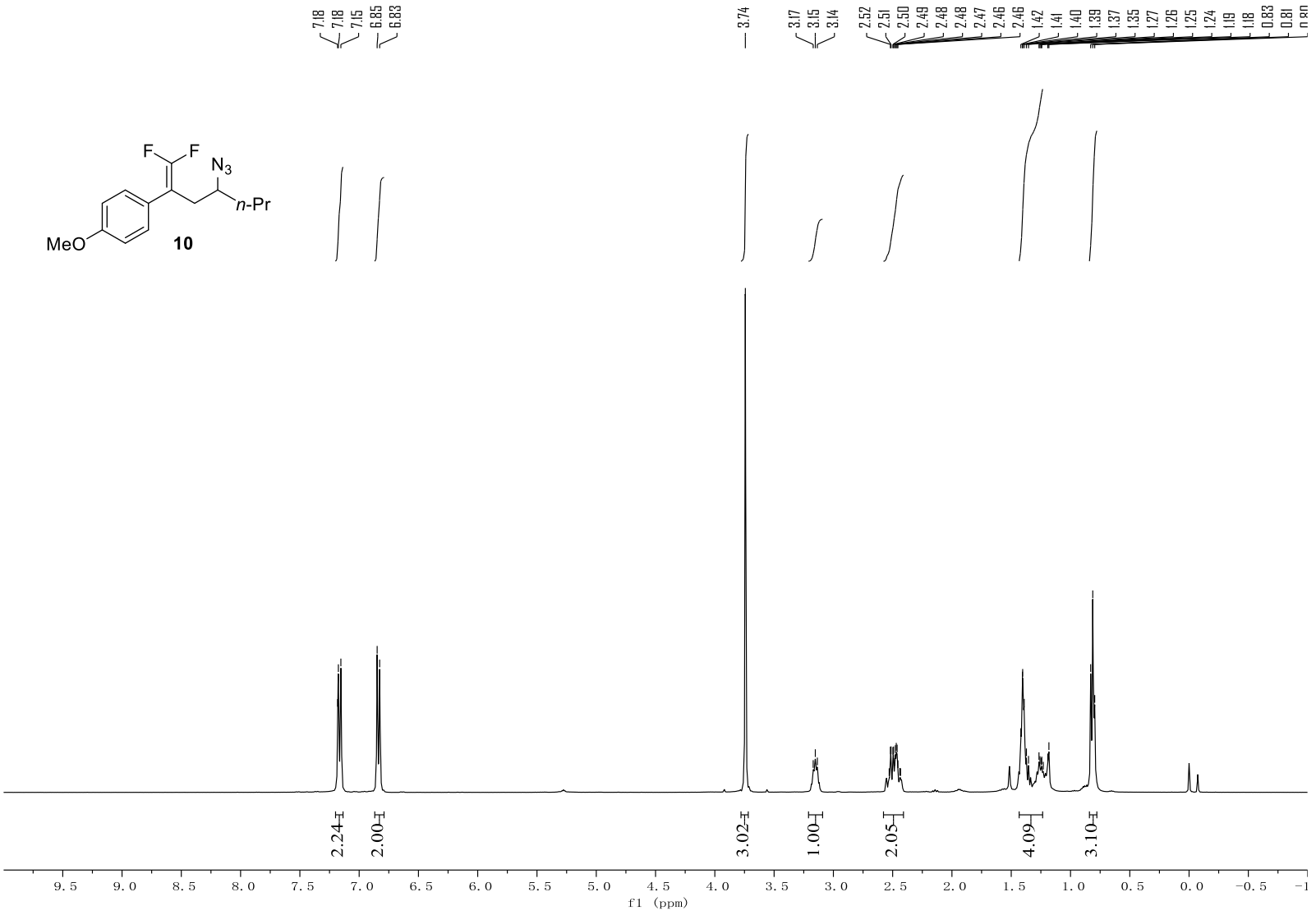
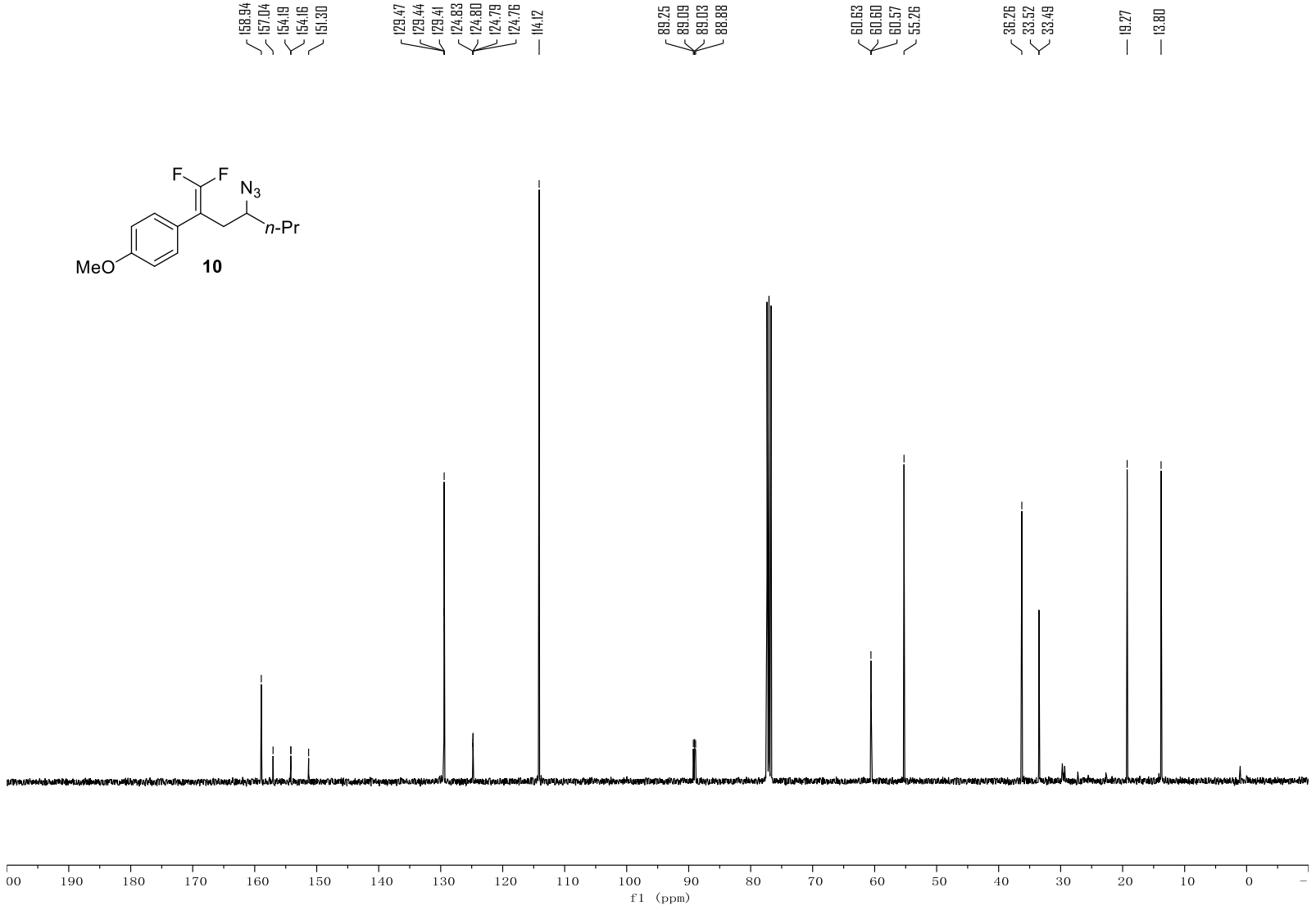
157.25
154.39
154.36
151.49
129.42
129.38
129.35
124.58
124.55
124.51
114.12
88.30
88.14
88.09
87.93
80.88
80.85
80.84
80.82
55.27
38.35
38.32
33.23
33.21
18.19
13.73
F
F
OMs
n-Pr
MeO
9
f1 (ppm)


F
F
OMs
n-Pr
MeO
9
-89.64
-89.74
-90.00
-90.11
1.00
1.01
-89.0
-89.5
-90.0
-90.5
-91.0
f1 (ppm)
1.00
1.01
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)


