Supporting Information

Chromium-Catalyzed Allylic Defluorinative Acylation of Trifluoromethyl-Substituted Alkenes with Acyl Oxime Esters

Hongzhang Shi, Haiyan Dong, and Chuan Wang*

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

E-mail: chuanw@ustc.edu.cn

Table of Contents

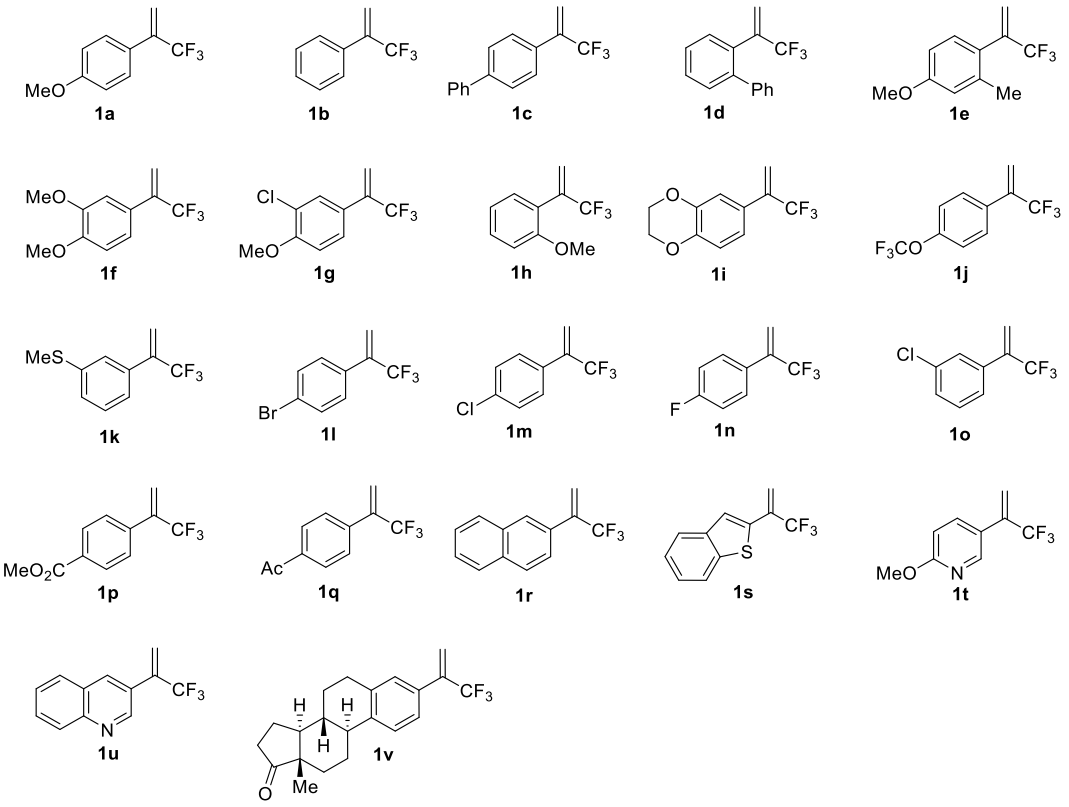
General Information

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 or 500M NMR spectrometers at ambient temperature in CDCl3 at 400 and 101 MHz or at 500 and 126 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); quin (quintet); 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. 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.

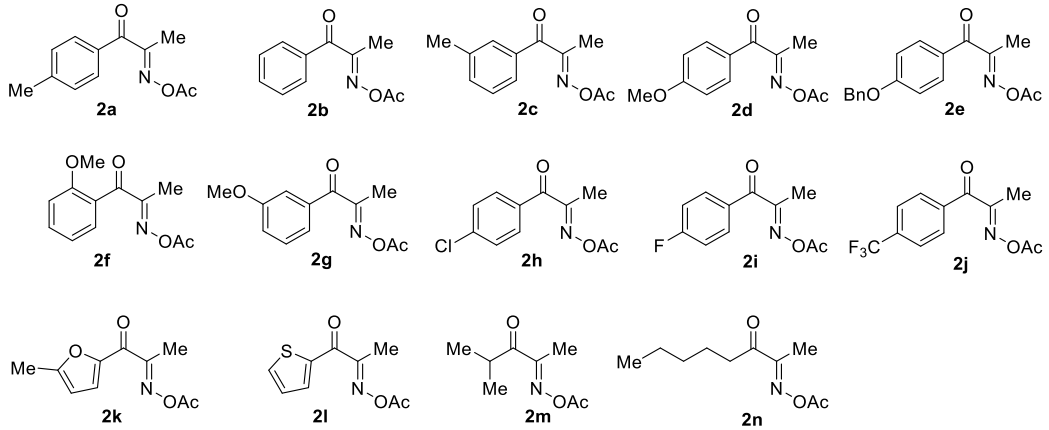
Preparation of Substrates

Synthesis of Trifluoromethyl-Substituted Alkenes



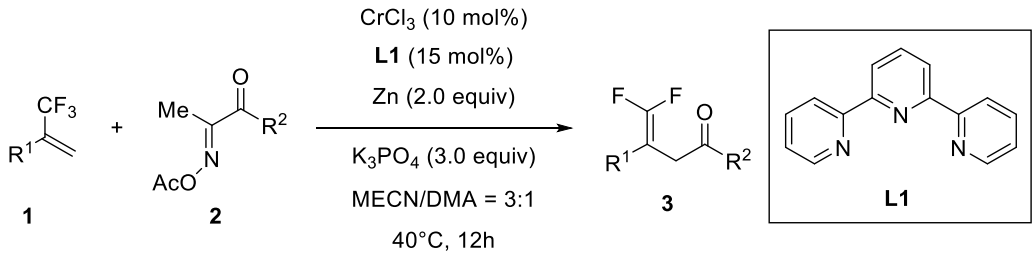
The trifluoromethyl-substituted alkenes **1a–e**,[1] **1f-j**,[2] **1k-u**,[1] and **1v**[2] are known compounds in the literature.

Synthesis of Oxime Esters



The Oxime Esters **1a–j**,[3] and **1k-n**[4] are known compounds in the literature.

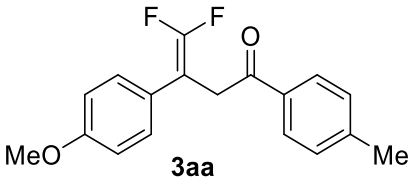
General Procedure for Chromium-Catalyzed Allylic Defluorinative Acylation of Trifluoromethyl-Substituted Alkenes with Acyl Oxime Esters



$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol%), 2,2':6',2''-terpyridine (**L1**) (7.0 mg, 0.03 mmol, 15 mol %), Zn (26.0 mg, 0.4 mmol, 2.0 equiv), K_3PO_4 (127.0 mg, 0.6 mmol, 3.0 qeuiv), and the oxime esters **2** (0.4 mmol, 2.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkenes **1** (0.2 mmol, 1.0 equiv) were added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to give the *gem*-difluoroalkenes **3** as the products.

Characterization Data of *gem*-Difluoroalkenes 3

4,4-Difluoro-3-(4-methoxyphenyl)-1-(*p*-tolyl)but-3-en-1-one (3aa)



3aa

The title compound **3aa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (48.3 mg, 80%).

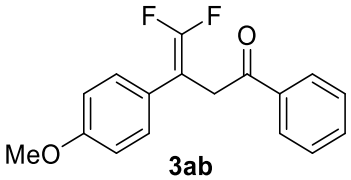
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.87 (d, *J* = 8.1 Hz, 2H), 7.29–7.22 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.01 (s, 2H), 3.78 (s, 3H), 2.42 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 195.3 (t, *J* = 2.9 Hz), 158.9, 154.6 (dd, *J* = 291.1, 287.5 Hz), 144.4, 134.0, 129.5(2C), 129.3 (t, *J* = 3.5 Hz, 2C), 128.4 (2C), 125.8 (t, *J* = 3.9 Hz), 114.0 (2C), 86.9 (dd, *J* = 21.9, 17.6 Hz), 55.3, 38.4 (d, *J* = 2.3 Hz), 21.8 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.39 (d, *J* = 40.1 Hz, 1F), −90.20 (d, *J* = 40.0 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}F_2O_2Na$ $[M+Na]^+$: 325.1011, found: 325.1011.

4,4-Difluoro-3-(4-methoxyphenyl)-1-phenylbut-3-en-1-one (3ab)



3ab

The title compound **3ab** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (32.8mg, 57%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.97 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.03 (s, 2H), 3.78 (s, 3H) ppm.

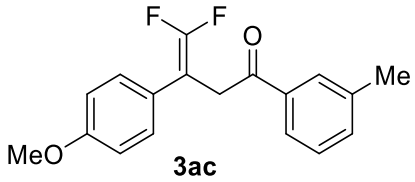
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 195.7 (t, *J* = 3.0 Hz), 158.9, 154.7 (dd, *J* =

291.0, 287.4 Hz), 136.4, 133.6, 129.3 (t, *J* = 3.5 Hz, 2C), 128.8 (2C), 128.3 (2C), 125.7 (t, *J* = 3.9 Hz), 114.1 (2C), 86.8 (dd, *J* = 21.9, 17.8 Hz), 55.4, 38.6 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.29 (d, *J* = 39.6 Hz, 1F), −90.11 (d, *J* = 39.6 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{15}F_2O_2$ $[M+H]^+$: 289.1035, found: 289.1039.

4,4-Difluoro-3-(4-methoxyphenyl)-1-(*m*-tolyl)but-3-en-1-one (3ac)



3ac

The title compound **3ac** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (45.3 mg, 75%).

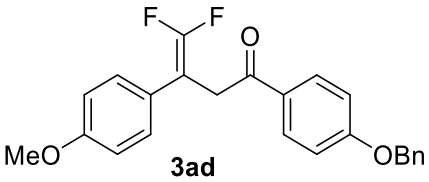
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79–7.74 (m, 2H), 7.42–7.33 (m, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.02 (s, 2H), 3.78 (s, 3H), 2.40 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 195.8 (t, *J* =2.8 Hz), 158.8, 154.6 (dd, *J* = 291.2, 287.4 Hz), 138.6, 136.4, 134.2, 129.2 (t, *J* = 3.5 Hz, 2C), 128.7, 128.6, 125.7 (t, *J* = 3.9 Hz), 125.4, 113.9 (2C), 86.8 (dd, *J* = 22.0, 17.6 Hz), 55.2, 38.5 (d, *J* = 2.5 Hz), 21.4 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.34 (d, *J* = 39.7 Hz, 1F), −90.12 (d, *J* = 39.6 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}F_2O_2Na$ $[M+Na]^+$: 325.1011, found: 325.1017.

1-(4-(Benzyloxy)phenyl)-4,4-difluoro-3-(4-methoxyphenyl)but-3-en-1-one (3ad)



3ad

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

petroleum ether/ethyl acetate 10:1) as a colorless oil (64.6 mg, 82%).

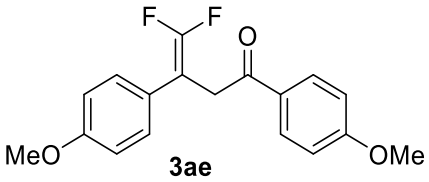
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.8 Hz, 2H), 7.47–7.32 (m, 5H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 2H), 3.98 (s, 2H), 3.78 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.2 (t, *J* = 2.8 Hz), 162.9, 158.8, 154.6 (dd, *J* = 291.0, 287.3 Hz), 136.2, 130.6 (2C), 129.7, 129.3 (t, *J* = 3.5 Hz, 2C), 128.8 (2C), 128.4, 127.6 (2C), 125.8 (t, *J* = 3.9 Hz), 114.8 (2C), 114.0 (2C), 87.0 (dd, *J* = 21.9, 17.5 Hz), 70.3, 55.3, 38.2 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −89.42 (d, *J* = 40.0 Hz, 1F), −90.22 (d, *J* = 39.9 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{21}F_2O_3$ $[M+H]^+$: 395.1453, found: 395.1465.

4,4-Difluoro-1,3-bis(4-methoxyphenyl)but-3-en-1-one (3ae)



3ae

The title compound **3ae** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (60.4 mg, 95%).

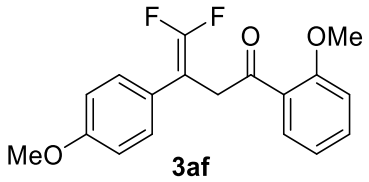
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.9 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.98 (s, 2H), 3.87 (s, 3H), 3.78 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 194.2 (t, *J* = 2.8 Hz), 163.8, 158.8, 154.6 (dd, *J* = 290.9, 287.3 Hz), 130.6 (2C), 129.5, 129.3 (t, *J* = 3.5 Hz, 2C), 125.8 (t, *J* = 3.9 Hz), 114.03 (2C), 113.96 (2C), 87.1 (dd, *J*= 21.9, 17.5 Hz), 55.6, 55.3, 38.2 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.48 (d, *J* = 40.0 Hz, 1F), −90.28 (d, *J* = 40.1 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}F_2O_3Na$ $[M+Na]^+$: 341.0960, found: 341.0968.

4,4-Difluoro-1-(2-methoxyphenyl)-3-(4-methoxyphenyl)but-3-en-1-one (3af)



3af

The title compound **3af** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (41.4 mg, 65%).

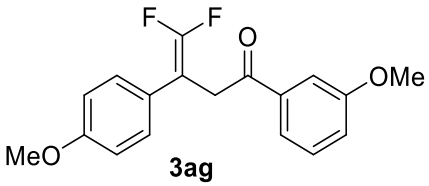
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.01–6.95 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.05 (s, 2H), 3.90 (s, 3H), 3.78 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.0 (t, *J* = 2.9 Hz), 158.7 (2C), 154.7 (dd, *J* = 290.9, 287.2 Hz), 133.9, 130.7, 129.2 (t, *J* = 3.5 Hz, 2C), 127.7, 126.1 (t, *J* = 4.0 Hz), 120.9, 113.9 (2C), 111.5, 87.3 (dd, *J* = 22.2, 16.7 Hz), 55.6, 55.3, 43.4 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.65 (d, *J* = 39.9 Hz, 1F), −90.72 (d, *J* = 40.2 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}F_2O_3Na$ $[M+Na]^+$: 341.0960, found: 341.0962.

4,4-Difluoro-1-(3-methoxyphenyl)-3-(4-methoxyphenyl)but-3-en-1-one (3ag)



3ag

The title compound **3ag** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (38.8 mg, 61%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.33 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 6.7 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 2H), 3.62 (s, 3H), 3.56 (s, 3H) ppm.

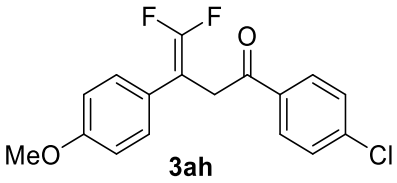
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 195.5 (t, *J* = 2.9 Hz), 160.0, 158.9, 154.7 (dd,

J = 291.1, 287.5 Hz), 137.8, 129.8, 129.3 (t, *J* = 3.5 Hz, 2C), 125.7 (t, *J* = 3.9 Hz), 120.8, 120.1, 114.1 (2C), 112.5, 86.9 (dd, *J* = 21.7, 17.9 Hz), 55.6, 55.4, 38.7 (d, *J* = 2.5 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.30 (d, *J* = 39.9 Hz, 1F), −90.13 (d, *J* = 40.0 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{17}F_2O_3$ $[M+H]^+$: 319.1140, found: 319.1167.

1-(4-Chlorophenyl)-4,4-difluoro-3-(4-methoxyphenyl)but-3-en-1-one (3ah)



3ah

The title compound **3ah** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (34.8 mg, 54%).

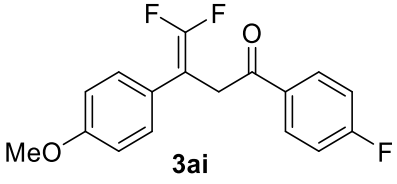
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.89 (d, *J* = 11.0 Hz, 2H), 7.44 (d, *J* = 10.8 Hz, 2H), 7.21 (d, *J* = 9.7 Hz, 2H), 6.85 (d, *J* = 11.0 Hz, 2H), 3.99 (s, 2H), 3.78 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.6 (t, *J* = 2.8 Hz), 159.0, 154.6 (dd, *J* = 291.1, 288.7 Hz), 140.1, 134.7, 129.7 (2C), 129.3 (t, *J* = 3.4 Hz, 2C), 129.2 (2C), 125.4 (t, *J* = 3.8 Hz), 114.1 (2C), 86.7 (dd, *J* = 21.8, 18.1 Hz), 55.4, 38.6 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.09 (d, *J* = 39.5 Hz, 1F), −89.89 (d, *J* = 39.7 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}{}^{35}ClF_2O_2$ $[M+H]^+$: 323.0645, found: 323.0617.

4,4-Difluoro-1-(4-fluorophenyl)-3-(4-methoxyphenyl)but-3-en-1-one (3ai)



3ai

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

petroleum ether/ethyl acetate 10:1) as a colorless oil (23.3 mg, 38%).

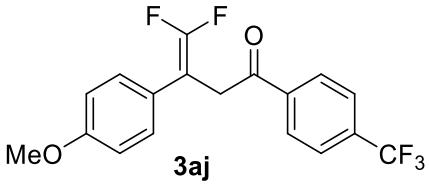
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.00 (s, 2H), 3.78 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.2 (t, *J* = 2.8 Hz), 166.0 (d, *J* = 255.3 Hz), 159.0, 154.6 (dd, *J* = 291.7, 287.6 Hz), 132.8 (d, *J* = 3.1 Hz), 131.0 (d, *J* = 9.3 Hz, 2C), 129.3 (t, *J* = 3.5 Hz, 2C), 125.5 (t, *J* = 3.8 Hz), 116.0 (d, *J* = 22.0 Hz, 2C), 114.1 (2C), 86.8 (dd, *J* = 21.7, 17.9 Hz), 55.4, 38.6 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.20 (d, *J* = 39.4 Hz, 1F), −90.00 (d, *J* = 39.4 Hz, 1F), -104.52(s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{15}F_3O_2$ $[M+H]^+$: 307.0940, found: 307.0951.

4,4-Difluoro-3-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-one (3aj)



3aj

The title compound **3aj** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (20.0 mg, 28%).

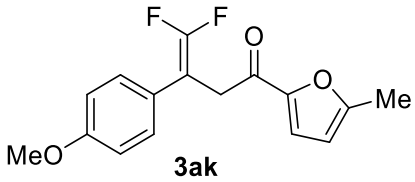
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.05 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.05 (s, 2H), 3.79 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.9 (t, *J* = 2.9 Hz), 159.1, 154.7 (dd, *J* = 291.7, 287.8 Hz), 139.0, 134.8 (q, *J* = 32.8 Hz), 129.3 (t, *J* = 3.4 Hz, 2C), 128.6 (2C), 125.9 (q, *J* = 3.7 Hz, 2C), 125.3 (t, *J* = 3.9 Hz), 123.6 (q, *J* = 272.6 Hz), 114.2 (2C), 86.6 (dd, *J* = 21.8, 18.2 Hz), 55.4, 39.0 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −63.15(s, 3F), −88.87 (d, *J* = 38.5 Hz, 1F), −89.68 (d, *J* = 38.5 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{13}F_5O_2Na$ $[M+Na]^+$: 379.0728, found: 379.0757.

4,4-Difluoro-3-(4-methoxyphenyl)-1-(5-methylfuran-2-yl)but-3-en-1-one (3ak)



3ak

The title compound **3ak** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (44.4 mg, 76%).

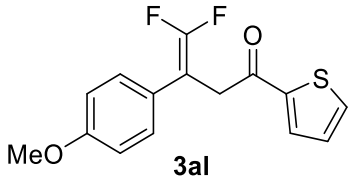
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.25 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.16 (d, *J* = 3.4 Hz, 1H) 3.83 (s, 2H), 3.78 (s, 3H), 2.39 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 184.2 (t, *J* = 3.0 Hz), 158.9, 158.1, 154.8 (dd, *J* = 291.2, 288.0 Hz), 151.1, 129.4 (t, *J* = 3.4 Hz, 2C), 125.6 (t, *J* = 3.8 Hz), 119.6, 114.0 (2C), 109.3, 86.7 (dd, *J* = 21.7, 18.0 Hz), 55.4, 38.0 (d, *J* = 2.3 Hz), 14.2 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.31 (d, *J* = 39.0 Hz, 1F), −89.86 (d, *J* = 39.0 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{14}F_2O_3Na$ $[M+Na]^+$: 315.0803, found: 315.0809.

4,4-Difluoro-3-(4-methoxyphenyl)-1-(thiophen-2-yl)but-3-en-1-one (3al)



3al

The title compound **3al** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (38.8 mg, 44%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.76 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 4.9 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.14 (t, *J* = 4.4 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H) ppm.

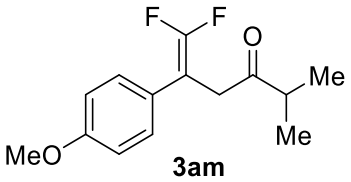
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 188.6 (t, *J* = 3.0 Hz), 159.0, 154.8 (dd, *J* = 291.4, 287.9 Hz), 143.4, 134.2, 132.3, 129.4 (t, *J* = 3.5 Hz, 2C), 128.3, 125.5 (t, *J* = 3.8

Hz), 114.1 (2C), 86.8 (dd, *J* = 21.6, 18.2 Hz), 55.4, 39.2 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −88.97 (d, *J* = 38.7 Hz, 1F), −89.79 (d, *J* = 38.4 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{15}H_{12}F_2O_2SNa$ $[M+Na]^+$: 317.0418, found: 317.0421.

6,6-Difluoro-5-(4-methoxyphenyl)-2-methylhex-5-en-3-one (3am)



3am

The title compound **3am** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (31.0 mg, 61%).

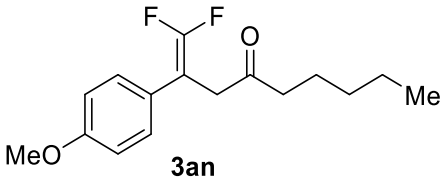
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.20 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.48 (s, 2H), 2.73 – 2.62 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 6H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 210.5 (t, *J* = 2.8 Hz), 158.9, 154.7 (dd, *J* = 291.5, 287.3 Hz), 129.2 (t, *J* = 3.5 Hz, 2C), 125.7 (t, *J* = 3.9 Hz), 114.1 (2C), 86.8 (dd, *J* = 22.1, 17.1 Hz), 55.4, 40.3, 40.2 (d, *J* = 2.2 Hz), 18.3 (2C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.64 (d, *J* = 39.9 Hz, 1F), −90.53 (d, *J* = 40.0 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{16}F_2O_2Na$ $[M+Na]^+$: 277.1011, found: 277.1009.

1,1-Difluoro-2-(4-methoxyphenyl)non-1-en-4-one (3an)



3an

The title compound **3an** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (52.5 mg, 93%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.22 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.8 Hz,

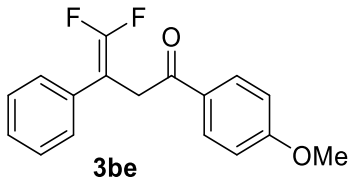
2H), 3.80 (s, 3H), 3.41 (s, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.59–1.49 (m, 2H), 1.32–1.17 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 207.3 (t, *J* = 2.8 Hz), 158.9, 154.6 (dd, *J* = 291.9, 287.4 Hz), 129.1 (t, *J* = 3.5 Hz, 2C), 125.4 (t, *J* = 3.9 Hz), 114.1 (2C), 86.9 (dd, *J* = 22.1, 16.7 Hz), 55.4, 42.4 (d, *J* = 1.9 Hz), 42.1, 31.4, 23.4, 22.5, 14.0 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −89.25 (d, *J* = 39.4 Hz, 1F), −90.26 (d, *J* = 39.4 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{20}F_2O_2Na$ $[M+Na]^+$: 305.1324, found: 305.1318.

4,4-Difluoro-1-(4-methoxyphenyl)-3-phenylbut-3-en-1-one (3be)



3be

The title compound **3be** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (48.4 mg, 84%).

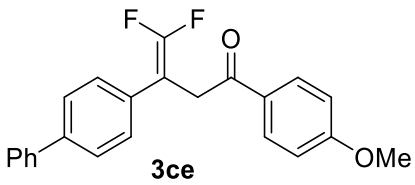
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.9 Hz, 2H), 7.35–7.30 (m, 4H), 7.28–7.22 (m, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.02 (s, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.0 (t, *J* = 2.8 Hz), 163.8, 154.8 (dd, *J* = 292.3, 288.0 Hz), 133.7 (t, *J* = 4.0 Hz), 130.6 (2C), 129.4, 128.6 (2C), 128.1 (t, *J* = 3.4 Hz, 2C), 127.5, 114.0 (2C), 87.5 (dd, *J* = 21.8, 17.1 Hz), 55.6, 38.1 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −88.27 (d, *J* = 37.5 Hz, 1F), −89.28 (d, *J* = 37.3 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}F_2O_2Na$ $[M+Na]^+$: 311.0854, found: 311.0854.

3-([1,1'-Biphenyl]-4-yl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3ce)



3ce

The title compound **3ce** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (59.7 mg, 82%).

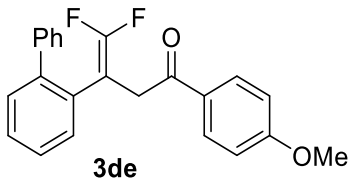
1H NMR (500 MHz, Chloroform-d) δ = 7.99 (d, *J* = 8.9 Hz, 2H), 7.62–7.53 (m, 4H), 7.47–7.39 (m, 4H), 7.37–7.33 (m, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.07 (s, 2H), 3.88 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.0 (t, *J* = 2.7 Hz), 163.9, 154.9 (dd, *J* = 292.8, 288.1 Hz), 140.6, 140.2, 132.6 (t, *J* = 4.1 Hz), 130.6 (2C), 129.4, 128.9 (2C), 128.4 (t, *J* = 3.6 Hz, 2C), 127.5, 127.3 (2C), 127.1 (2C), 114.0 (2C), 87.3 (dd, *J* = 22.0, 16.9 Hz), 55.6, 37.9 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −87.68 (d, *J* = 36.7 Hz, 1F), −88.64 (d, *J* = 36.6 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{18}F_2O_2Na$ $[M+Na]^+$: 387.1167, found: 387.1165.

3-([1,1'-Biphenyl]-2-yl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3de)



3de

The title compound **3de** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (59.9 mg, 82%).

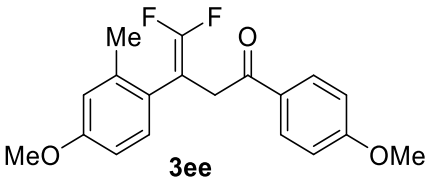
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.68 (d, *J* = 8.9 Hz, 2H), 7.53–7.29 (m, 9H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.39 (s, 2H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.9 (t, *J* = 2.8 Hz), 163.5, 154.7 (dd, *J* = 289.4, 287.2 Hz), 141.2 (d, *J* = 3.1 Hz), 141.1, 131.7 (dd, *J* = 4.5, 2.2 Hz), 131.6 (t, *J* = 2.3 Hz, 2C), 130.4 (2C), 130.2, 129.4, 128.9, 128.4 (2C), 128.3, 127.5, 127.4, 113.7 (2C), 87.6 (dd, *J* = 22.3, 21.1 Hz), 55.5, 37.8 (d, *J* = 2.1 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −89.02 (d, *J* = 38.6 Hz, 1F), −90.78 (d, *J* = 38.9 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{18}F_2O_2Na$ $[M+Na]^+$: 387.1167, found: 387.1172.

4,4-Difluoro-3-(4-methoxy-2-methylphenyl)-1-(4-methoxyphenyl)but-3-en-1-one (3ee)



3ee

The title compound **3ee** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (57.1 mg, 86%).

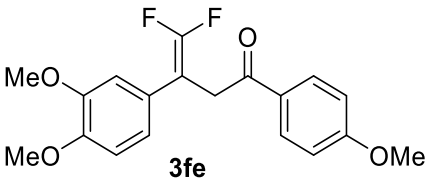
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.89 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.73 (d, *J* = 2.7 Hz, 1H), 6.71–6.67 (m, 1H), 3.89 (s, 2H), 3.86 (s, 3H), 3.76 (s, 3H), 2.30 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.2 (t, *J* = 2.8 Hz), 163.7, 159.2, 153.9 (dd, *J* = 289.8, 286.6 Hz), 138.6, 130.9, 130.6 (2C), 129.5, 125.1 (dd, *J* = 4.7, 2.1 Hz), 115.7, 113.9 (2C), 111.4, 85.7 (dd, *J* = 22.1, 21.6 Hz), 55.6, 55.2, 39.2, 19.9 (d, *J* = 2.2 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −88.14 (d, *J* = 39.1 Hz, 1F), −91.26 (d, *J* = 39.1 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{19}F_2O_3$ $[M+H]^+$: 333.1297, found: 333.1302.

3-(3,4-Dimethoxyphenyl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3fe)



3fe

The title compound **3fe** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (66.1 mg, 95%).

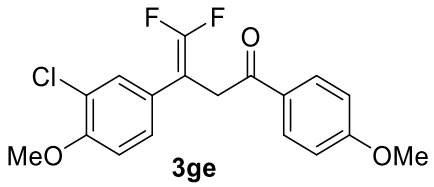
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.87 (s, 1H), 6.84–6.78 (m, 2H), 3.98 (s, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 194.3 (t, *J* = 2.6 Hz), 163.8, 154.7 (dd, *J* = 290.9, 287.6 Hz), 148.8, 148.4, 130.6 (2C), 129.5, 126.1 (t, *J* = 3.8 Hz), 120.5 (t, *J* = 3.3 Hz), 114.0 (2C), 111.5 (t, *J* = 3.4 Hz), 111.1, 87.4 (dd, *J* = 21.9, 17.4 Hz), 55.95, 55.92, 55.6, 38.2 (d, *J* = 2.2 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.20 (d, *J* = 39.5 Hz, 1F), −89.68 (d, *J* = 39.7 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{18}F_2O_4Na$ $[M+Na]^+$: 371.1065, found: 371.1064

3-(3-Chloro-4-methoxyphenyl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3ge)



3ge

The title compound **3ge** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (65.5 mg, 93%).

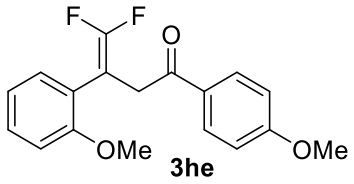
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.7 Hz, 2H), 7.33 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.9 (t, *J* = 2.8 Hz), 163.9, 154.7 (dd, *J* = 291.8, 288.1 Hz), 154.2, 130.6 (2C), 129.8 (t, *J* = 3.7 Hz), 129.3, 127.7 (t, *J* = 3.5 Hz), 126.8 (t, *J* = 4.0 Hz), 122.4, 114.0 (2C), 111.9, 86.4 (dd, *J* = 22.7, 17.2 Hz), 56.2, 55.6, 37.9 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −88.40 (d, *J* = 37.8 Hz, 1F), −89.12 (d, *J* = 37.8 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}{}^{35}ClF_2O_3$ $[M+H]^+$: 353.0751, found: 353.0751.

4,4-Difluoro-3-(2-methoxyphenyl)-1-(4-methoxyphenyl)but-3-en-1-one (3he)



3he

The title compound **3he** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (48.4 mg, 76%).

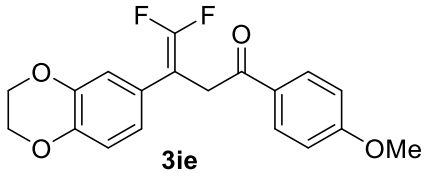
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.92 (d, *J* = 8.9 Hz, 2H), 7.32–7.23 (m, 2H), 6.97–6.89 (m, 3H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.96 (s, 2H), 3.86 (s, 3H), 3.74 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 194.5 (t, *J* = 2.8 Hz), 163.6, 157.2 (d, *J* = 2.9 Hz), 154.5 (t, *J* = 288.3 Hz), 131.7, 130.5 (2C), 129.8, 129.4, 122.1 (dd, *J* = 4.8, 2.3 Hz), 120.7, 113.8 (2C), 110.9, 85.1 (dd, *J* = 23.5, 20.2 Hz), 55.6, 55.4, 37.6 (d, *J* = 2.0 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −89.27 (d, *J* = 38.1 Hz, 1F), −90.86 (d, *J* = 38.3 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}F_2O_3Na$ $[M+Na]^+$: 341.0960, found: 341.0963.

3-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3ie)



3ie

The title compound **3ie** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (64.4 mg, 93%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 6.80 (s, 2H), 4.22 (s, 4H), 3.96 (s, 2H), 3.87 (s, 3H) ppm.

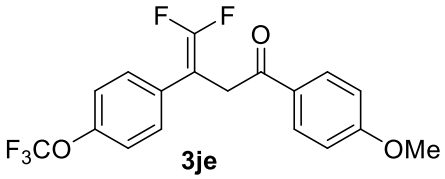
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.0 (t, *J* = 2.5 Hz), 162.8, 153.7 (dd, *J* =

291.7, 287.4 Hz), 142.4, 141.9, 129.6 (2C), 128.4, 125.7 (t, *J* = 3.9 Hz), 120.2 (t, *J* = 3.6 Hz), 116.3, 116.0 (t, *J* = 3.6 Hz), 112.9 (2C), 85.9 (dd, *J* = 22.1, 17.0 Hz), 63.45, 63.36, 54.6, 37.0 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −88.93 (d, *J* = 39.1 Hz, 1F), −89.52 (d, *J* = 39.3 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{16}F_2O_4Na$ $[M+Na]^+$: 369.0909, found: 369.0915.

4,4-Difluoro-1-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)but-3-en-1-one (3je)



3je

The title compound **3he** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (50.6 mg, 68%).

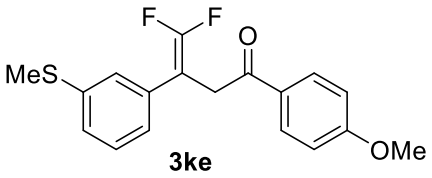
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 1.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.01 (s, 2H), 3.88 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.7 (t, *J* = 2.8 Hz), 164.0, 154.9 (dd, *J* = 292.5, 288.5 Hz), 148.4, 132.4 (t, *J* = 4.1 Hz), 130.6 (2C), 129.6 (t, *J* = 3.6 Hz, 2C), 129.3, 121.1 (2C), 120.5 (q, *J* = 257.4 Hz), 114.0 (2C), 86.7 (dd, *J* = 22.9, 17.0 Hz), 55.6, 37.9 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −57.84 (s, 3F), -87.53 (d, *J* = 35.6 Hz), −88.51 (d, *J* = 35.8 Hz) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{14}F_5O_3$ $[M+H]^+$: 373.0858, found: 373.0873.

4,4-Difluoro-1-(4-methoxyphenyl)-3-(3-(methylthio)phenyl)but-3-en-1-one (3ke)



3ke

The title compound **3ke** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (33.4 mg, 50%).

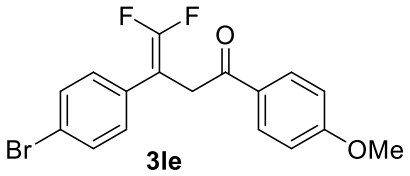
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.98 (d, *J* = 8.9 Hz, 2H), 7.29 (s, 1H), 7.25–7.23(m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.02 (s, 2H), 3.90 (s, 3H), 2.46 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 193.7 (t, *J* = 2.5 Hz), 163.8, 154.8 (dd, *J* = 292.6, 288.3 Hz), 138.8, 134.3 (t, *J* = 4.1 Hz), 130.5 (2C), 129.3, 128.9, 126.1 (t, *J* = 3.6 Hz), 125.6, 124.8 (t, *J* = 3.4 Hz), 113.9 (2C), 87.2 (dd, *J* = 22.1, 17.2 Hz), 55.5, 37.9 (d, *J* = 2.3 Hz), 15.8 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −87.77 (d, *J* = 36.0 Hz, 1F), −88.48 (d, *J* = 36.2 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{16}F_2O_2{}^{32}SNa$ $[M+Na]^+$: 357.0731, found: 357.0730.

3-(4-Bromophenyl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3le)



3le

The title compound **3le** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (70.3 mg, 96%).

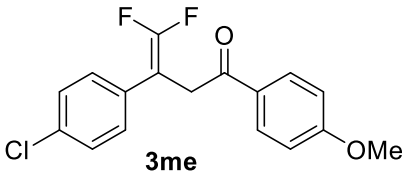
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.99 (s, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.7 (t, *J* = 2.8 Hz), 163.9, 154.6 (dd, *J* = 292.8, 288.6 Hz), 132.6 (t, *J* = 4.1 Hz), 131.7 (2C), 130.5 (2C), 129.7 (t, *J* = 3.5 Hz, 2C), 129.2, 121.4, 113.9 (2C), 86.8 (dd, *J* = 22.5, 17.0 Hz), 55.6, 37.7 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −87.44 (d, *J* = 35.5 Hz, 1F), −88.33 (d, *J* = 35.4 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{13}{}^{79}BrF_2O_2Na$ $[M+Na]^+$: 388.9969, found: 388.9962.

3-(4-Chlorophenyl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3me)



3me

The title compound **3me** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (61.8 mg, 96%).

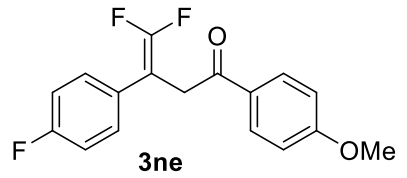
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.93 (d, *J* = 8.9 Hz, 2H), 7.31–7.20 (m, 4H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.98 (s, 2H), 3.86 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.8 (t, *J* = 2.8 Hz), 164.0, 154.8 (dd, *J* = 292.7, 288.5 Hz), 133.3, 132.2 (t, *J* = 4.1 Hz), 130.6 (2C), 129.5 (t, *J* = 3.6 Hz, 2C), 129.3, 128.8 (2C), 114.0 (2C), 86.9 (dd, *J* = 22.6, 17.0 Hz), 55.6, 37.9 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −87.59 (d, *J* = 36.1 Hz, 1F), −88.48 (d, *J* = 35.5 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{13}ClF_2O_2Na$ $[M+Na]^+$: 345.0464, found: 345.0461.

4,4-Difluoro-3-(4-fluorophenyl)-1-(4-methoxyphenyl)but-3-en-1-one (3ne)



3ne

The title compound **3ne** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (56.9 mg, 93%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 9.0 Hz, 2H), 7.29 (dd, *J* = 8.0,

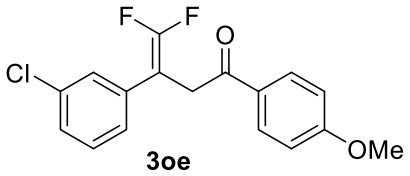
5.5 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.99 (s, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.9 (t, *J* = 2.8 Hz), 163.9, 162.0 (d, *J* = 247.1 Hz), 154.8 (dd, *J* = 292.6, 289.5 Hz), 130.6 (2C), 129.9 (dt, *J* = 7.4, 3.5 Hz, 2C), 129.6 (q, *J* = 3.6 Hz), 129.3, 115.6 (d, *J* = 21.6 Hz, 2C), 114.0 (2C), 86.8 (dd, *J* = 22.5, 17.5 Hz), 55.6, 38.1 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −88.58 (d, *J* = 38.0 Hz, 1F), −89.46 (d, *J* = 38.0 Hz, 1F), −114.41 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{13}F_3O_2Na$ $[M+Na]^+$: 329.0760, found: 329.0771.

3-(3-Chlorophenyl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3oe)



3oe

The title compound **3oe** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (52.7 mg, 81%).

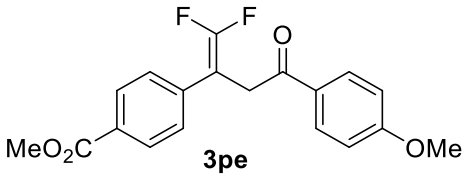
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.90 (d, *J* = 8.7 Hz, 2H), 7.23–7.12 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.94 (s, 2H), 3.82 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.5 (t, *J* = 2.7 Hz), 163.9, 154.9 (dd, *J* = 293.3, 288.8 Hz), 135.5 (t, *J* = 4.2 Hz), 134.3, 130.5 (2C), 129.7, 129.1, 128.1 (t, *J* = 3.7 Hz), 127.6, 126.2 (t, *J* = 3.6 Hz), 113.9 (2C), 86.7 (dd, *J* = 22.8, 16.8 Hz), 55.6, 37.7 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −87.00 (d, *J* = 34.5 Hz, 1F), −87.86 (d, *J* = 34.7 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{13}{}^{35}ClF_2O_2Na$ $[M+Na]^+$: 345.0464, found: 345.0486.

Methyl 4-(1,1-difluoro-4-(4-methoxyphenyl)-4-oxobut-1-en-2-yl)benzoate (3pe)



3pe

The title compound **3pe** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (51.0 mg, 74%).