F
F
N3
n-Pr
MeO
10
7.18
7.18
7.15
6.85
6.83
3.74
3.17
3.15
3.14
2.52
2.51
2.50
2.49
2.48
2.48
2.47
2.46
2.46
1.42
1.41
1.40
1.39
1.37
1.35
1.27
1.26
1.25
1.24
1.19
1.18
0.83
0.81
2.24
2.00
3.02
1.00
2.05
4.09
3.10
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 −1
f1 (ppm)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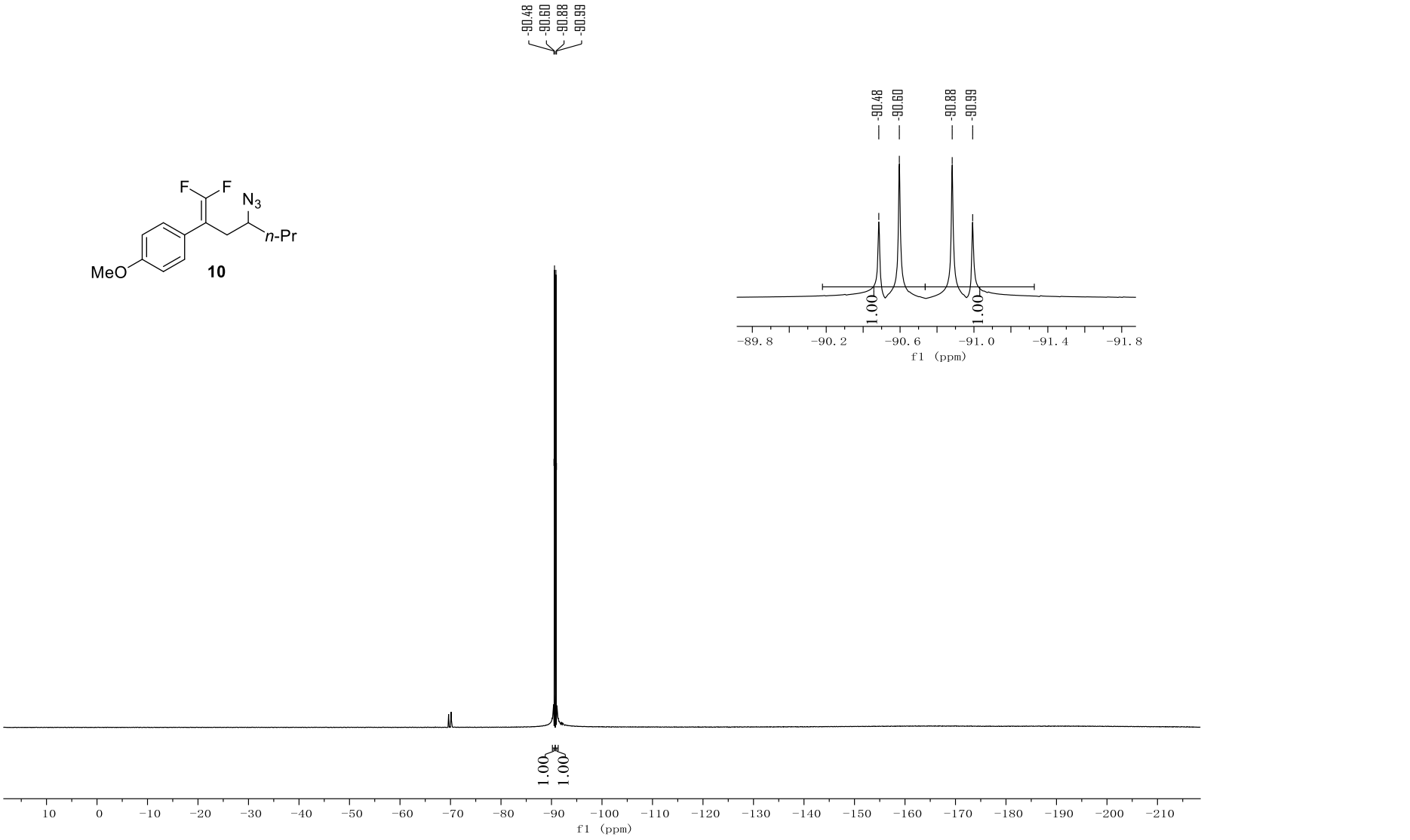
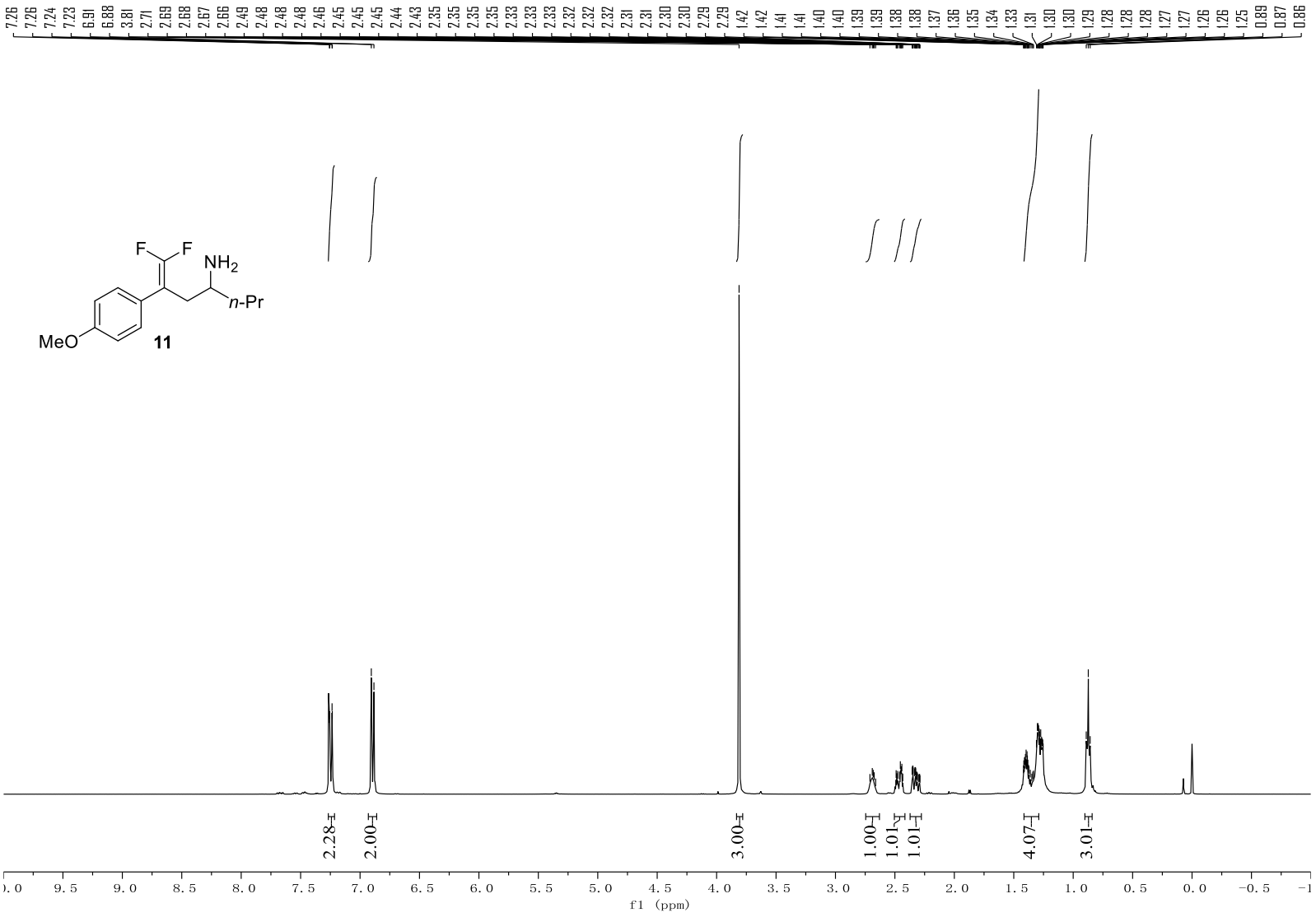
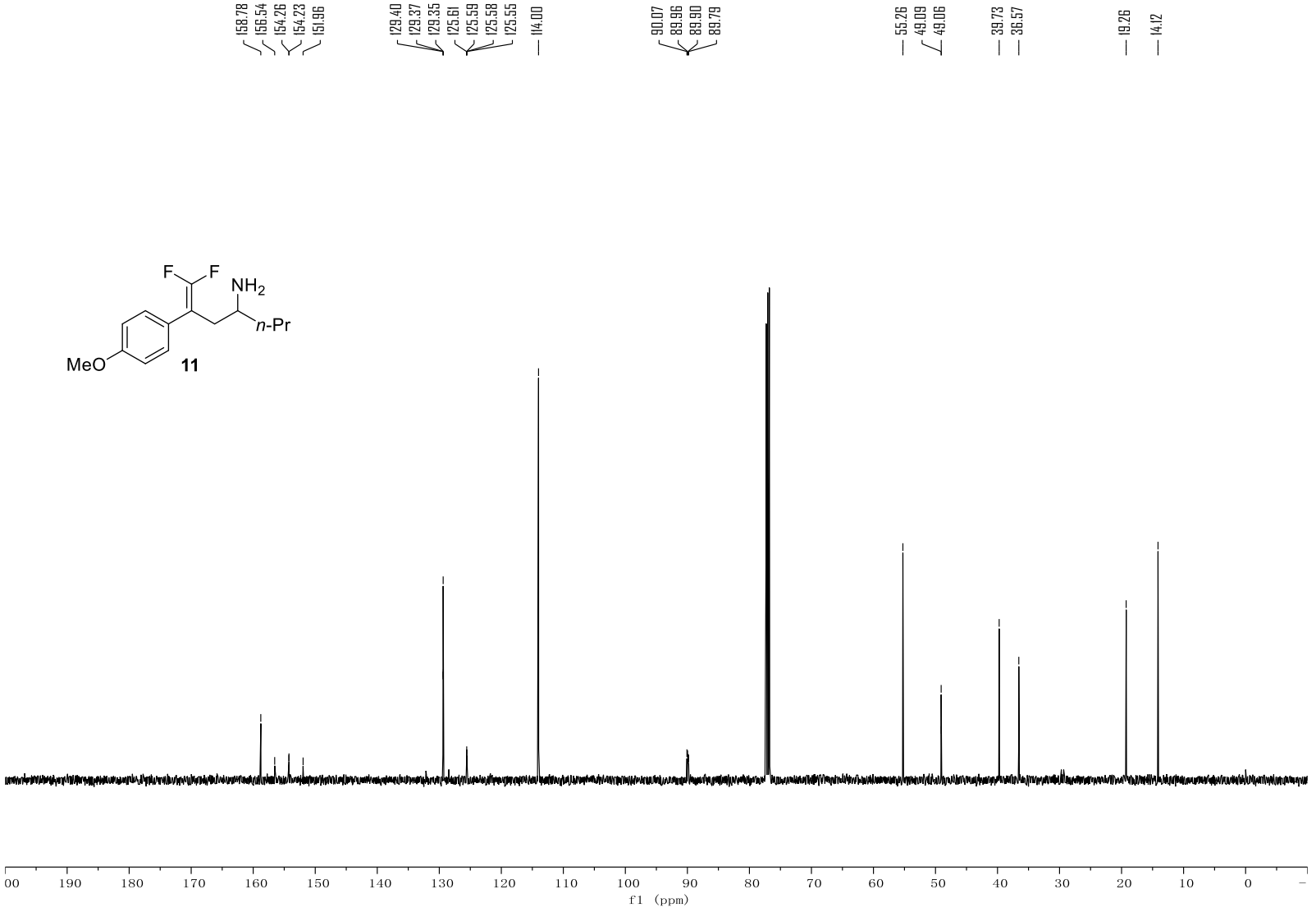
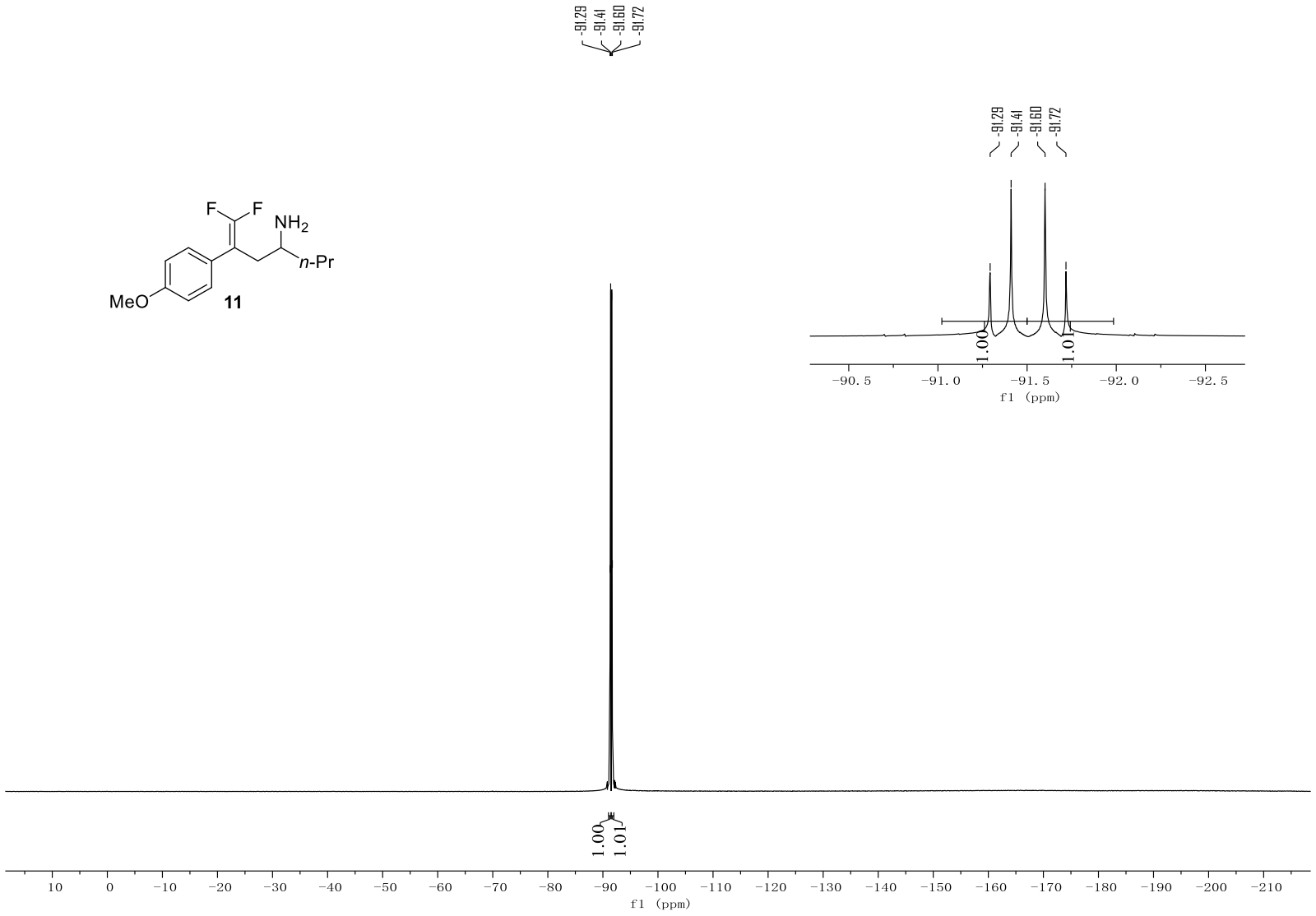
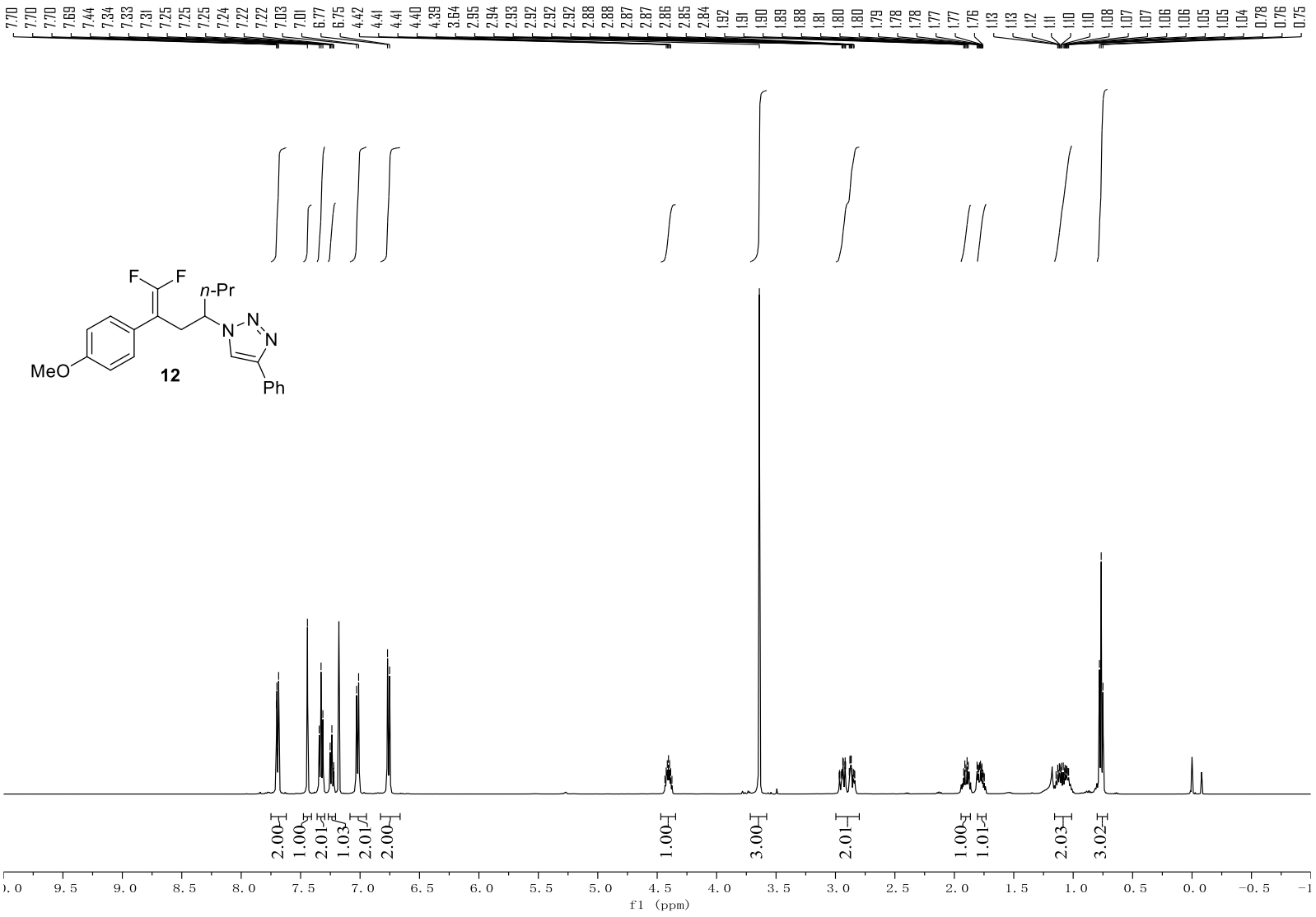
157.04
154.19
154.16
151.30
129.47
129.44
129.41
124.83
124.80
124.79
124.76
114.12
89.25
89.09
89.03
88.88
60.63
60.60
60.57
55.26
36.26
33.52
33.49
19.27
13.80
F
F
N3
n-Pr
MeO
10
f1 (ppm)

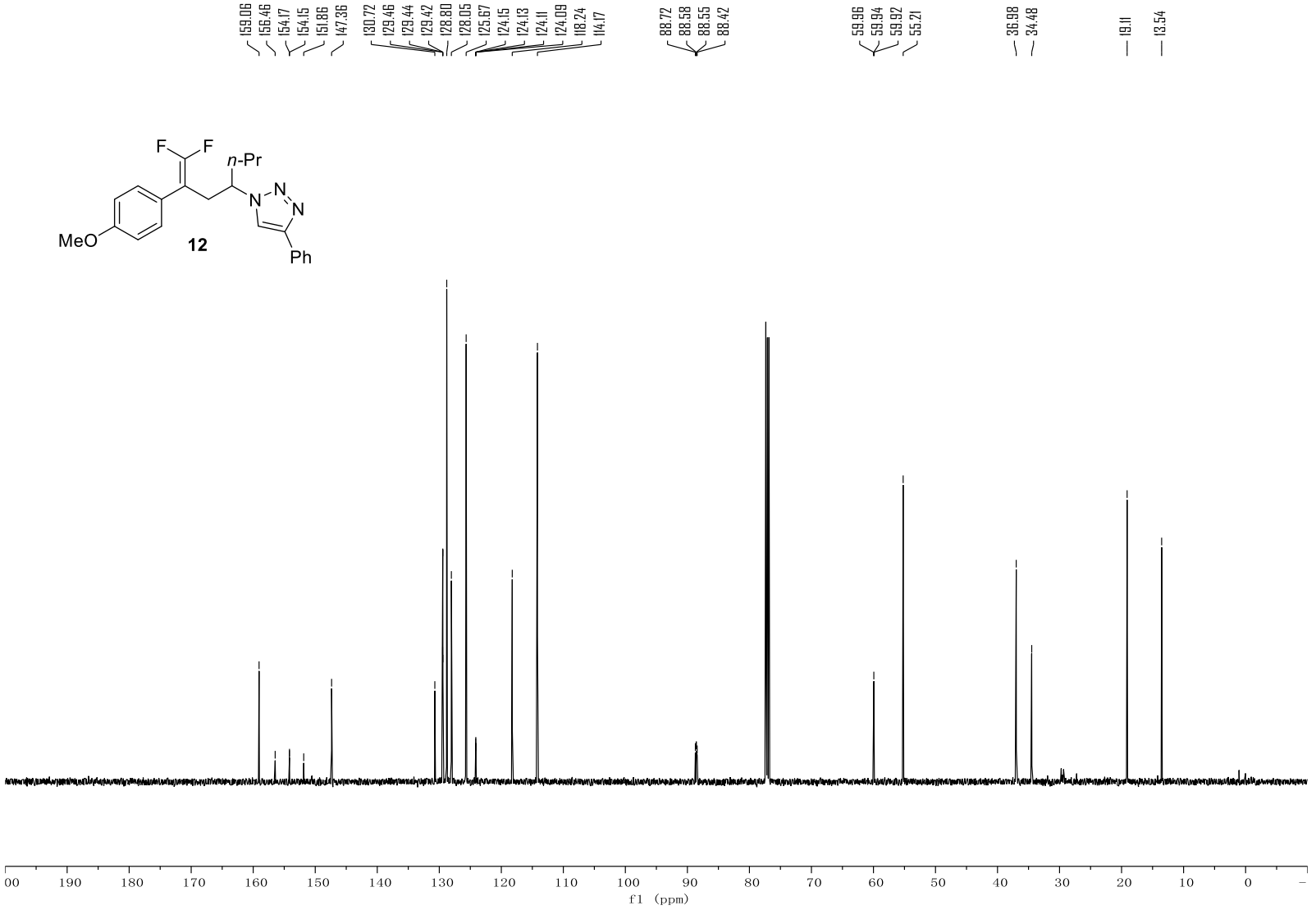

-90.48
-90.60
-90.88
-90.99
F
F
N3
n-Pr
MeO
10
1.00
1.00
-89.8
-90.2
-90.6
-91.0
-91.4
-91.8
f1 (ppm)
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


F
F
NH2
n-Pr
MeO
11
2.28
2.00
3.00
1.00
1.01
1.01
4.07
3.01
f1 (ppm)


158.78
156.54
154.26
154.23
151.96
129.40
129.37
129.35
125.61
125.59
125.58
125.55
114.00
90.07
89.96
89.90
89.79
55.26
49.09
49.06
39.73
36.57
19.26
14.12
F
F
NH2
n-Pr
MeO
11
f1 (ppm)


-91.29
-91.41
-91.60
-91.72
F
F
NH2
n-Pr
MeO
11
1.00
1.01
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)
-91.29
-91.41
-91.60
-91.72
1.00
1.01
−90.5 −91.0 −91.5 −92.0 −92.5
f1 (ppm)


7.70
7.70
7.70
7.69
7.44
7.34
7.33
7.31
7.25
7.25
7.25
7.24
7.22
7.22
7.03
7.01
6.77
6.75
4.42
4.41
4.41
4.40
4.39
3.64
2.95
2.94
2.93
2.92
2.92
2.92
2.88
2.88
2.87
2.87
2.86
2.85
2.84
1.92
1.91
1.90
1.89
1.88
1.81
1.80
1.80
1.79
1.78
1.78
1.77
1.77
1.76
1.13
1.13
1.12
1.11
1.10
1.10
1.08
1.07
1.07
1.06
1.06
1.05
1.05
1.04
0.78
0.76
0.75
F
F
n-Pr
N
N
N
MeO
12
Ph
2.00
1.00
2.01
1.03
2.01
2.00
1.00
3.00
2.01
1.00
1.01
2.03
3.02
f1 (ppm)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129.46
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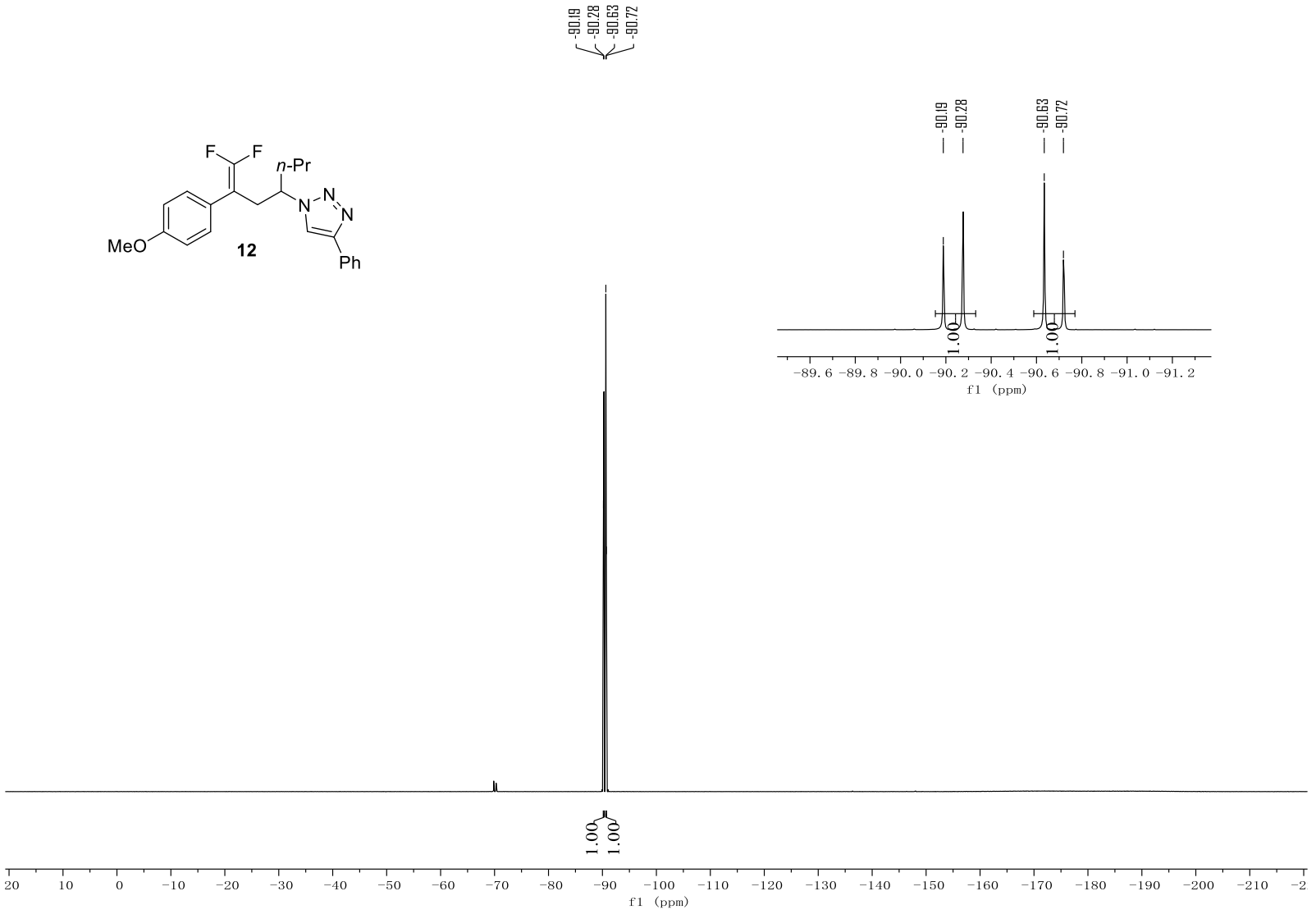
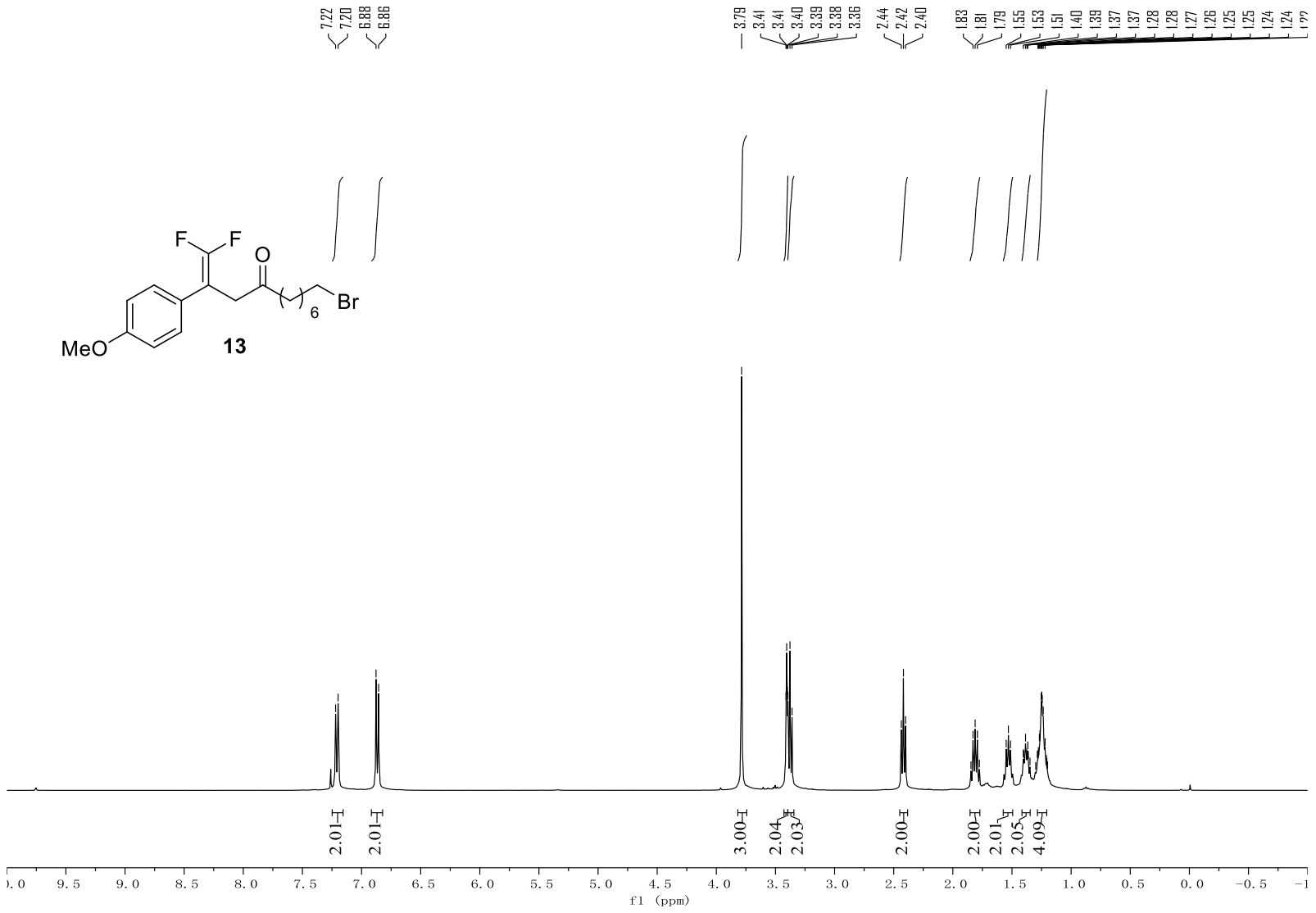
128.05
125.67
124.15
124.13
124.11
124.09
118.24
114.17
88.72
88.58
88.55
88.42
59.96
59.94
59.92
55.21
36.88
34.48
19.11
13.54
F
F
n-Pr
N
N
N
MeO
Ph
12
f1 (ppm)