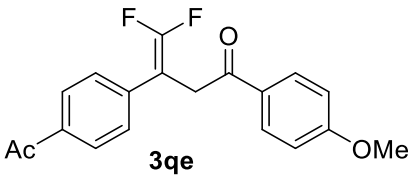
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.01–7.93 (m, 4H), 7.39 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.04 (s, 2H), 3.89 (s, 3H), 3.87 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.6 (t, *J* = 2.7 Hz), 166.8, 164.0, 155.1 (dd, *J* = 294.6, 289.4 Hz), 138.5 (t, *J* = 4.4 Hz), 130.6 (2C), 129.8 (2C), 129.2, 129.0, 128.0 (t, *J* = 3.7 Hz, 2C), 114.0 (2C), 87.3 (dd, *J* = 22.5, 16.4 Hz), 55.7, 52.3, 37.6 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −85.91 (d, *J* = 32.1 Hz, 1F), −86.96 (d, *J* = 32.1 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{17}F_2O_4$ $[M+H]^+$: 347.1089, found: 347.1080.

3-(3-Acetylphenyl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3qe)



3qe

The title compound **3qe** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (37.7 mg, 57%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.06 (s, 3H), 3.88 (s, 2H), 2.57 (s, 3H) ppm.

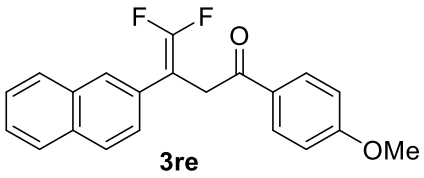
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 197.6, 193.6 (t, *J* = 2.8 Hz), 164.0, 155.1 (dd, *J* = 294.7, 289.4 Hz), 138.7 (t, *J* = 4.4 Hz), 135.9, 130.6 (2C), 129.2, 128.6 (2C), 128.2

(t, *J* = 3.5 Hz, 2C), 114.1 (2C), 87.3 (dd, *J* = 22.5, 16.1 Hz), 55.7, 37.6 (d, *J* = 2.3 Hz), 26.7 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −85.73 (d, *J* = 31.8 Hz, 1F), −86.77 (d, *J* = 32.0 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{17}F_2O_3$ $[M+H]^+$: 331.1140, found: 331.1150.

4,4-Difluoro-1-(4-methoxyphenyl)-3-(naphthalen-2-yl)but-3-en-1-one (3re)



3re

The title compound **3re** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (54.8 mg, 84%).

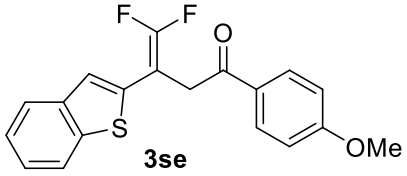
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.98 (d, *J* = 8.8 Hz, 2H), 7.85–7.69 (m, 4H), 7.55–7.37 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.12 (s, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.9 (t, *J* = 2.7 Hz), 163.8, 154.9 (dd, *J* = 292.6, 288.3 Hz), 133.2, 132.5, 131.1 (t, *J* = 4.0 Hz), 130.5 (2C), 129.4, 128.2, 128.0, 127.6, 127.1 (t, *J* = 3.6 Hz), 126.3, 126.2, 125.9 (t, *J* = 3.5 Hz), 113.9 (2C), 87.6 (dd, *J* = 22.1, 17.0 Hz), 55.5, 38.1 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −87.73 (d, *J* = 36.5 Hz, 1F), −88.93 (d, *J* = 36.6 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{17}F_2O_2$ $[M+H]^+$: 339.1191, found: 339.1200.

3-(Benzo[b]thiophen-2-yl)-4,4-difluoro-1-(4-methoxyphenyl)but-3-en-1-one (3se)



3se

The title compound **3se** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (53.7 mg, 78%).

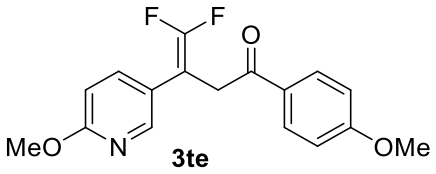
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.45–7.34 (m, 3H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.02 (s, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 192.8 (t, *J* = 2.9 Hz), 162.8, 153.9 (t, *J* = 290.5 Hz), 138.9, 136.7, 129.5 (2C), 128.4, 127.9 (dd, *J* = 4.8, 2.1 Hz), 125.3 (dd, *J* = 4.2, 1.6 Hz), 123.6, 123.5, 121.9, 121.6 (d, *J* = 2.1 Hz), 112.9 (2C), 80.8 (dd, *J* = 24.6, 21.0 Hz), 54.6, 37.7 (d, *J* = 2.4 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −84.99 (d, *J* = 33.4 Hz, 1F), −88.39 (d, *J* = 33.8 Hz, 1F).

HRMS (ESI) m/z calculated for $C_{19}H_{15}F_2O_2S$ $[M+H]^+$: 345.0755, found: 345.0765.

4,4-Difluoro-1-(4-methoxyphenyl)-3-(6-methoxypyridin-3-yl)but-3-en-1-one (3te)



3te

The title compound **3se** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (60.4 mg, 95%).

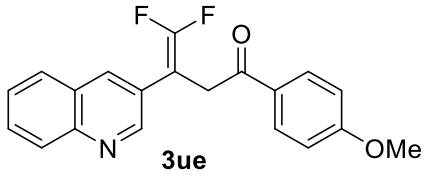
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.09 (s, 1H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.56 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H) ppm.

13C NMR (126 MHz, Chloroform-d) δ = 193.8 (t, *J* = 2.8 Hz), 164.0, 163.3, 154.8 (dd, *J* = 291.5, 288.4 Hz), 146.1, 138.6 (t, *J* = 3.5 Hz), 130.6 (2C), 129.3, 122.7, 114.0 (2C), 110.8, 84.7 (dd, *J* = 23.4, 17.9 Hz), 55.6, 53.6, 37.7 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −88.18 (d, *J* = 37.6 Hz, 1F), −88.96 (d, *J* = 37.6 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{16}F_2NO_3$ $[M+H]^+$: 320.1093, found: 320.1097.

4,4-Difluoro-1-(4-methoxyphenyl)-3-(quinolin-3-yl)but-3-en-1-one (3ue)



3ue

The title compound **3ue** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (60.4 mg, 89%).

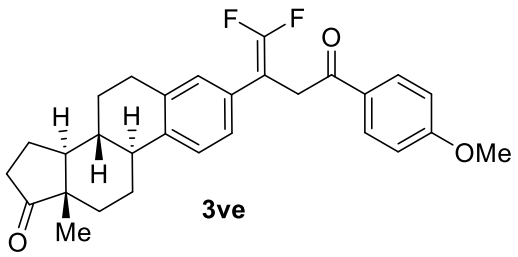
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.90 (s, 1H), 8.09–8.04 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.68 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.13 (s, 2H), 3.86 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 193.5 (t, *J* = 2.7 Hz), 164.0, 155.2 (dd, *J* = 293.3, 290.0 Hz), 150.0 (dd, *J* = 5.0, 2.7 Hz), 147.1, 134.9 (t, *J* = 3.5 Hz), 130.5 (2C), 129.7, 129.2, 129.1, 127.9, 127.6, 127.0, 126.9 (d, *J* = 4.3 Hz), 114.0 (2C), 85.2 (dd, *J* = 23.4, 17.5 Hz), 55.6, 37.7 (d, *J* = 2.3 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −86.25 (d, *J* = 33.5 Hz, 1F), −87.51 (d, *J* = 33.8 Hz, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{16}F_2NO_2$ $[M+H]^+$: 340.1144 found: 340.1148.

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



3ve

The title compound **3ve** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a colorless oil (85.4 mg, 92%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.9 Hz, 2H), 7.24 (d, *J* = 8.2 Hz,

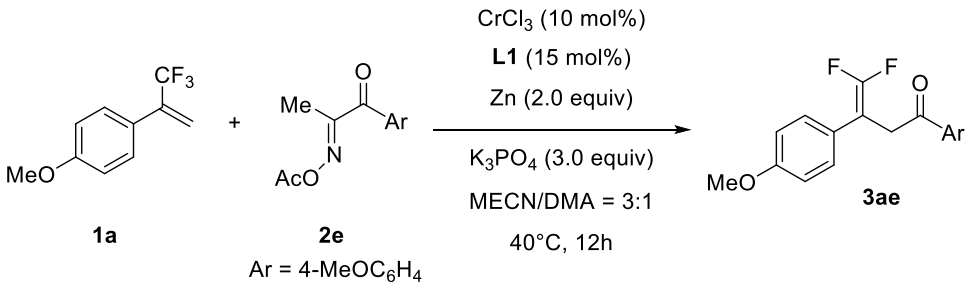
1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.07 (s, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.00 (s, 2H), 3.87 (s, 3H), 2.88 (dd, *J* = 9.1, 4.2 Hz, 2H), 2.50 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.41–2.24 (m, 2H), 2.18–2.09 (m, 1H), 2.06–1.92 (m, 2H), 1.70–1.37 (m, 7H), 0.89 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 221.0, 194.0 (t, *J* = 2.8 Hz), 163.8, 154.7 (dd, *J* = 291.9, 287.7 Hz), 139.1, 136.7, 131.1 (t, *J* = 3.9 Hz), 130.5 (2C), 129.4, 128.6 (t, *J* = 3.4 Hz), 125.6, 125.4 (t, *J* = 3.4 Hz), 113.9 (2C), 87.2 (dd, *J* = 21.6, 17.2 Hz), 55.6, 50.5, 48.0, 44.4, 38.1, 37.9 (d, *J* = 2.4 Hz), 35.9, 31.6, 29.5, 26.5, 25.6, 21.6, 13.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −88.56 (d, *J* = 38.1 Hz, 1F), −89.43 (d, *J* = 38.2 Hz, 1F) ppm.

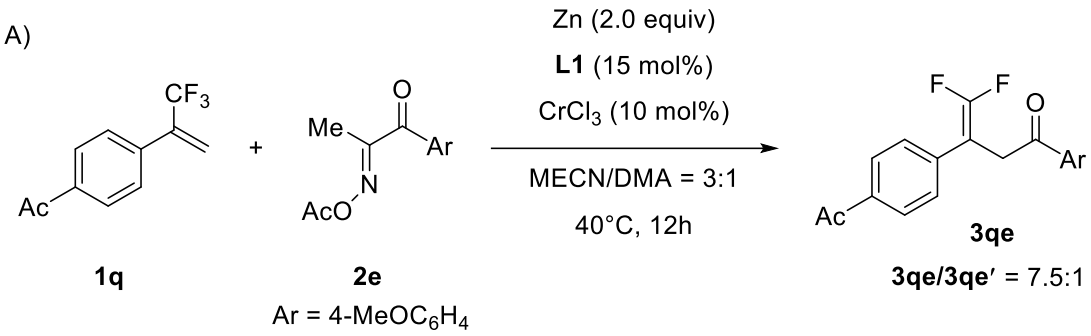
HRMS (ESI) m/z calculated for $C_{29}H_{31}F_2O_3$ $[M+H]^+$: 465.2236, found: 465.2239.

Synthesis of the *gem*-Difluoroalkene 3ae on 2 mmol Scale of 1a

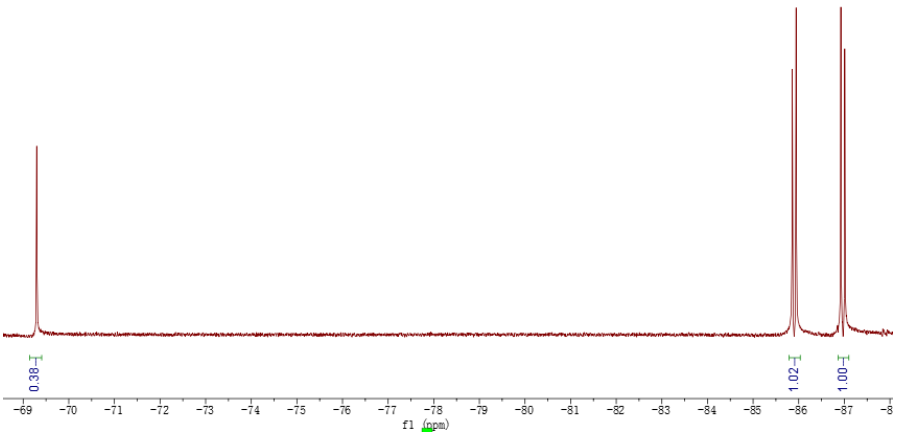


$CrCl_3$ (32 mg, 0.2 mmol, 10 mol%), 2,2':6',2''-terpyridine (**L1**) (70 mg, 0.3 mmol, 15 mol %) , Zn (260 mg, 4 mmol, 2.0 equiv), K_3PO_4 (1.27 g, 6 mmol, 3.0 qeuiv), and the oxime ester **2e** (940 mg, 4 mmol, 2.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, CH_3CN/DMA (3:1) (10 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkene **1a** (404 mg, 2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. 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 crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give *4,4-difluoro-1,3-bis(4-methoxyphenyl)but-3-en-1-one* **3ae** (553 mg, 87%) as the product.

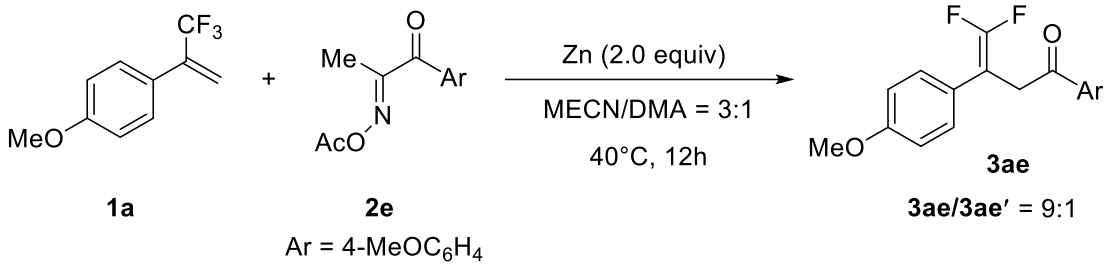
Control Experiments.



$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol%), 2,2':6',2''-terpyridine (**L1**) (7.0 mg, 0.03 mmol, 15 mol %), Zn (26.0 mg, 0.4 mmol, 2.0 equiv), and the oxime ester **2e** (94.0 mg, 0.4 mmol, 2.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkene **1q** (42.8 mg, 0.2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the mixture of **3qe** and **3qe′** (25.1 mg, combined yield 43%, **3qe**:**3qe'** = 7.5:1) as the products.



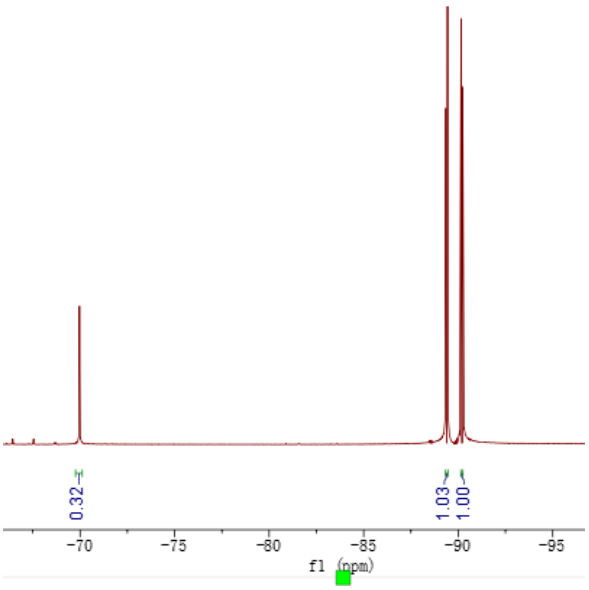
B)



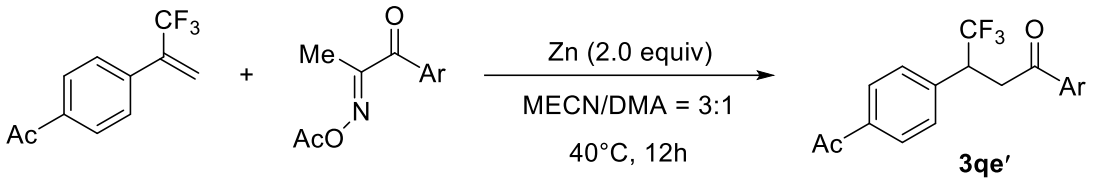
1a **2e** **3ae/3ae′** = 9:1

Ar = 4-$MeOC_6H_4$

Zn (26.0 mg, 0.4 mmol, 2.0 equiv) and the oxime ester **2e** (94.0 mg, 0.4 mmol, 2.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkenes **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the mixture of **3ae** and **3ae′** (6.4 mg, combined yield: 10%, **3ae** : **3ae'** = 9:1) as the products.



C1)



1q **2e**

Ar = 4-$MeOC_6H_4$

Zn (26.0 mg, 0.4 mmol, 2.0 equiv) and the oxime ester **2e** (94.0 mg, 0.4 mmol, 2.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkene **1q** (42.8 mg, 0.2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give *3-(4-acetylphenyl)-1-argio-4,4,4-trifluorobutan-1-one* (**3qe′**) (8.4 mg, 12%) as a colorless oil.

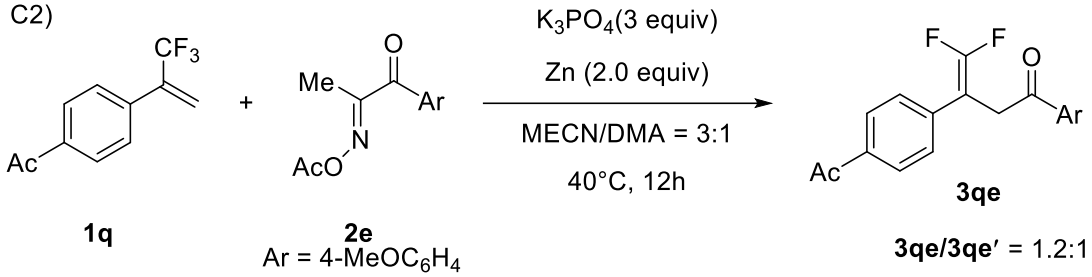
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.95–7.88 (m, 4H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.62–4.07 (m, 1H), 3.86 (s, 3H), 3.73–3.53 (m, 2H), 2.57 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 197.7, 193.5, 164.1, 140.0, 137.0, 130.5 (2C), 129.5 (2C), 129.2, 128.8 (2C), 126.8 (q, *J* = 279.4 Hz), 114.1 (2C), 55.7, 45.0 (q, *J* = 27.6 Hz), 37.7, 26.7 ppm.

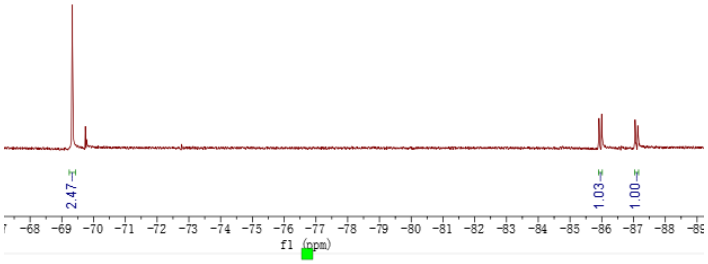
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −69.3 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{18}F_3O_3$ $[M+H]^+$: 351.1203, found: 351.1208.

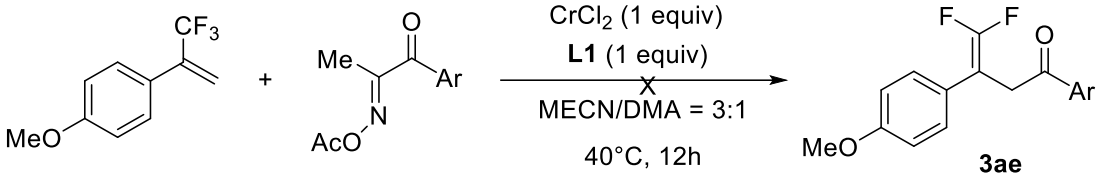
C2)



Zn (26.0 mg, 0.4 mmol, 2.0 equiv) and the oxime ester **2e** (94.0 mg, 0.4 mmol, 2.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkene **1q** (42.8 mg, 0.2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the mixture of **3qe** and **3qe′**(18.5 mg, combined yield : 28%, **3qe** : **3qe′** = 1.2:1) as the products.



D)

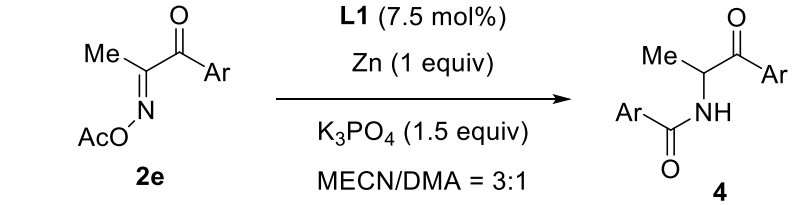


1a **2e** **3ae**

Ar = 4-$MeOC_6H_4$

$CrCl_2$ (24.6 mg, 0.2 mmol, 1.0 equiv), 2,2':6',2''-terpyridine (**L1**) (46.6 mg, 0.2 mmol, 1.0 equiv), and the oxime ester **2e** (94.0 mg, 0.4 mmol, 2.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkene **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 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, the product **3ae** was not observed, and neither **1a** nor **2e** was converted.

E)



2e **4**

Ar = 4-$MeOC_6H_4$

$CrCl_3$ (3.2 mg, 0.02 mmol, 5 mol%), 2,2':6',2''-terpyridine (**L1**) (7.0 mg, 0.03 mmol, 7.5 mol %) , Zn (26.0 mg, 0.4 mmol, 1.0 equiv), K_3PO_4 (127.0 mg, 0.6 mmol, 1.5 qeuiv), and the oxime ester **2e** (94.0 mg, 0.4 mmol, 1.0 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 this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. The reaction mixture was stirred at 40 ℃ for 12 hours before it was

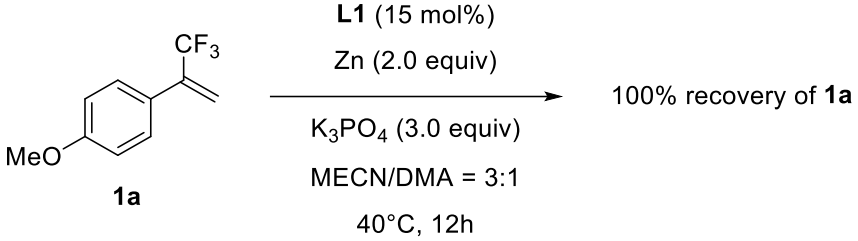
quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified through column chromatography (petroleum ether/ethyl acetate = 3:1) on silica gel, to give *4-methoxy-N-(1-(4-methoxyphenyl)-1-oxopropan-2-yl)benzamide* (**4**) (34.4 mg, 55%) as a yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.04 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.71 (quint, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 1.53 (d, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 197.9, 166.3, 164.4, 162.4, 131.4 (2C), 129.0 (2C), 126.8, 126.6, 114.3 (2C), 113.9 (2C), 55.7, 55.6, 50.2, 20.5 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{20}NO_4$ $[M+H]^+$: 314.1387, found: 314.1392.

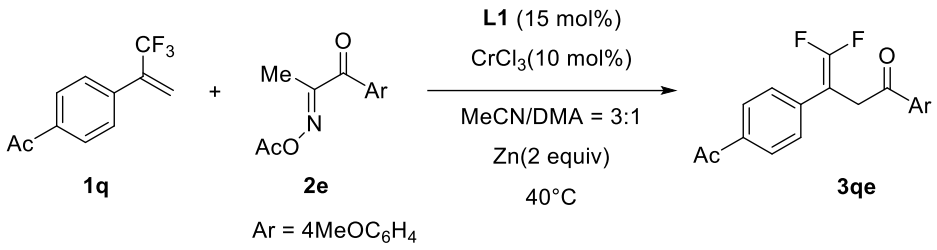
F)



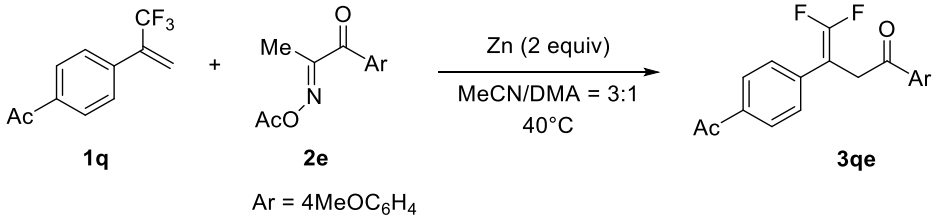
$CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol%), 2,2':6',2"-terpyridine (**L1**) (7.0 mg, 0.03 mmol, 15 mol %), Zn (26.0 mg, 0.4 mmol, 2.0 equiv), and K_3PO_4 (127.0 mg, 0.6 mmol, 3.0 qeuiv) were placed in a Schlenk tube equipped with a stir bar. Next, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, CH_3CN/DMA (3:1) (1.0 mL) was added under nitrogen atmosphere. After stirring at 40 ℃ for 15 minutes, the trifluoromethyl-substituted alkene **1a** (40.4 mg, 0.2 mmol, 1.0 equiv) was added under a positive flow of nitrogen. The reaction mixture was stirred at 40 ℃ for 12 hours before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 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 **1a** was not observed.

Kinetic Studies

A) Kinetic Progress Analysis for the Reaction between 1q and 2e

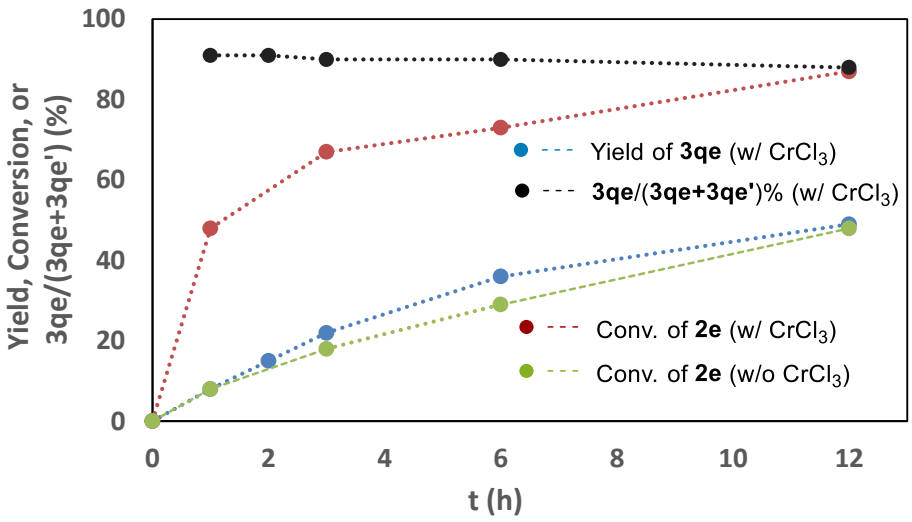


A Schlenk tube was charged with the acyl oxime esters **2e** (94 mg, 0.4 mmol, 2 equiv**)**, the trifluoromethyl styrene **1q** (42.8 mg, 0.2 mmol, 1 equiv), $CrCl_3$ (3.2 mg, 0.02 mol, 10 mol%), the ligand 2,2':6',2''-terpyridine (**L1**)(7.0 mg, 0.03 mol, 15 mol%), and Zn (26 mg, 0.4 mmol, 2 equiv) in MeCN/DMA (3:1). After stirring for 1h, 2h, 3h, 6h, 12h at 40 ˚C, the reaction was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo.The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to provide the recovered acyl oxime ester **2e** and the *gem*-difluoroalkenes **3qe** as the products.



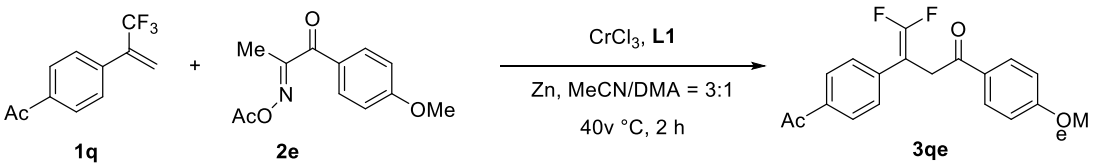
A Schlenk tube was charged with the acyl oxime esters **2e (**94 mg, 0.4 mmol, 2 equiv**)**, the trifluoromethyl styrene **1q** (42.8 mg, 0.2 mmol, 1 equiv), and Zn (26 mg, 0.4 mmol, 2 equiv) in MeCN/DMA (3:1). After stirring for 1h, 3h, 6h, 12h at 40 ˚C, the reaction was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo.The crude materials were purified through column

chromatography on silica gel (petroleum ether/ethyl acetate) to provide the recovered acyl oxime ester **2e** and the *gem*-difluoroalkenes **3qe** as the products.



T (h)	Conv. of **2e** (w/ $CrCl_3$)	Conv. of **2e** (w/o $CrCl_3$)	Yield of **2e** (w/ $CrCl_3$)	**3qe**/(**3qe**+**3qe'**) (w/$CrCl_3$)
1	48%	8%	8%	91%
2	n.d.	n.d.	15%	91%
3	67%	18%	22%	90%
6	73%	29%	36%	90%
12	87%	48%	49%	88%

Determination of the Reaction Order of the Reactants and Catalyst

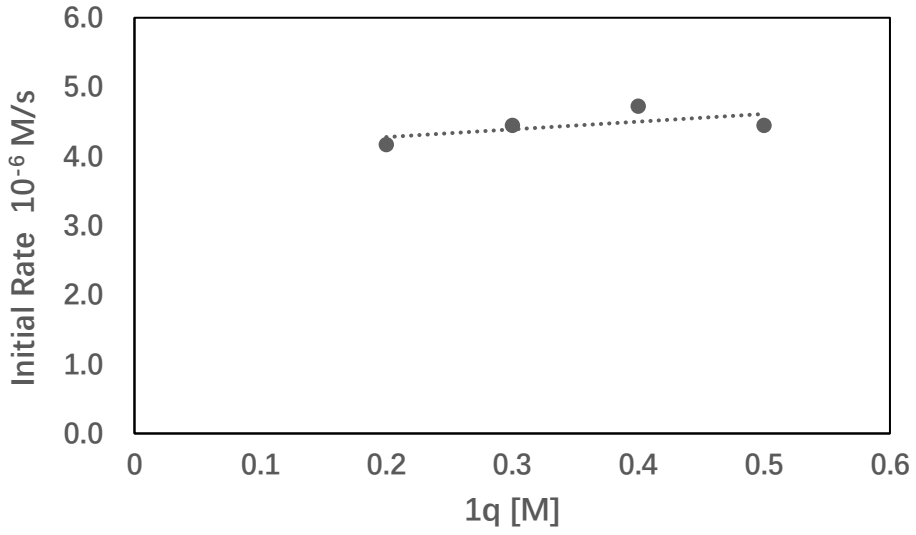


A Schlenk tube was charged with the indicated concentration of the acyl oxime ester **2e**, the trifluoromethyl styrene **1q**, $CrCl_3$, the ligand 2,2':6',2''-terpyridine (**L1**), and Zn in MeCN/DMA (3:1). After stirring for 2h at 40 ˚C, the reaction was quenched by

addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to give the *gem*-difluoroalkenes **3qe** as the product. The initial rates were calculated and plotted against the reactant or catalyst concentration to determine the reaction orders.

B) Determination of the Reaction Order in the α-Trifluoromethyl Styrene 1q

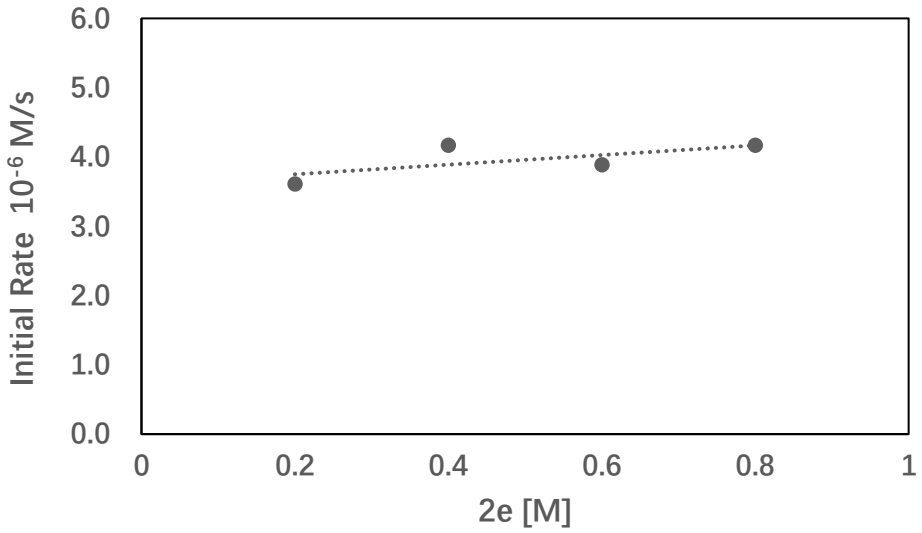
The reaction was performed with acyl oxime esters **2e** (94.0 mg, 0.4 mmol, 1.0 equiv, 0.4 M), $CrCl_3$ (3.2 mg, 0.02 mmol, 5 mol %), the ligand 2,2':6',2''-terpyridine (**L1**) (7.0 mg, 0.03 mmol, 7.5 mol %), and Zn (26.0 mg, 0.4 mmol, 1.0 equiv) in MeCN/DMA (3:1) (1.0 mL) in the presence of 0.2 M, 0.3 M, 0.4M and 0.5 M the α-trifluoromethyl styrene **1q** with the reaction time of 2 h. The initial rates at various **1q** were similar, showing the reaction exhibits zero-order rate dependence on the concentration of **1q**.



[**1a**] (M)	Yield (%)	[**3qe**] (10^{-2}M)	Initial Rate (10^{-6}M/s)
0.2	15	3.00	4.17
0.3	11	3.20	4.44
0.4	8.5	3.40	4.72
0.5	6.4	3.20	4.44

C) Determination of the Reaction Order in the Acyl Oxime Esters 2e

The reaction was performed with the α-trifluoromethyl styrene **1q** (42.8 mg, 0.2 mmol, 1.0 equiv, 0.2 M), $CrCl_3$ (3.2 mg, 0.02 mmol, 10 mol%), the ligand 2,2':6',2"-terpyridine (**L1**) (7.0 mg, 0.03 mmol, 15 mol%), and Zn (26.0 mg, 0.4 mmol, 2.0 equiv) in MeCN/DMA (3:1) (1.0 mL) in the presence of 0.2 M, 0.4 M, 0.6 M, and 0.8 M the acyl oxime ester **2e** with the reaction time of 2 h. The initial rates at various **2e** were similar, showing the reaction exhibits zero-order rate dependence on the concentration of **2e**.

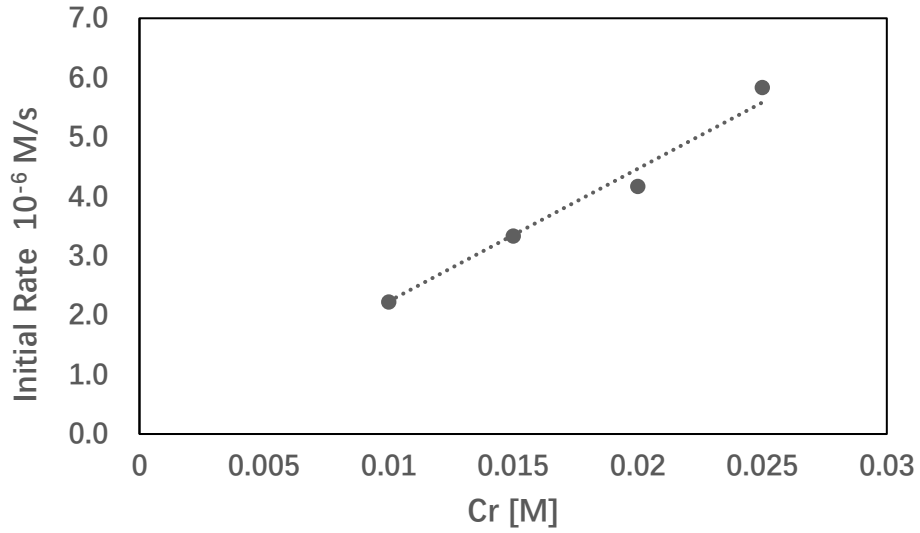


[**2e**] (M)	Yield (%)	[**3qe**] (10^{-2}M)	Initial Rate (10^{-6}M/s)
0.2	13	2.60	3.61
0.4	15	3.00	4.17
0.6	14	2.80	3.89
0.8	15	3.00	4.17

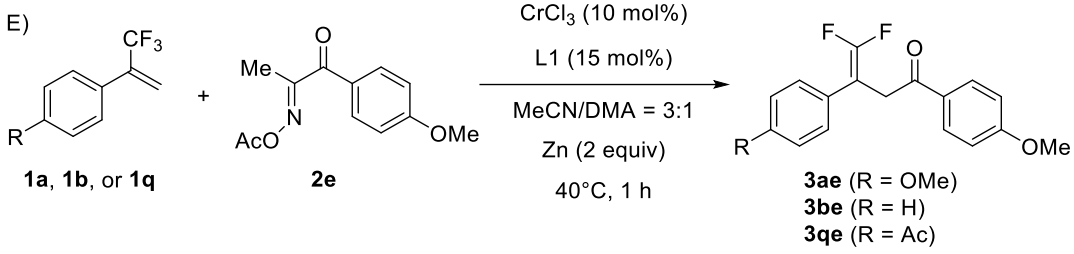
D) Determination of the Reaction Order in the Cr Catalyst

The reaction was performed with α-trifluoromethyl styrene **1q** (42.8 mg, 0.2 mmol, 2.0 equiv, 0.2 M), the oxime ester **2e** (94.0 mg, 0.4 mmol, 2.0 equiv, 0.4 M), and Zn (26.0 mg, 0.4 mmol, 2.0 equiv) in MeCN/DMA (3:1) (1.0 mL) in the presence of 0.01 M, 0.015 M, 0.02 M, and 0.025 M $CrCl_3$ with 0.015 M, 0.0225 M, 0.30 M, and 0.375 M **L1**, respectively, with the reaction time of 2 h. 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)	Yield (%)	[**3qe**] (10^{-2}M)	Initial Rate (10^{-6}M/s)
0.010	8	1.60	2.22
0.015	12	2.40	3.33
0.020	15	3.00	4.17
0.025	21	4.20	5.83



A Schlenk tube was charged with the acyl oxime ester **2e** (188 mg, 0.8 mmol, 2 equiv**)**, the indicated trifluoromethyl styrene **1a**, **1b**, or **1q** (0.4 mmol, 1 equiv), $CrCl_3$ (6.4 mg, 0.04 mol, 10mol%), the ligand 2,2':6',2"-terpyridine (**L1**)(14.0 mg, 0.06 mol, 15mol%), and Zn (52 mg, 0.8 mmol, 2 equiv) in MeCN/DMA (3:1) (2.0 mL). After stirring for 1 h at 40 ˚C, the reaction was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed

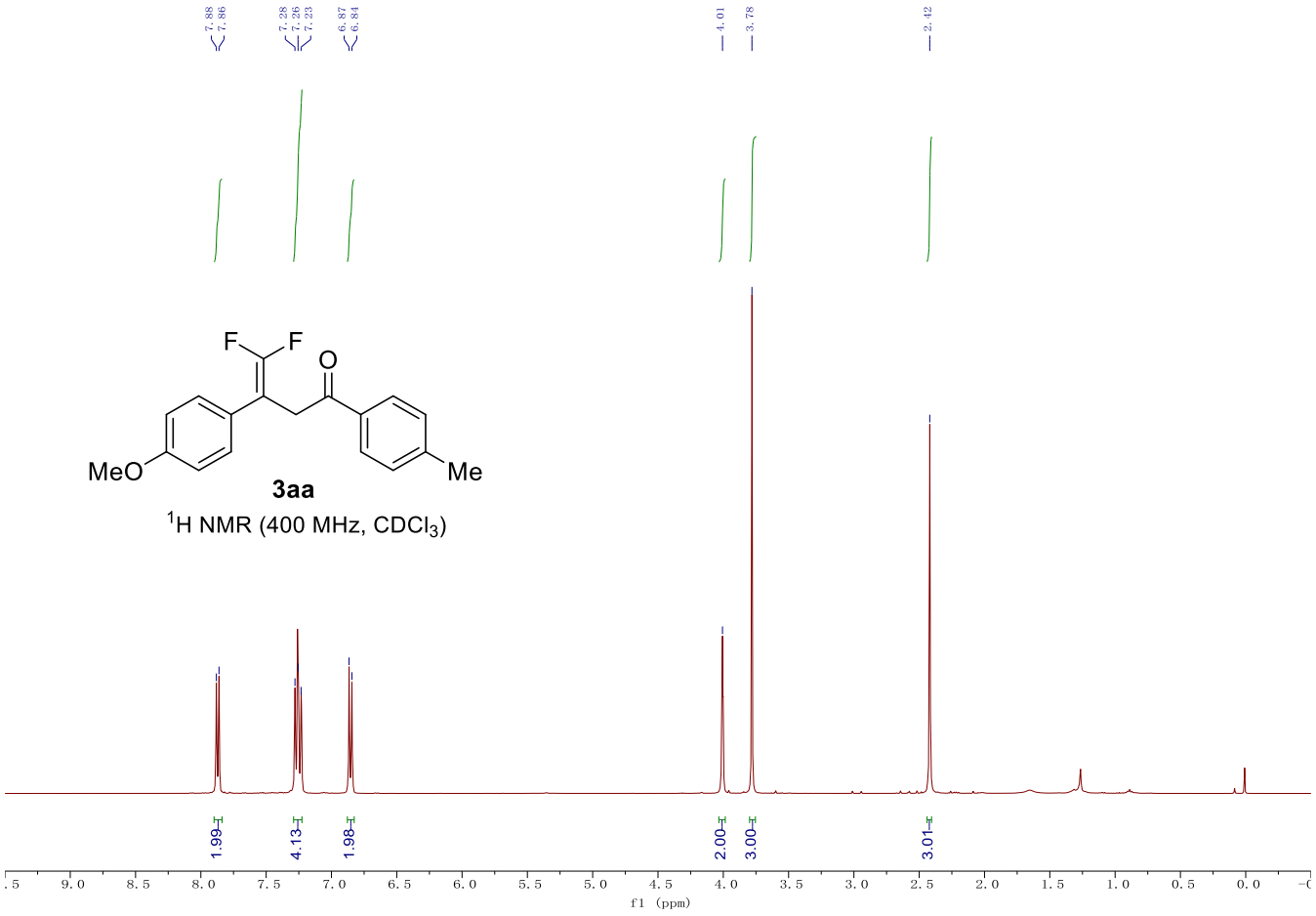
with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the *gem*-difluoroalkenes **3ae**, **1be**, or **3qe** as the products.

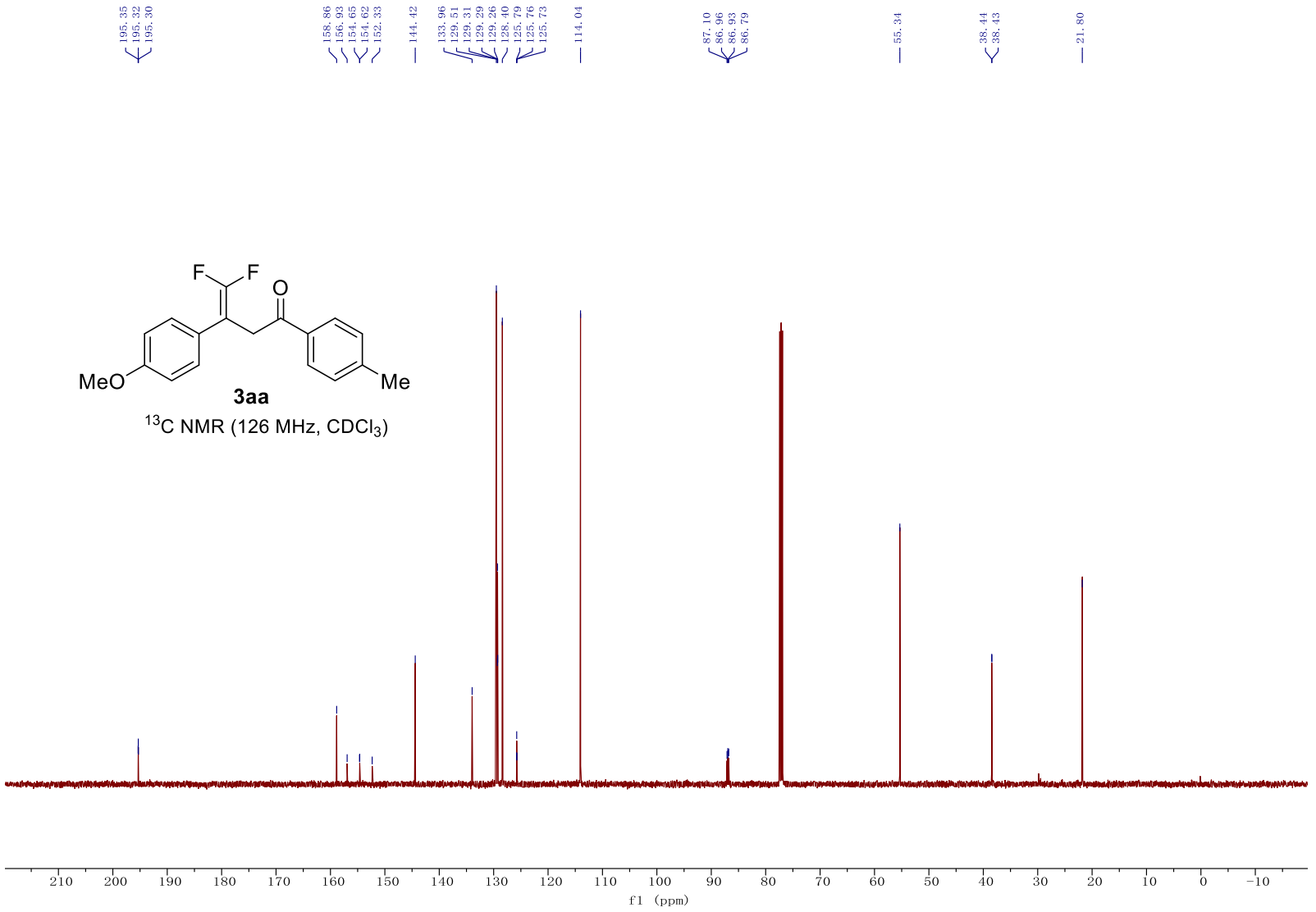
R	Yield (%)	[**3**] (10^{-2}M)	Initial Rate (10^{-6}M/s)
OMe	14	2.80	7.80
H	11	2.20	6.11
Ac	8	1.60	4.44

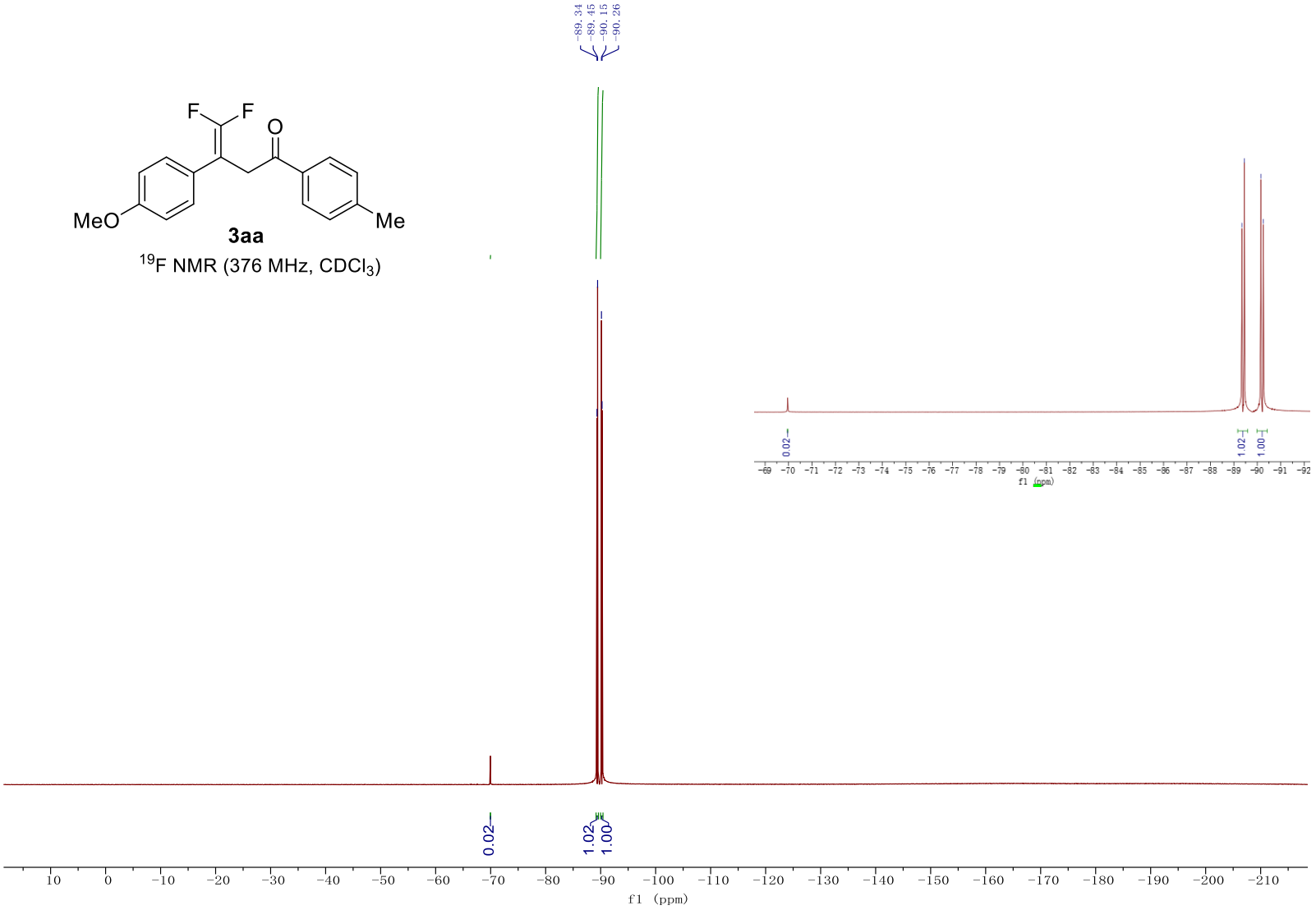
References

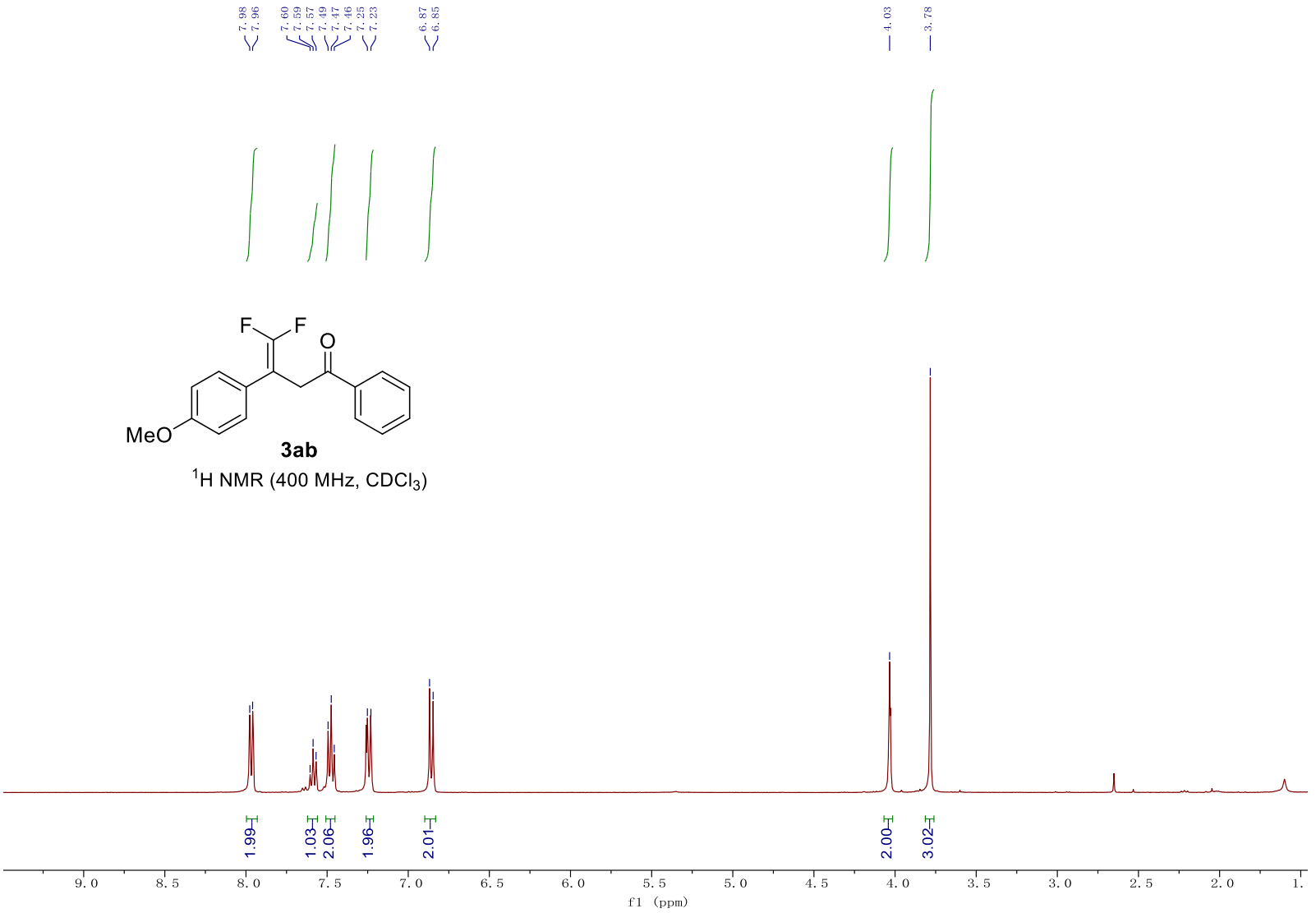
1. Liu, Y.; Zhou, Y.; Zhao, Y.; Qu, J. Synthesis of *gem*-Difluoroallylboronates via $FeCl_2$-Catalyzed Boration/β-Fluorine Elimination of Trifluoromethyl Alkenes. *Org. Lett.* **2017**, *19*, 946–949.
2. Lan, Y.; Yang, F.; Wang, C. Synthesis of *gem*-Difluoroalkenes via Nickel-Catalyzed Allylic Defluorinative Reductive Cross-Coupling. *ACS Catal*. **2018**, *8*, 9245–9251.
3. Cheng, Y.-Y.; Lei, T.; Su, L.; Fan, X.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Visible Light Irradiation of Acyl Oxime Esters and Styrenes Efficiently Constructs β-Carbonyl Imides by a Scission and Four-Component Reassembly Process. *Org. Lett.* **2019**, *21*, 8789−8794
4. Fan, X.; Lei, T.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Photocatalytic C−C Bond Activation of Oxime Ester for Acyl Radical Generation and Application. *Org. Lett.* **2019**, *21*, 4153−4158.

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



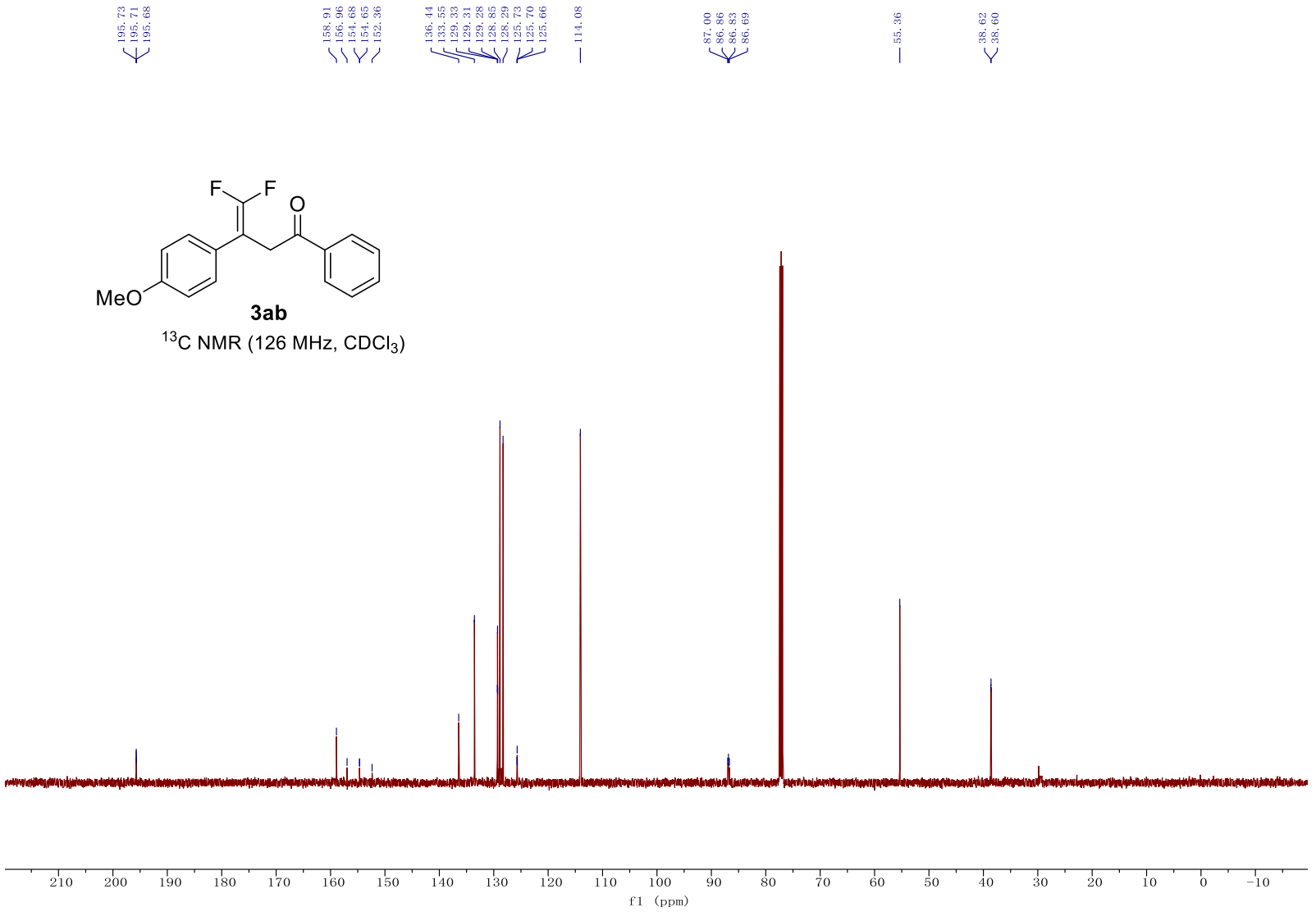

195.35
195.32
195.30
158.86
156.93
154.65
154.62
152.33
144.42
133.96
129.51
129.31
129.29
129.26
128.40
125.79
125.76
125.73
114.04
87.10
86.96
86.93
86.79
55.34
38.44
38.43
21.80
F
F
O
MeO
Me
3aa
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

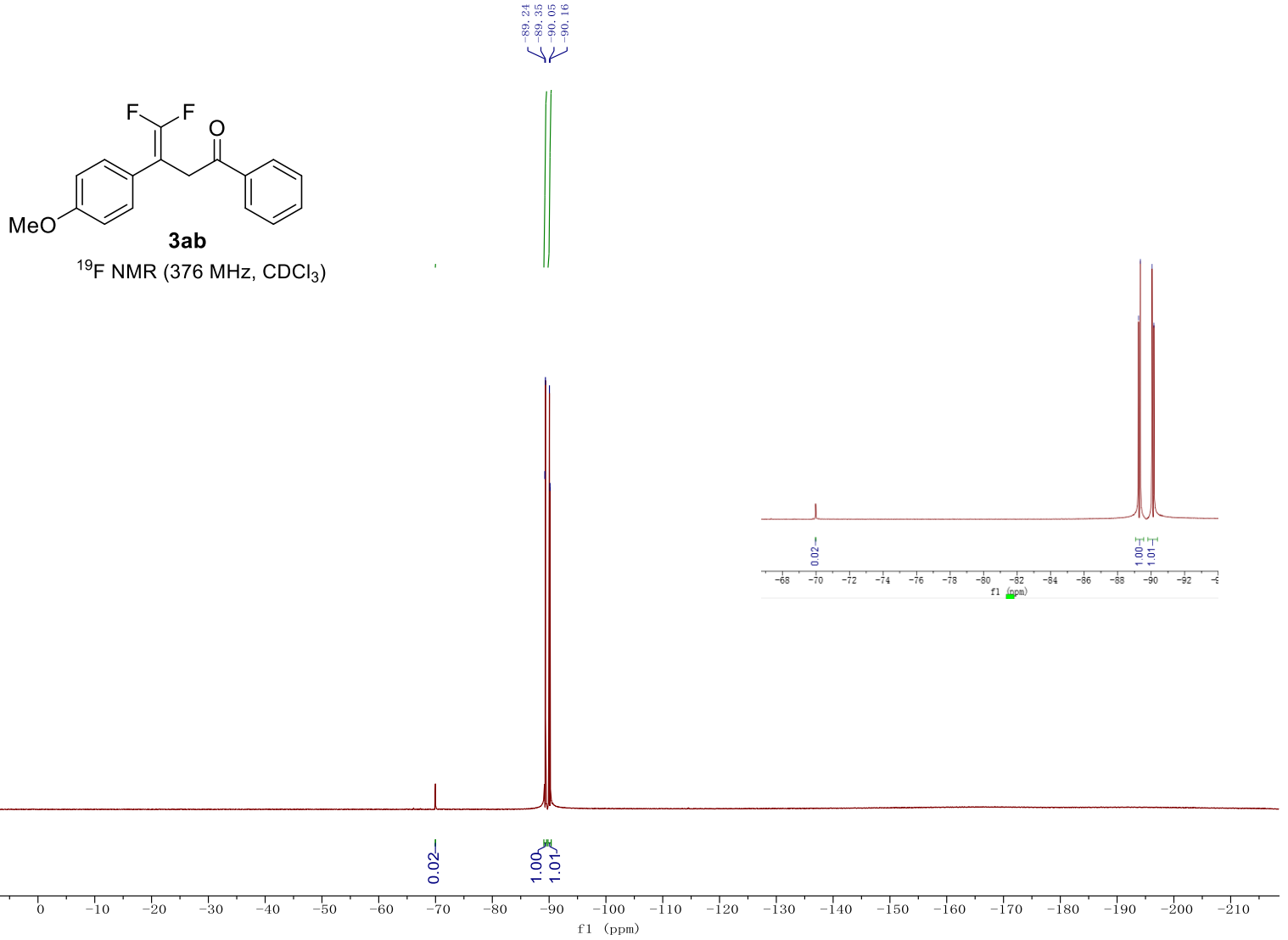

F
F
O
MeO
Me
3aa
19F NMR (376 MHz, CDCl3)
-89.34
-89.45
-90.15
-90.26
0.02
1.02
1.00
f1 (ppm)

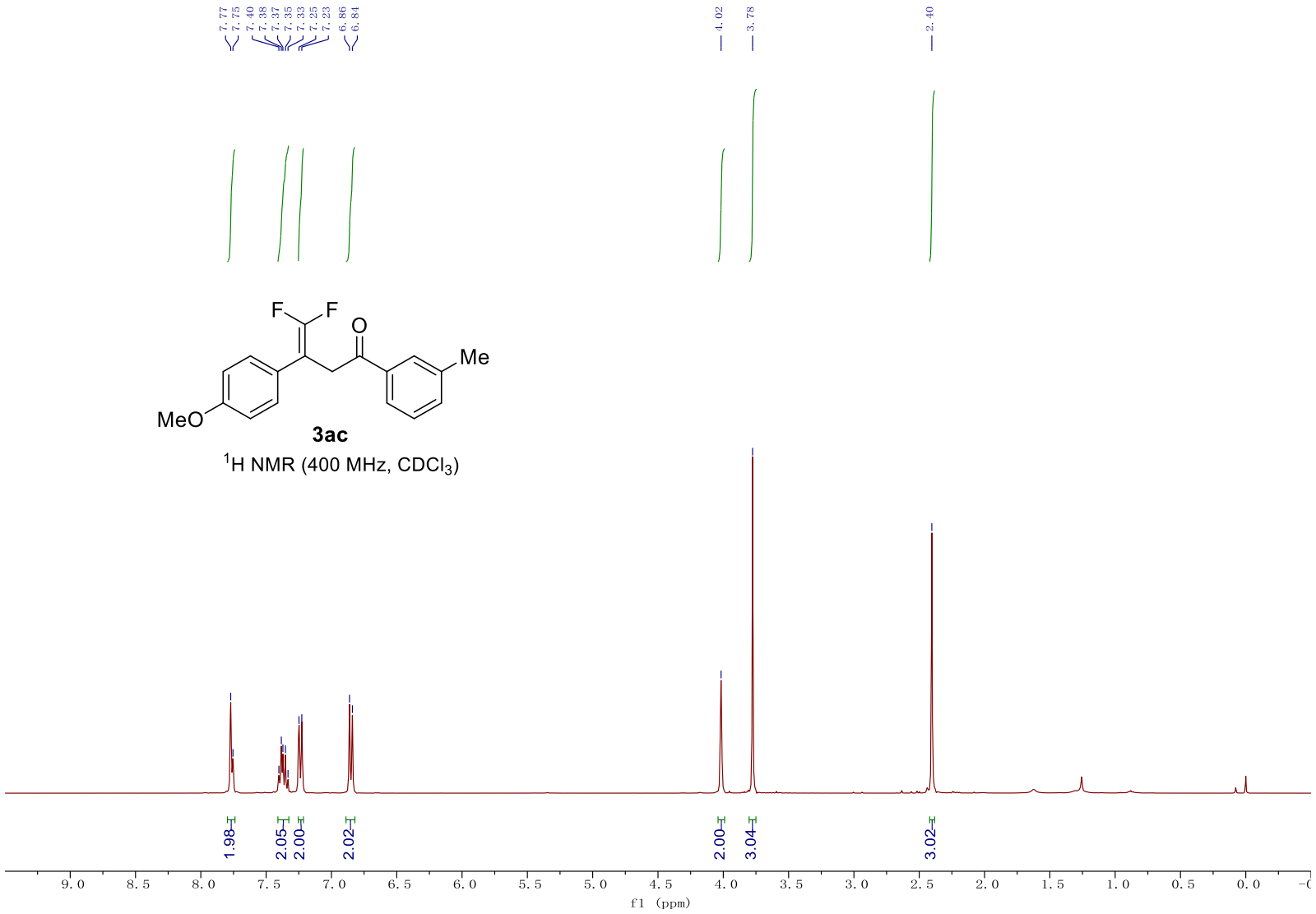


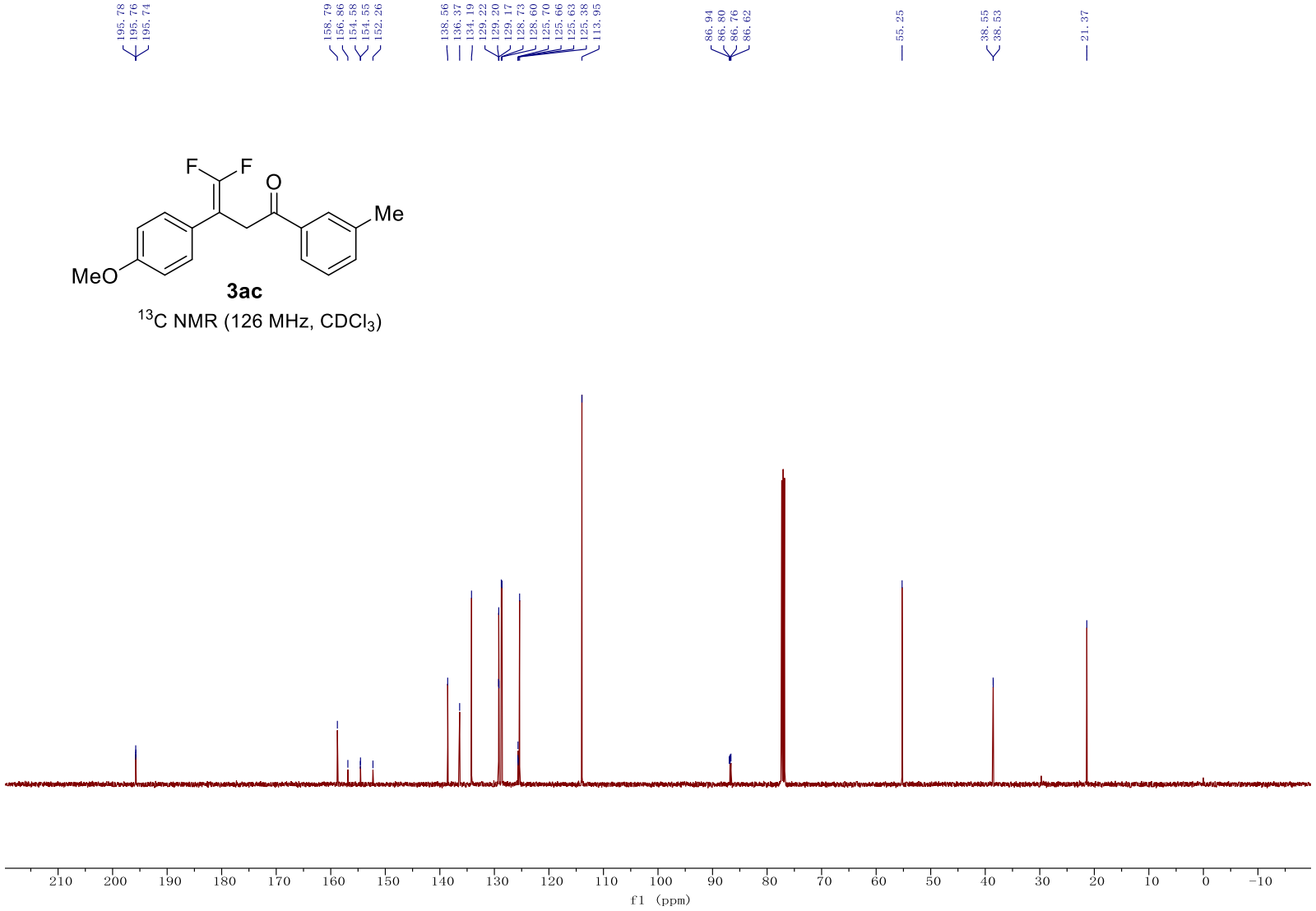
3ab

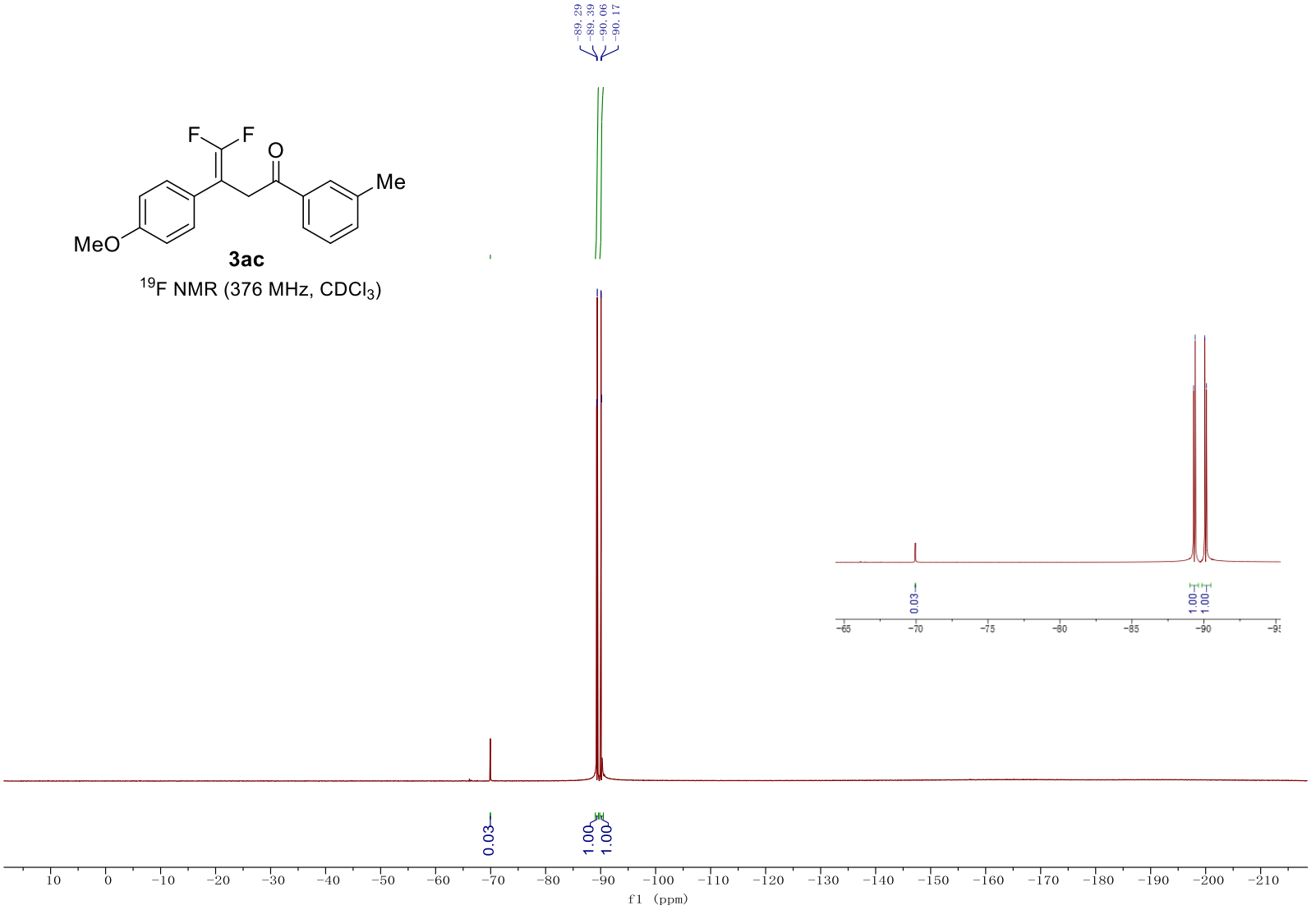
^{1}H NMR (400 MHz, $CDCl_3$)


195.73
195.71
195.68
158.91
156.96
154.68
154.65
152.36
136.44
133.55
129.33
129.31
129.28
128.85
128.29
125.73
125.70
125.66
114.08
87.00
86.86
86.83
86.69
55.36
38.62
38.60
F
F
O
MeO
3ab
^{13}C NMR (126 MHz, CDCl$_3$)
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
MeO
3ab
19F NMR (376 MHz, CDCl3)
-89.24
-89.35
-90.05
-90.16
0.02
1.00
1.01
f1 (ppm)

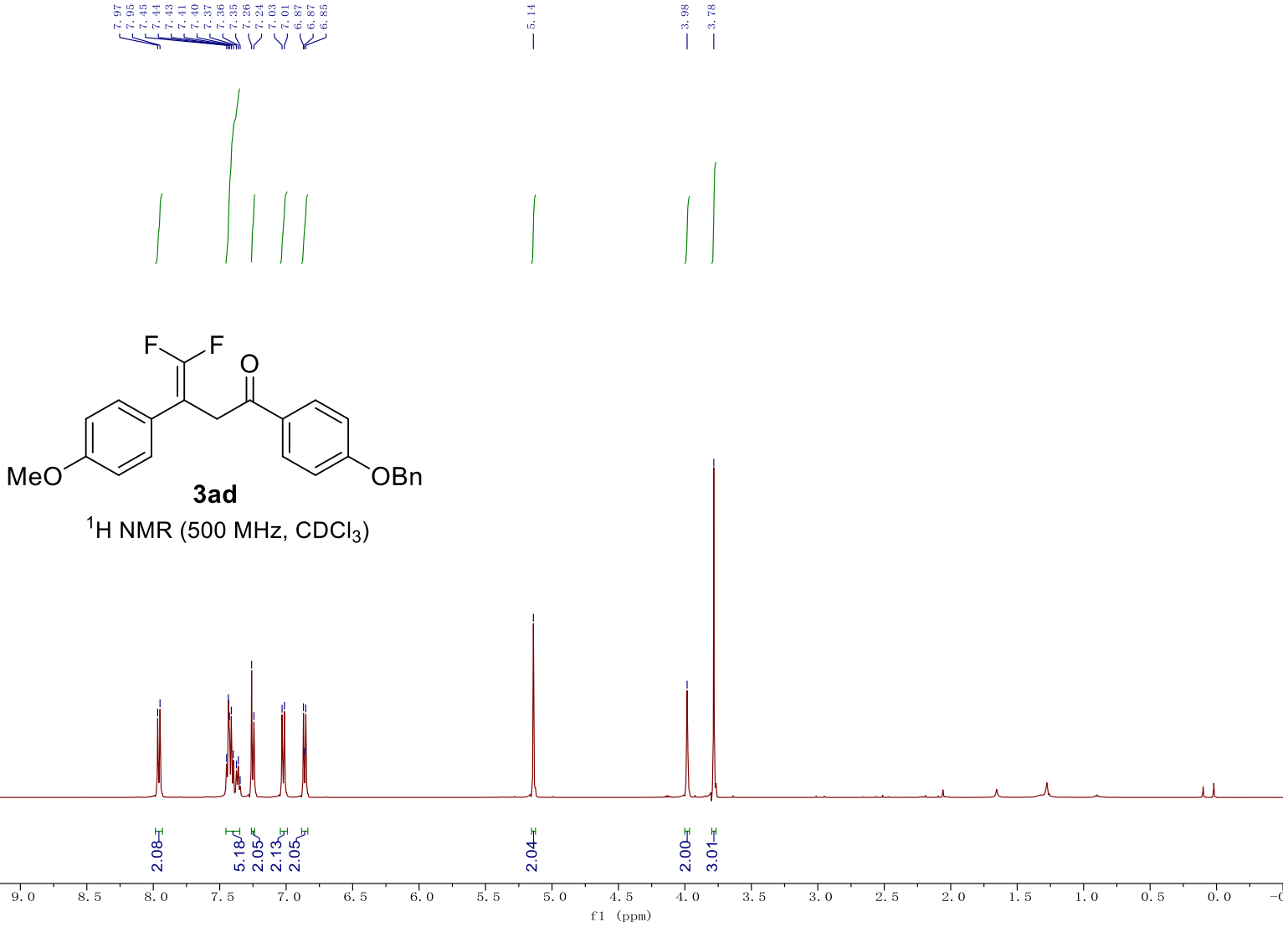

7.77
7.75
7.40
7.38
7.37
7.35
7.33
7.25
7.23
6.86
6.84
4.02
3.78
2.40
F
F
O
Me
MeO
3ac
1H NMR (400 MHz, CDCl3)
1.98
2.05
2.00
2.02
2.00
3.04
3.02
f1 (ppm)

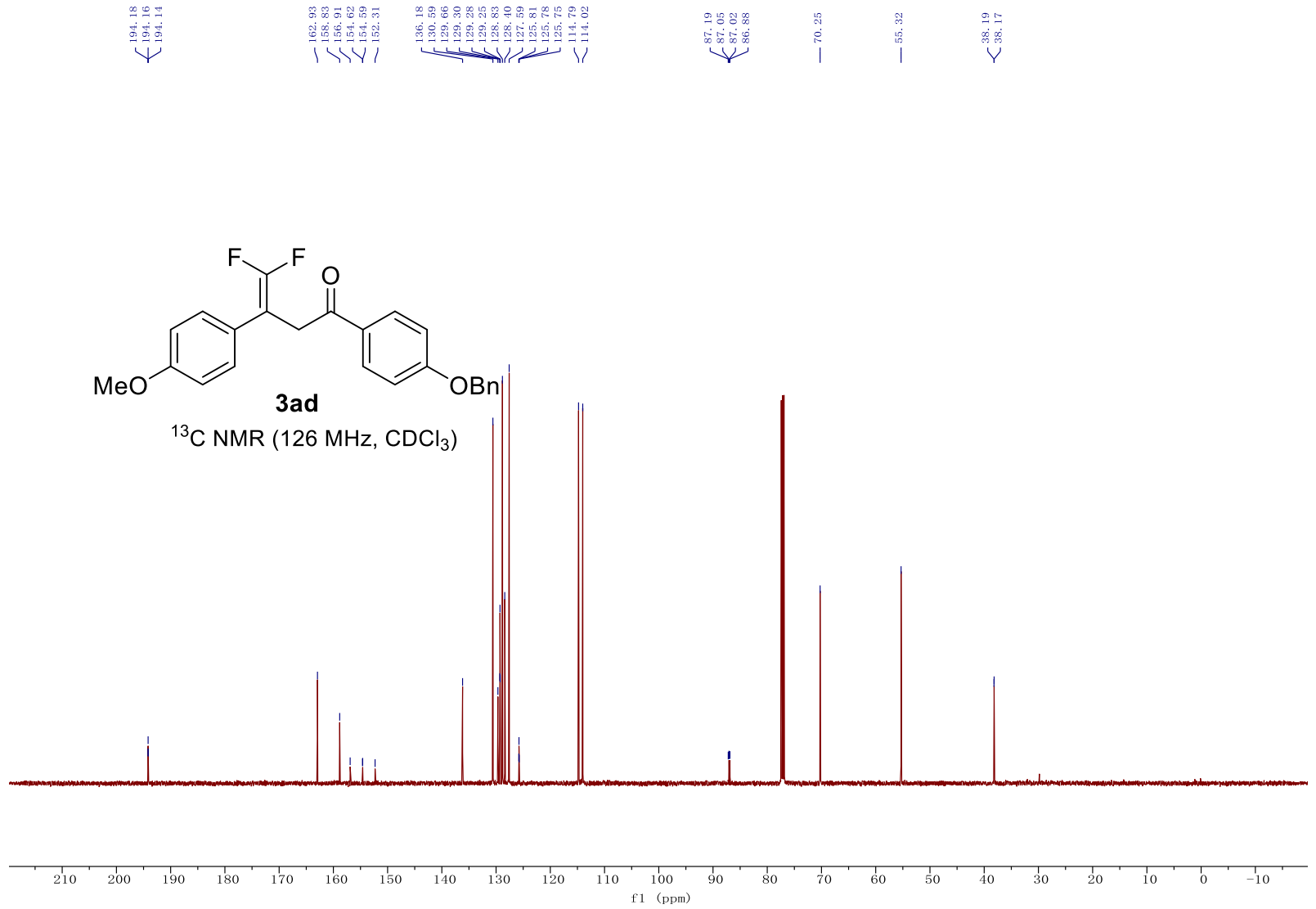

195.78
195.76
195.74
158.79
156.86
154.58
154.55
152.26
138.56
136.37
134.19
129.22
129.20
129.17
128.73
128.60
125.70
125.66
125.63
125.38
113.95
86.94
86.80
86.76
86.62
55.25
38.55
38.53
21.37
F
F
O
Me
MeO
3ac
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