-90.19
-90.28
-90.63
-90.72
F
F
n-Pr
N
N
N
MeO
12
Ph
1.00
1.00
-89.6 -89.8 -90.0 -90.2 -90.4 -90.6 -90.8 -91.0 -91.2
f1 (ppm)
1.00
1.00
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)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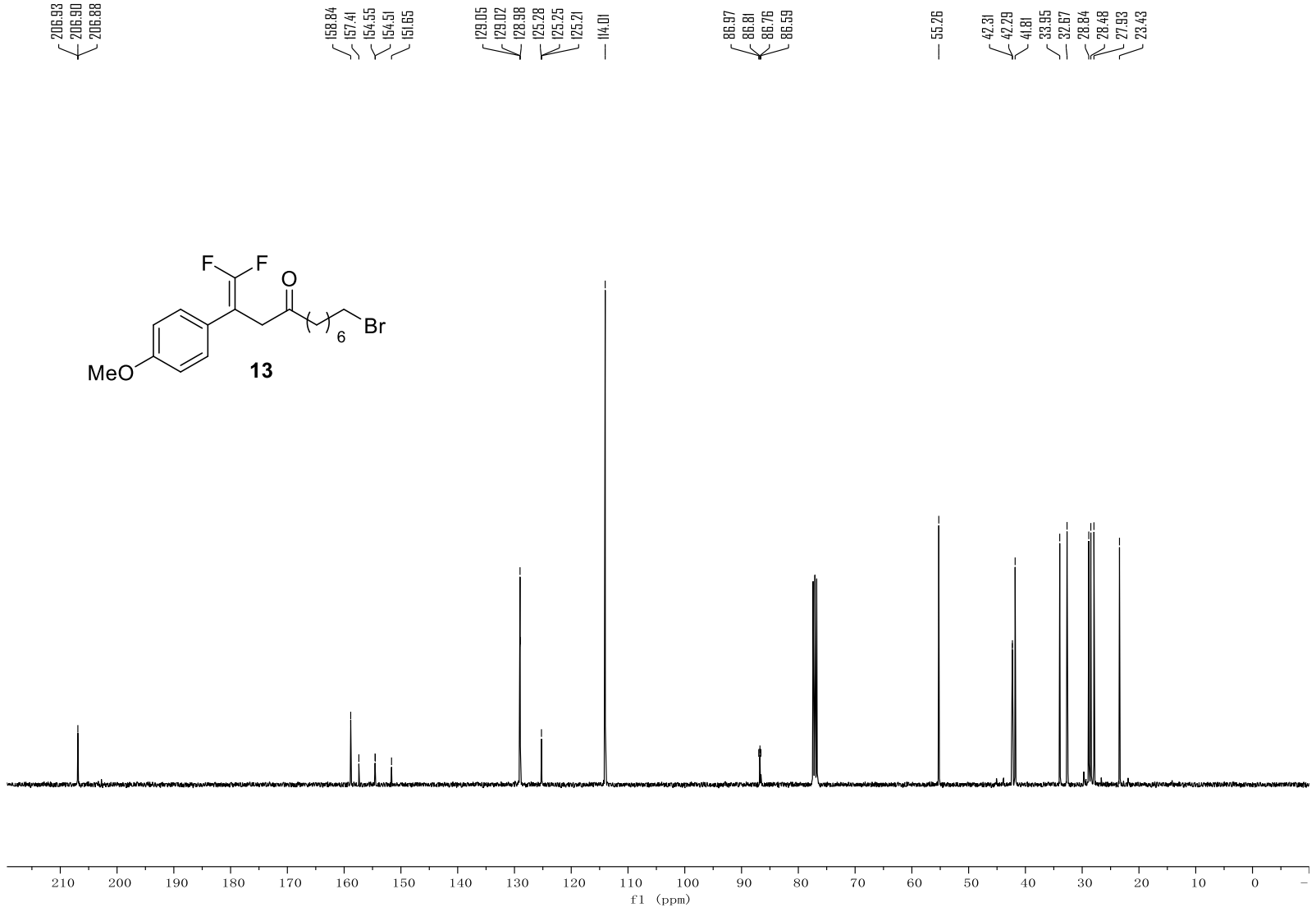
6.86
3.79
3.41
3.41
3.40
3.39
3.38
3.36
2.44
2.42
2.40
1.83
1.81
1.79
1.55
1.53
1.51
1.40
1.39
1.37
1.37
1.28
1.28
1.27
1.26
1.25
1.25
1.24
1.24
F
F
O
Br
6
MeO
13
2.01
2.01
3.00
2.04
2.03
2.00
2.00
2.01
2.05
4.09
f1 (ppm)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206.90
206.88
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154.55
154.51
151.65
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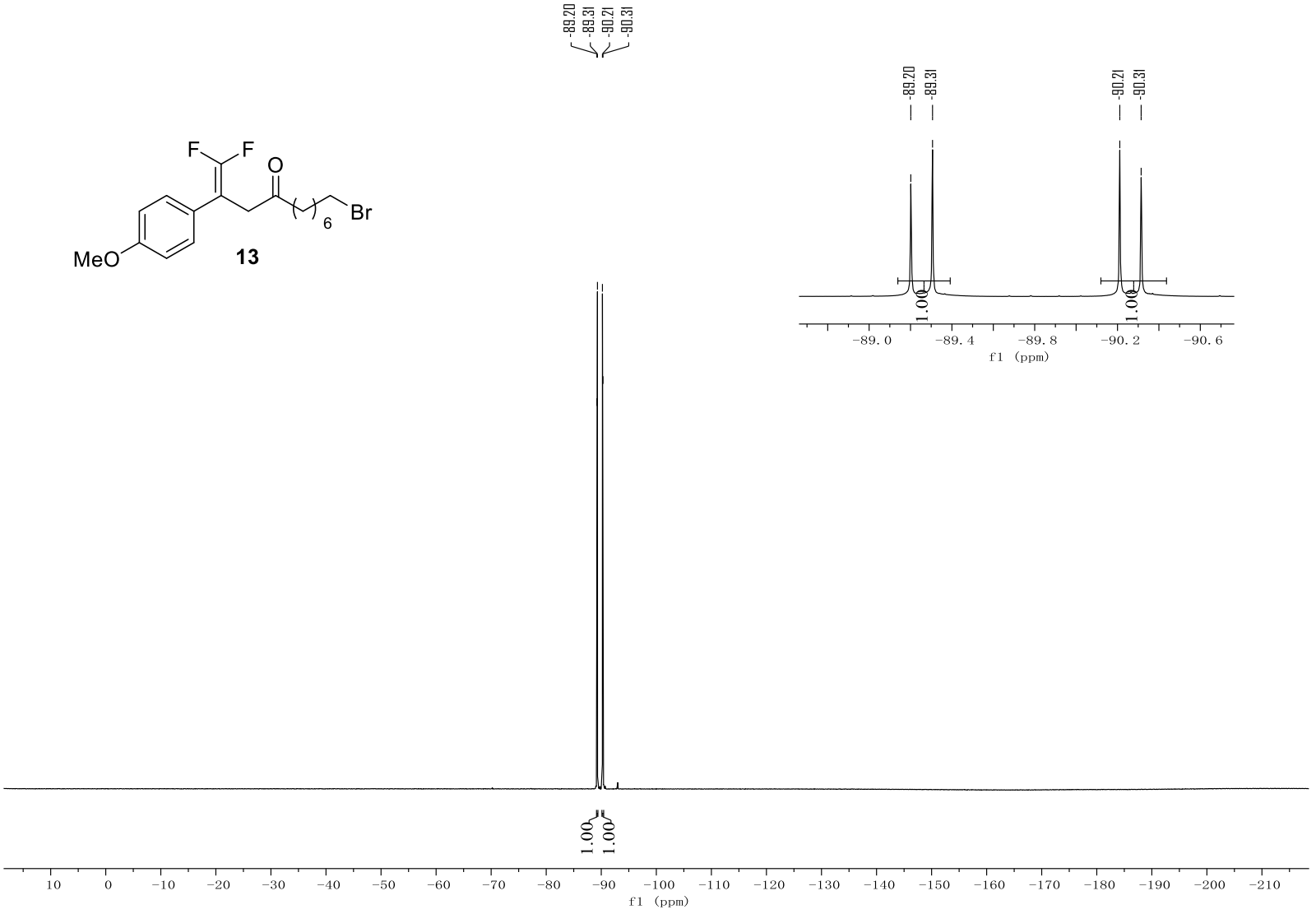
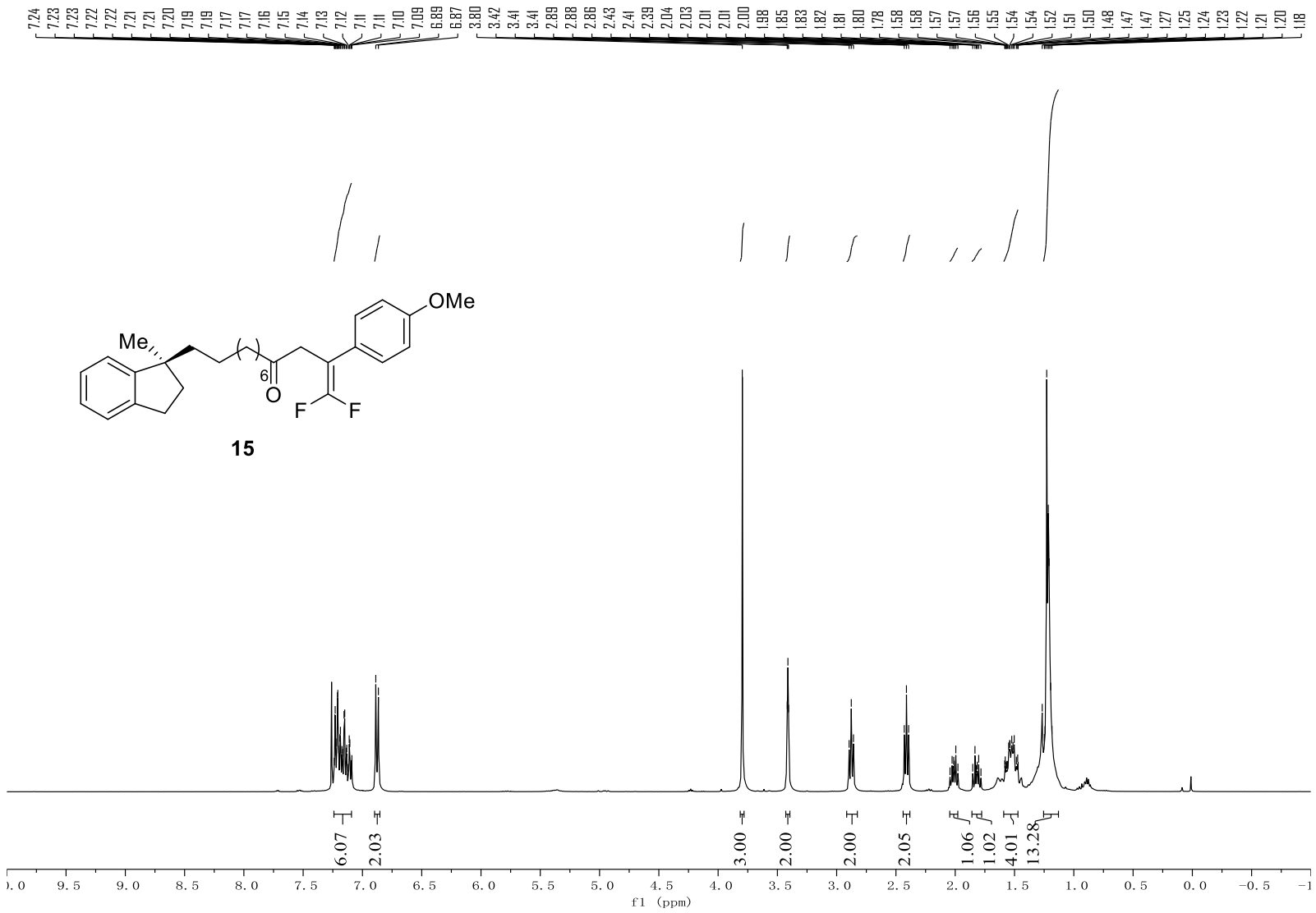
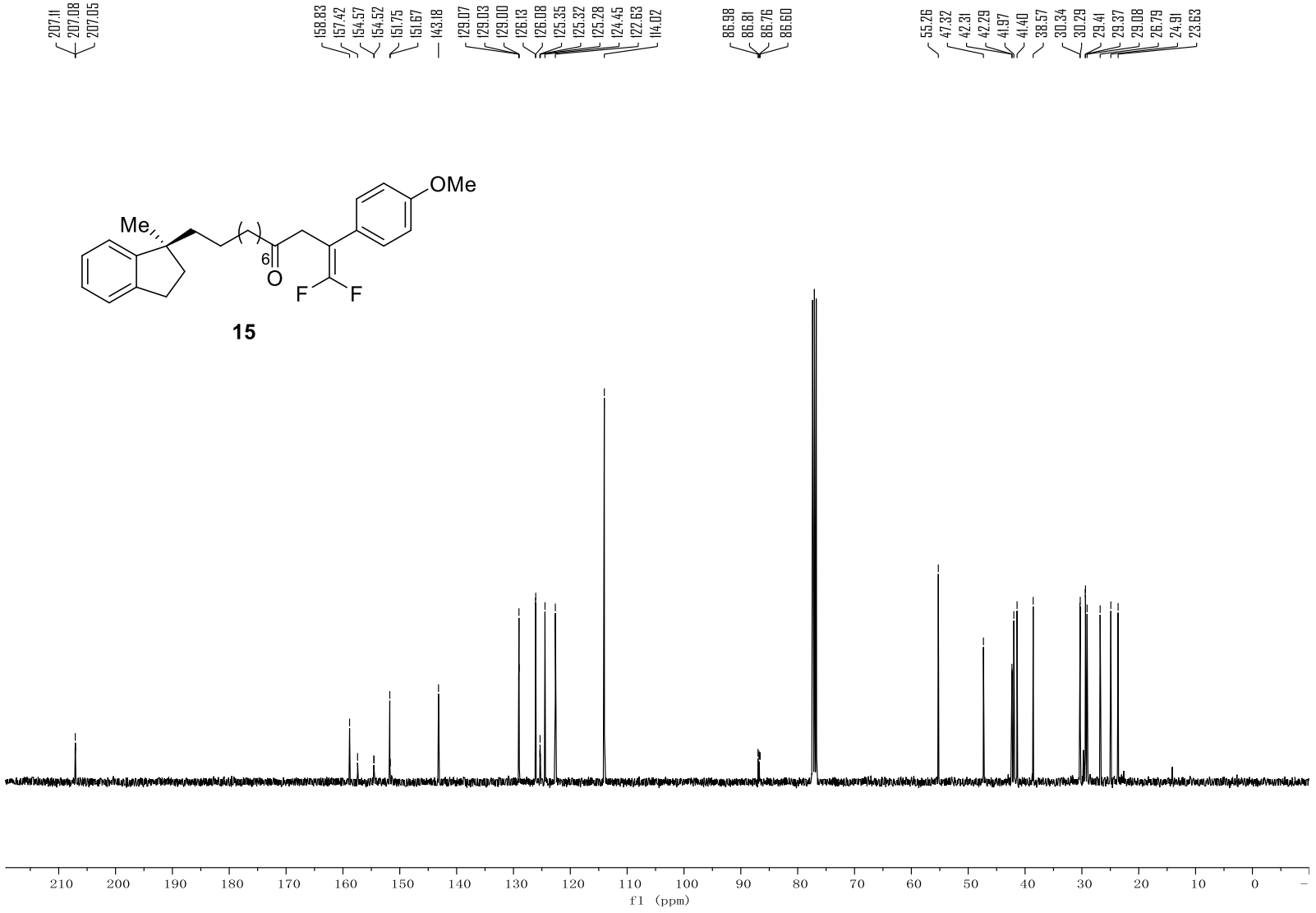
129.02
128.98
125.28
125.25
125.21
114.01
86.97
86.81
86.76
86.59
55.26
42.31
42.29
41.81
33.95
32.67
28.84
28.48
27.93
23.43
F
F
O
Br
6
MeO
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
6
Br
MeO
13
-89.20
-89.31
-90.21
-90.31
1.00
1.00
-89.0
-89.4
-89.8
-90.2
-90.6
f1 (ppm)
1.00
1.00
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)


7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.19 7.17 7.17 7.16 7.15 7.14 7.13 7.12 7.11 7.11 7.10 7.09 6.89 6.87
3.80 3.42 3.41 3.41 2.89 2.88 2.86 2.43 2.41 2.39 2.04 2.03 2.01 2.01 2.00 1.98 1.85 1.83 1.82 1.81 1.80 1.78 1.58 1.58 1.57 1.57 1.56 1.55 1.54 1.54 1.52 1.51 1.50 1.48 1.47 1.47 1.27 1.25 1.24 1.23 1.22 1.21 1.20 1.18
OMe
Me
6
O
F
F
15
6.07
2.03
3.00
2.00
2.00
2.05
1.06
1.02
4.01
13.28
f1 (ppm)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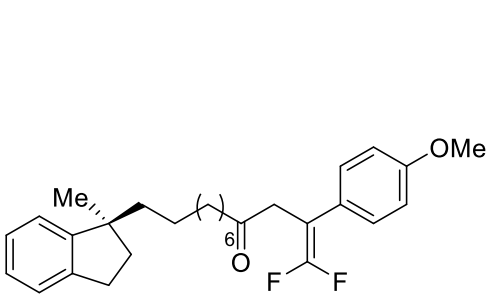
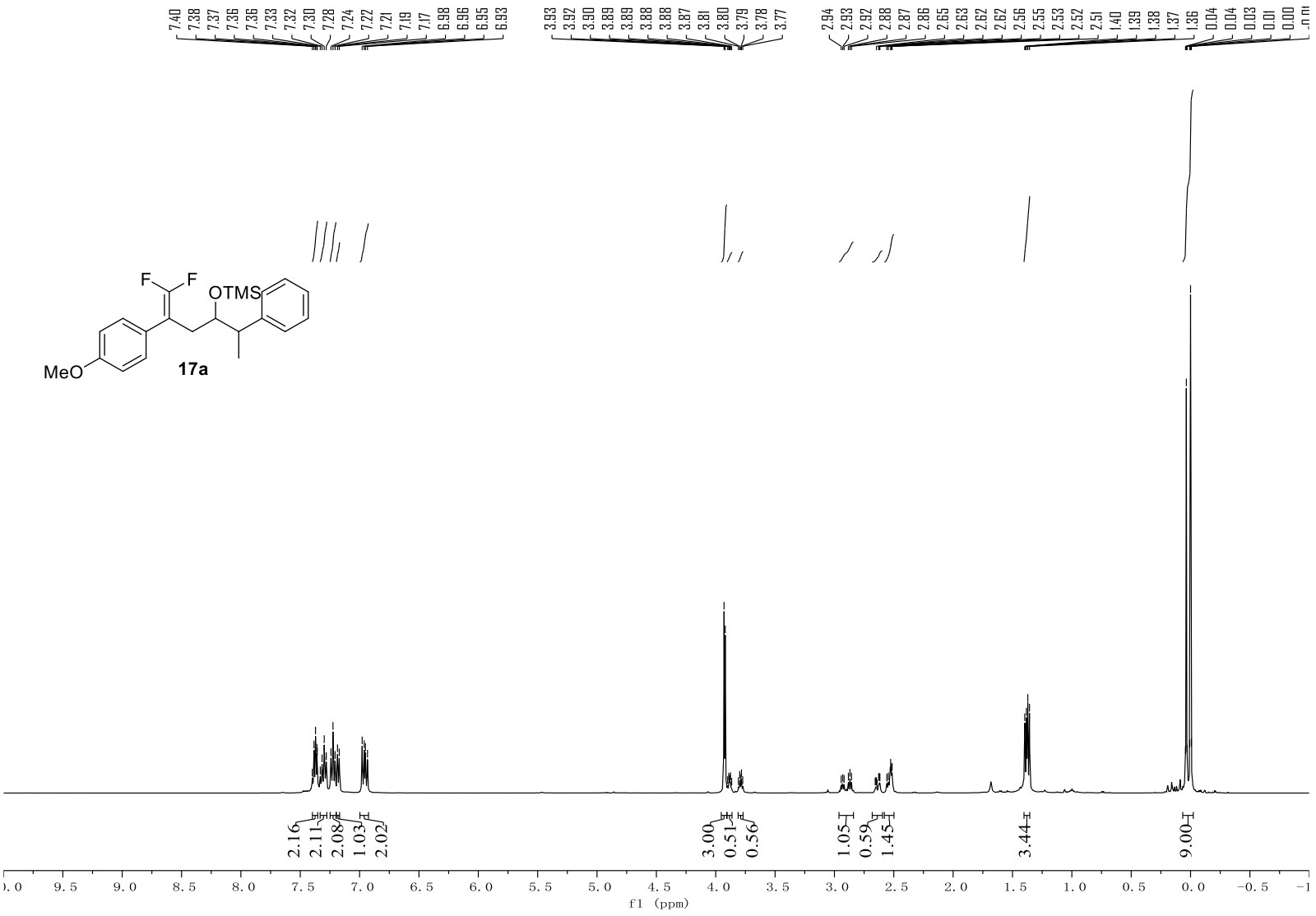
207.08
207.05
158.83
157.42
154.57
154.52
151.75
151.67
143.18
129.07
129.03
129.00
126.13
126.08
125.35
125.32
125.28
124.45
122.63
114.02
86.98
86.81
86.76
86.60
55.26
47.32
42.31
42.29
41.97
41.40
38.57
30.34
30.29
29.41
29.37
29.08
26.79
24.91
23.63
OMe
Me
6
O
F
F
15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
6
O
F
F
OMe

15

-89.19
-89.29
-90.20
-90.30
1.01
1.00
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)

-89.19
-89.29
-90.20
-90.30
1.01
1.00
−89.0 −89.5 −90.0 −90.5
f1 (ppm)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7.33
7.32
7.30
7.28
7.24
7.22
7.21
7.19
7.17
6.98
6.96
6.95
6.93
3.93
3.92
3.90
3.89
3.89
3.88
3.88
3.87
3.81
3.80
3.79
3.78
3.77
2.94
2.93
2.92
2.88
2.87
2.86
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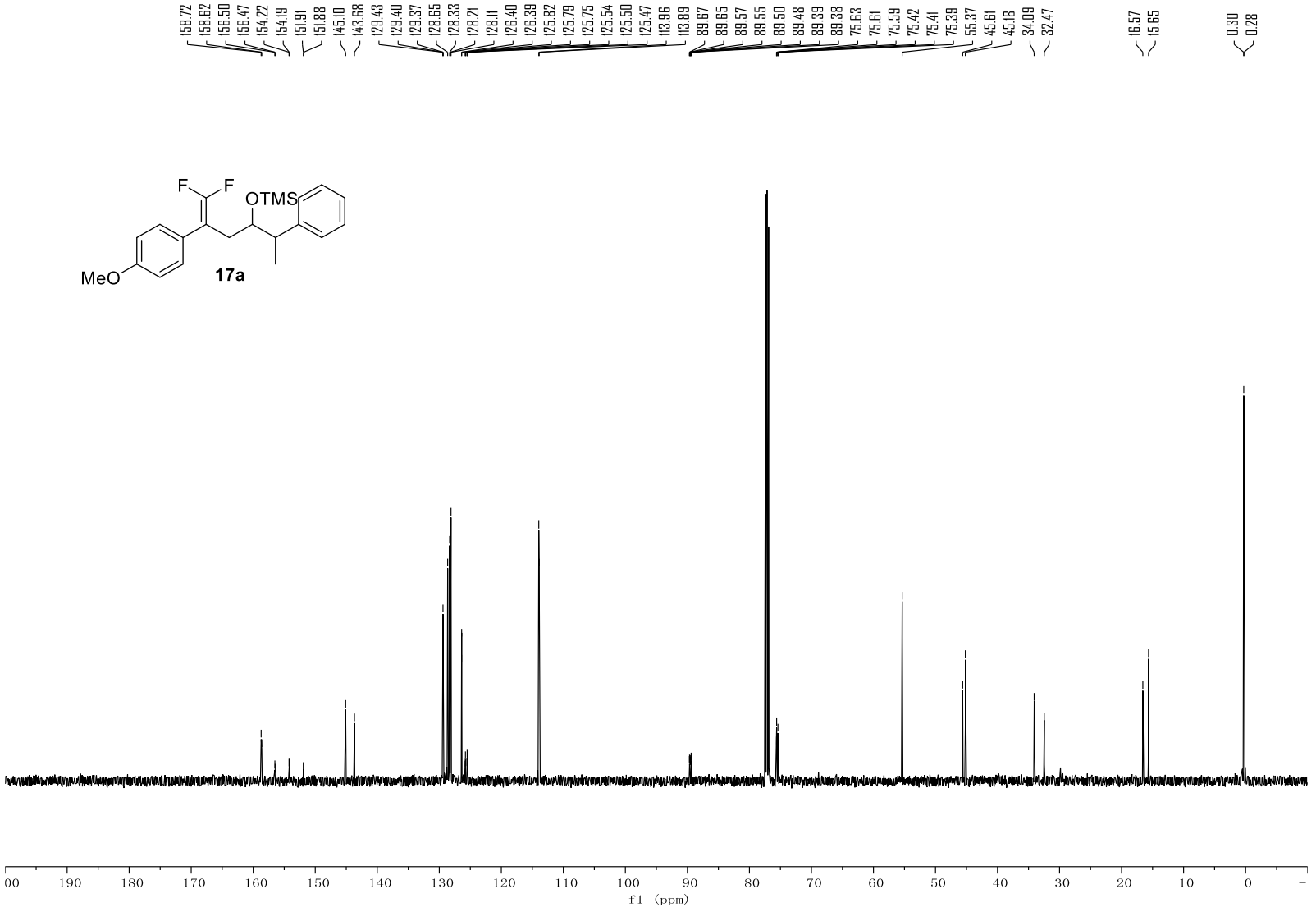
2.63
2.62
2.62
2.56
2.55
2.53
2.52
2.51
1.40
1.39
1.38
1.37
1.36
0.04
0.04
0.03
0.01
0.00
F
F
OTMS
MeO
17a
2.16
2.11
2.08
1.03
2.02
3.00
0.51
0.56
1.05
0.59
1.45
3.44
9.00
f1 (ppm)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151.88
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143.68
129.43
129.40
129.37
128.65
128.33
128.21
128.11
126.40
126.39
125.82
125.79
125.75
125.54
125.50
125.47
113.96
113.89
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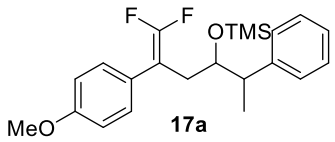
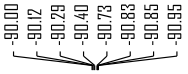
89.57
89.55
89.50
89.48
89.39
89.38
75.63
75.61
75.59
75.42
75.41
75.39
55.37
45.61
45.18
34.09
32.47
16.57
15.65
0.30
0.28
F
F
OTMS
MeO
17a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
OTMS
MeO

17a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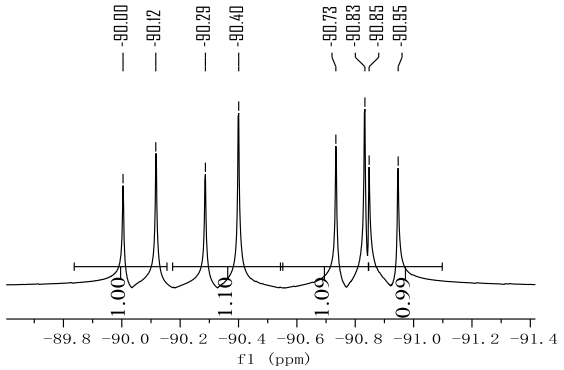
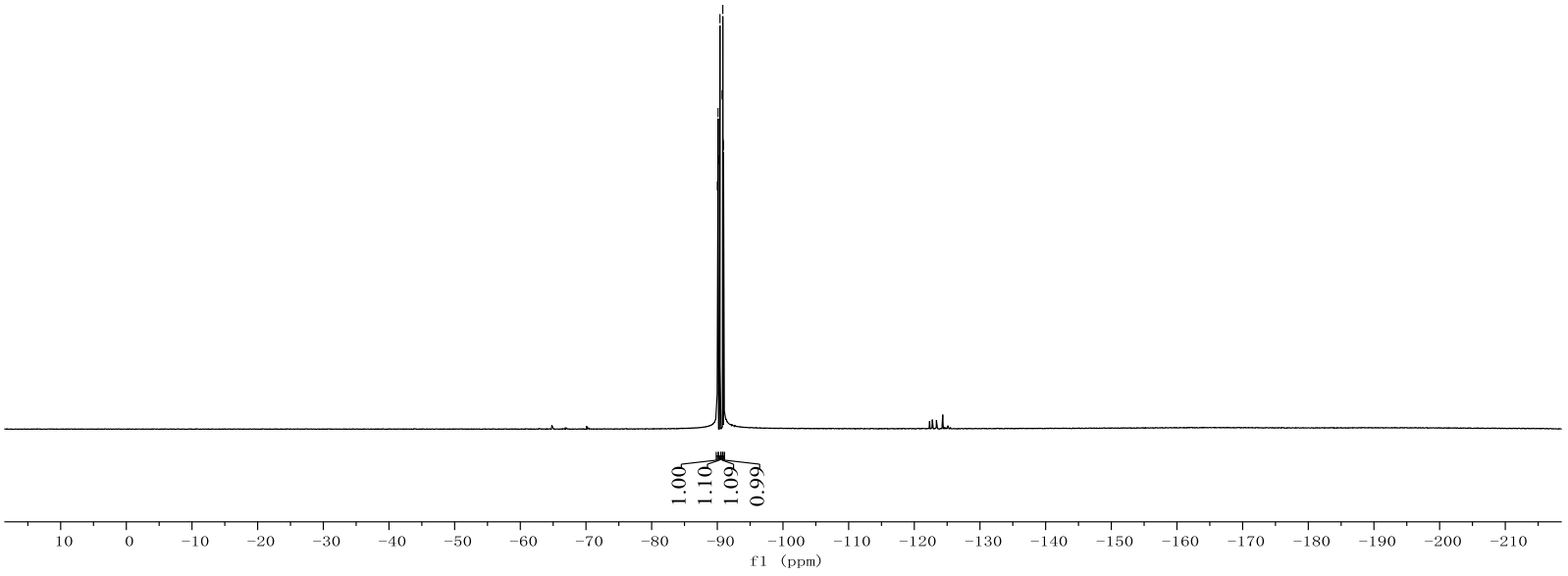
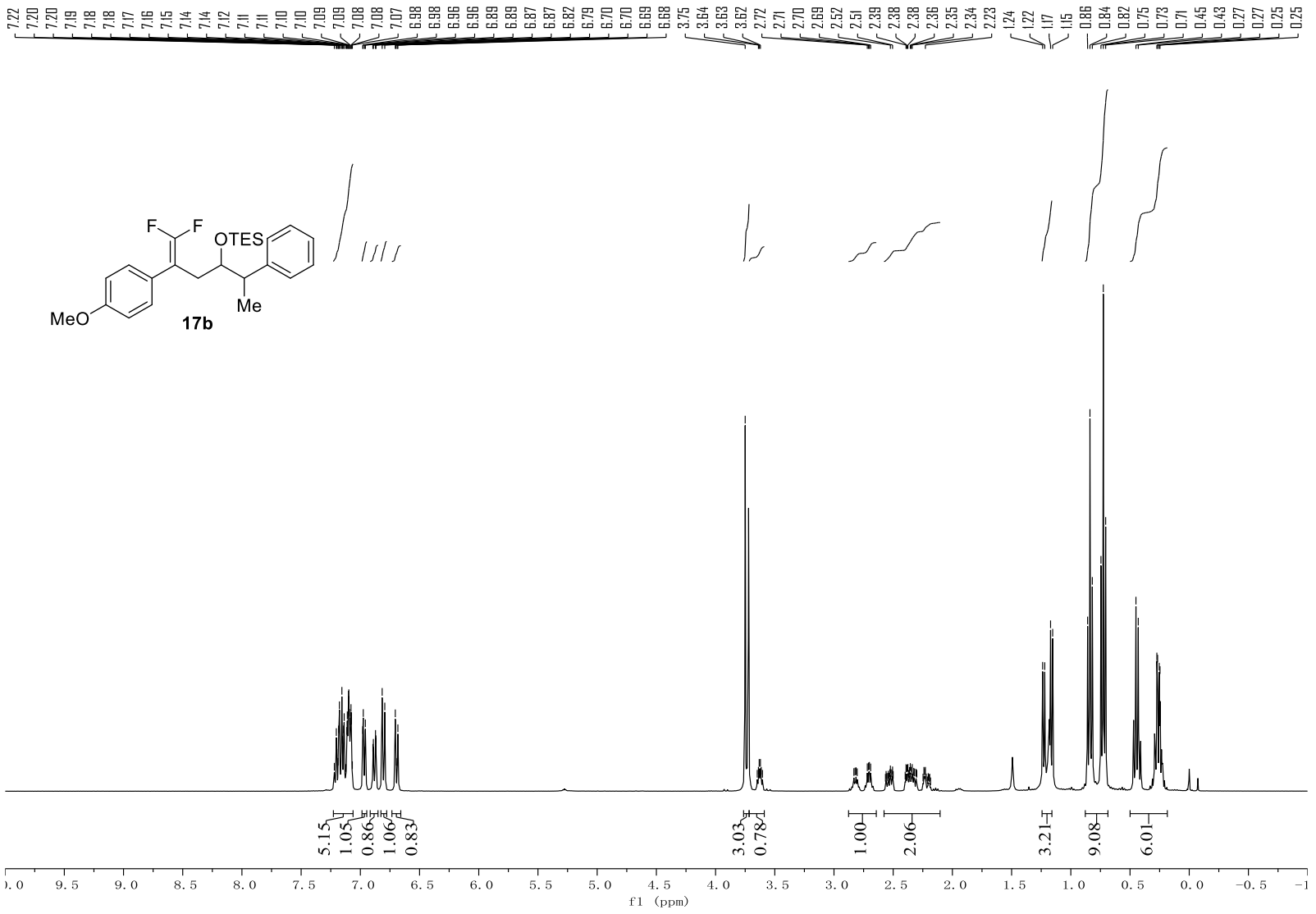
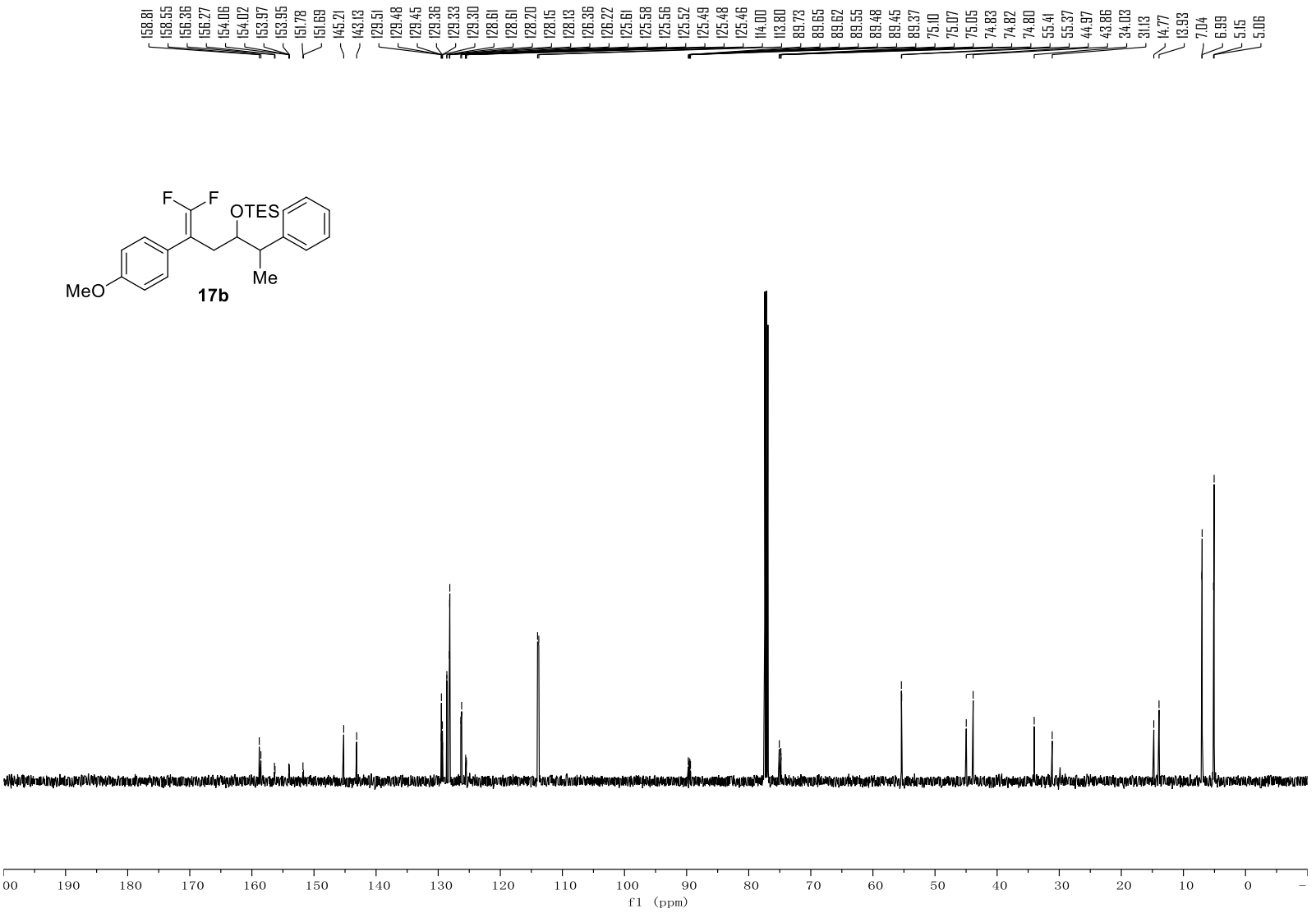
-90.12
-90.29
-90.40
-90.73
-90.83
-90.85
-90.95