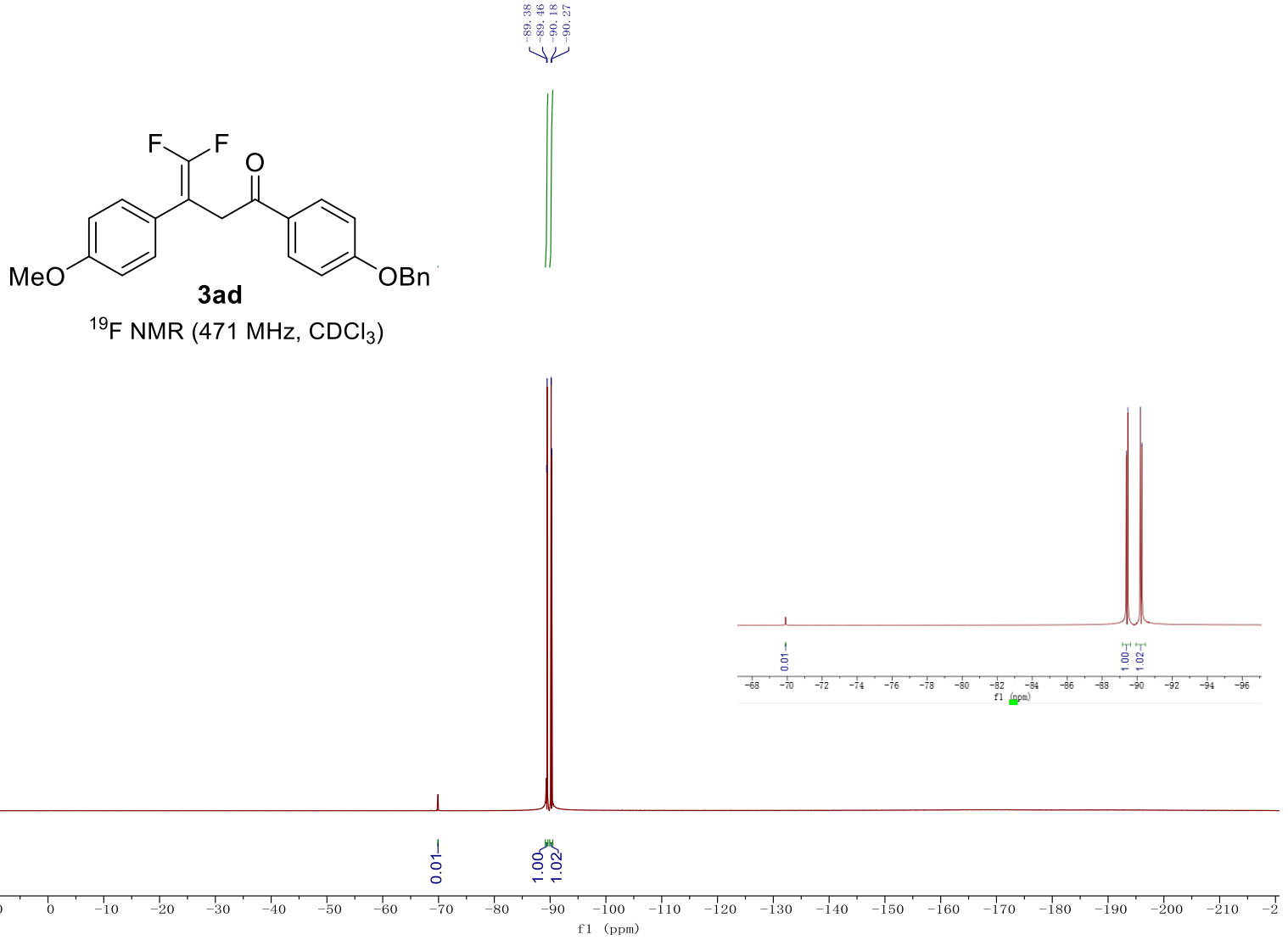


3ac

^{19}F NMR (376 MHz, $CDCl_3$)

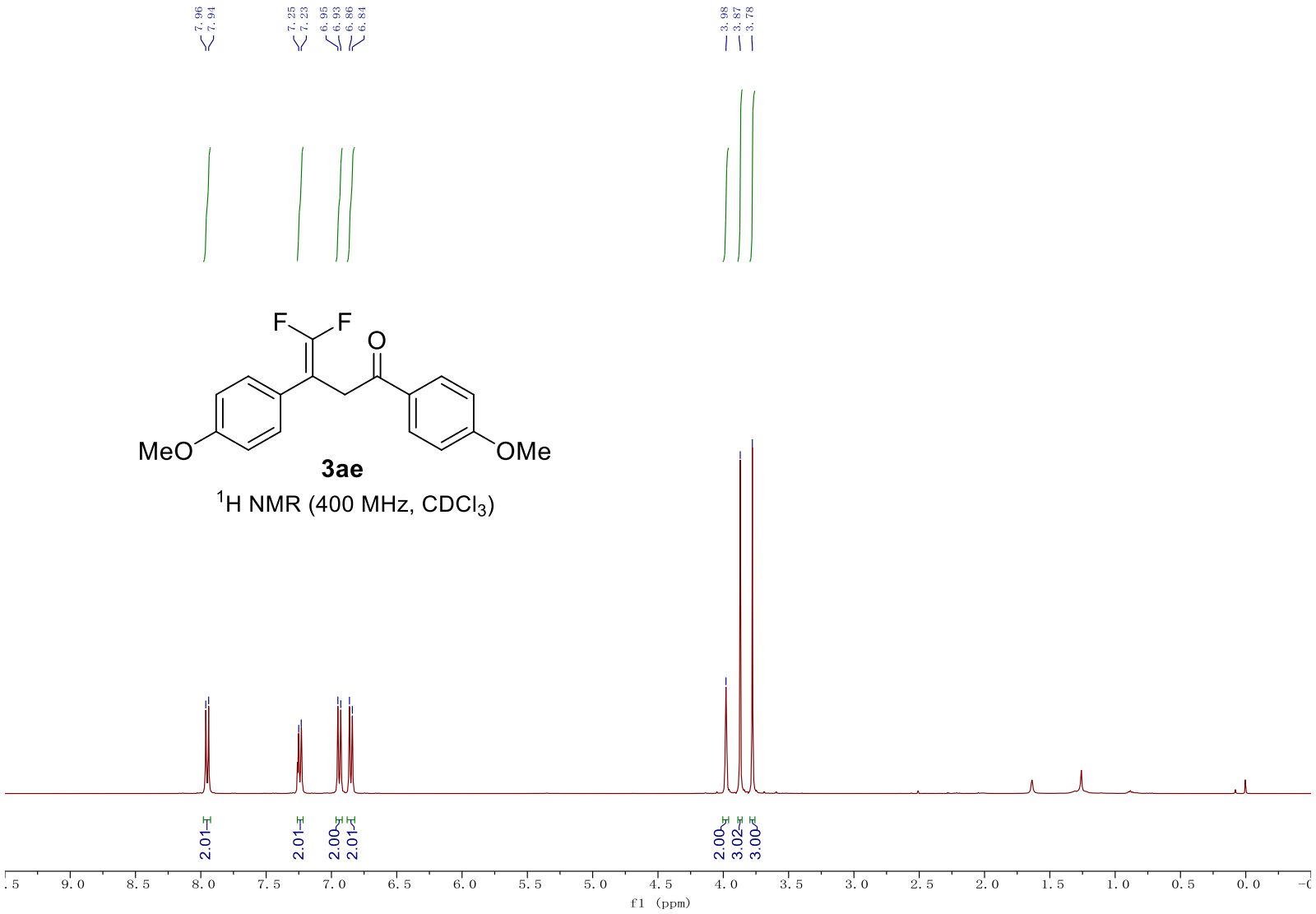

7.97
7.95
7.45
7.44
7.43
7.41
7.40
7.37
7.36
7.35
7.26
7.24
7.03
7.01
6.87
6.85
5.14
3.98
3.78
F
F
O
MeO
OBn
3ad
1H NMR (500 MHz, CDCl3)
2.08
5.18
2.05
2.13
2.05
2.04
2.00
3.01
f1 (ppm)


194.18
194.16
194.14
162.93
158.83
156.91
154.62
154.59
152.31
136.18
130.59
129.66
129.30
129.28
129.25
128.83
128.40
127.59
125.81
125.78
125.75
114.79
114.02
87.19
87.05
87.02
86.88
70.25
55.32
38.19
38.17
F
F
O
MeO
OBn
3ad
^{13}C NMR (126 MHz, $CDCl_3$)
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)



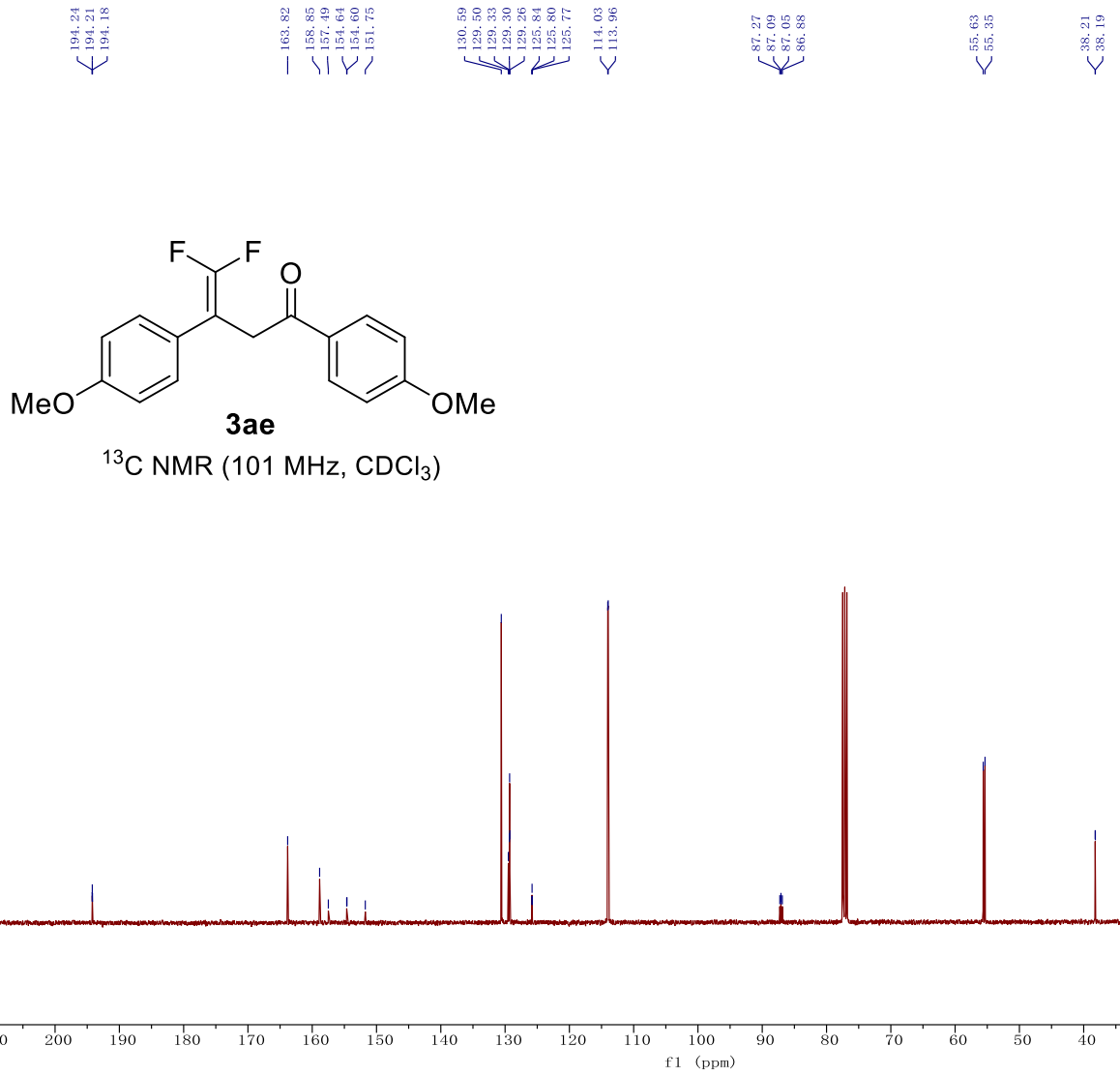
3ad

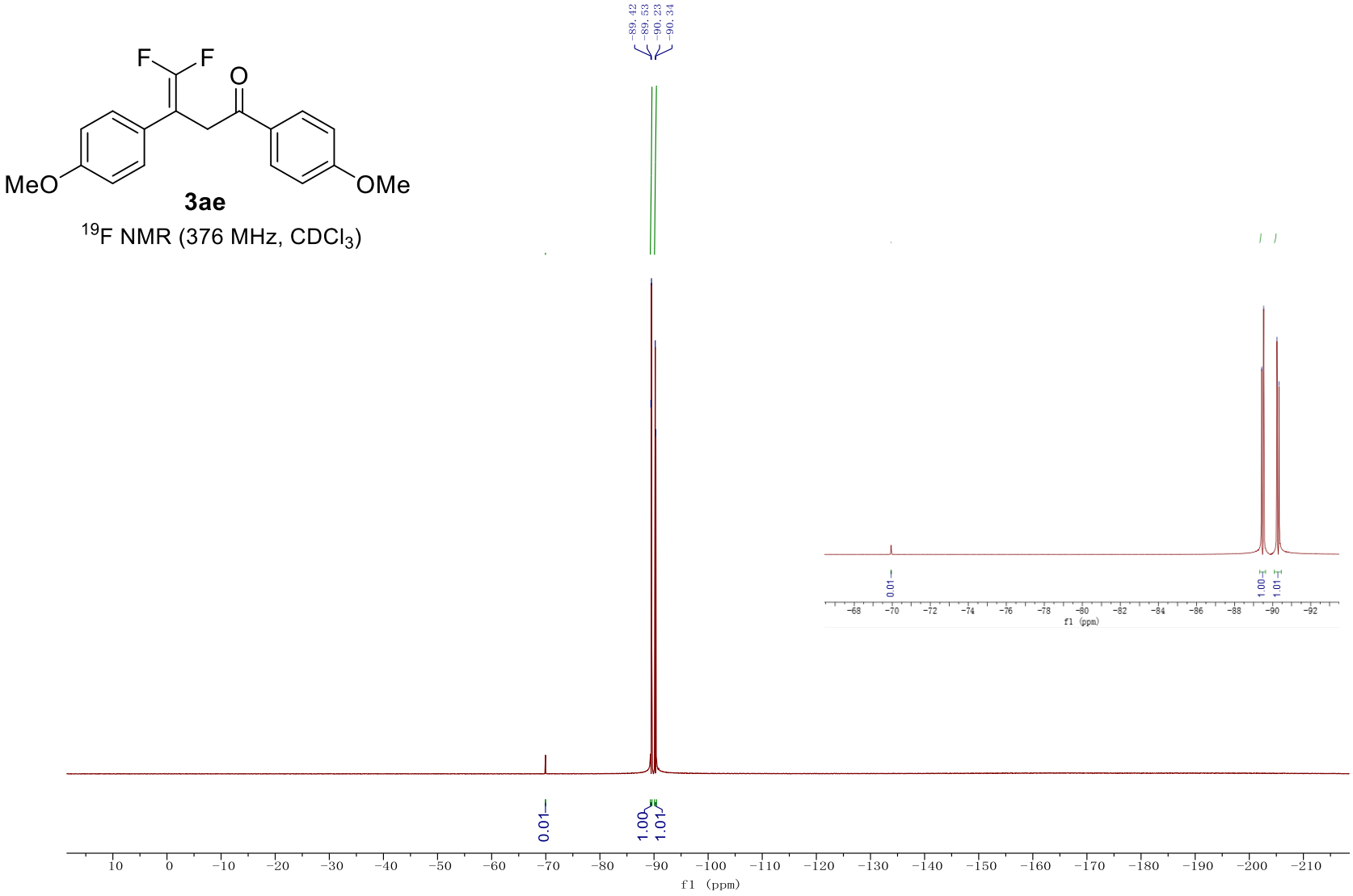
^{19}F NMR (471 MHz, $CDCl_3$)



3ae

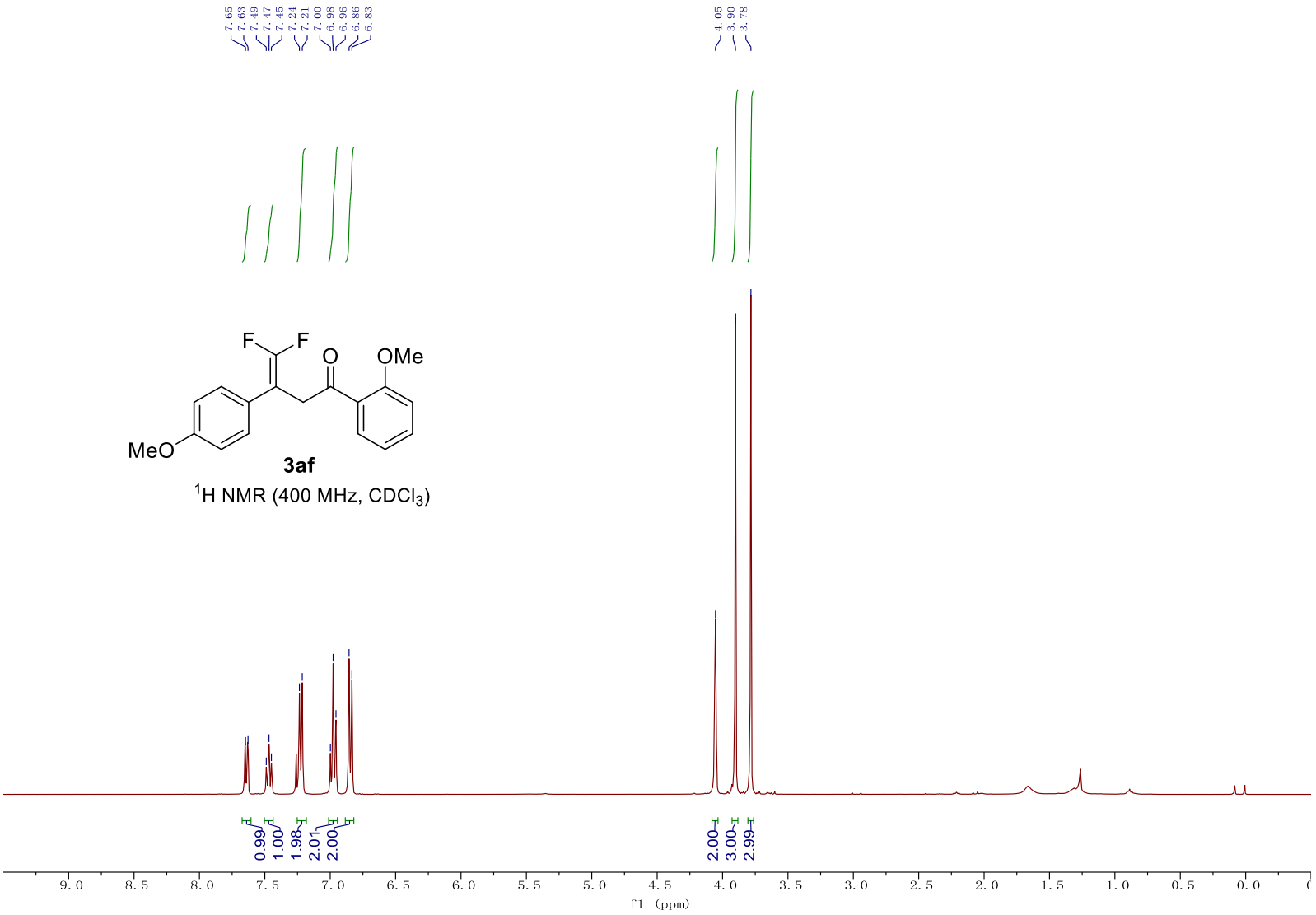
^{1}H NMR (400 MHz, $CDCl_3$)


194.24
194.21
194.18
163.82
158.85
157.49
154.64
154.60
151.75
130.59
129.50
129.33
129.30
129.26
125.84
125.80
125.77
114.03
113.96
87.27
87.09
87.05
86.88
55.63
55.35
38.21
38.19
F
F
O
MeO
OMe
3ae
13C NMR (101 MHz, CDCl3)
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)



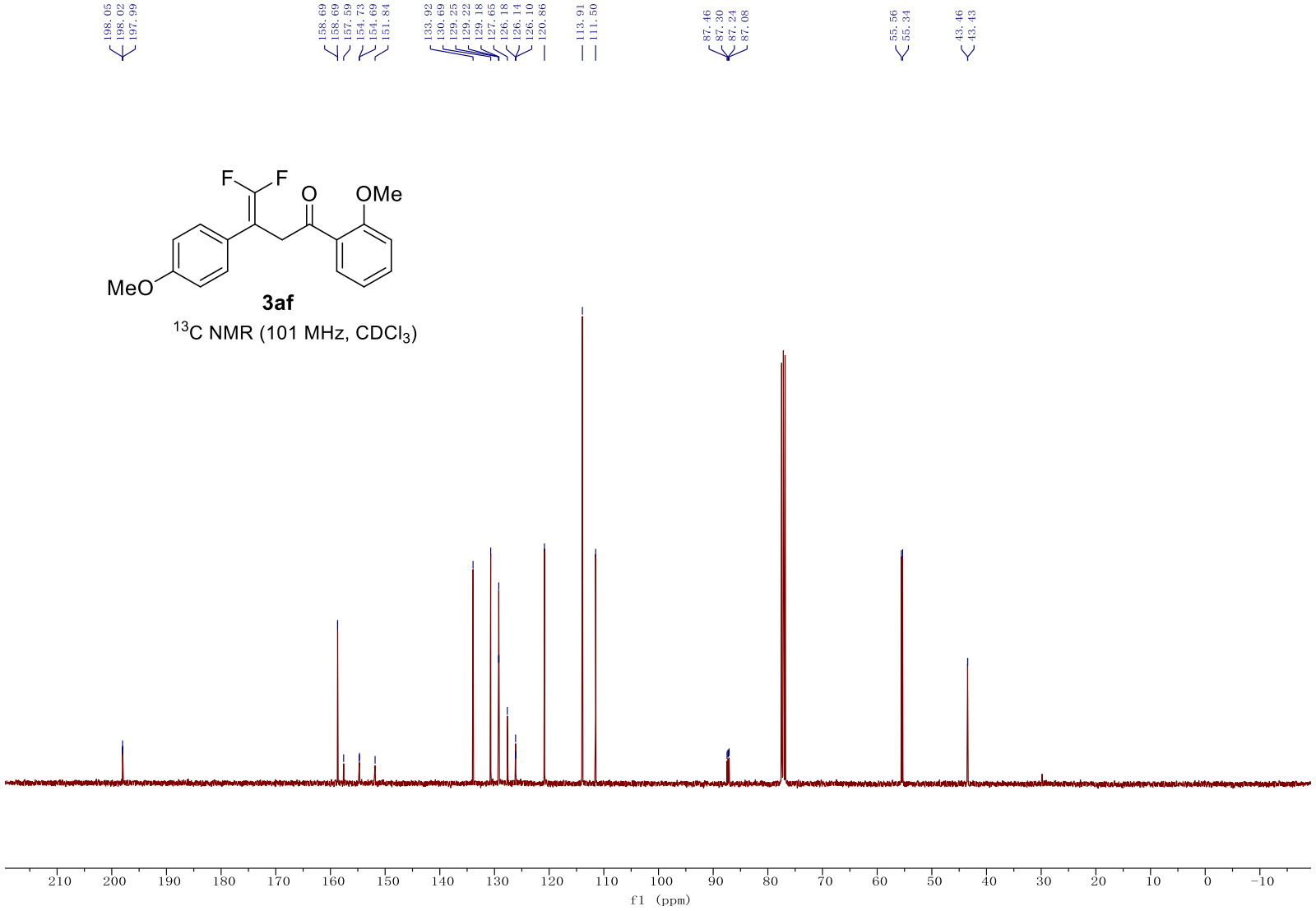
3ae

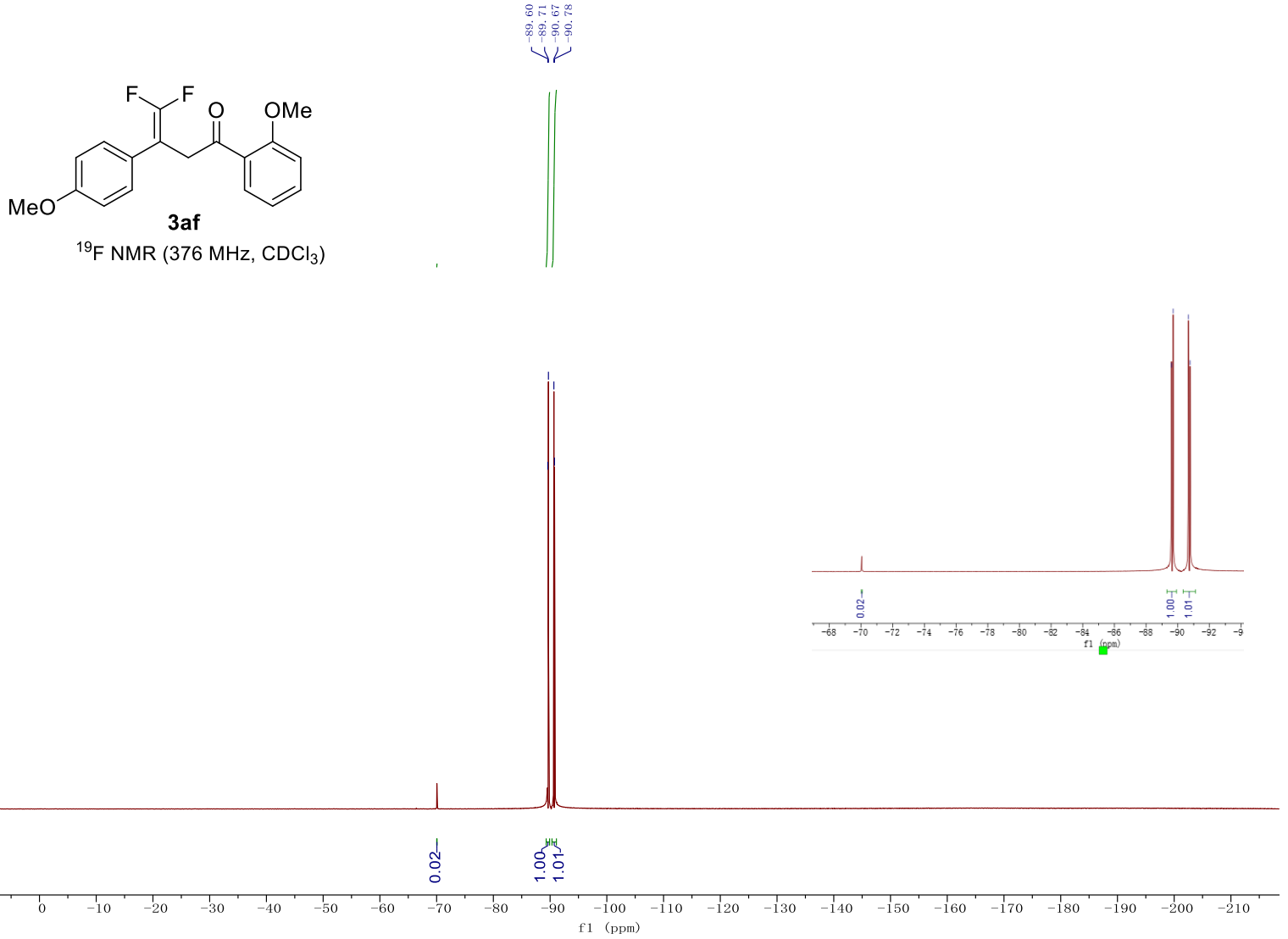
^{19}F NMR (376 MHz, $CDCl_3$)

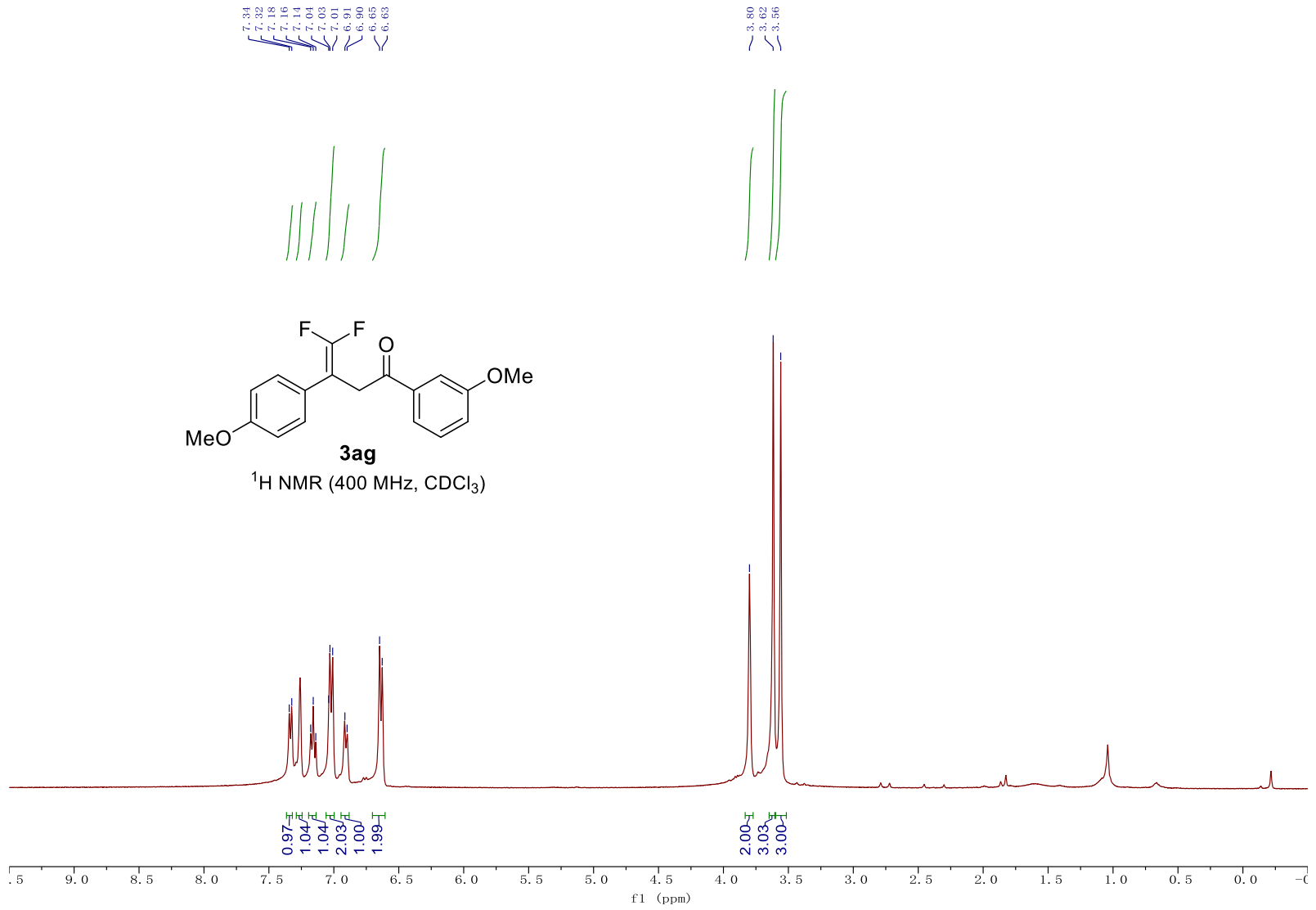


3af

^{1}H NMR (400 MHz, $CDCl_3$)

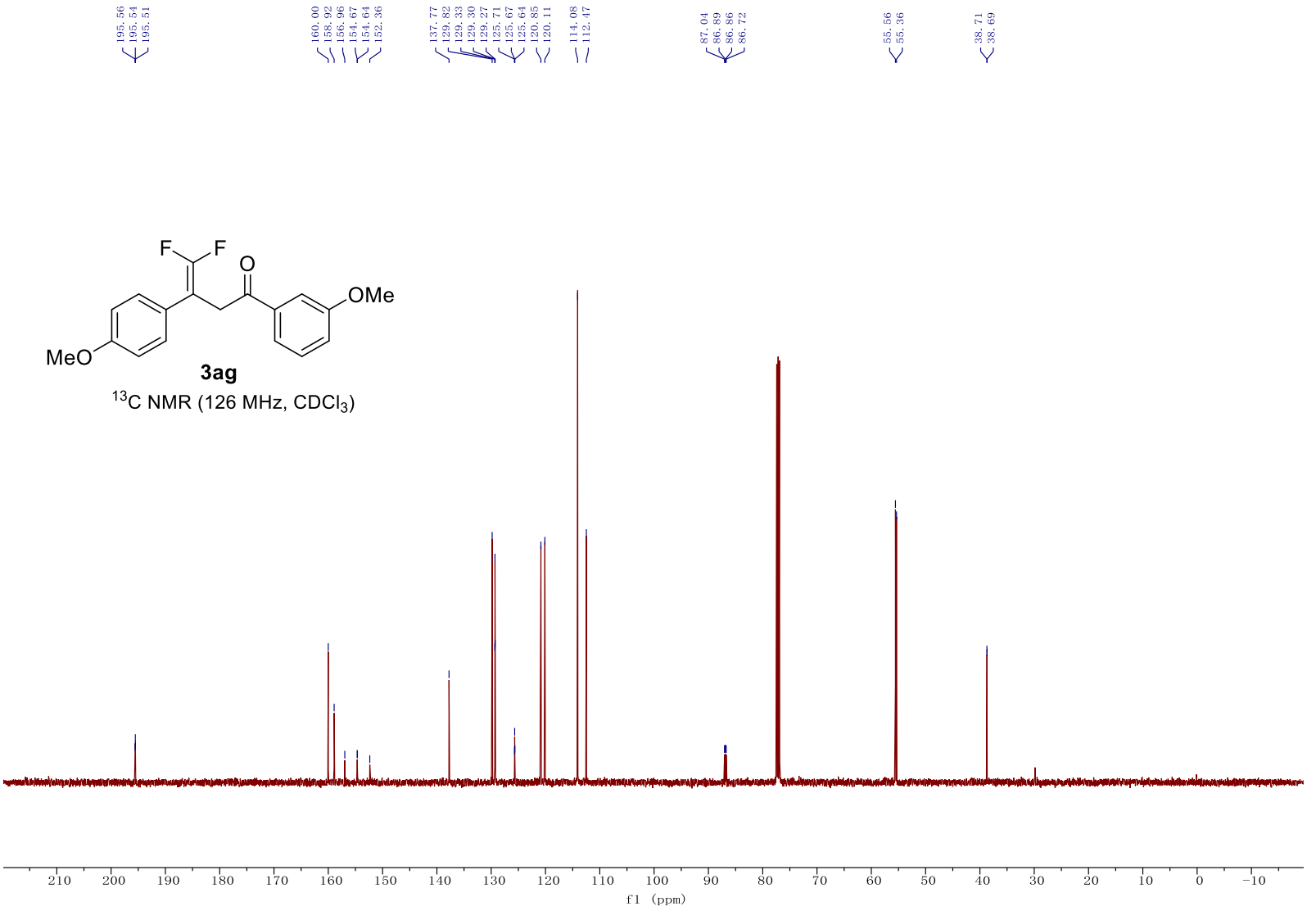

198.05
198.02
197.99
158.69
158.69
157.59
154.73
154.69
151.84
133.92
130.69
129.25
129.22
129.18
127.65
126.18
126.14
126.10
120.86
113.91
111.50
87.46
87.30
87.24
87.08
55.56
55.34
43.46
43.43
F
F
O
OMe
MeO
3af
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

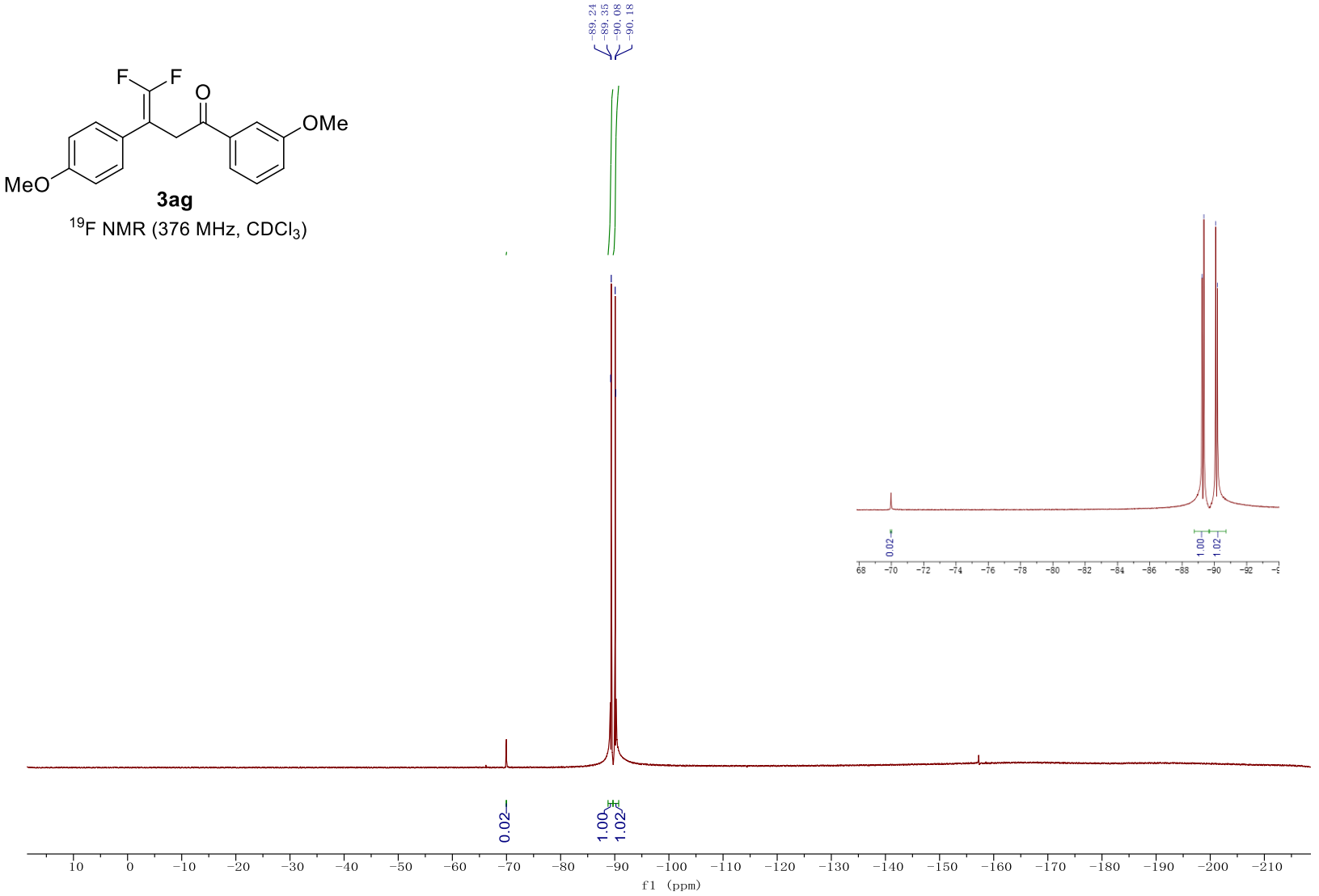

F
F
O
OMe
MeO
3af
^{19}F NMR (376 MHz, $CDCl_3$)
-89.60
-89.71
-90.67
-90.78
0.02
1.00
1.01
f1 (ppm)