-90.00
-90.12
-90.29
-90.40
-90.73
-90.83
-90.85
-90.95
1.00
1.10
1.09
0.99
-89.8 -90.0 -90.2 -90.4 -90.6 -90.8 -91.0 -91.2 -91.4
f1 (ppm)


1.00
1.10
1.09
0.99
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)


F
F
OTES
Me
MeO
17b
7.22 7.20 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.14 7.14 7.12 7.11 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.07 6.98 6.98 6.96 6.96 6.89 6.89 6.87 6.87 6.82 6.79 6.70 6.70 6.69 6.68
3.75 3.64 3.63 3.62 2.72 2.71 2.70 2.69 2.52 2.51 2.39 2.38 2.38 2.36 2.35 2.34 2.23
1.24 1.22 1.17 1.15 0.86 0.84 0.82 0.75 0.73 0.71 0.45 0.43 0.27 0.27 0.25 0.25
5.15 1.05 0.86 1.06 0.83 3.03 0.78 1.00 2.06 3.21 9.08 6.01
f1 (ppm)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153.95
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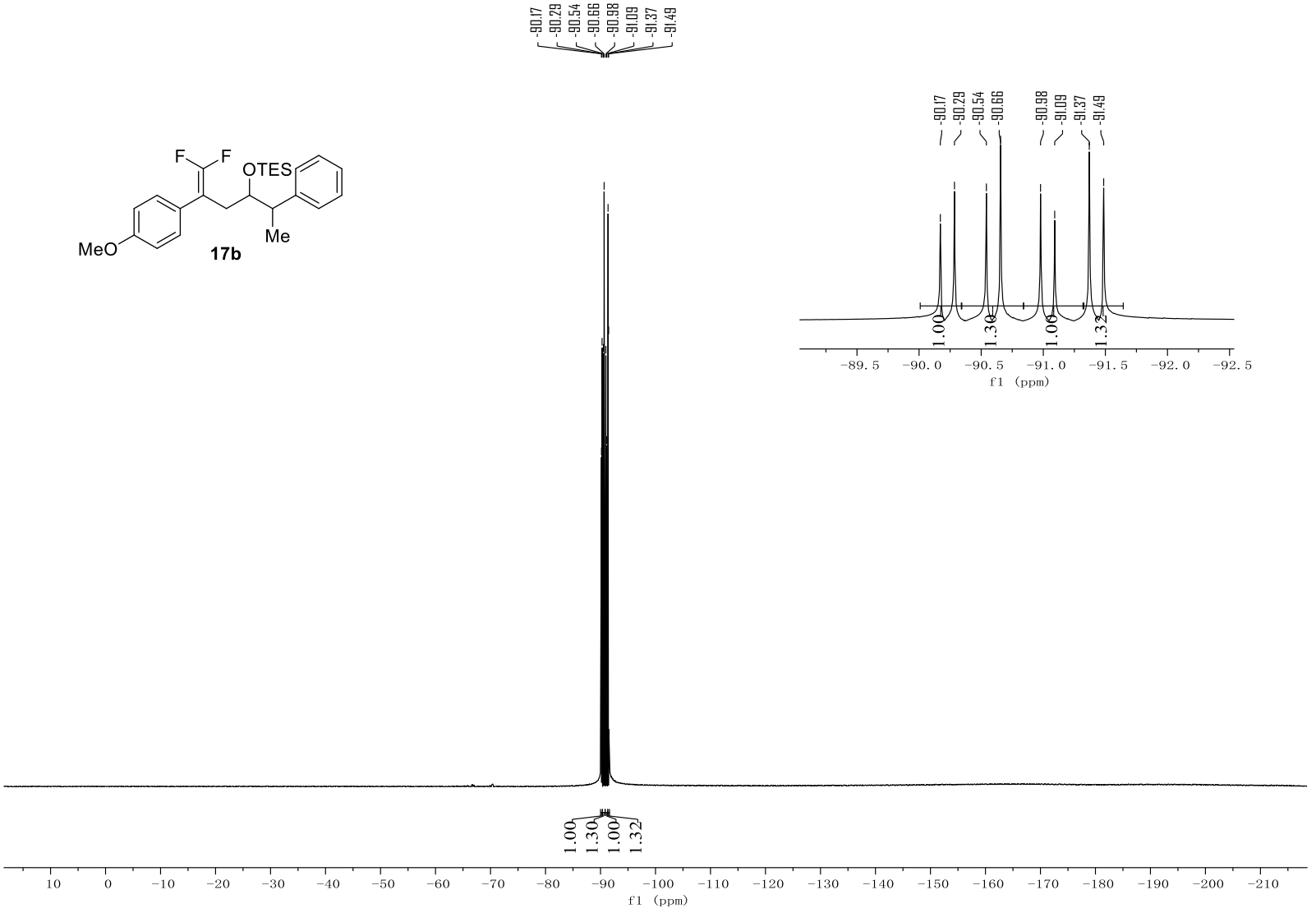
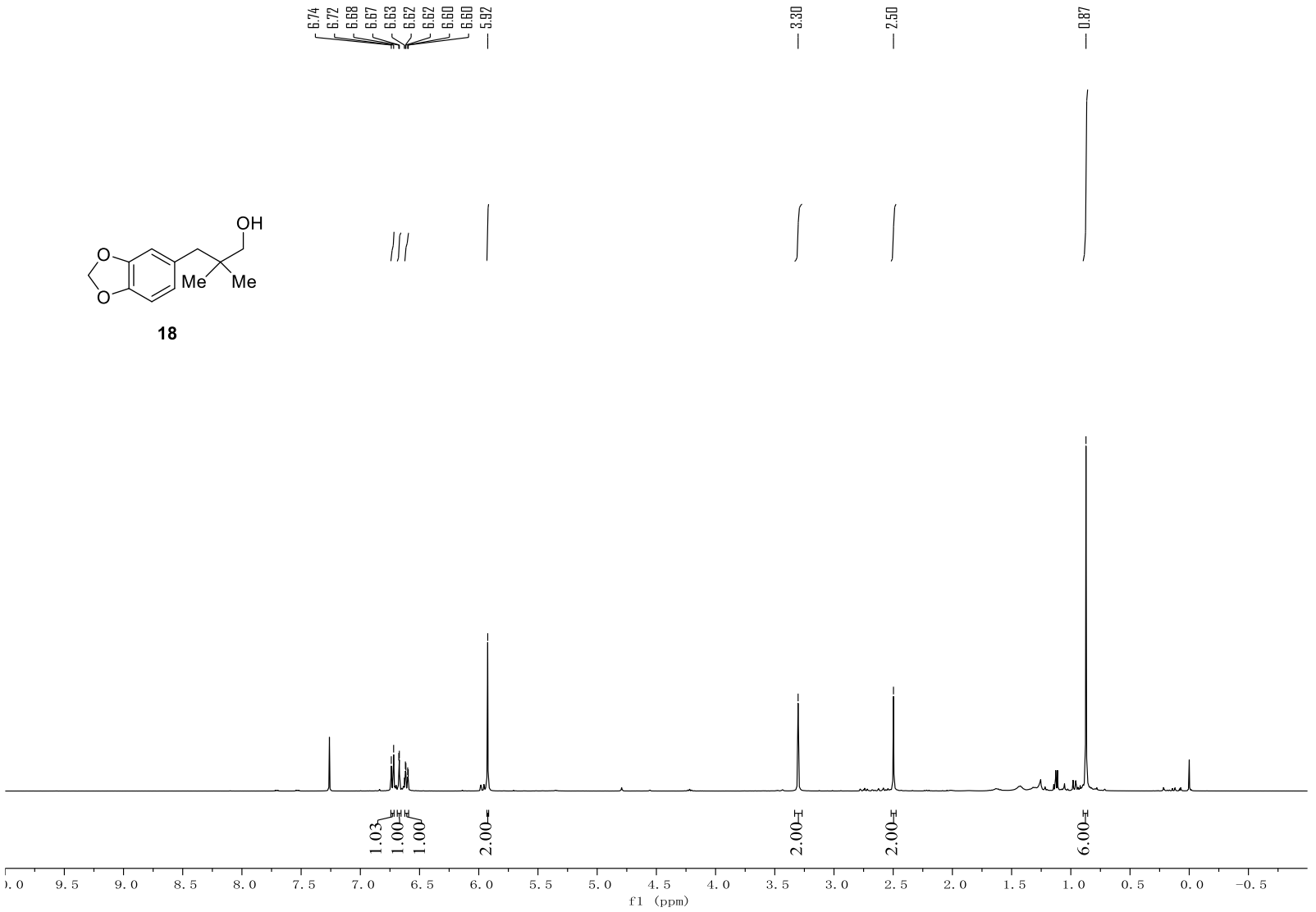
151.69
145.21
143.13
129.51
129.48
129.45
129.38
129.33
129.30
128.61
128.61
128.20
128.15
128.13
126.36
126.22
125.61
125.58
125.56
125.52
125.49
125.48
125.46
114.00
113.80
89.73
89.65
89.62
89.55
89.48
89.45
89.37
75.10
75.07
75.05
74.83
74.82
74.80
55.41
55.37
44.97
43.86
34.03
31.13
14.77
13.93
7.04
6.99
5.15
5.06
F
F
OTES
Me
MeO
17b
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-90.17
-90.29
-90.54
-90.66
-90.98
-91.09
-91.37
-91.49
F
F
OTES
MeO
Me
17b
1.00
1.30
1.00
1.32
f1 (ppm)


6.74
6.72
6.68
6.67
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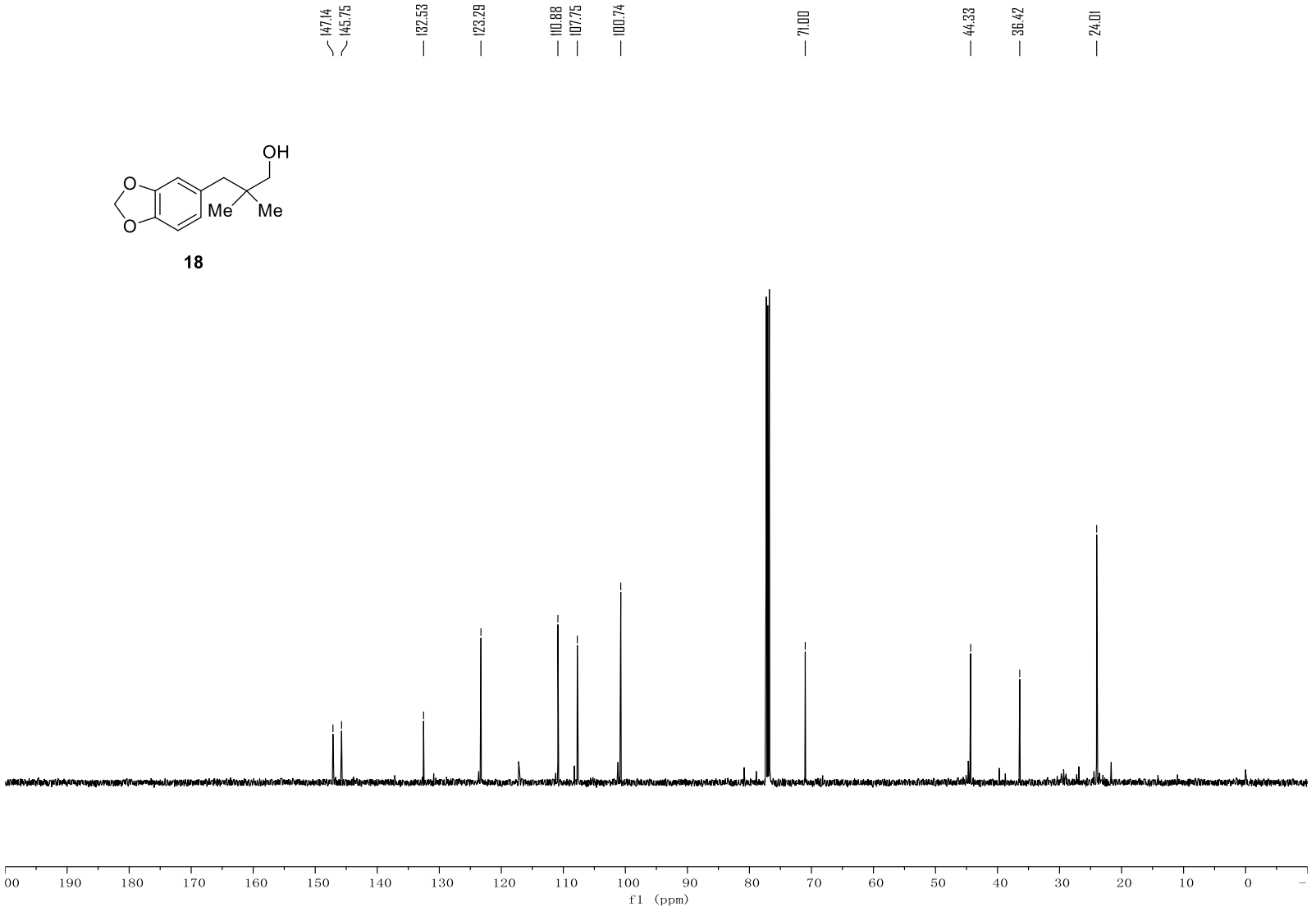
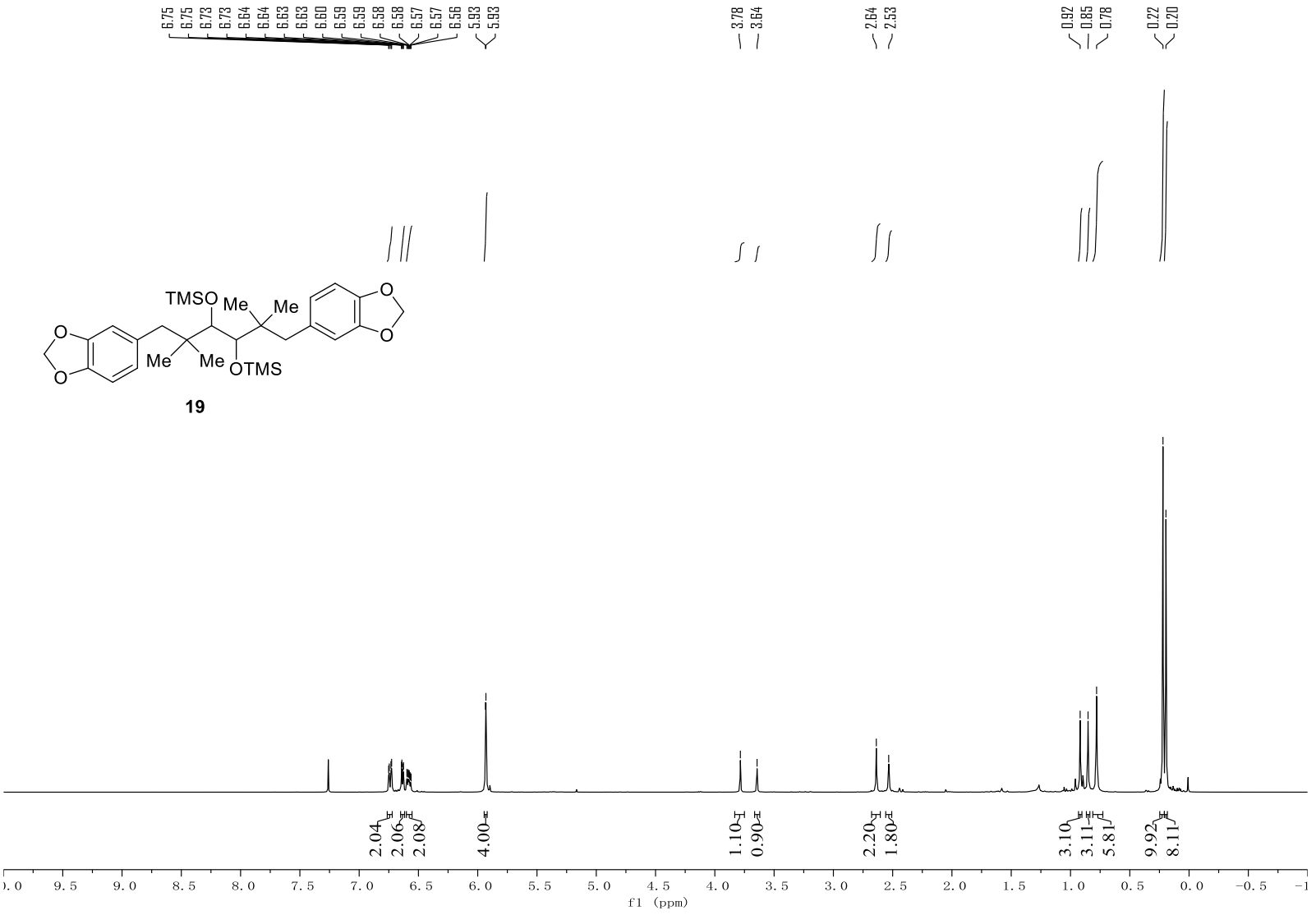
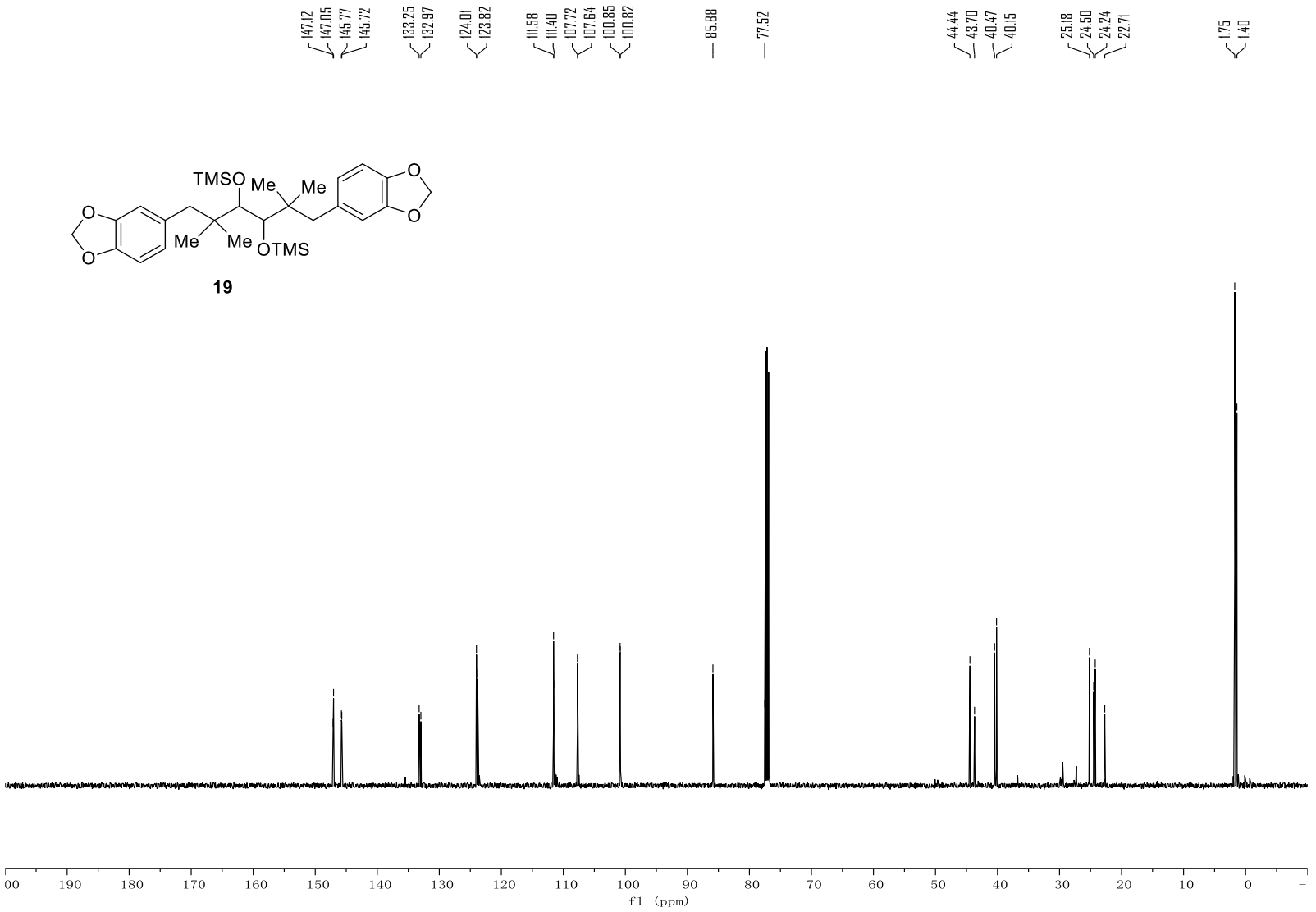
6.62
6.62
6.60
6.60
5.92
3.30
2.50
0.87
OH
O
O
Me
Me
1.03
1.00
1.00
2.00
2.00
2.00
6.00
f1 (ppm)

18


147.14
145.75
132.53
123.29
110.88
107.75
100.74
71.00
44.33
36.42
24.01
OH
Me
Me
O
O
18
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.75
6.75
6.73
6.73
6.64
6.64
6.63
6.63
6.60
6.59
6.59
6.58
6.58
6.57
6.57
6.56
5.93
5.93
3.78
3.64
2.64
2.53
0.92
0.85
0.78
0.72
0.20
TMSO
Me
Me
Me
Me
OTMS
O
O
O
O
2.04
2.06
2.08
4.00
1.10
0.90
2.20
1.80
3.10
3.11
5.81
9.92
8.11
f1 (ppm)