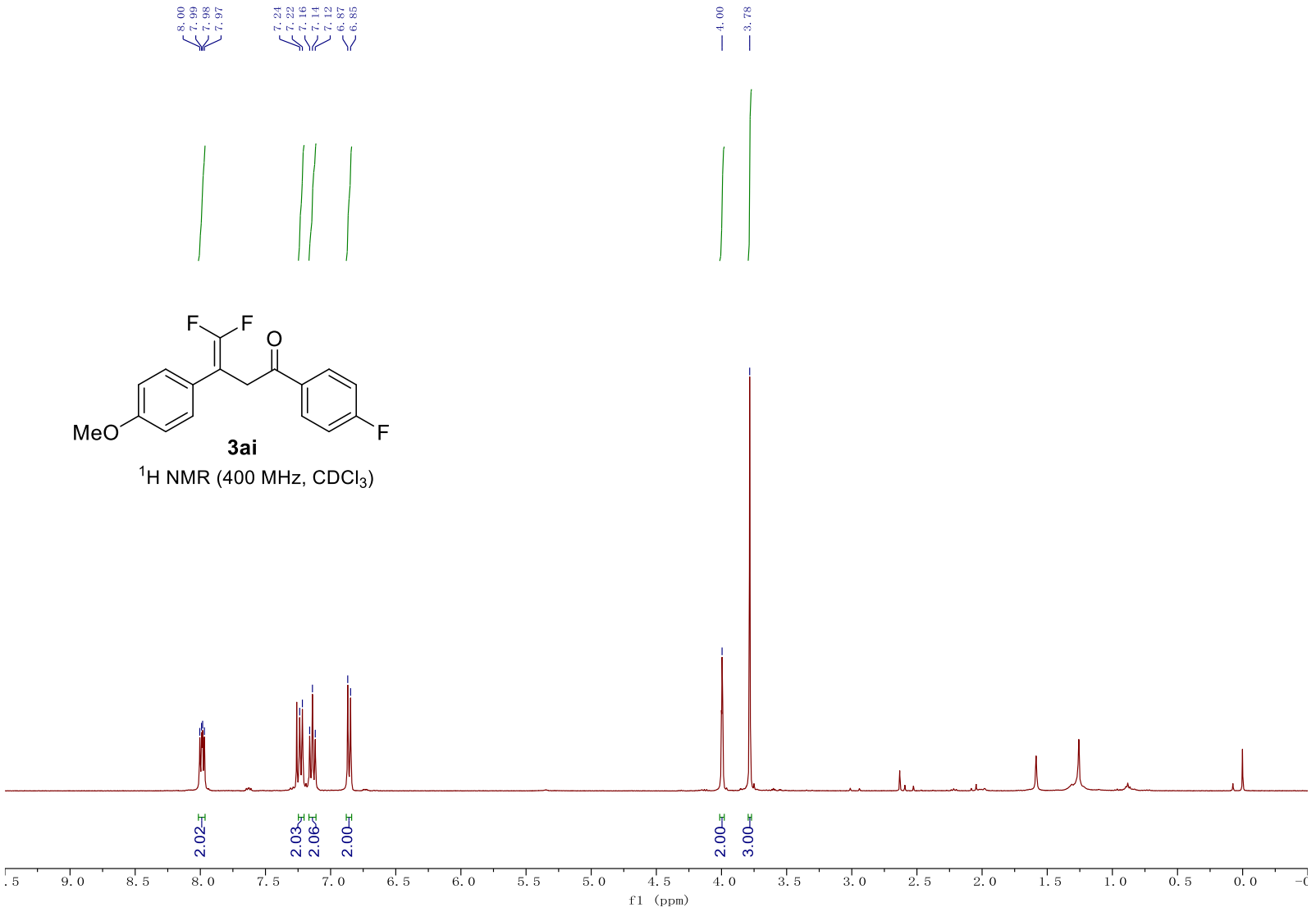


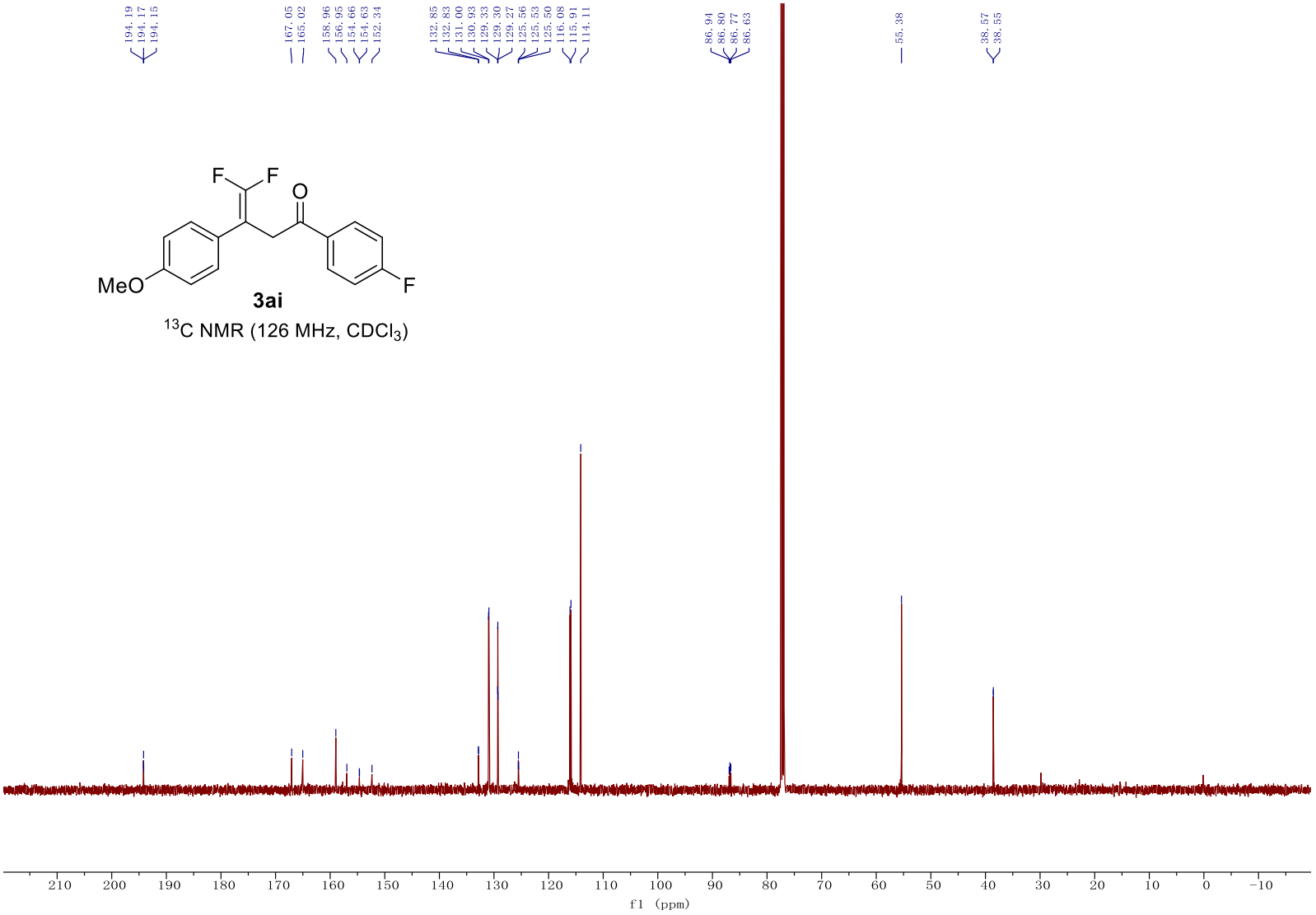
3ag

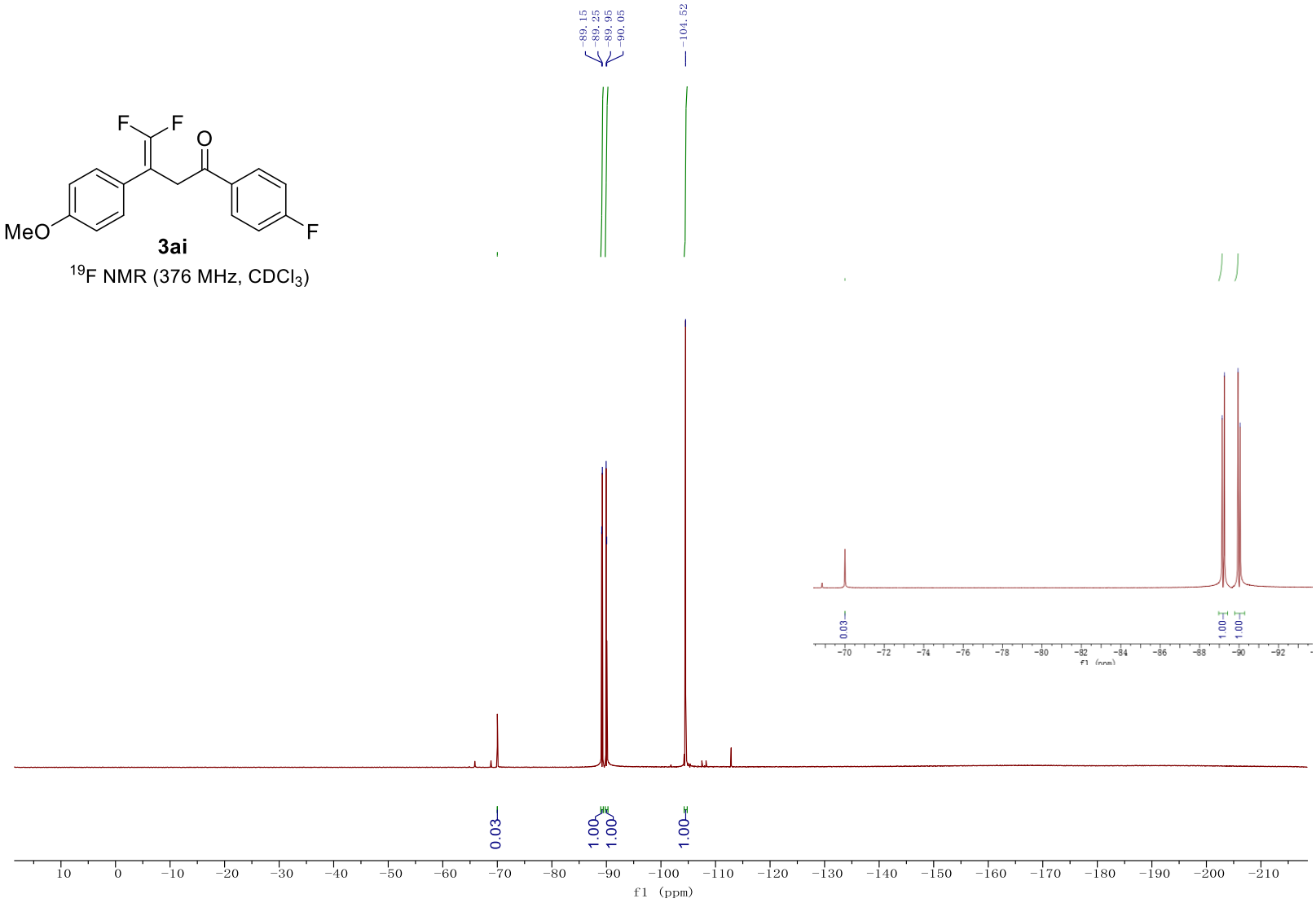
^{1}H NMR (400 MHz, $CDCl_3$)

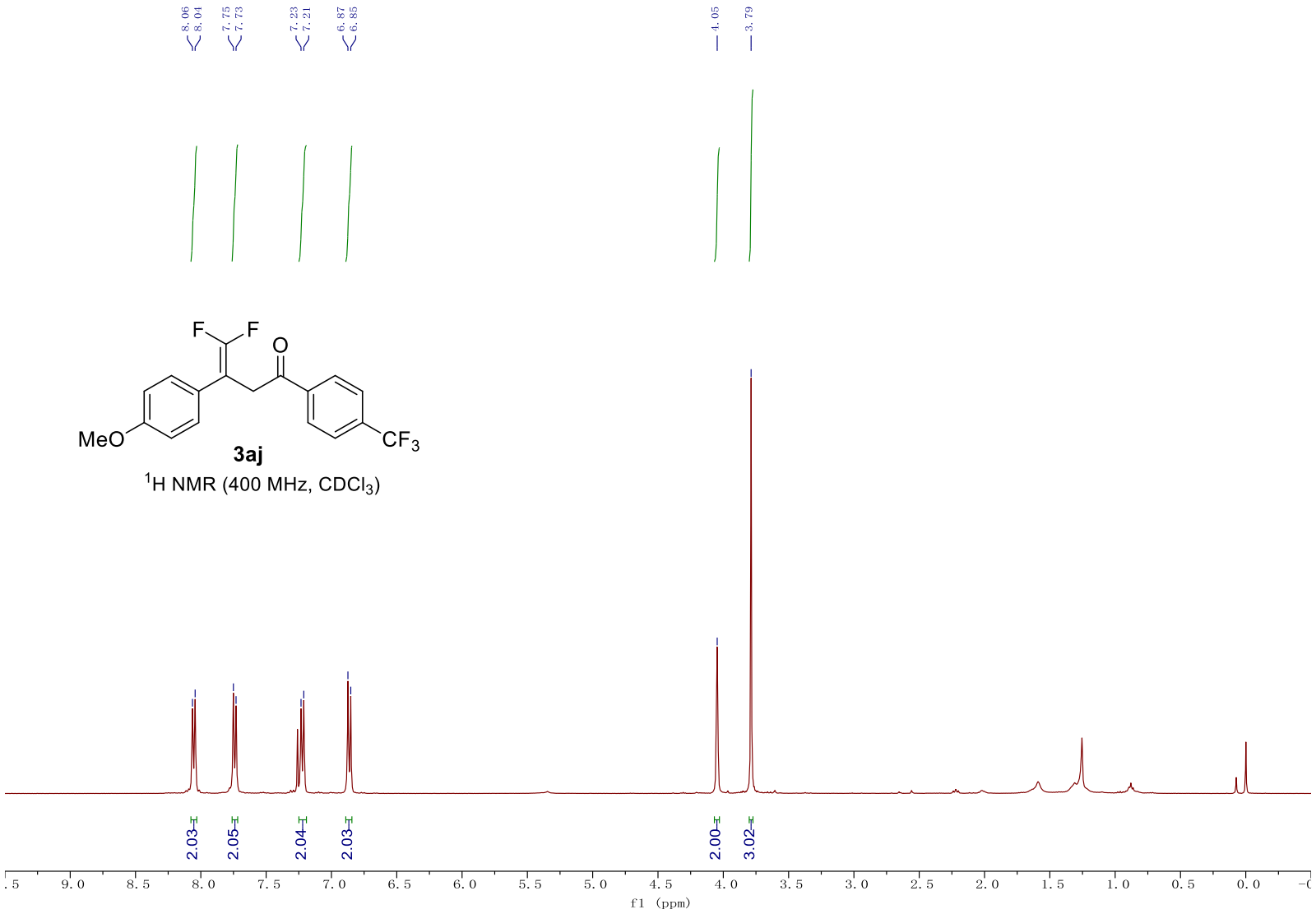

195.56
195.54
195.51
160.00
158.92
156.96
154.67
154.64
152.36
137.77
129.82
129.33
129.30
129.27
125.71
125.67
125.64
120.85
120.11
114.08
112.47
87.04
86.89
86.86
86.72
55.56
55.36
38.71
38.69
F
F
O
OMe
MeO
3ag
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

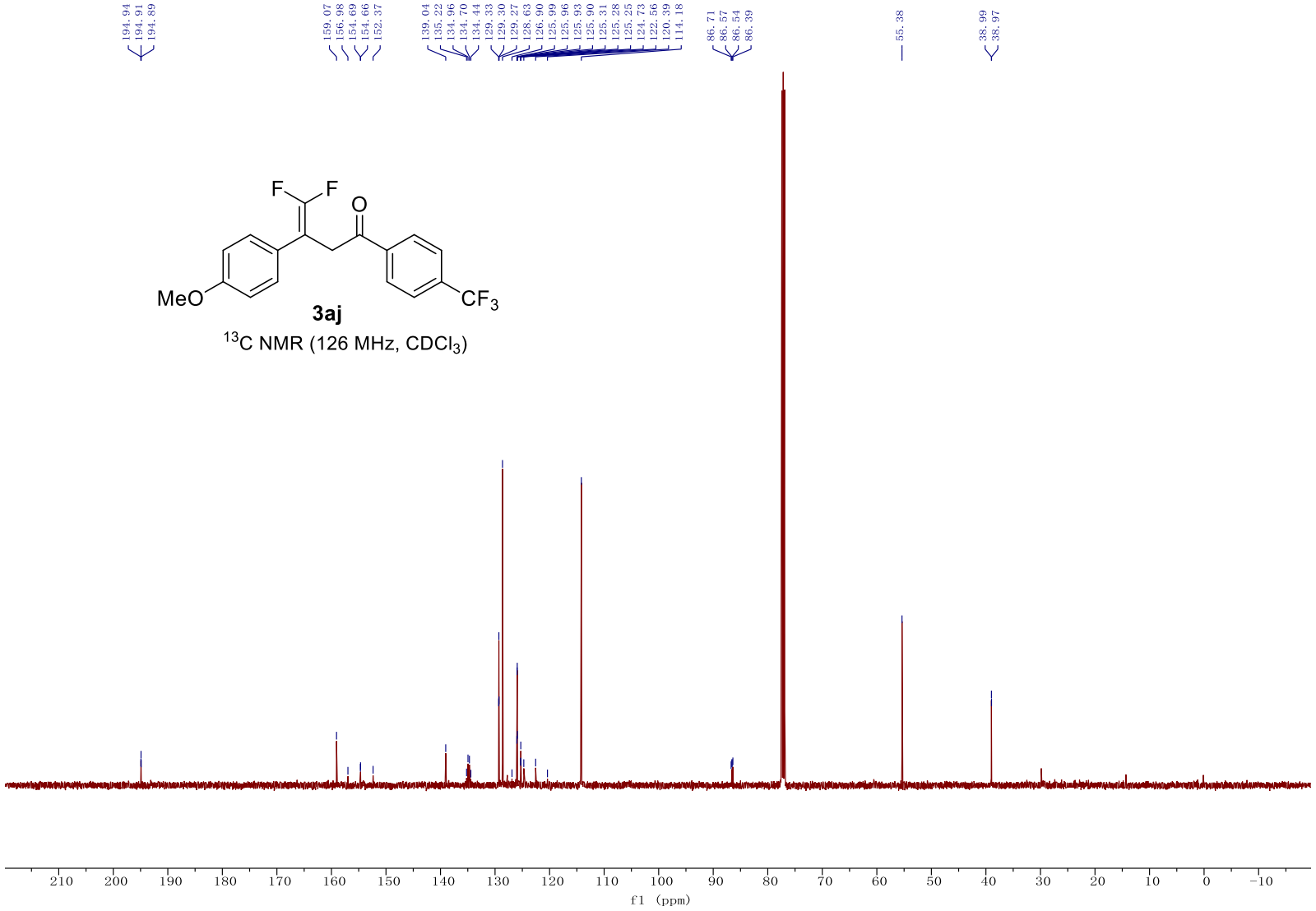

F
F
O
OMe
MeO
3ag
^{19}F NMR (376 MHz, $CDCl_3$)
-89.24
-89.35
-90.08
-90.18
0.02
1.00
1.02
f1 (ppm)

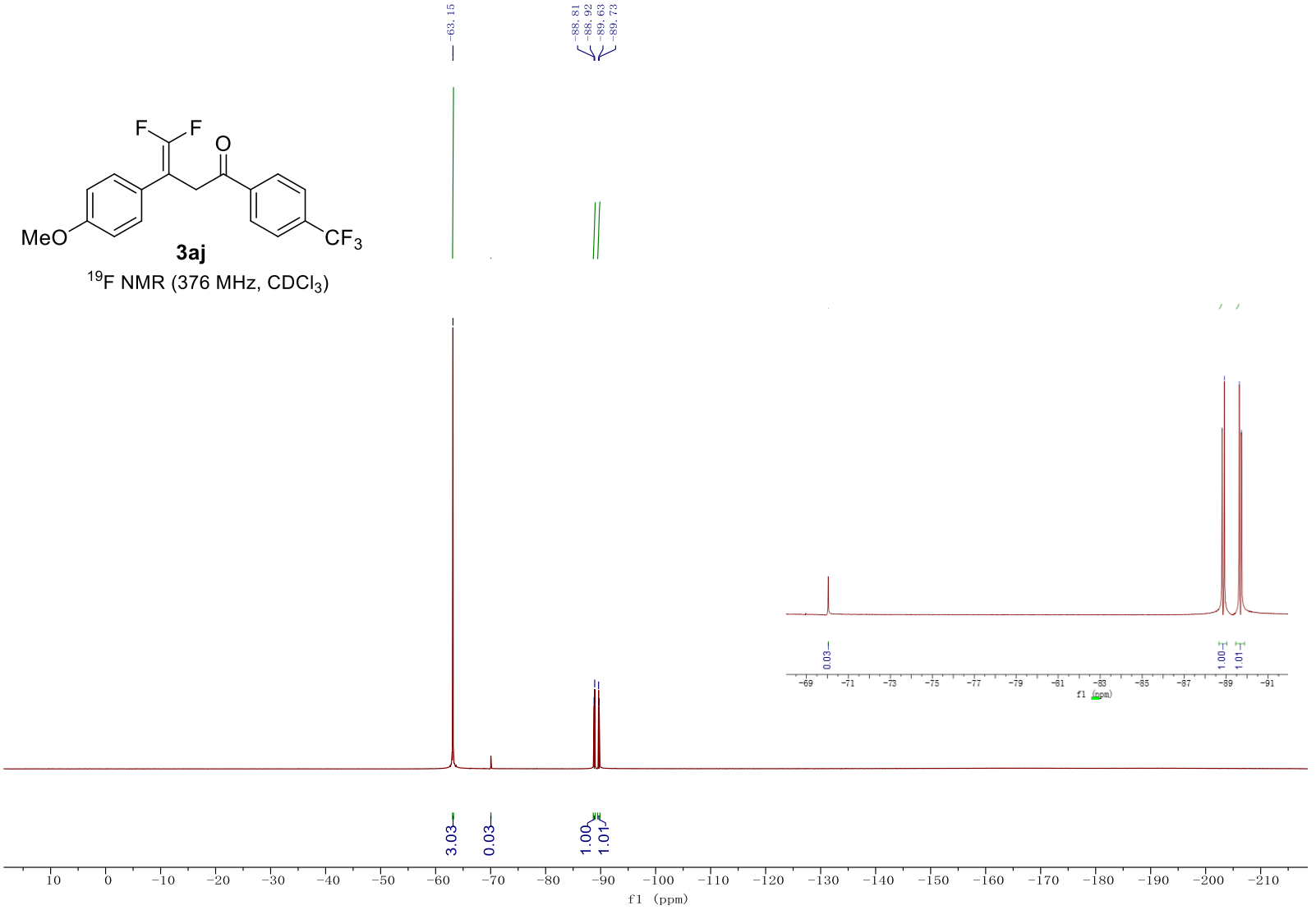

8.00
7.99
7.98
7.97
7.24
7.22
7.16
7.14
7.12
6.87
6.85
4.00
3.78
F
F
O
MeO
F
3ai
1H NMR (400 MHz, CDCl3)
2.02
2.03
2.06
2.00
2.00
3.00
f1 (ppm)

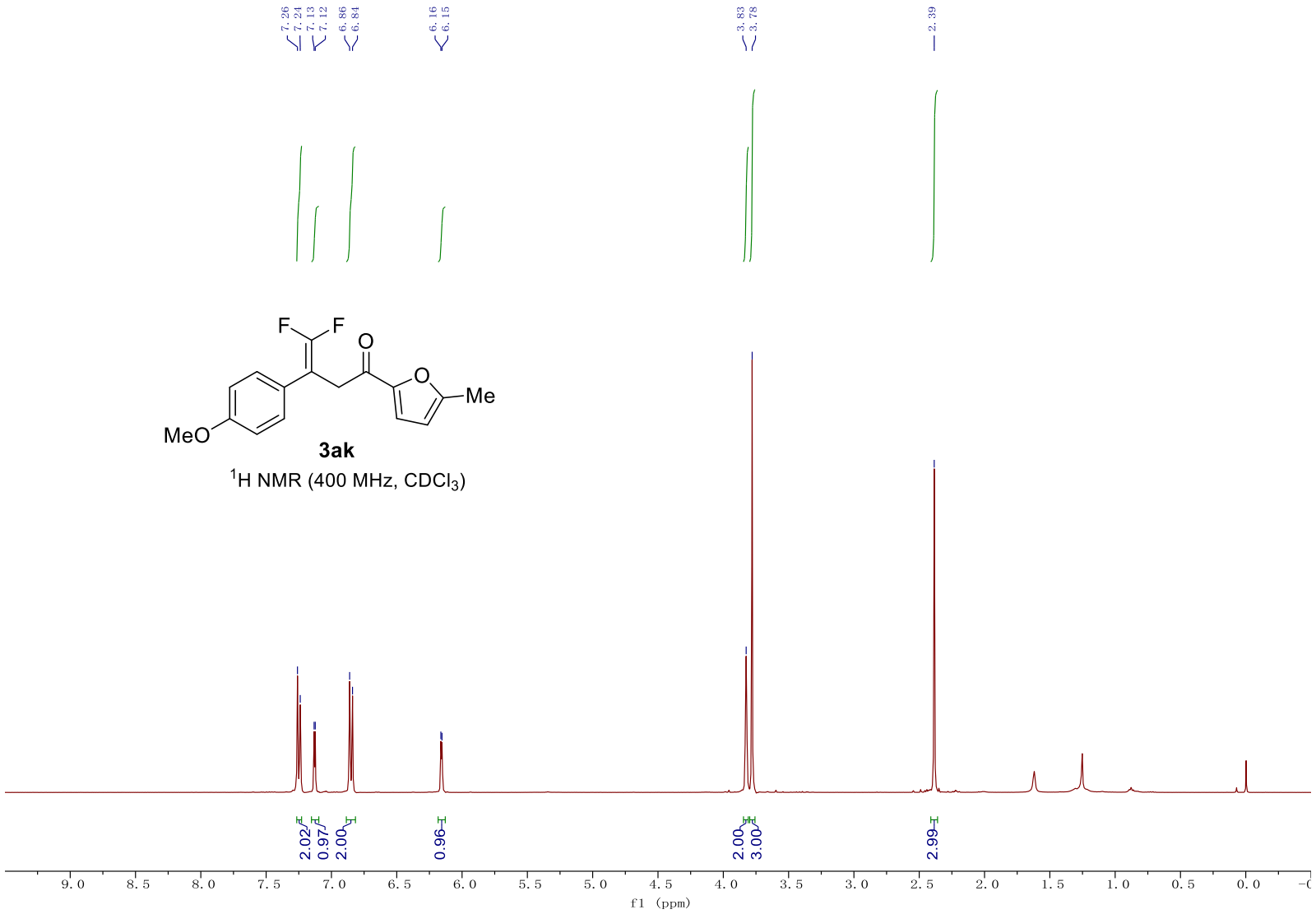

194.19
194.17
194.15
167.05
165.02
158.96
156.95
154.66
154.63
152.34
132.85
132.83
131.00
130.93
129.33
129.30
129.27
125.56
125.53
125.50
116.08
115.91
114.11
86.94
86.80
86.77
86.63
55.38
38.57
38.55
F
F
O
MeO
F
3ai
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
F
O
MeO
F
3ai
19F NMR (376 MHz, CDCl3)
-89.15
-89.25
-89.95
-90.05
-104.52
0.03
1.00
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)


8.06
8.04
7.75
7.73
7.23
7.21
6.87
6.85
4.05
3.79
F
F
O
MeO
CF3
3aj
1H NMR (400 MHz, CDCl3)
2.03
2.05
2.04
2.03
2.00
3.02
f1 (ppm)

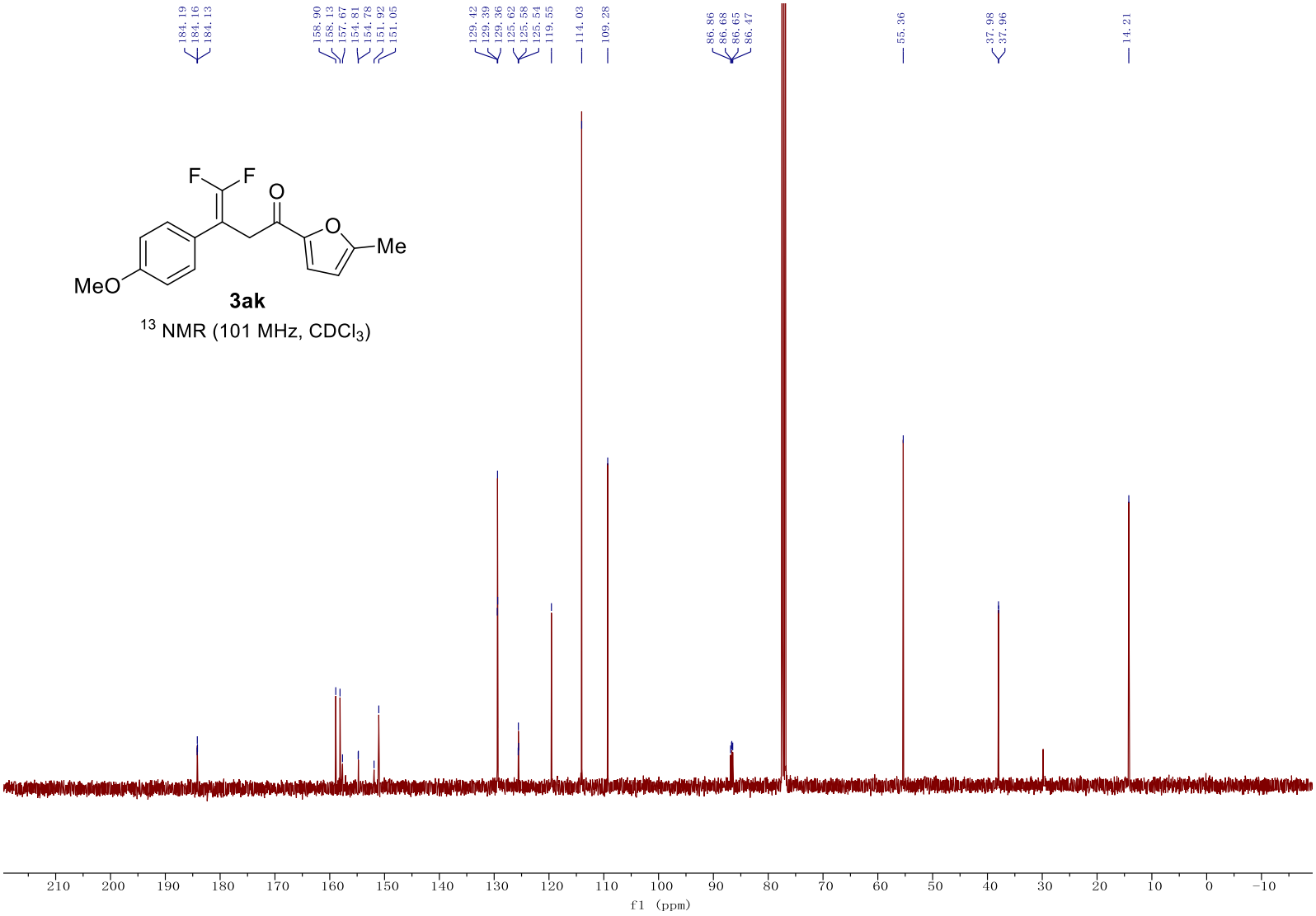

194.94
194.91
194.89
159.07
156.98
154.69
154.66
152.37
139.04
135.22
134.96
134.70
134.44
129.33
129.30
129.27
128.63
126.90
125.99
125.96
125.93
125.90
125.31
125.28
125.25
124.73
122.56
120.39
114.18
86.71
86.57
86.54
86.39
55.38
38.99
38.97
F
F
O
MeO
CF3
3aj
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

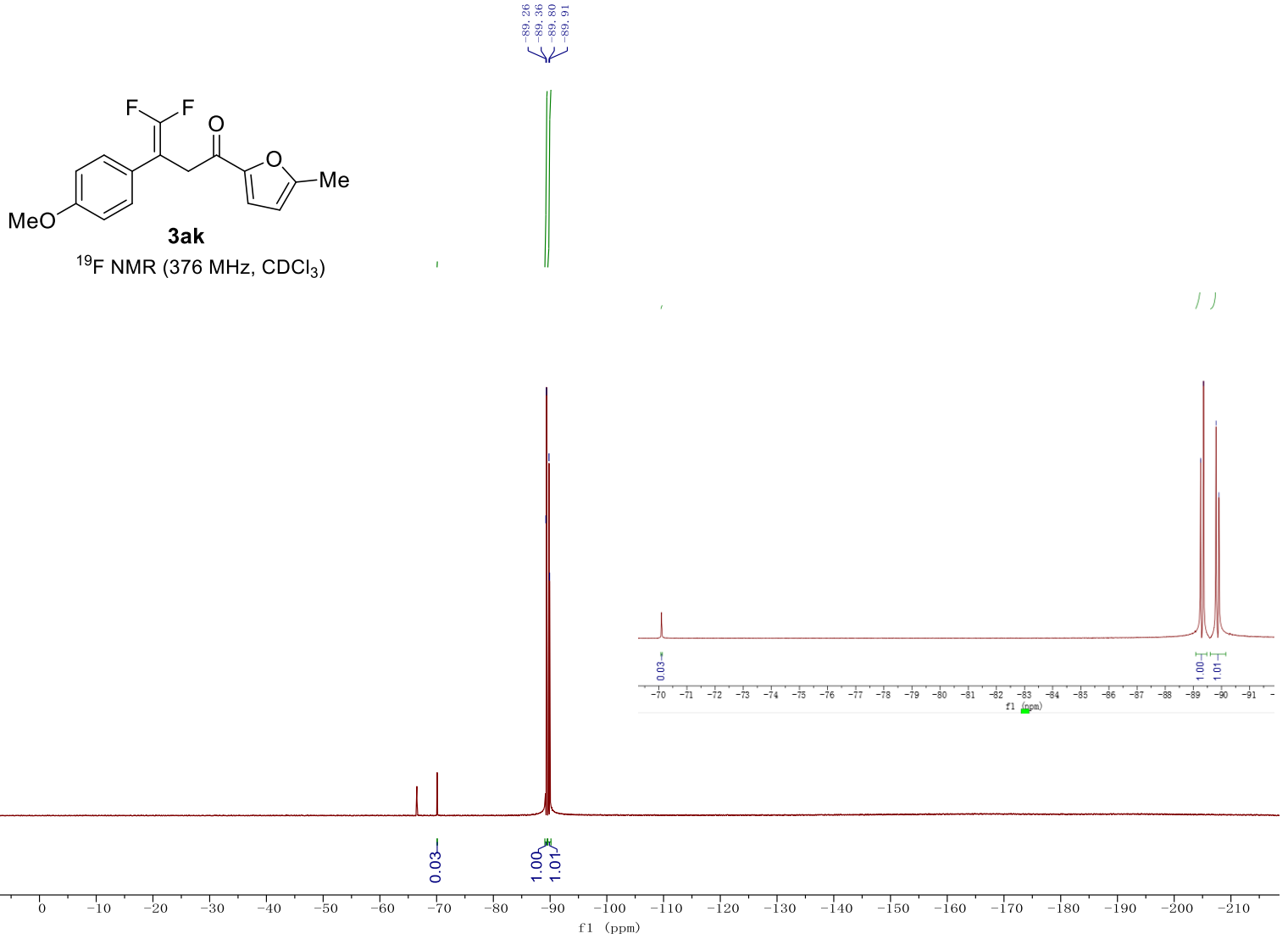

F
F
O
MeO
CF3
3aj
19F NMR (376 MHz, CDCl3)
-63.15
-88.81
-88.92
-89.63
-89.73
3.03
0.03
1.00
1.01
f1 (ppm)



3ak

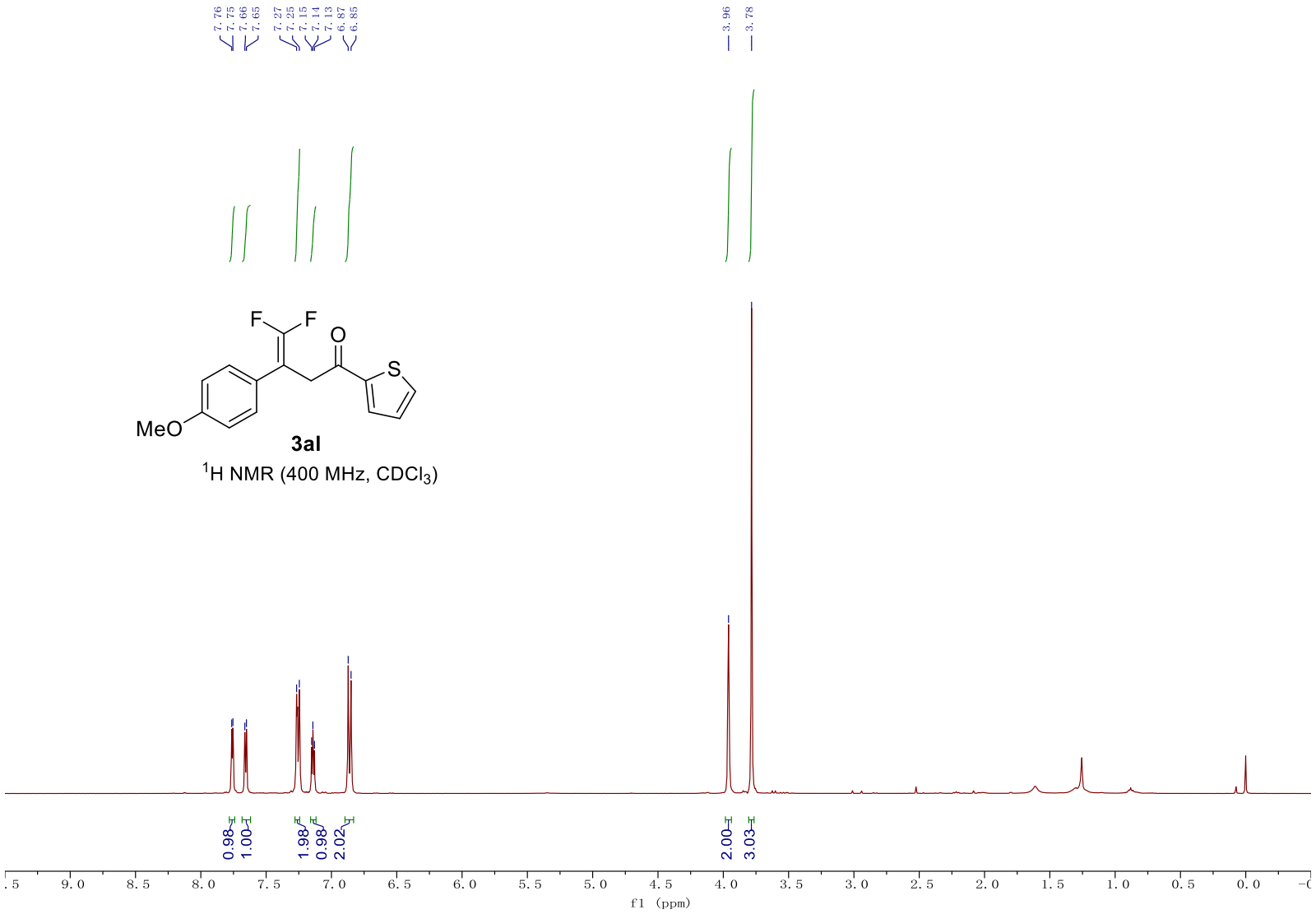
^{1}H NMR (400 MHz, $CDCl_3$)


184.19
184.16
184.13
158.90
158.13
157.67
154.81
154.78
151.92
151.05
129.42
129.39
129.36
125.62
125.58
125.54
119.55
114.03
109.28
86.86
86.68
86.65
86.47
55.36
37.98
37.96
14.21
F
F
O
O
Me
MeO
3ak
13 NMR (101 MHz, CDCl3)
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)