19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145.77
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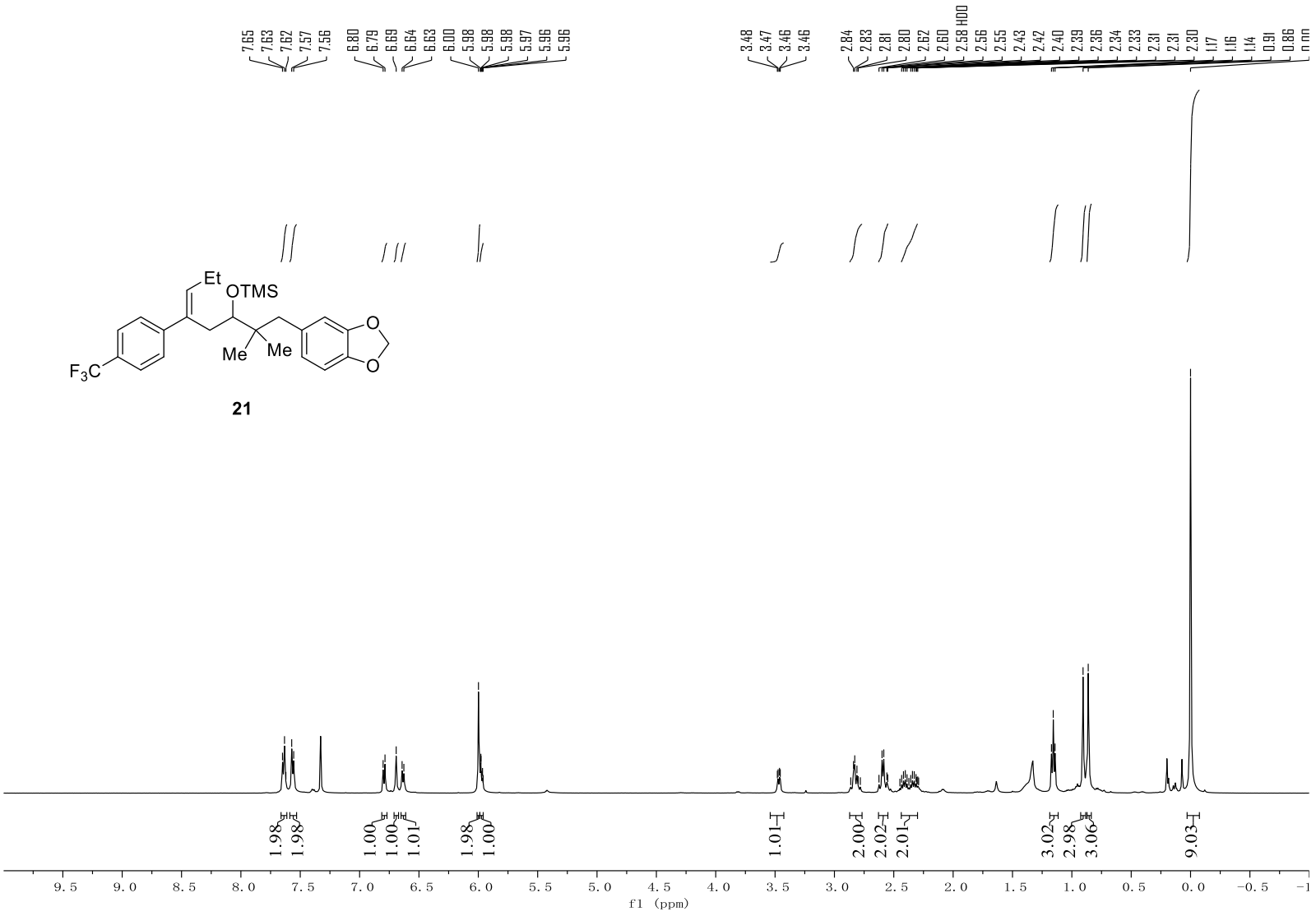
132.97
124.01
123.82
111.58
111.40
107.72
107.64
100.85
100.82
85.88
77.52
44.44
43.70
40.47
40.15
25.18
24.50
24.24
22.71
1.75
1.40
TMSO
Me
Me
Me
Me
OTMS
O
O
O
O
19
f1 (ppm)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6.79
6.69
6.64
6.63
6.00
5.98
5.98
5.98
5.97
5.96
5.96
3.48
3.47
3.46
3.46
2.84
2.83
2.81
2.80
2.67
2.60
2.58 HDO
2.56
2.55
2.43
2.42
2.40
2.39
2.36
2.34
2.33
2.31
2.31
2.30
1.17
1.16
1.14
0.91
0.88
Et
OTMS
Me
Me
O
O
F3C
21
1.98
1.98
1.00
1.00
1.01
1.98
1.00
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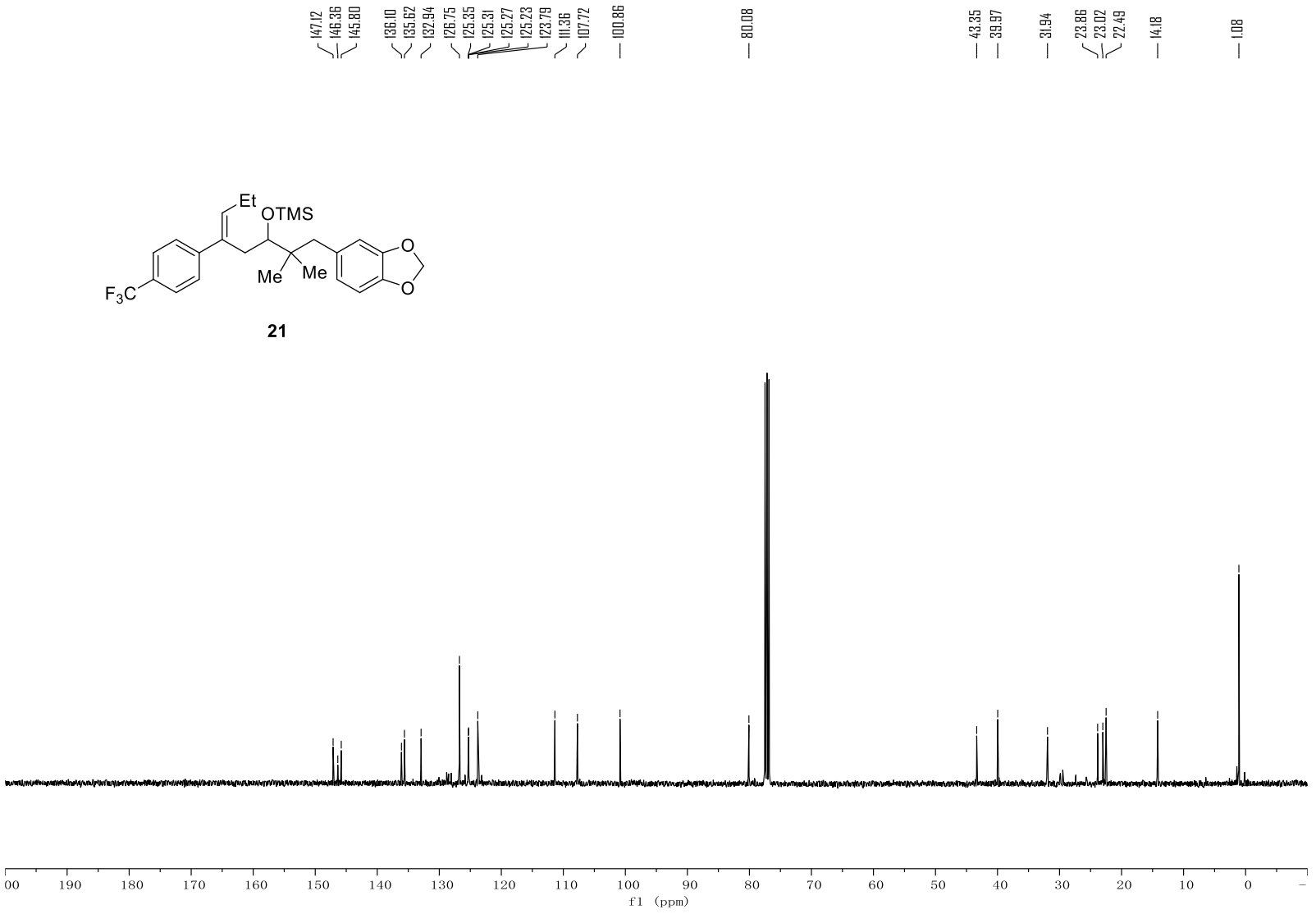
3.02
2.98
3.06
9.03
f1 (ppm)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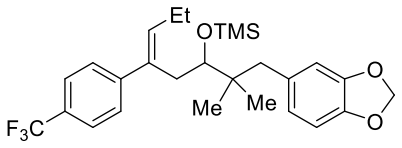
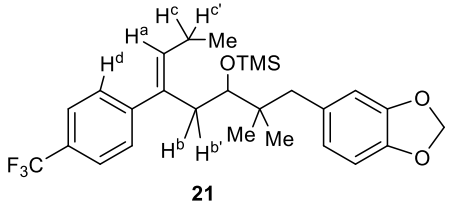
135.62
132.94
126.75
125.35
125.31
125.27
125.23
123.79
111.36
107.72
100.86
80.08
43.35
39.97
31.94
28.86
28.02
22.49
14.18
1.08
Et
OTMS
Me
Me
F3C
O
O
21
f1 (ppm)


Et
OTMS
Me
Me
O
O
F3C

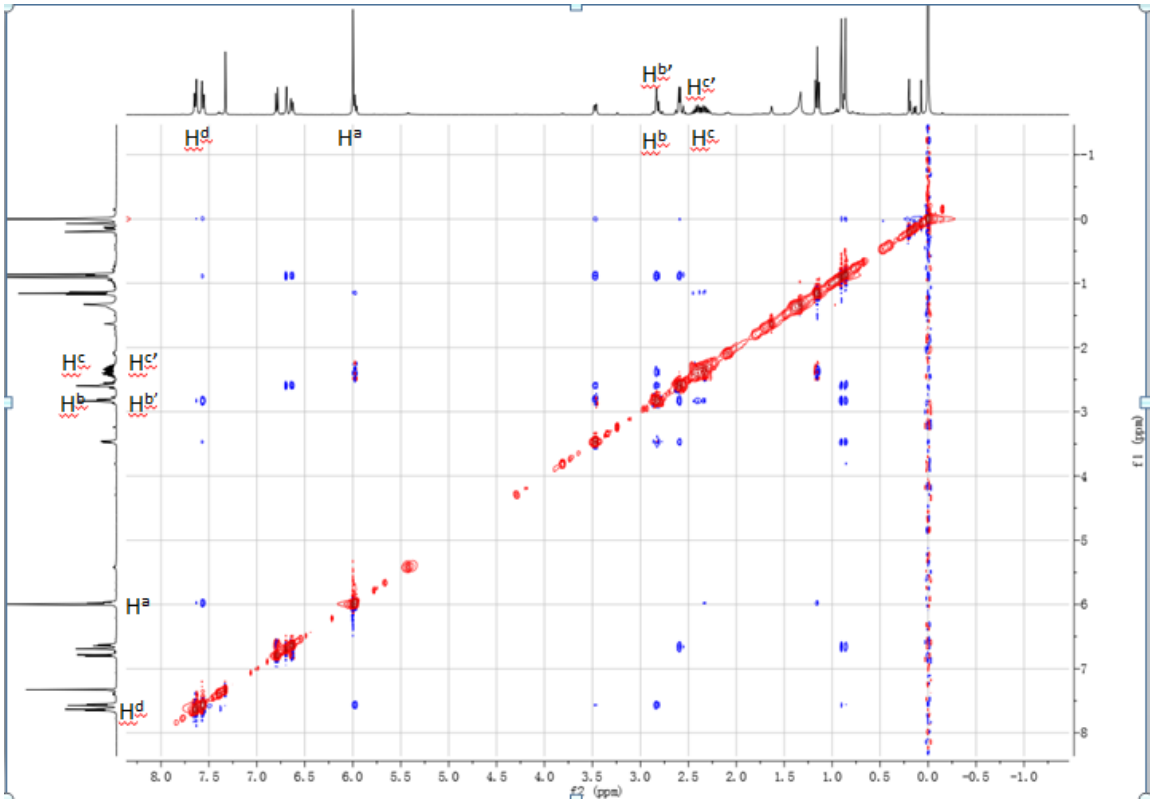
21

-62.29
3.00
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)

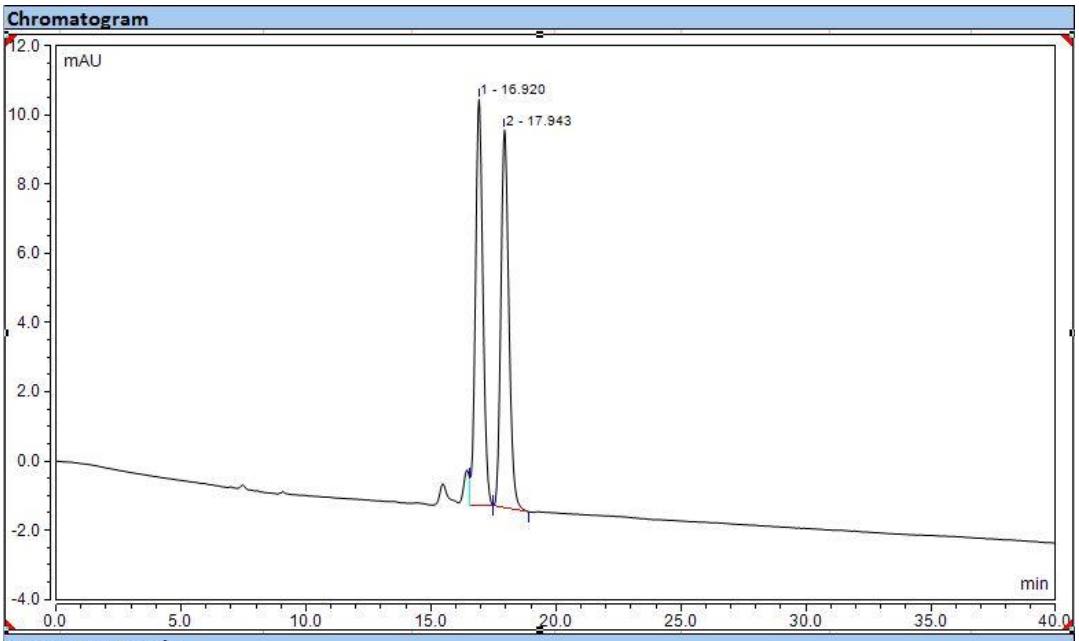
-62.29
3.00
-61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0
f1 (ppm)


Hc
Hc'
Ha
Me
Hd
OTMS
Hb
Hb'
Me
Me
O
O
F3C

21

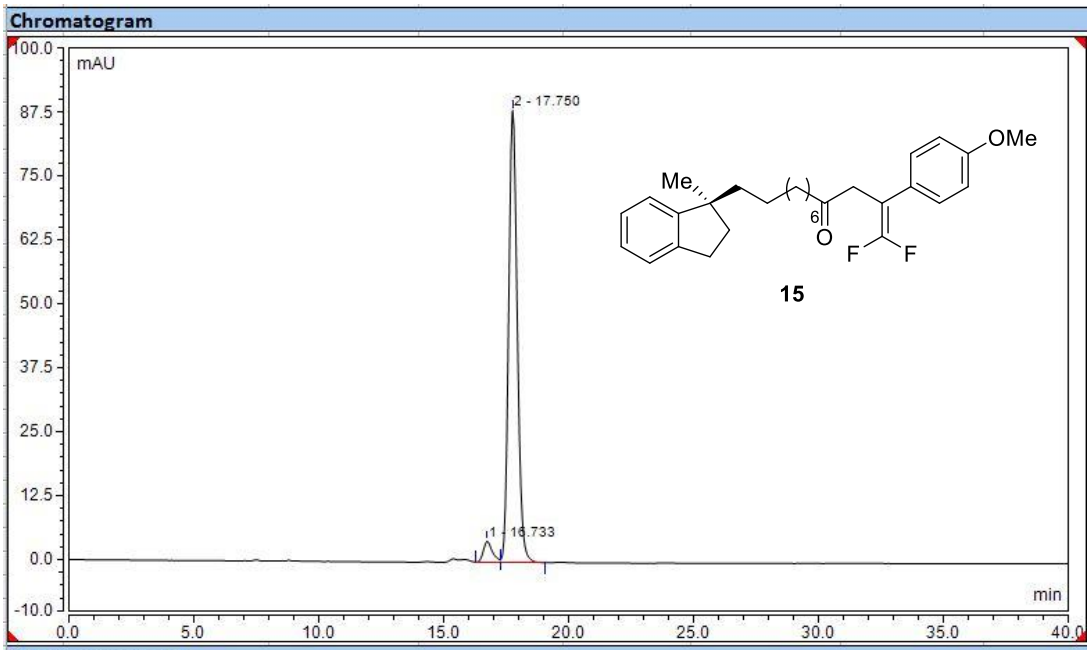

Hb'
Hc'
Hd
Ha
Hb
Hc
Hc
Hc'
Hb
Hb'
Ha
Hd
f2 (ppm)
f1 (ppm)

HPLC Chromatograms



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.920	4.048	11.750	50.10	51.84	n.a.
2		17.943	4.032	10.917	49.90	48.16	n.a.
Total:			**8.081**	**22.667**	**100.00**	**100.00**	



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Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.733	1.696	4.085	4.58	4.42	n.a.
2		17.750	35.378	88.374	95.42	95.58	n.a.
Total:			**37.074**	**92.459**	**100.00**	**100.00**	

HPLC (Chiralpak AD-H): t_R= 16.7 (minor), 17.8 (major)
Condition: 98:2 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25 ℃