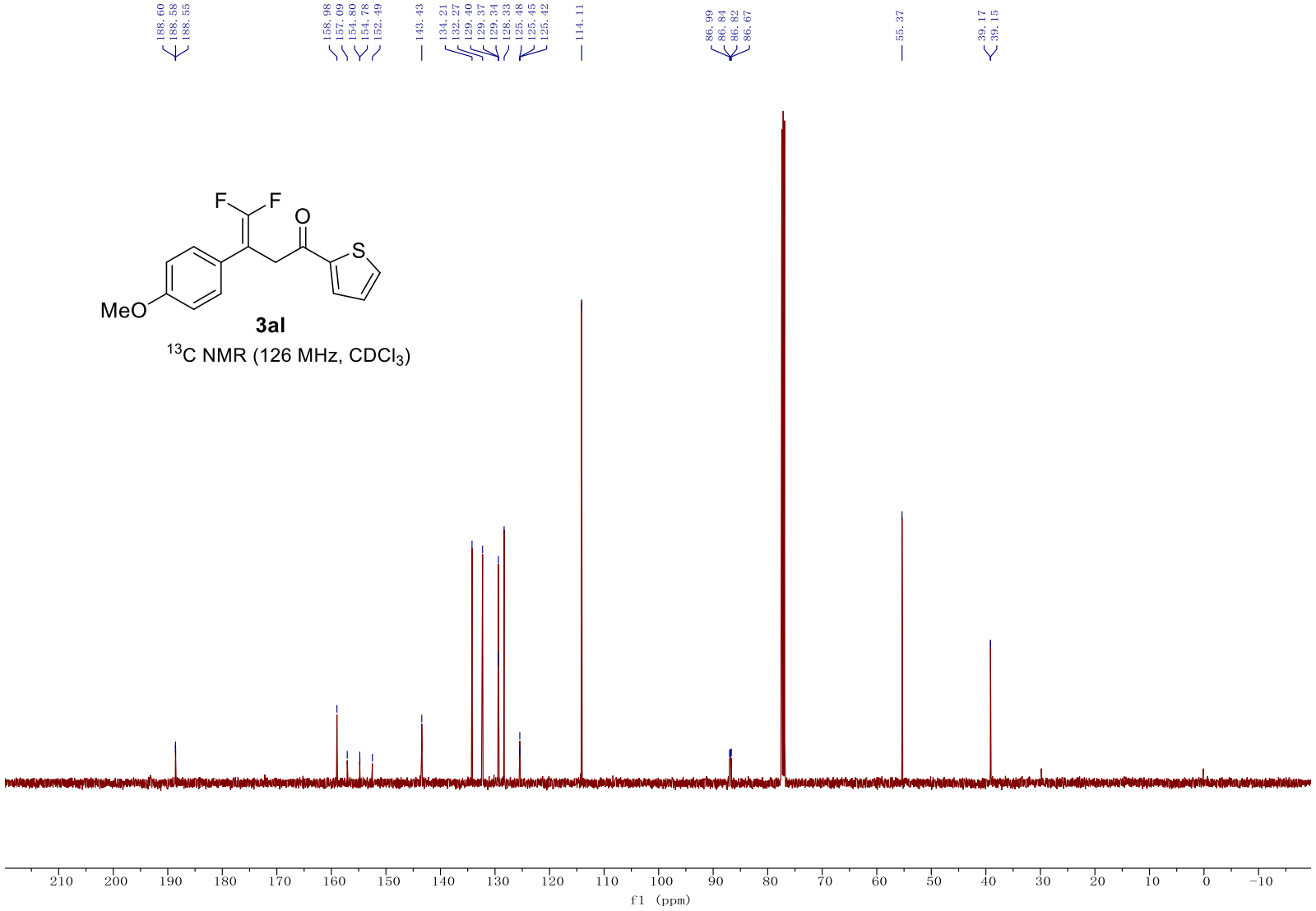
3ak

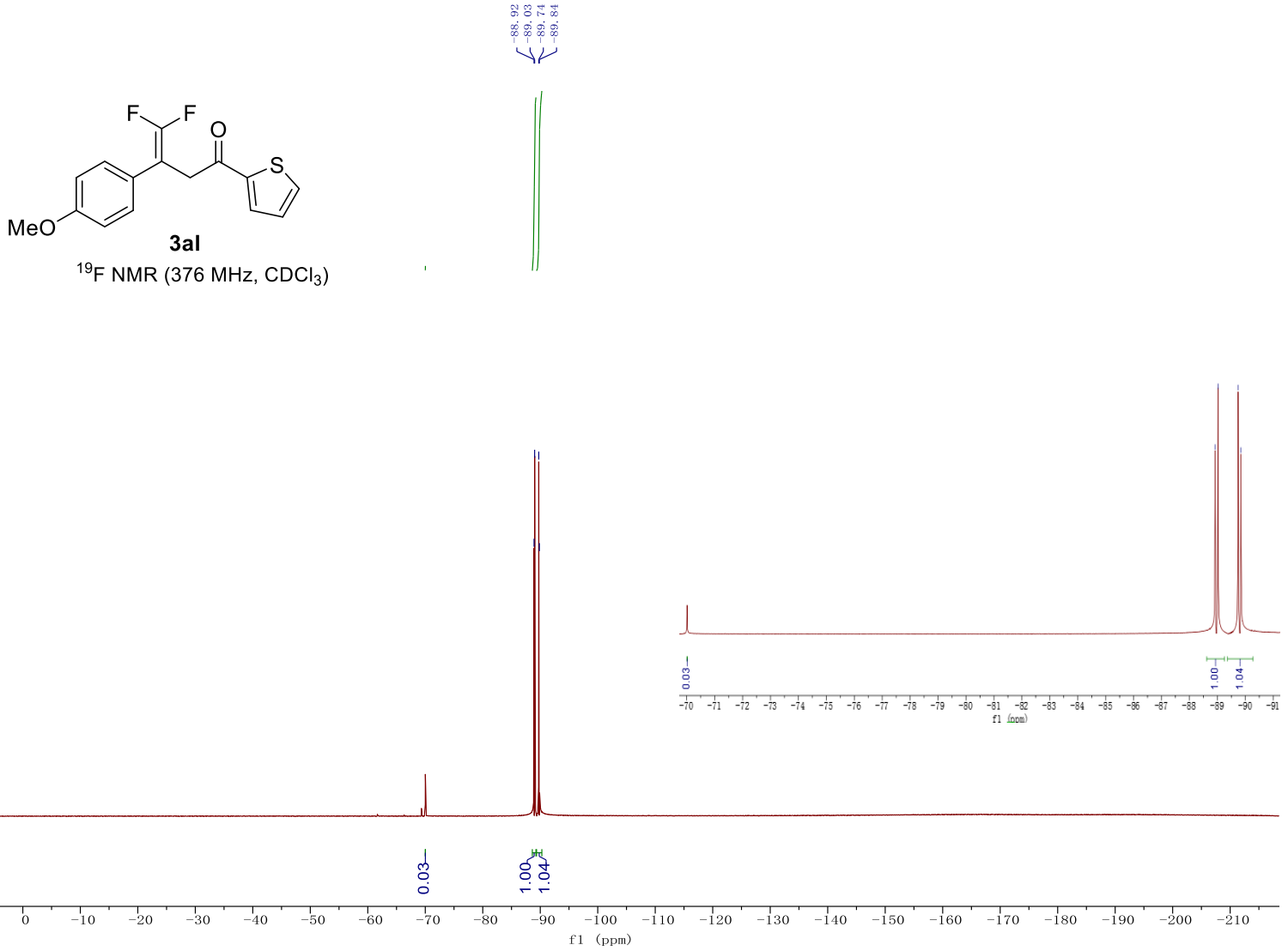
^{19}F NMR (376 MHz, $CDCl_3$)



3al

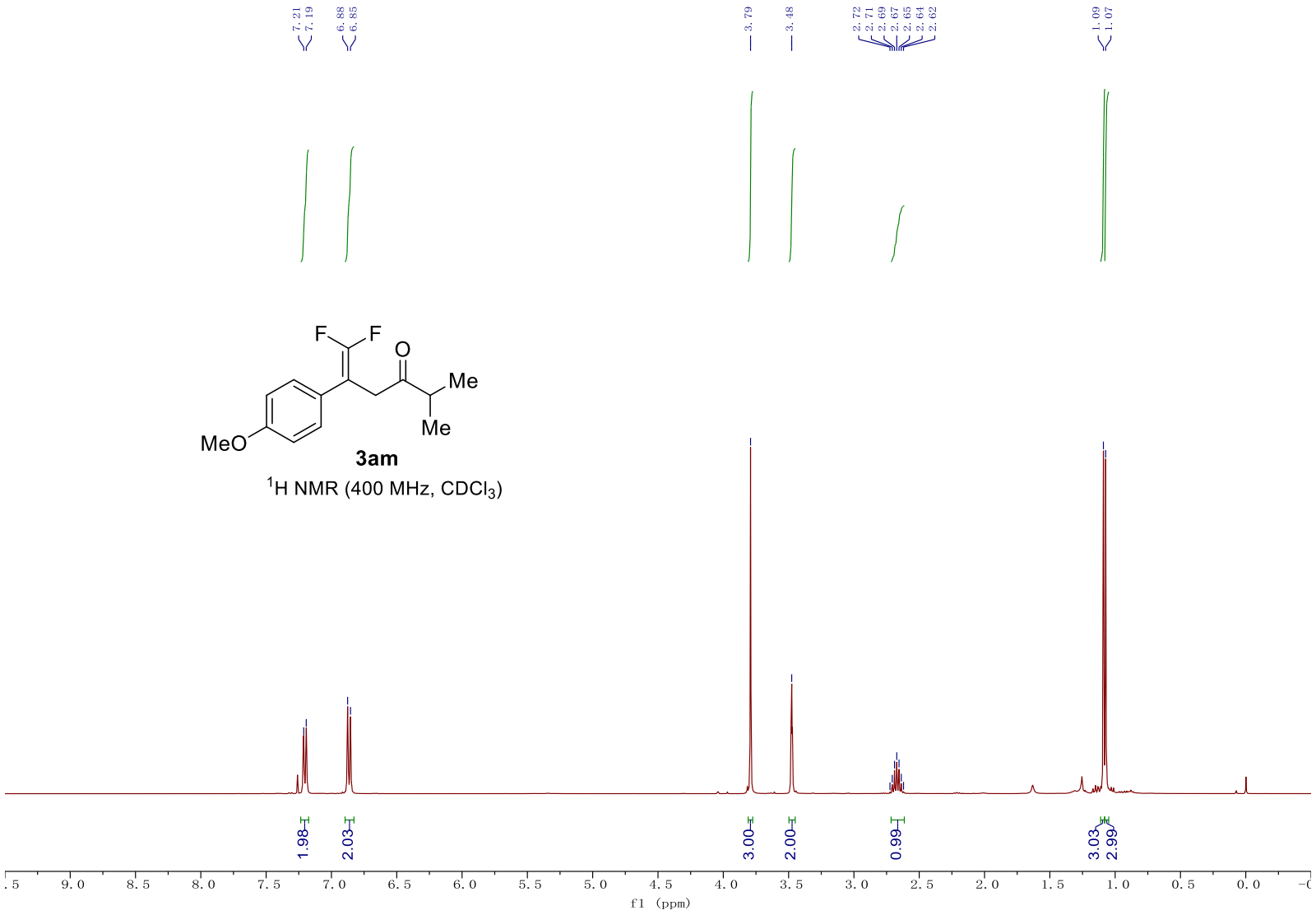
^{1}H NMR (400 MHz, $CDCl_3$)


188.60
188.58
188.55
158.98
157.09
154.80
154.78
152.49
143.43
134.21
132.27
129.40
129.37
129.34
128.33
125.48
125.45
125.42
114.11
86.99
86.84
86.82
86.67
55.37
39.17
39.15
F
F
O
S
MeO
3al
^{13}C NMR (126 MHz, CDCl$_3$)
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)



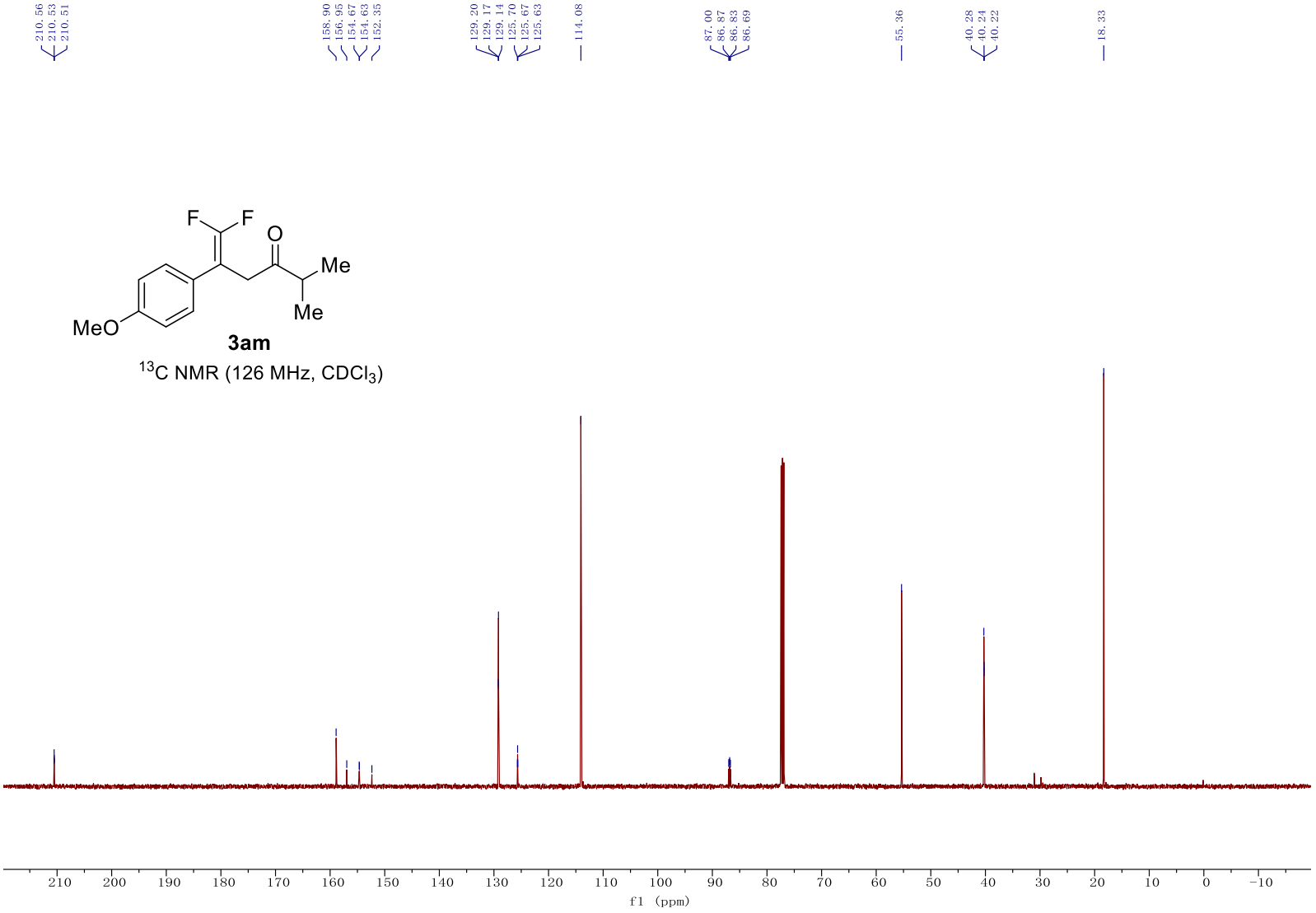
3al

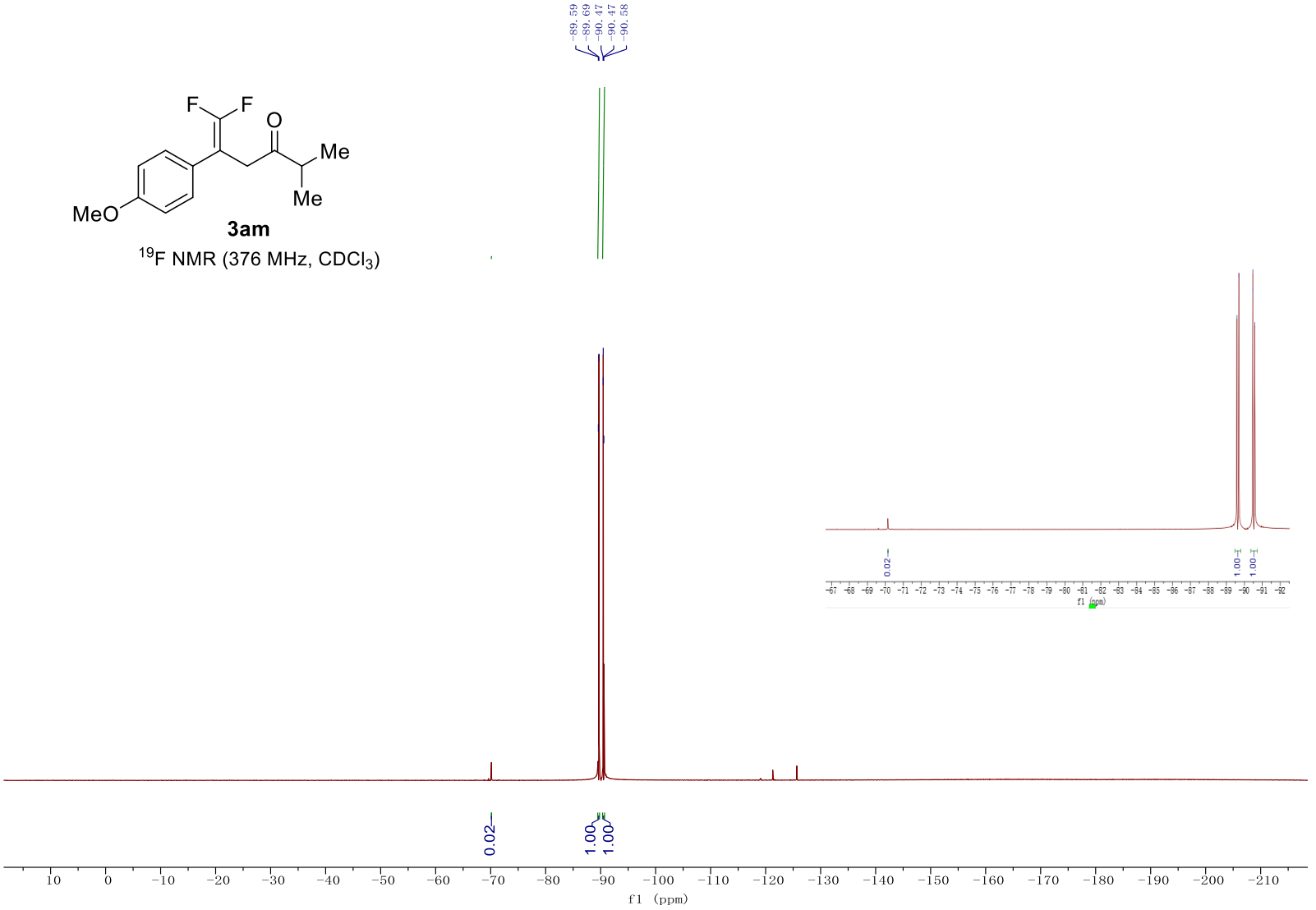
^{19}F NMR (376 MHz, $CDCl_3$)



3am

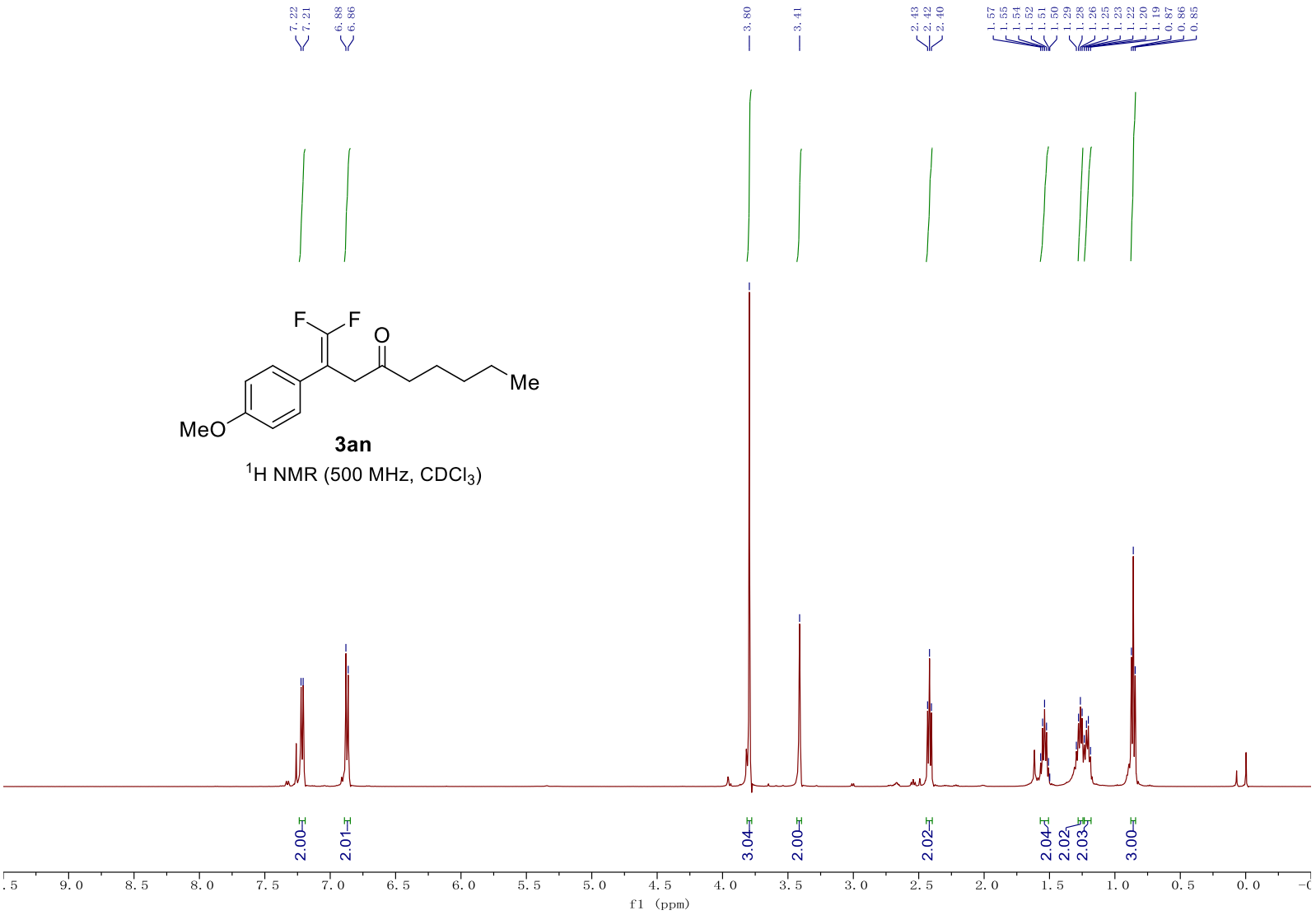
^{1}H NMR (400 MHz, $CDCl_3$)


210.56
210.53
210.51
158.90
156.95
154.67
154.63
152.35
129.20
129.17
129.14
125.70
125.67
125.63
114.08
87.00
86.87
86.83
86.69
55.36
40.28
40.24
40.22
18.33
F
F
O
Me
Me
MeO
3am
13C NMR (126 MHz, CDCl3)
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)



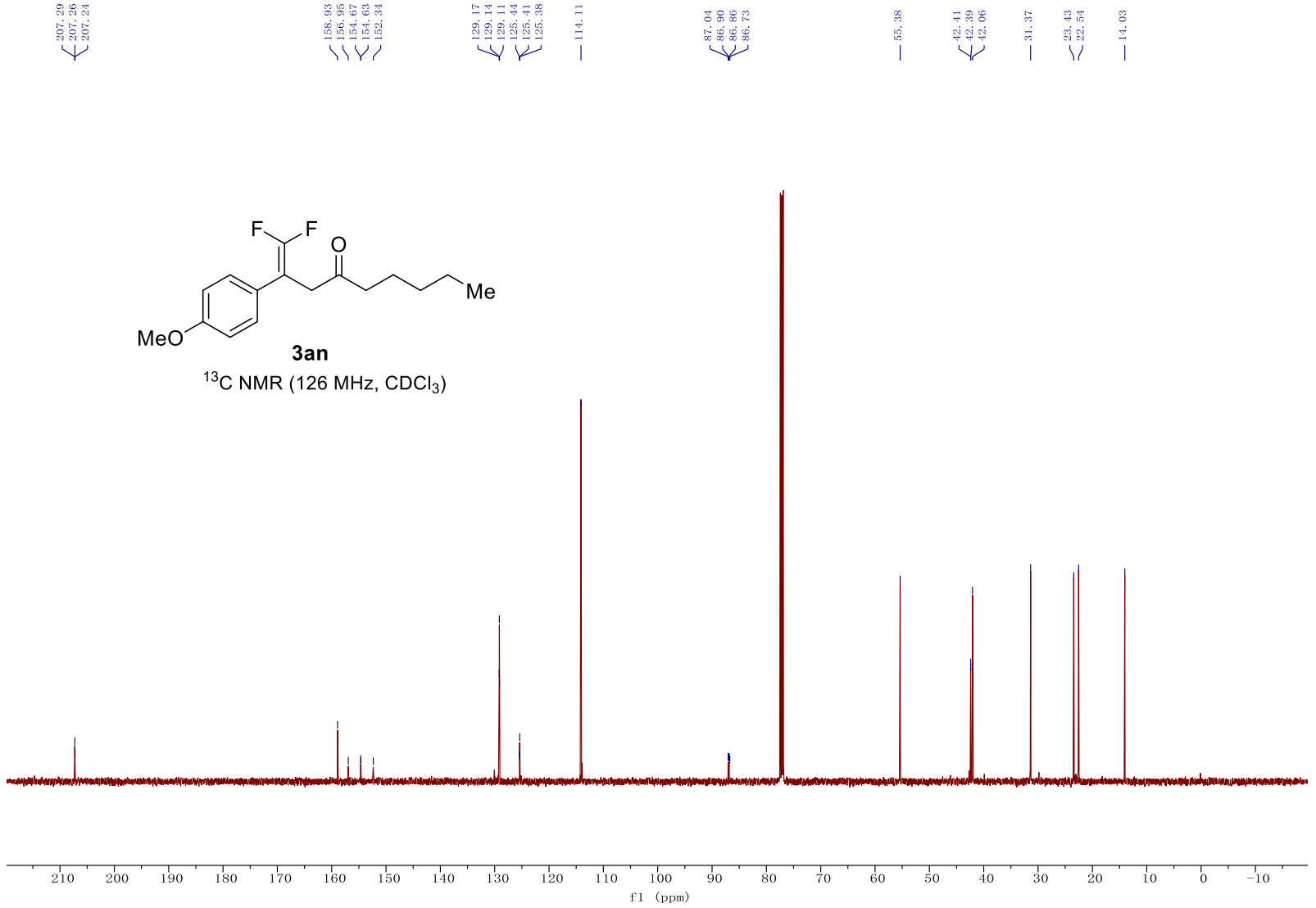
3am

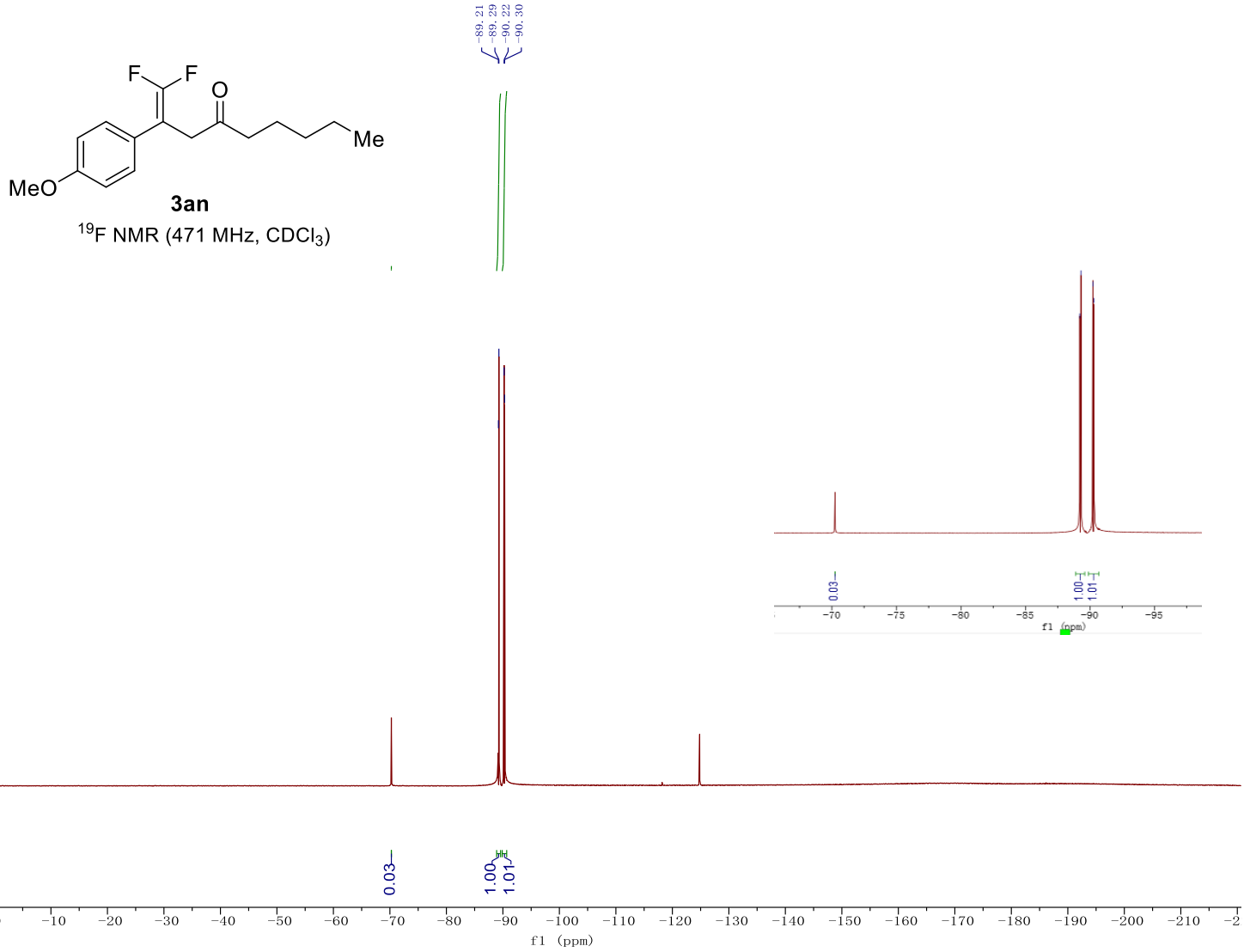
^{19}F NMR (376 MHz, $CDCl_3$)



3an

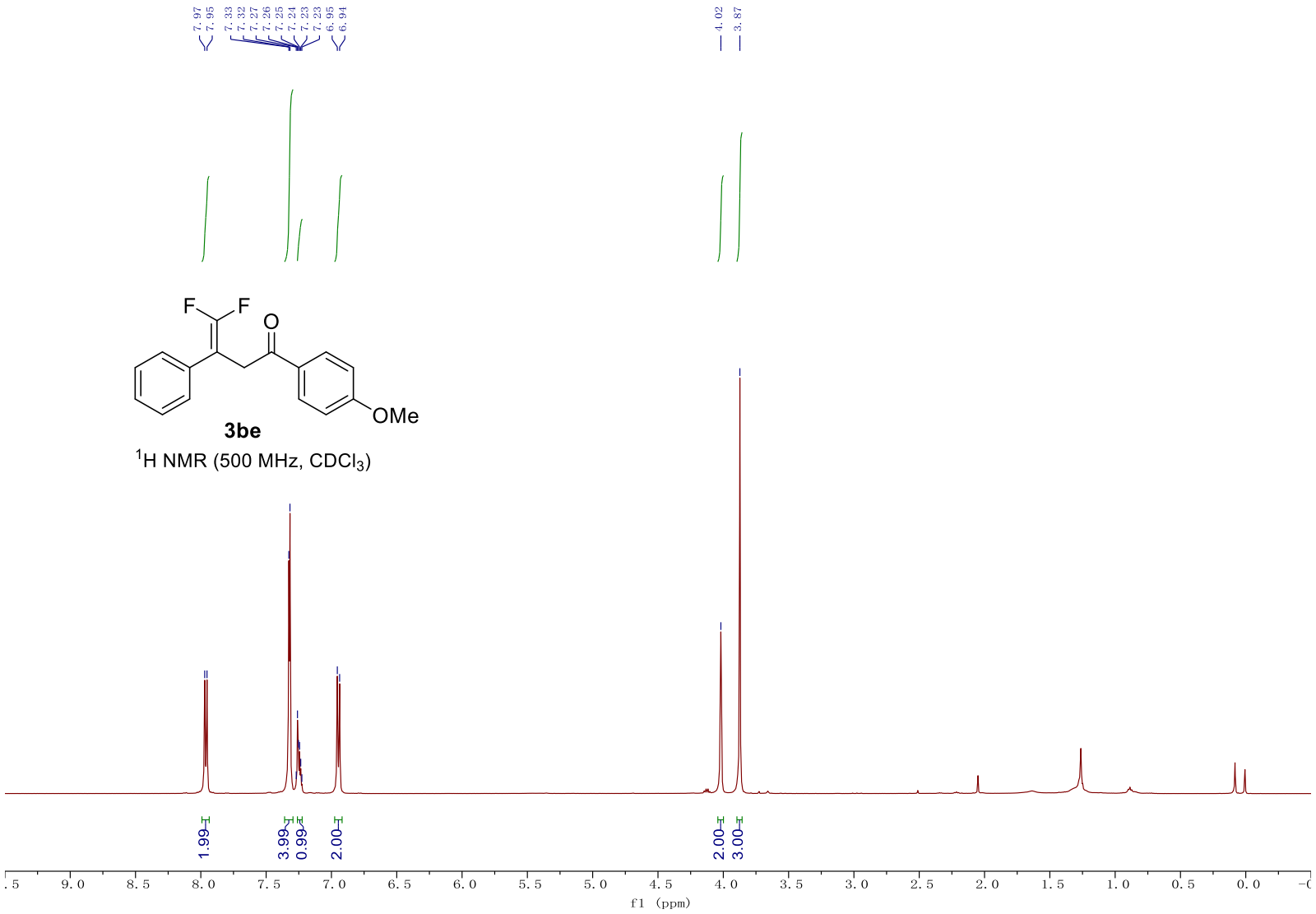
^{1}H NMR (500 MHz, $CDCl_3$)

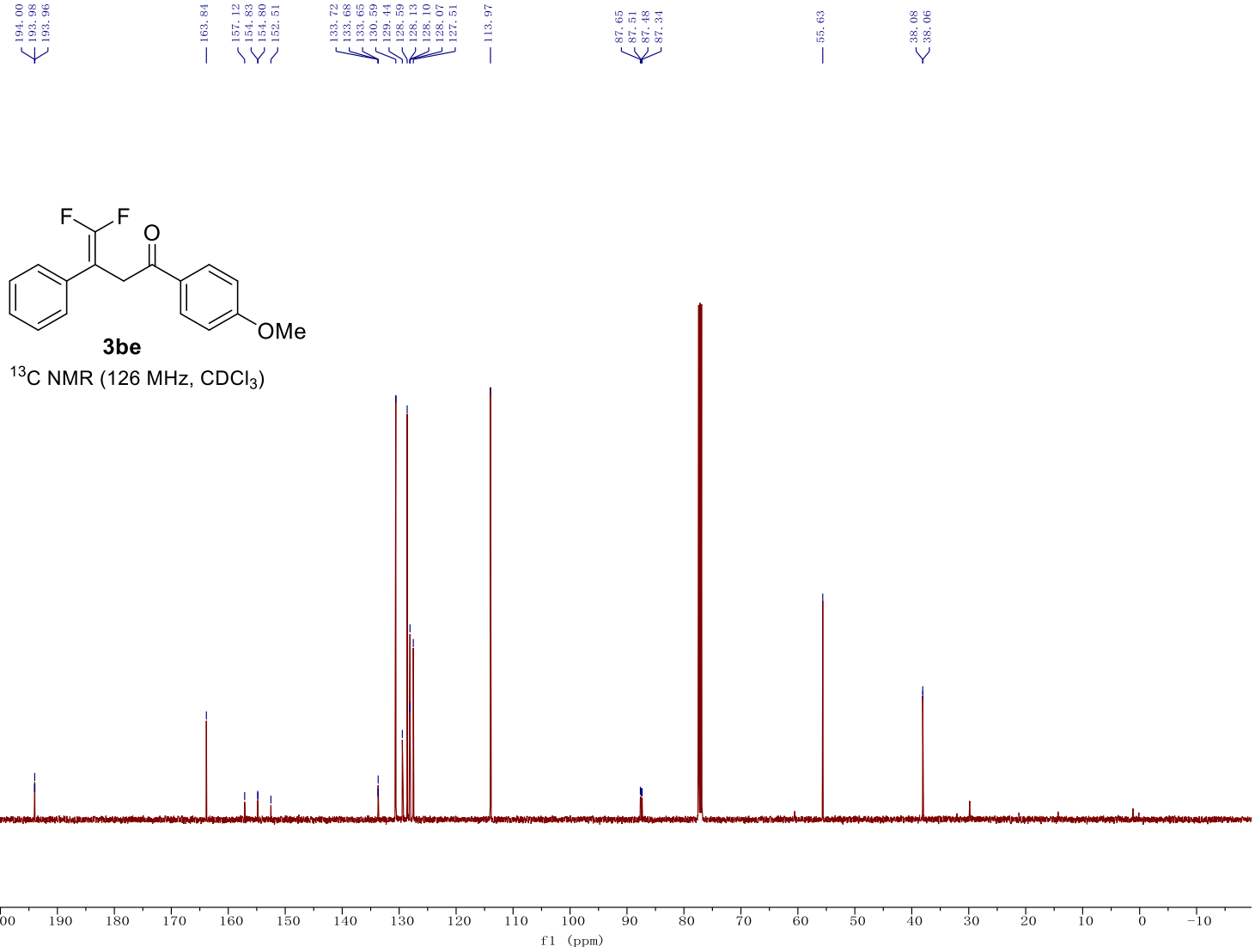

207.29
207.26
207.24
158.93
156.95
154.67
154.63
152.34
129.17
129.14
129.11
125.44
125.41
125.38
114.11
87.04
86.90
86.86
86.73
55.38
42.41
42.39
42.06
31.37
23.43
22.54
14.03
F
F
O
Me
MeO
3an
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

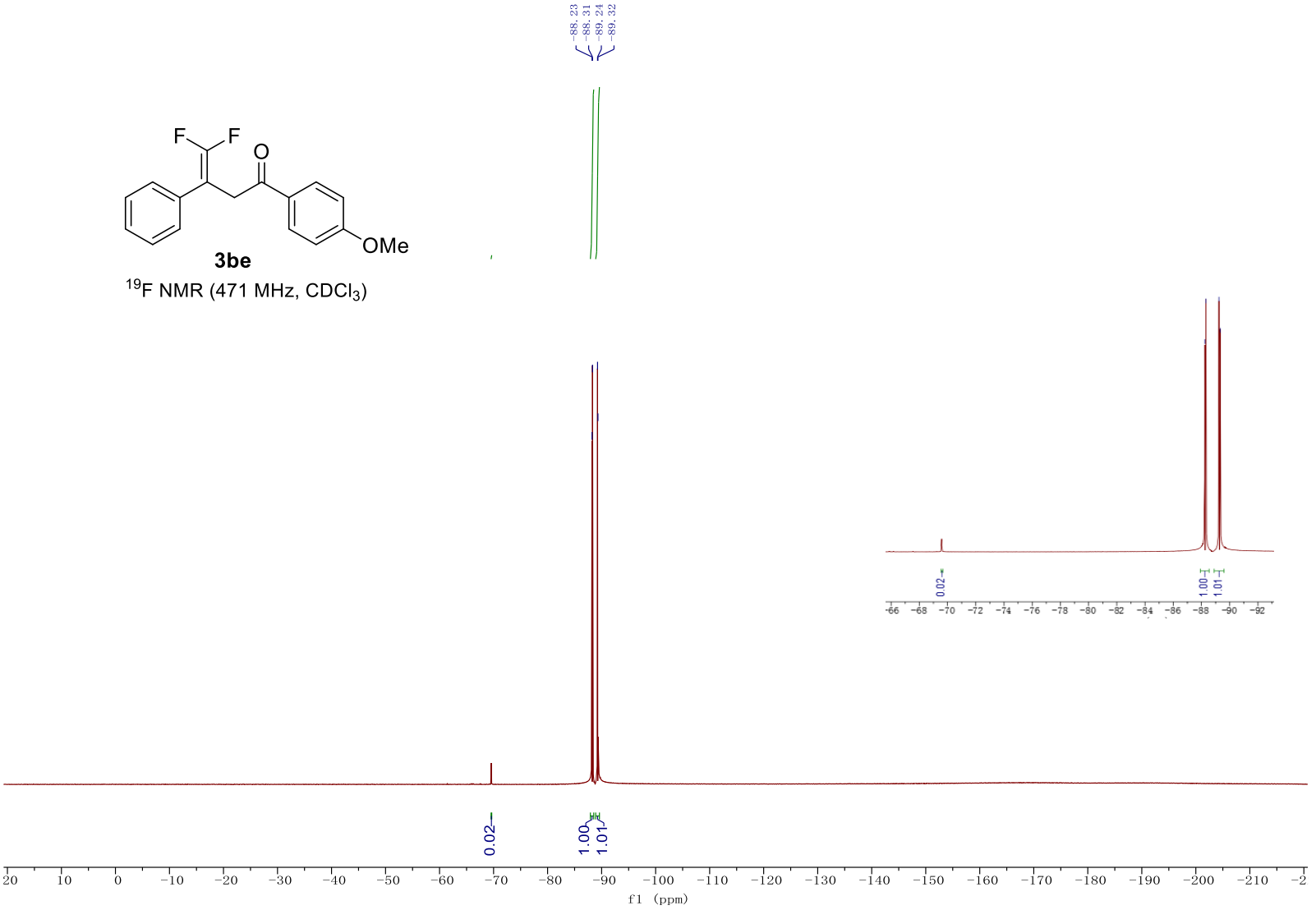


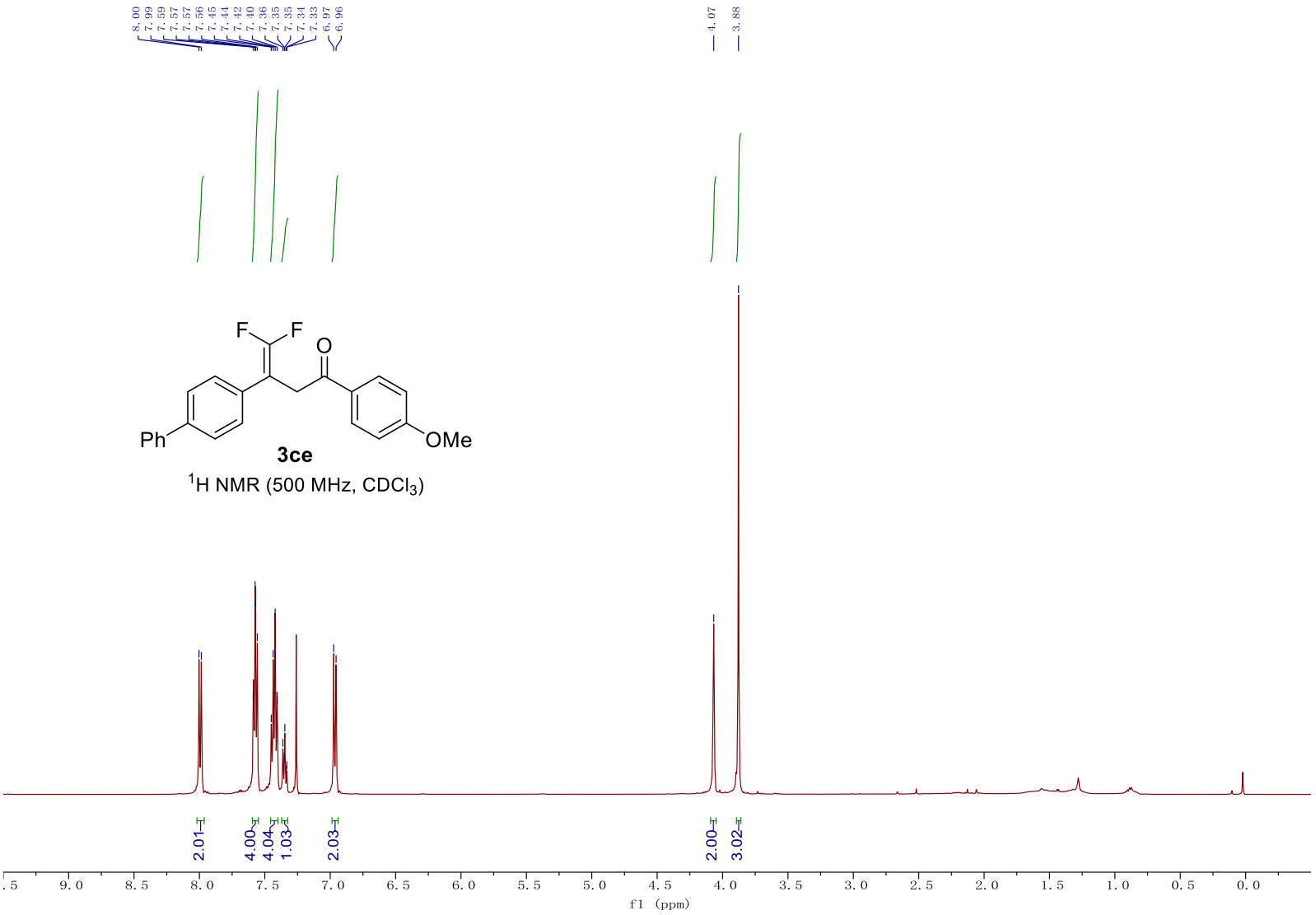
3an

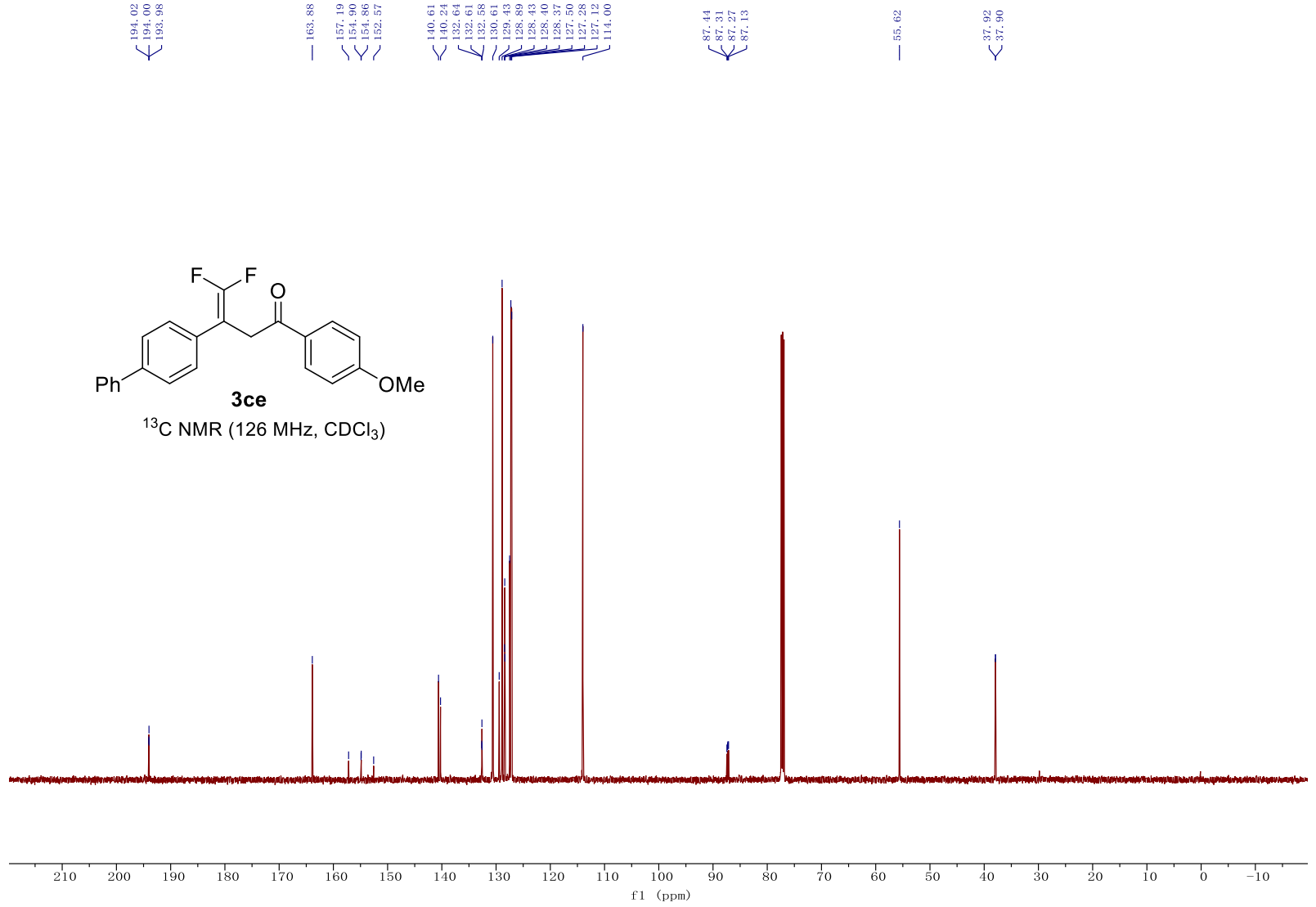
^{19}F NMR (471 MHz, $CDCl_3$)

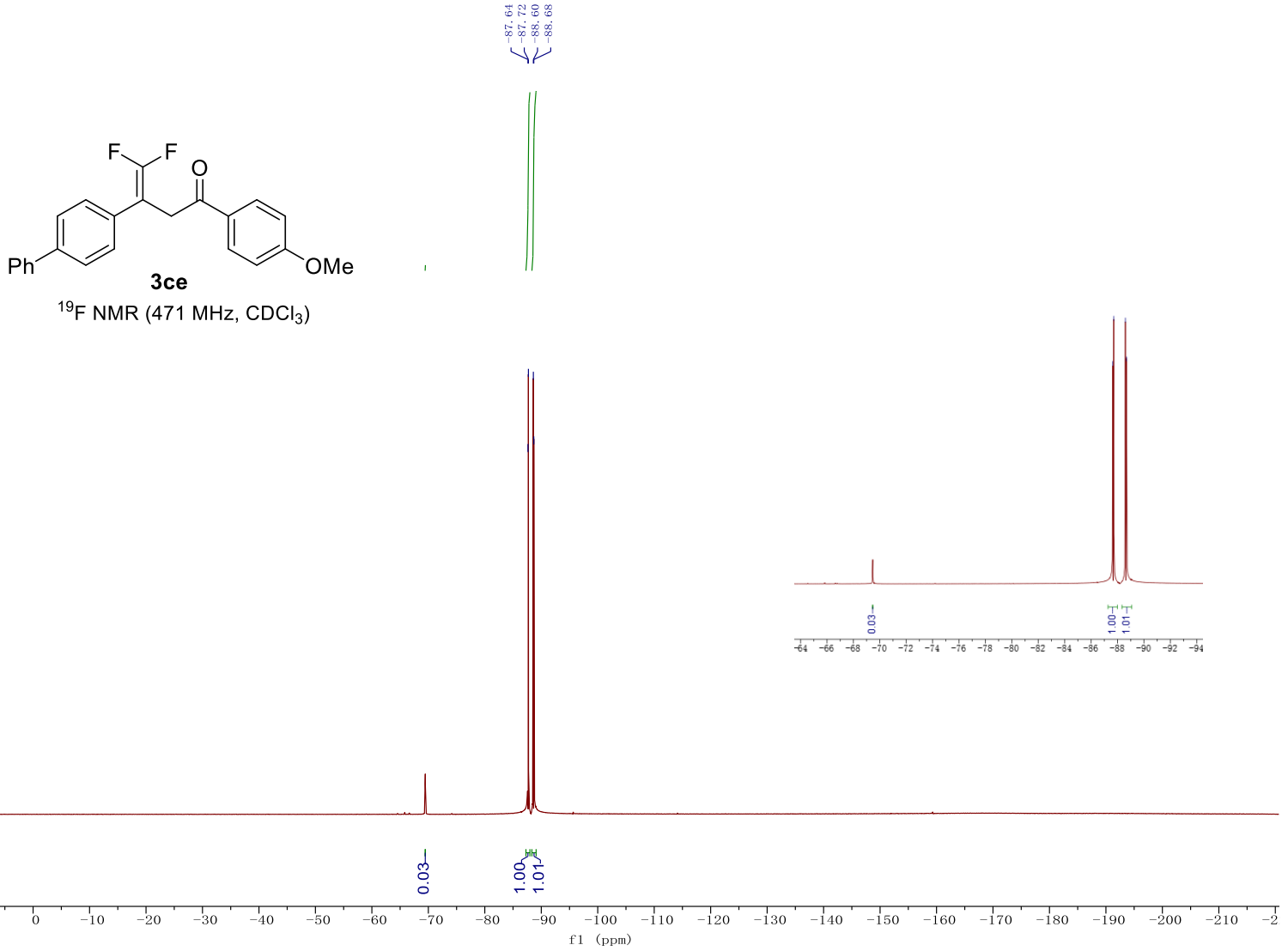

7.97
7.95
7.33
7.32
7.27
7.26
7.25
7.24
7.23
7.23
6.95
6.94
4.02
3.87
F
F
O
OMe
3be
1H NMR (500 MHz, CDCl3)
1.99
3.99
0.99
2.00
2.00
3.00
f1 (ppm)

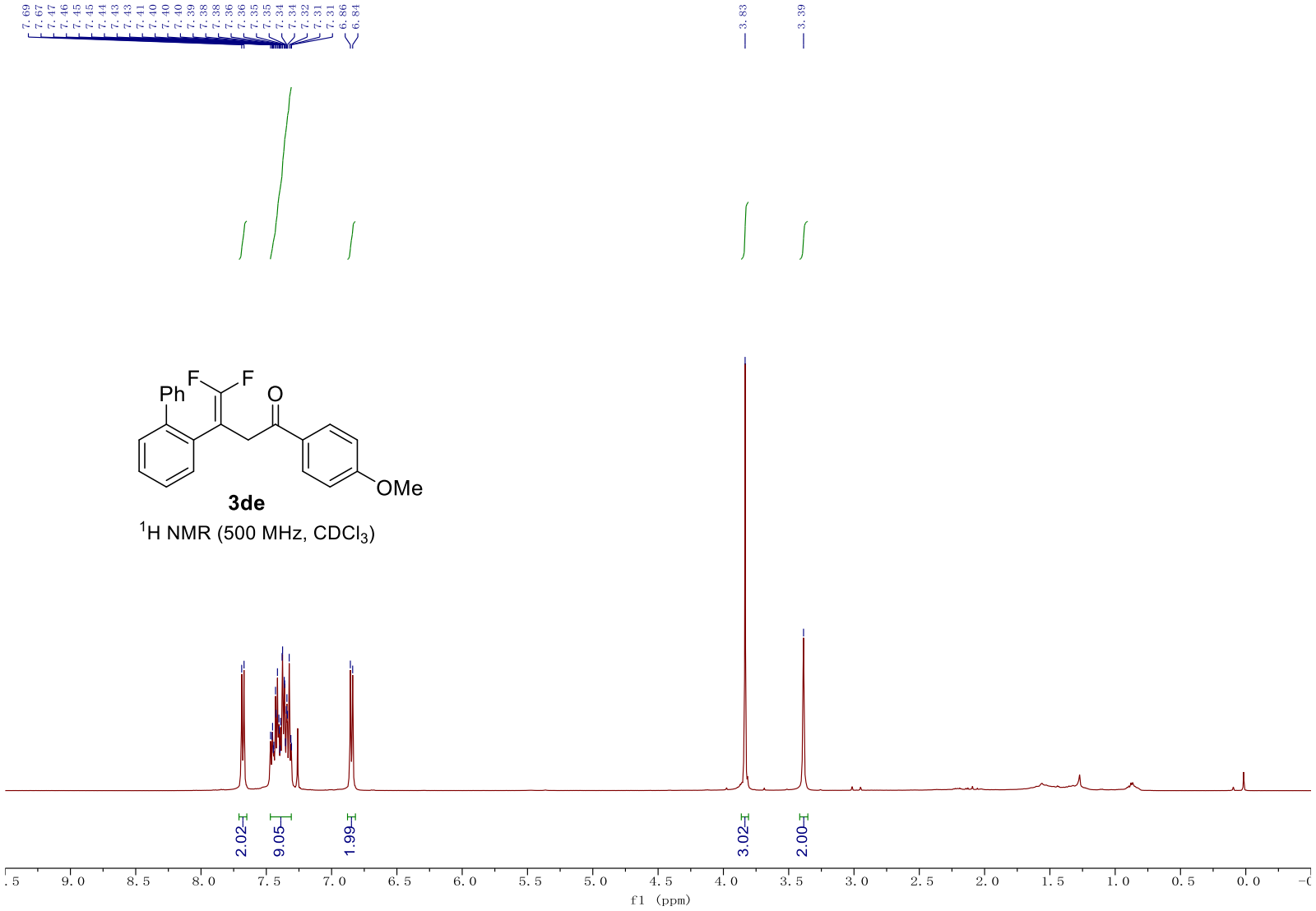

194.00
193.98
193.96
163.84
157.12
154.83
154.80
152.51
133.72
133.68
133.65
130.59
129.44
128.59
128.13
128.10
128.07
127.51
113.97
87.65
87.51
87.48
87.34
55.63
38.08
38.06
F
F
O
OMe
3be
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

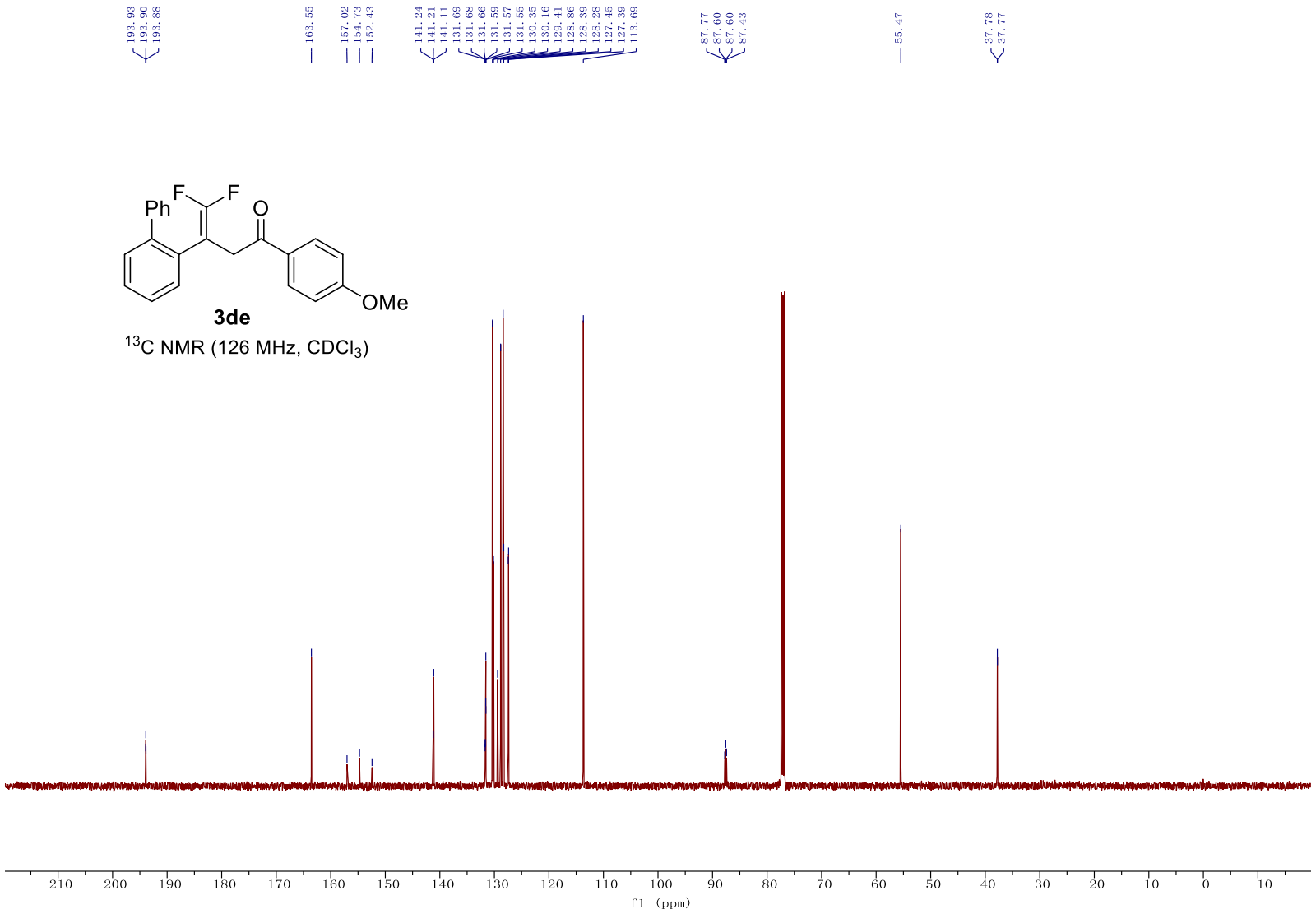

F
F
O
OMe
3be
^{19}F NMR (471 MHz, $CDCl_3$)
-88.23
-88.31
-89.24
-89.32
0.02
1.00
1.01
f1 (ppm)

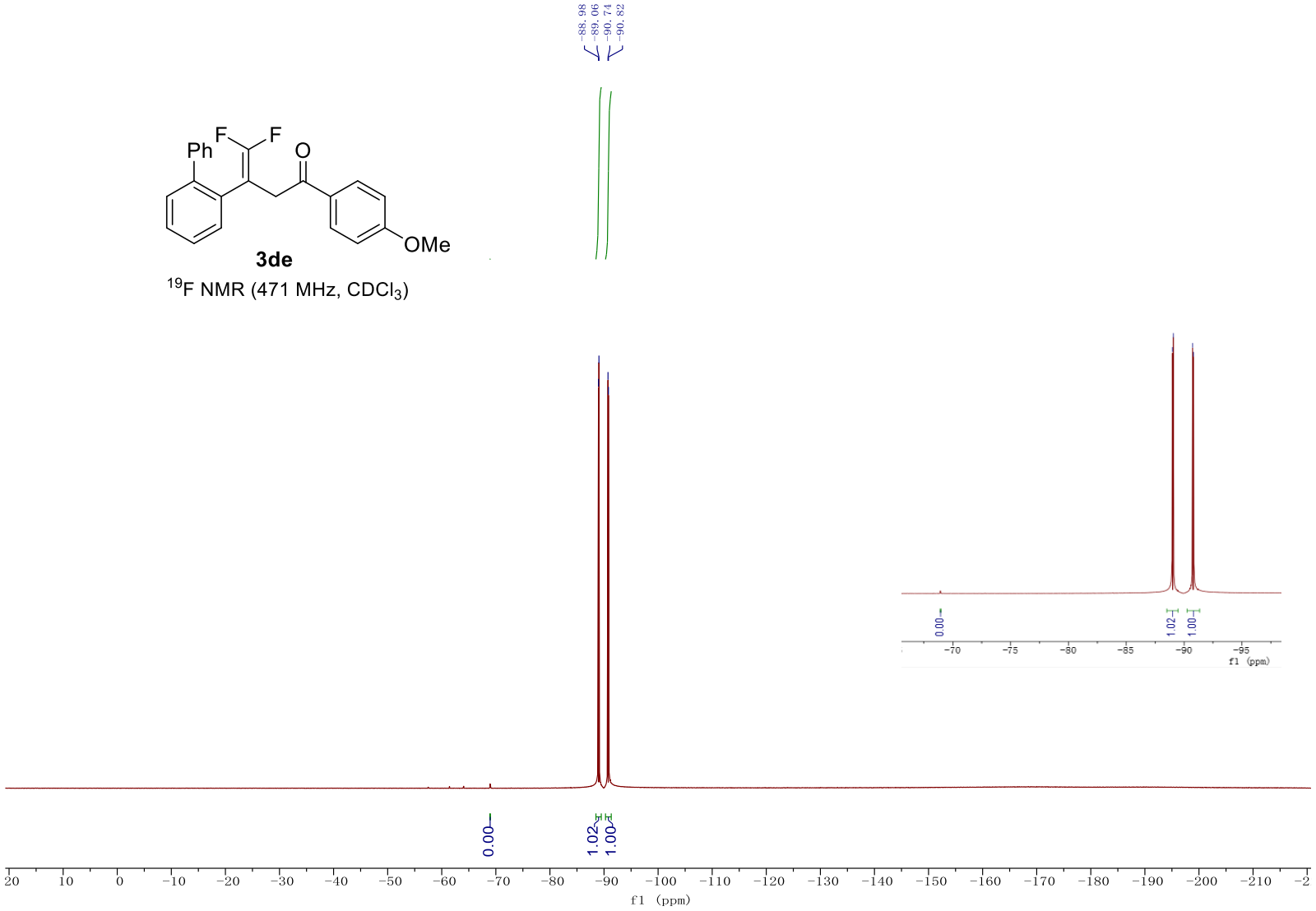

8.00
7.99
7.59
7.57
7.57
7.56
7.45
7.44
7.42
7.40
7.36
7.35
7.34
7.33
6.97
6.96
4.07
3.88
F
F
O
Ph
OMe
3ce
1H NMR (500 MHz, CDCl3)
2.01
4.00
4.04
1.03
2.03
2.00
3.02
f1 (ppm)

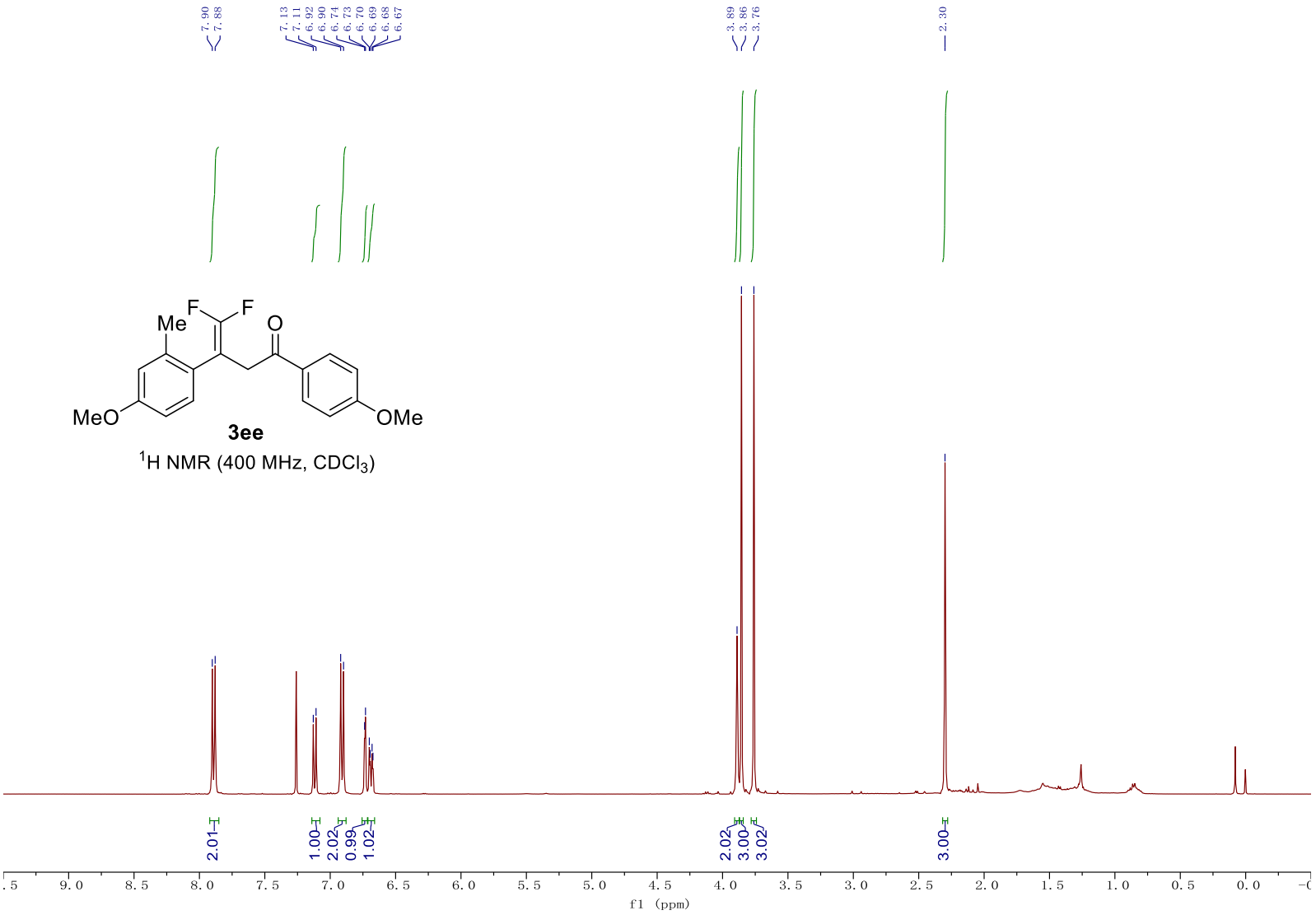

194.02
194.00
193.98
163.88
157.19
154.90
154.86
152.57
140.61
140.24
132.64
132.61
132.58
130.61
129.43
128.89
128.43
128.40
128.37
127.50
127.28
127.12
114.00
87.44
87.31
87.27
87.13
55.62
37.92
37.90
F
F
O
Ph
OMe
3ce
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

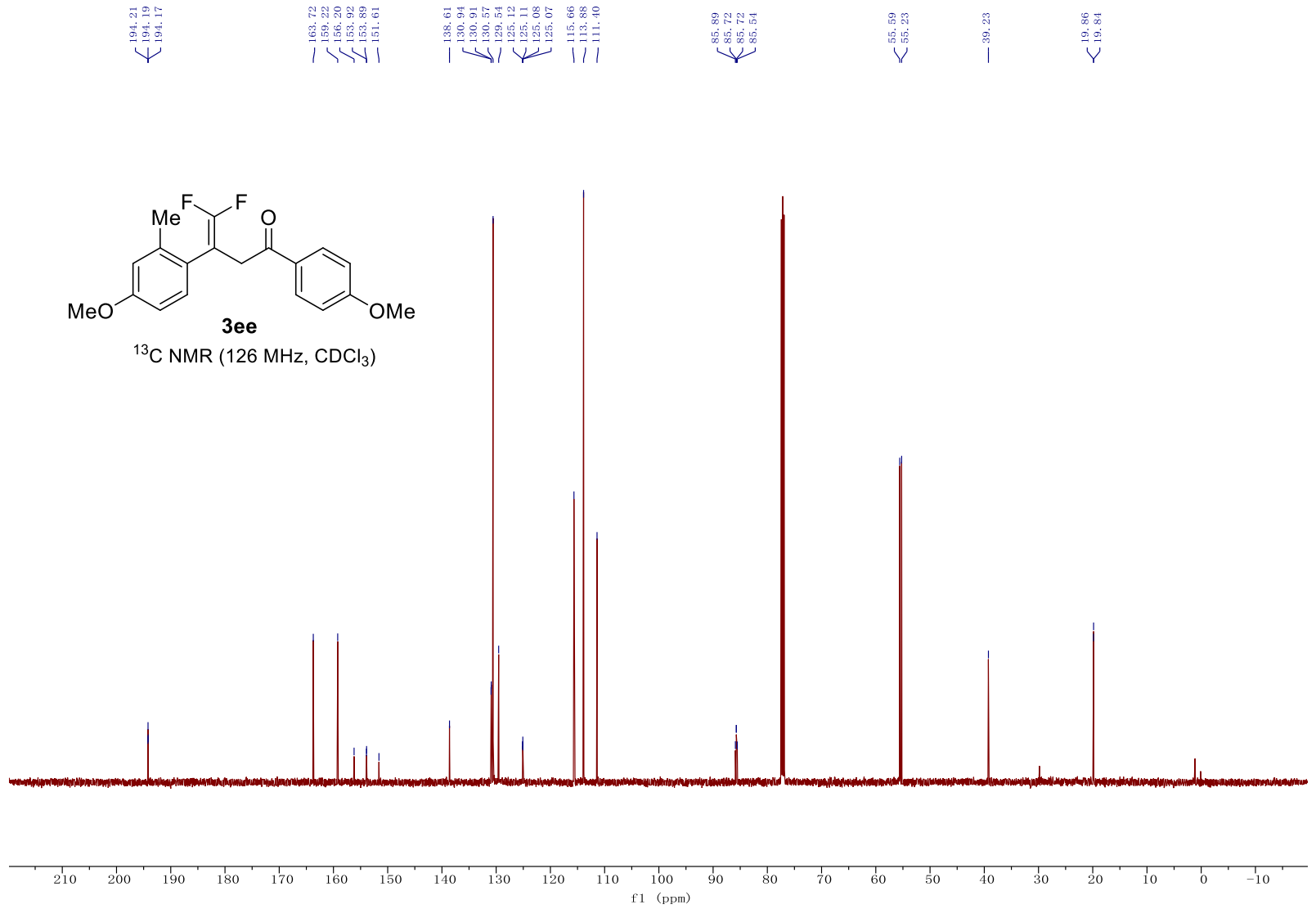

F
F
O
Ph
OMe
3ce
^{19}F NMR (471 MHz, $CDCl_3$)
-87.64
-87.72
-88.60
-88.68
0.03
1.00
1.01
f1 (ppm)

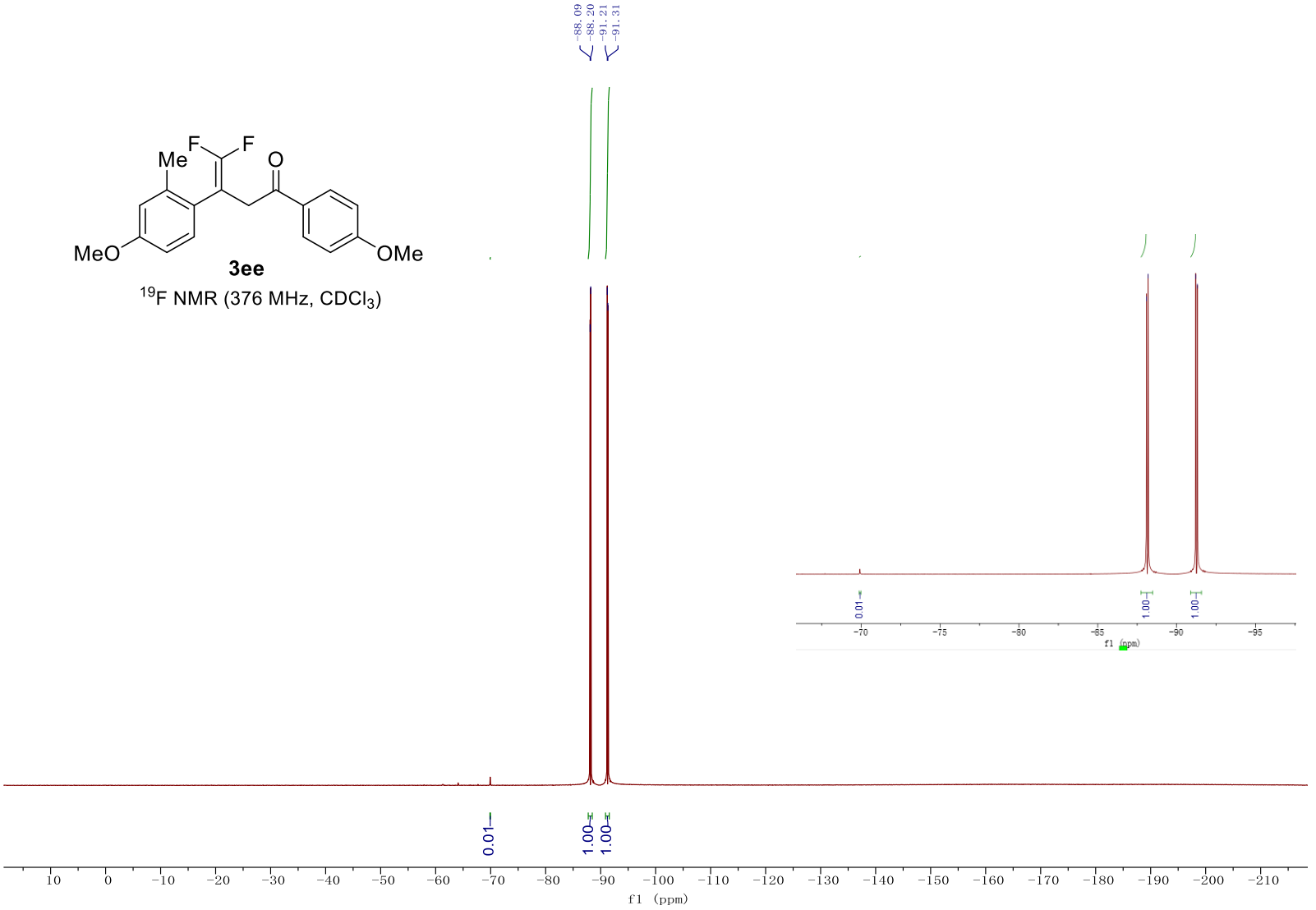

7.69
7.67
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.32
7.31
7.31
6.86
6.84
3.83
3.39
F
F
Ph
O
OMe
3de
^{1}H NMR (500 MHz, $CDCl_3$)
2.02
9.05
1.99
3.02
2.00
f1 (ppm)

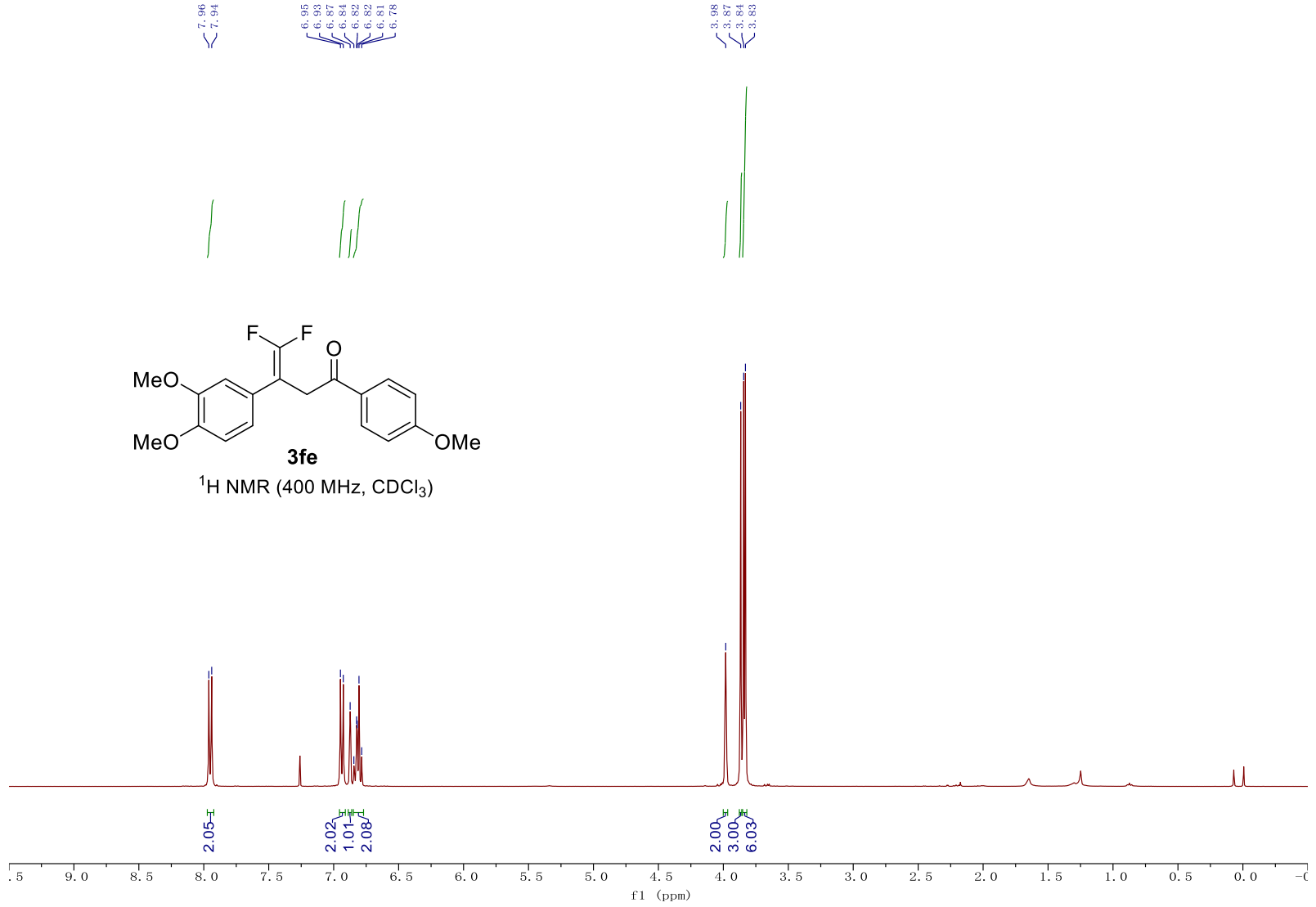

193.93
193.90
193.88
163.55
157.02
154.73
152.43
141.24
141.21
141.11
131.69
131.68
131.66
131.59
131.57
131.55
130.35
130.16
129.41
128.86
128.39
128.28
127.45
127.39
113.69
87.77
87.60
87.60
87.43
55.47
37.78
37.77
F
F
Ph
O
OMe
3de
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-88.98
-89.06
-90.74
-90.82
F
F
Ph
O
OMe
3de
19F NMR (471 MHz, CDCl3)
0.00
1.02
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)
−70 −75 −80 −85 −90 −95
f1 (ppm)


7.90
7.88
7.13
7.11
6.92
6.90
6.74
6.73
6.70
6.69
6.68
6.67
3.89
3.86
3.76
2.30
F
F
Me
O
MeO
OMe
3ee
1H NMR (400 MHz, CDCl3)
2.01
1.00
2.02
0.99
1.02
2.02
3.00
3.02
3.00
f1 (ppm)

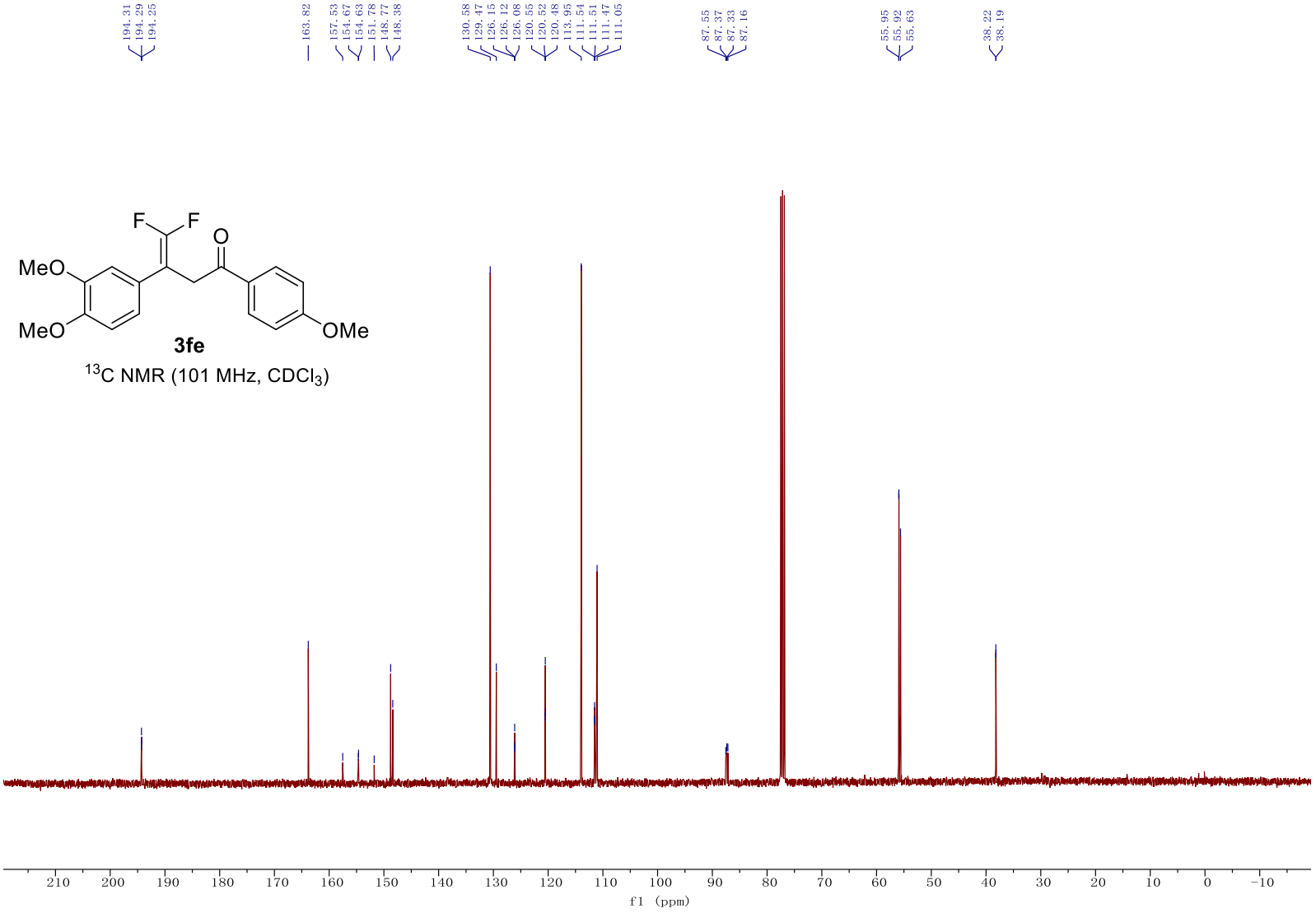

194.21
194.19
194.17
163.72
159.22
156.20
153.92
153.89
151.61
138.61
130.94
130.91
130.57
129.54
125.12
125.11
125.08
125.07
115.66
113.88
111.40
85.89
85.72
85.72
85.54
55.59
55.23
39.23
19.86
19.84
F
F
Me
O
MeO
OMe
3ee
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

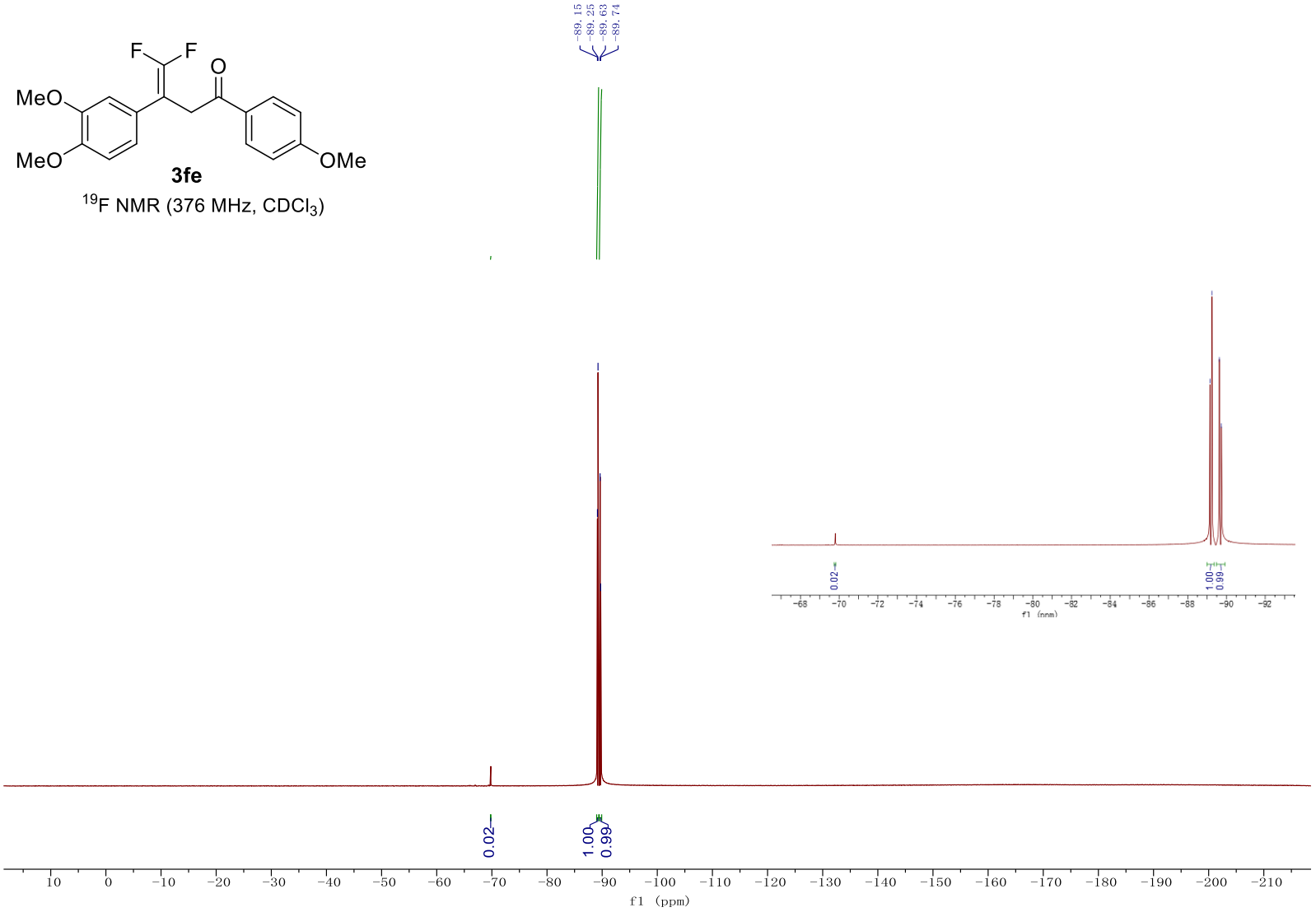

F
F
Me
O
MeO
OMe
3ee
^{19}F NMR (376 MHz, $CDCl_3$)
-88.09
-88.20
-91.21
-91.31
0.01
1.00
1.00
f1 (ppm)

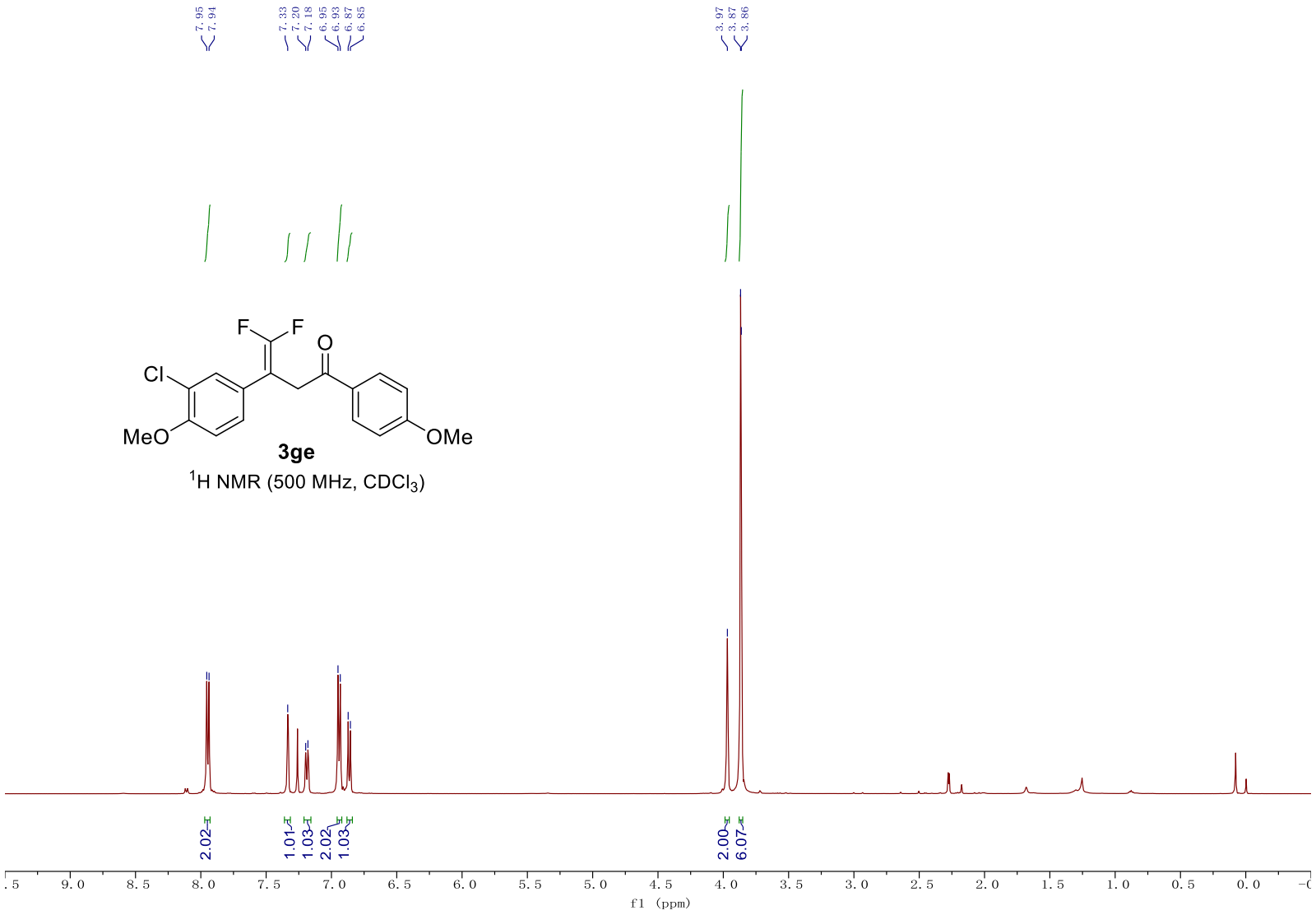


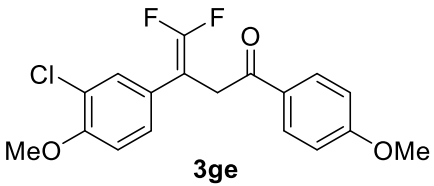
3fe

^{1}H NMR (400 MHz, $CDCl_3$)


194.31
194.29
194.25
163.82
157.53
154.67
154.63
151.78
148.77
148.38
130.58
129.47
126.15
126.12
126.08
120.55
120.52
120.48
113.95
111.54
111.51
111.47
111.05
87.55
87.37
87.33
87.16
55.95
55.92
55.63
38.22
38.19
F
F
O
MeO
MeO
OMe
3fe
13C NMR (101 MHz, CDCl3)
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)

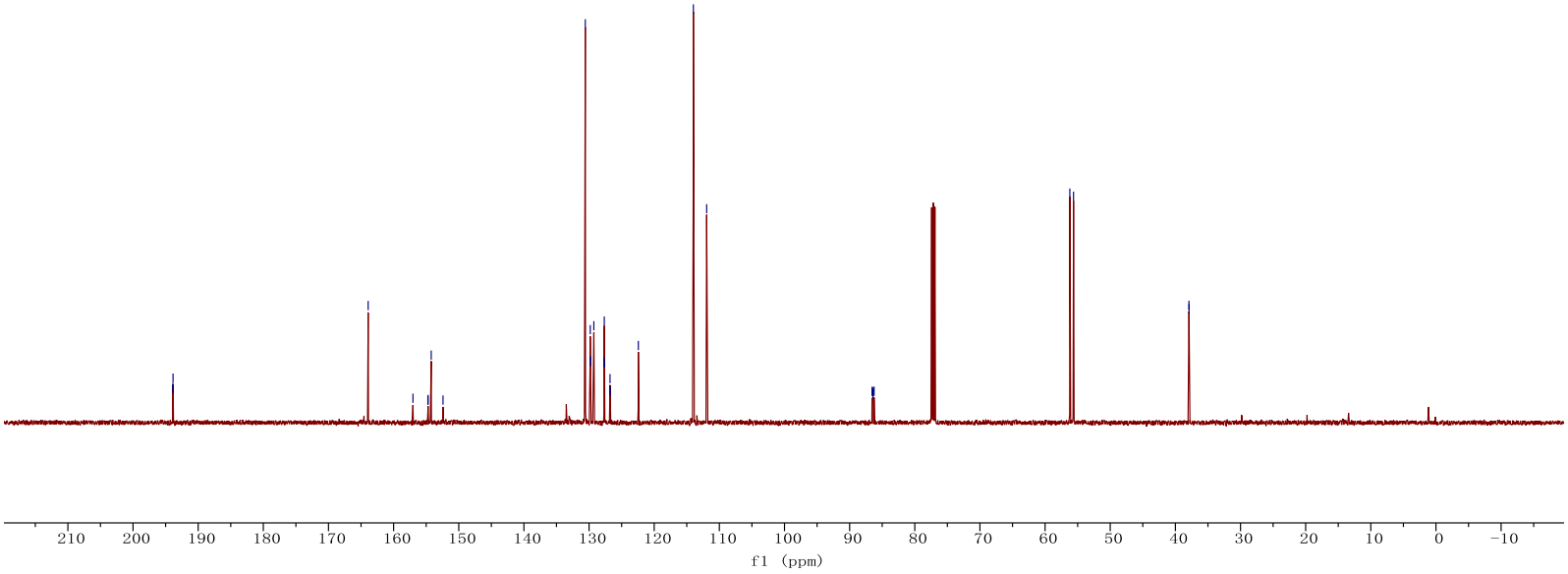

F
F
O
MeO
MeO
OMe
3fe
^{19}F NMR (376 MHz, $CDCl_3$)
-89.15
-89.25
-89.63
-89.74
0.02
1.00
0.99
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)
−68 −70 −72 −74 −76 −78 −80 −82 −84 −86 −88 −90 −92
f1 (ppm)

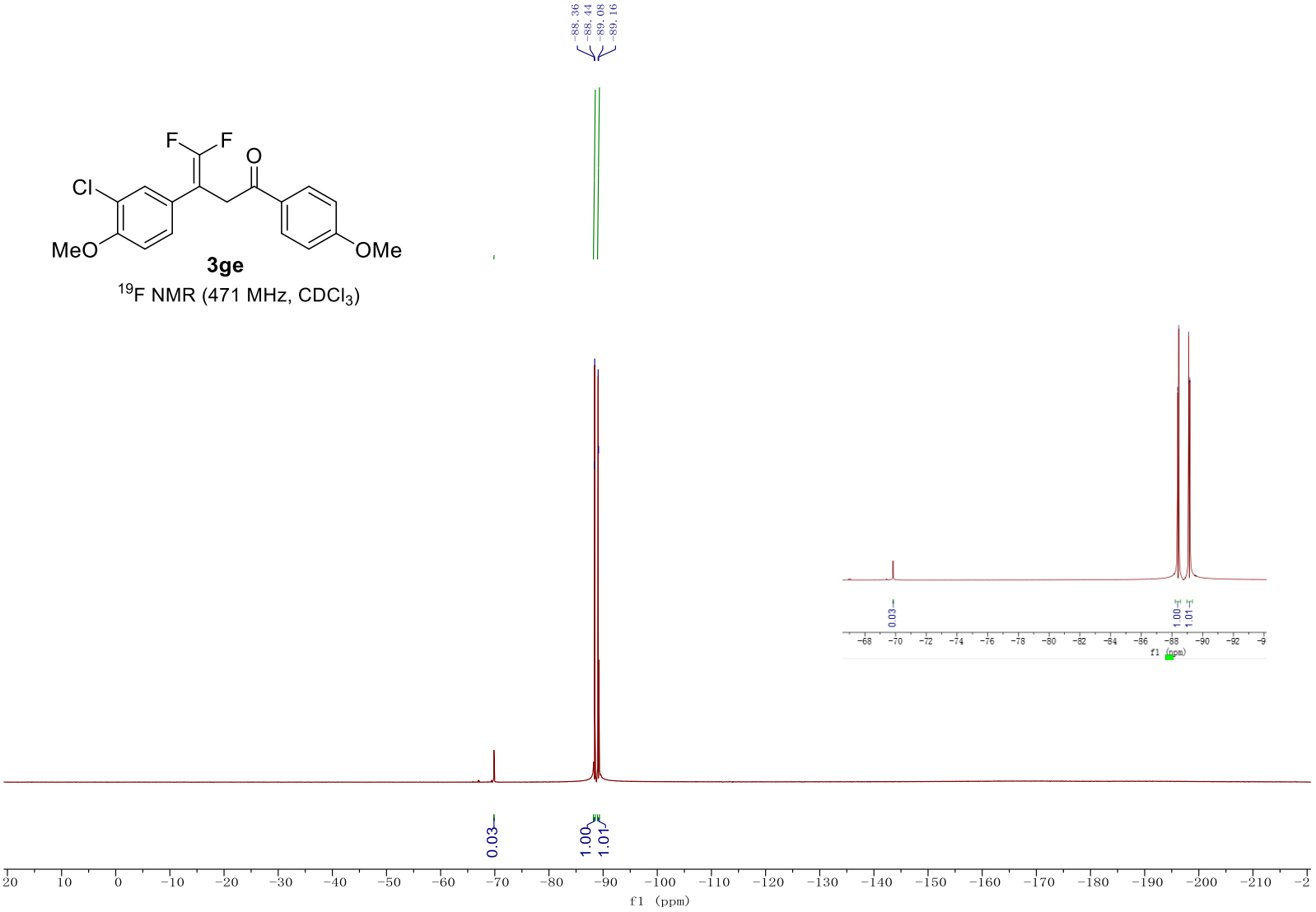

7.95
7.94
7.33
7.20
7.18
6.95
6.93
6.87
6.85
3.97
3.87
3.86
F
F
O
Cl
MeO
OMe
3ge
1H NMR (500 MHz, CDCl3)
2.02
1.01
1.03
2.02
1.03
2.00
6.07
f1 (ppm)

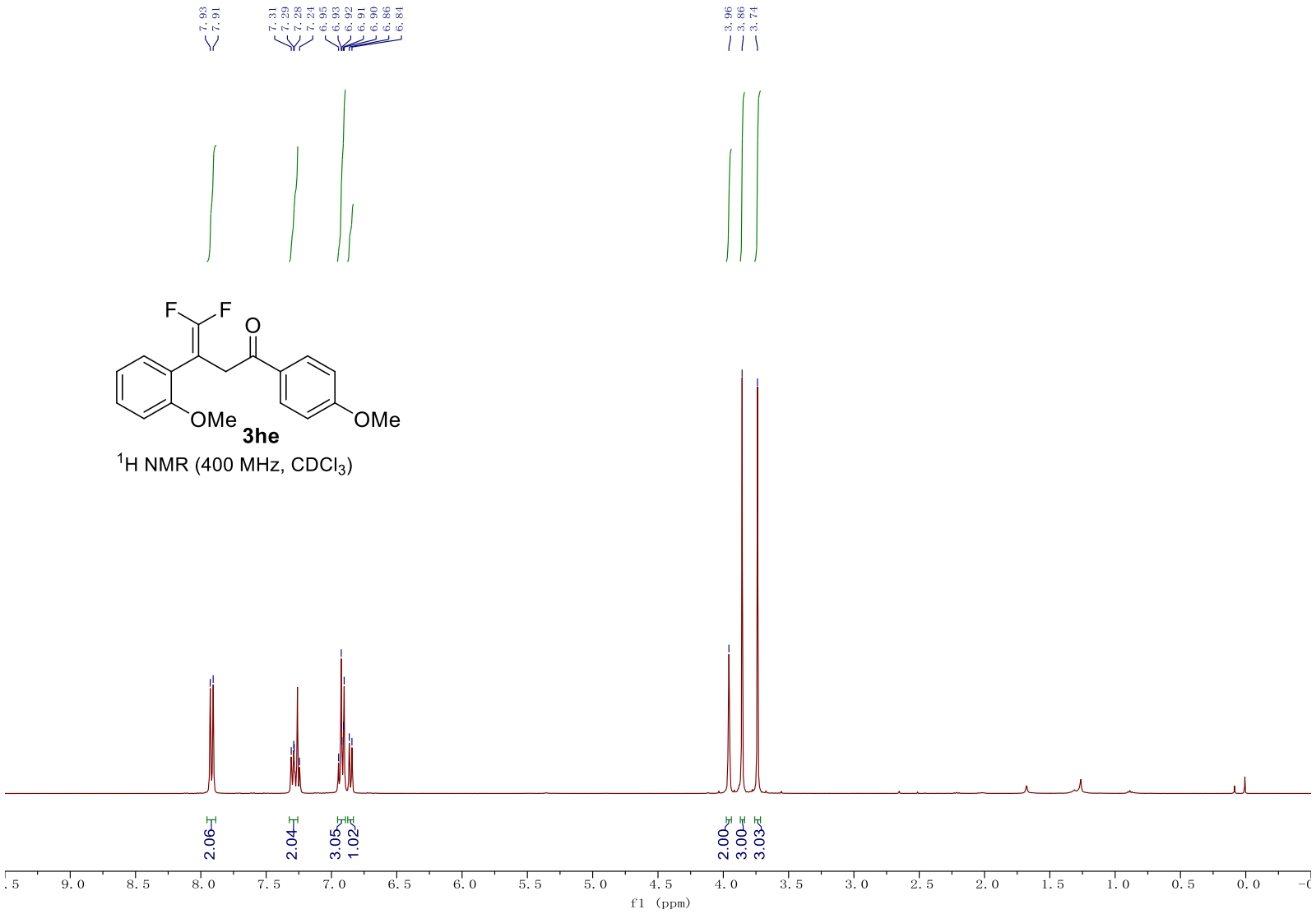


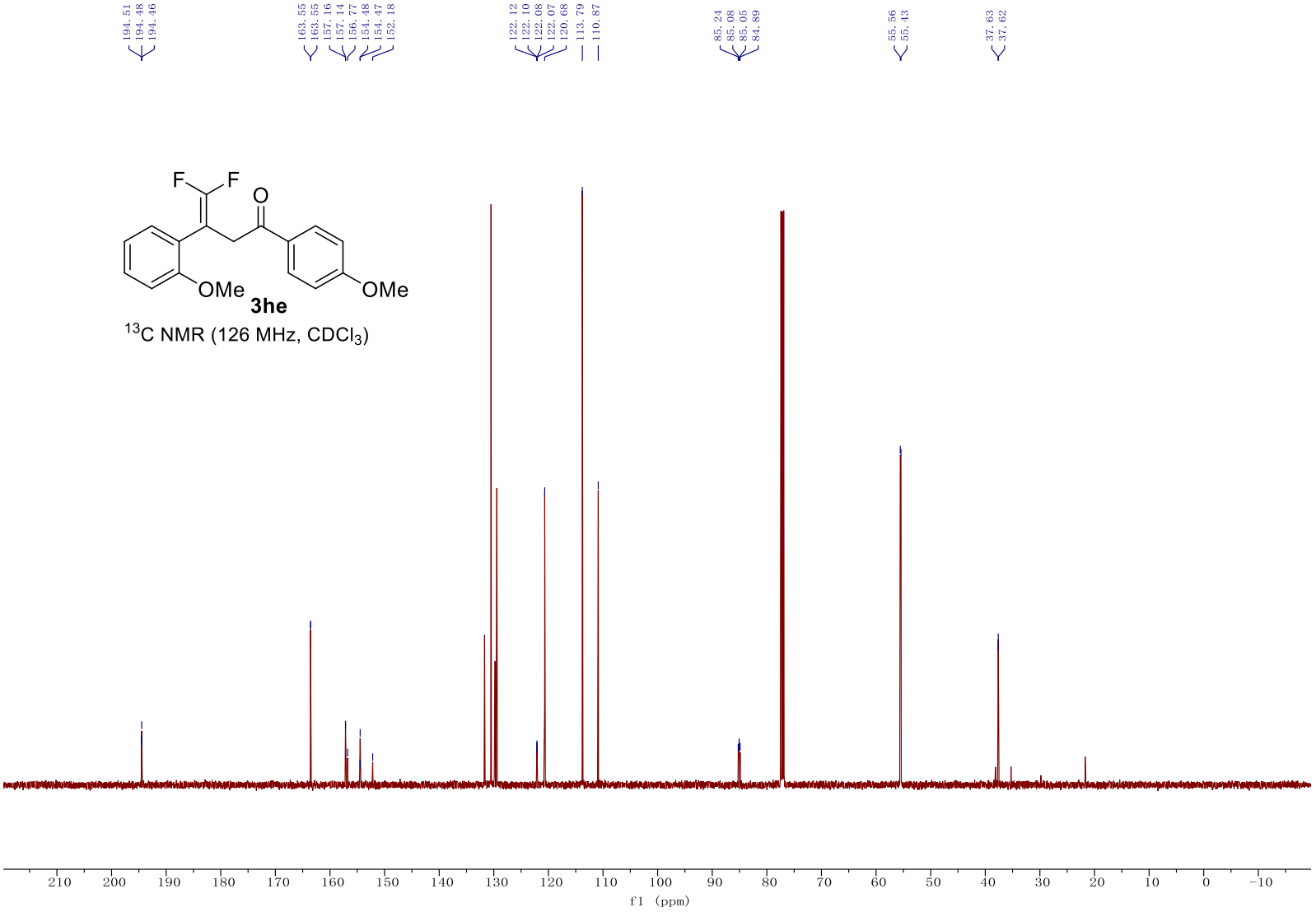
3ge

^{13}C NMR (126 MHz, $CDCl_3$)



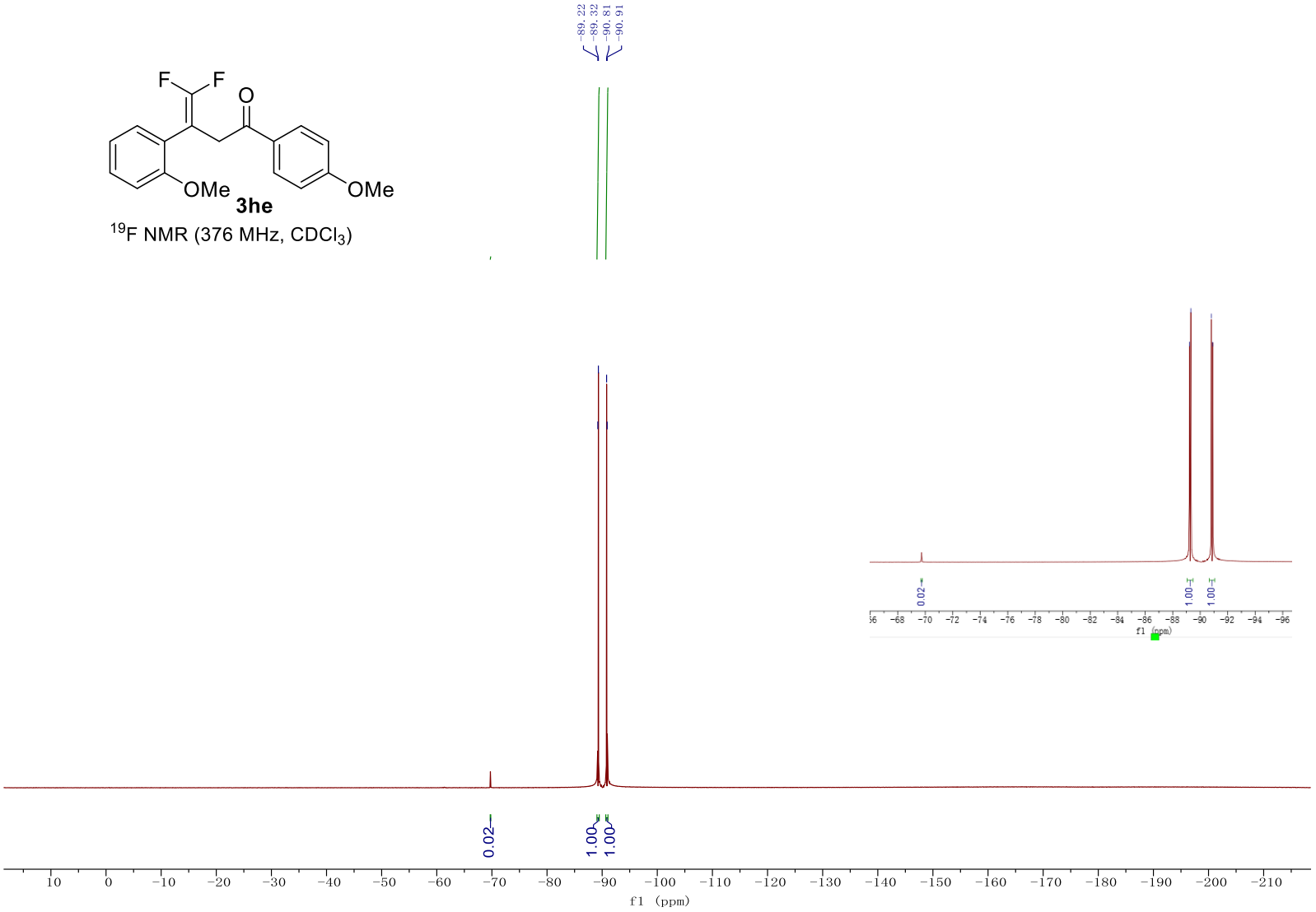

F
F
O
Cl
MeO
OMe
3ge
19F NMR (471 MHz, CDCl3)
-88.36
-88.44
-89.08
-89.16
0.03
1.00
1.01
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)
-68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -9
f1 (ppm)

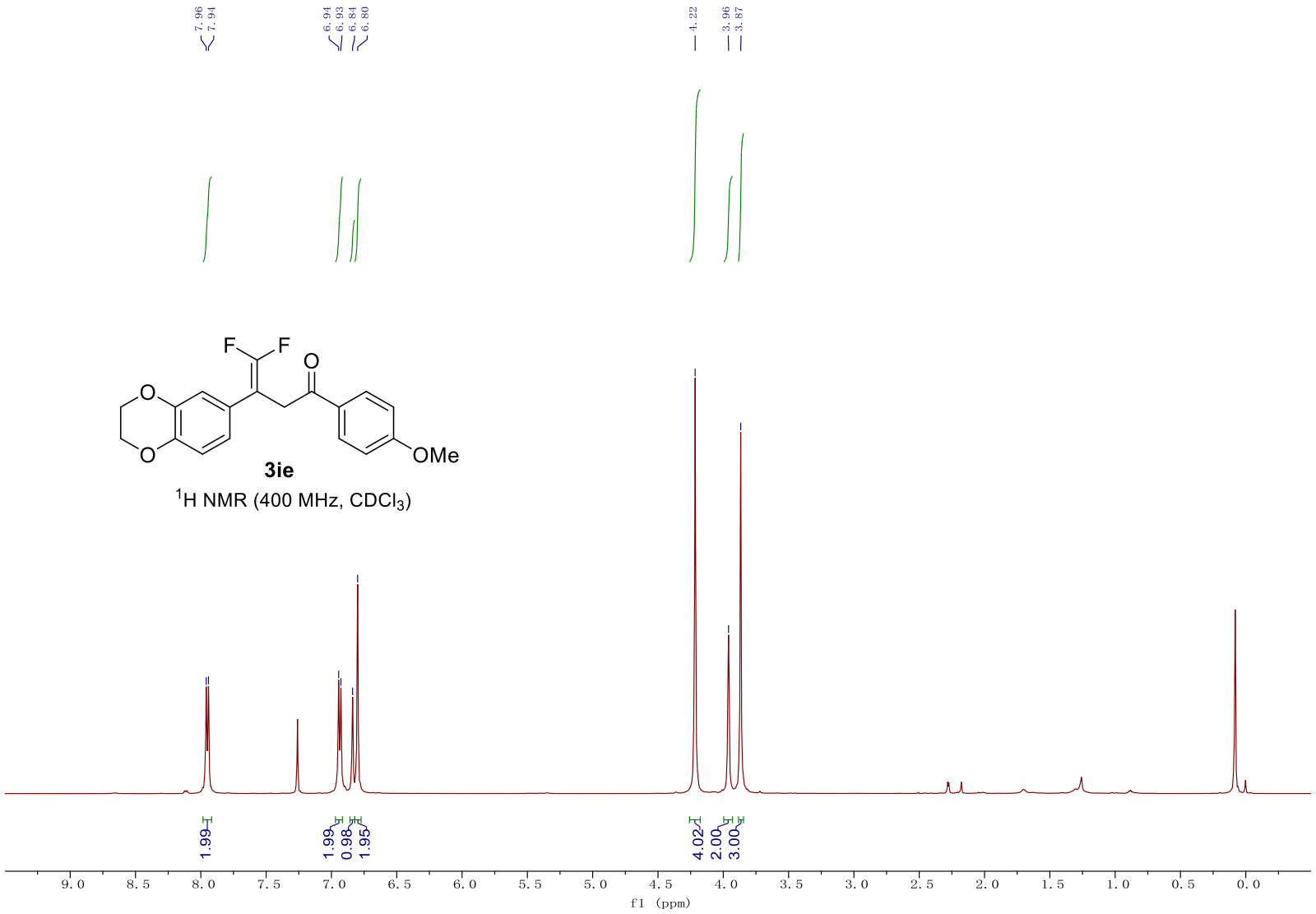

7.93
7.91
7.31
7.29
7.28
7.24
6.95
6.93
6.92
6.91
6.90
6.86
6.84
3.96
3.86
3.74
F
F
O
OMe
OMe
3he
1H NMR (400 MHz, CDCl3)
2.06
2.04
3.05
1.02
2.00
3.00
3.03
f1 (ppm)

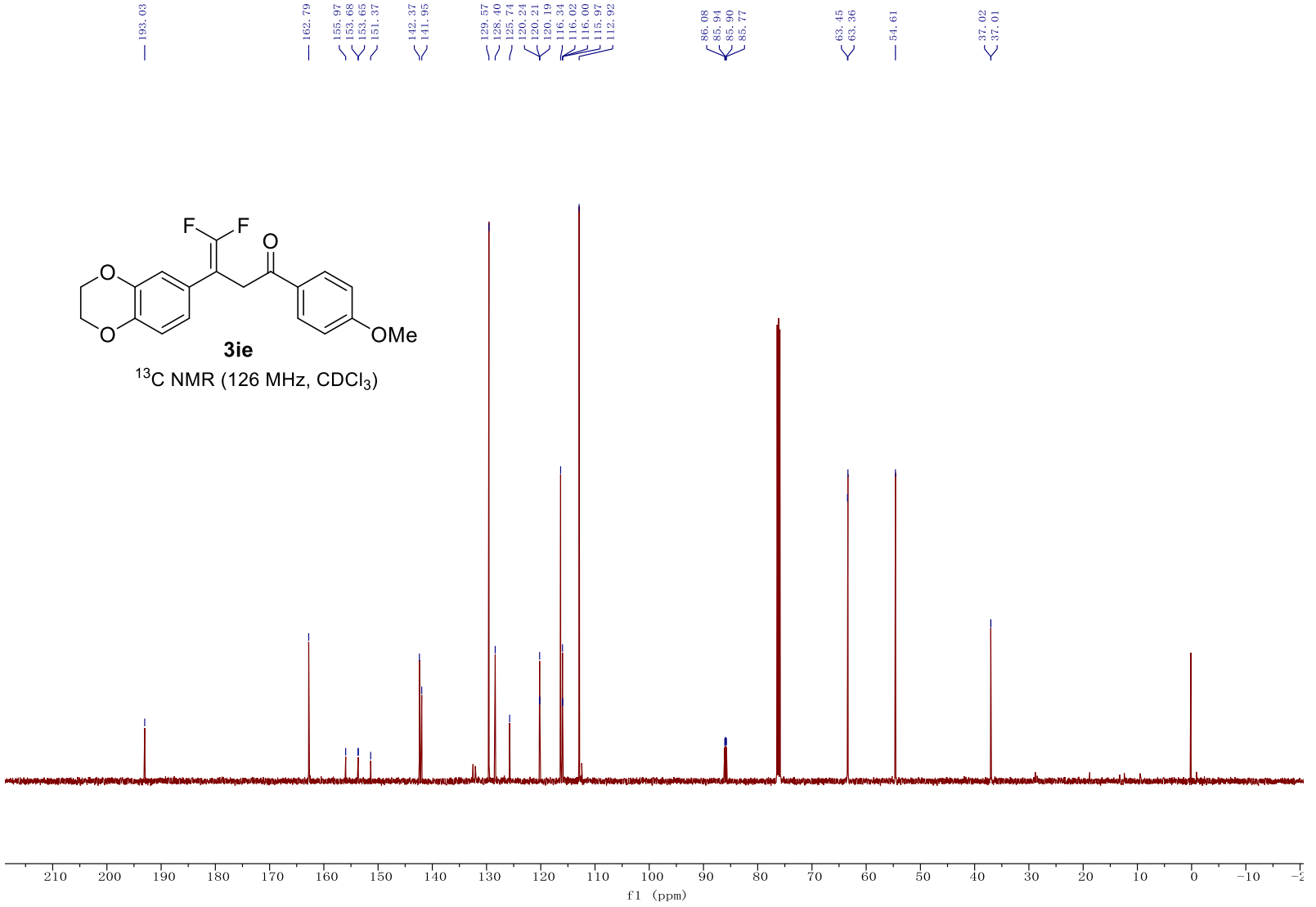

194.51
194.48
194.46
163.55
163.55
157.16
157.14
156.77
154.48
154.47
152.18
122.12
122.10
122.08
122.07
120.68
113.79
110.87
85.24
85.08
85.05
84.89
55.56
55.43
37.63
37.62
F
F
O
OMe
OMe
3he
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

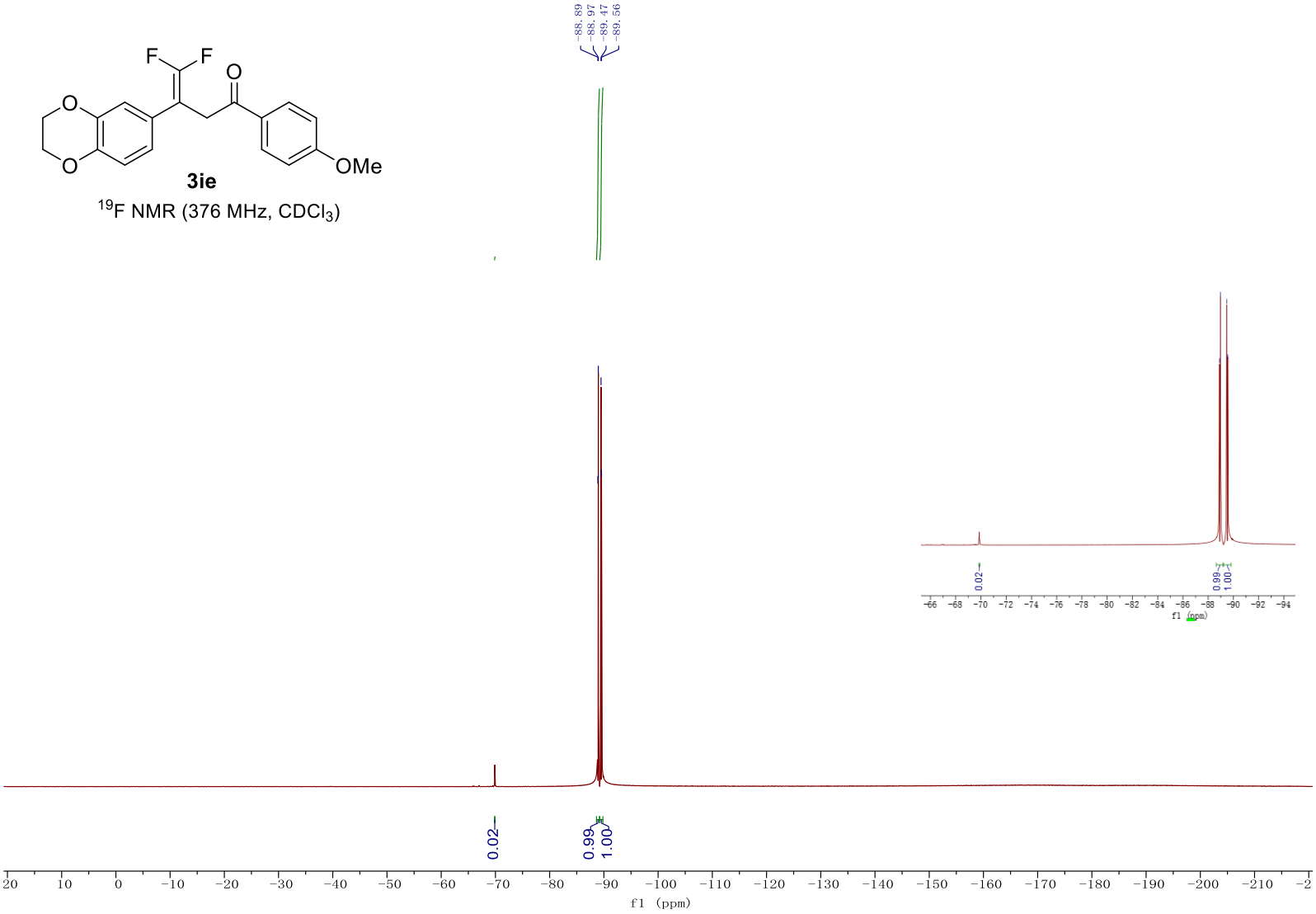
3he

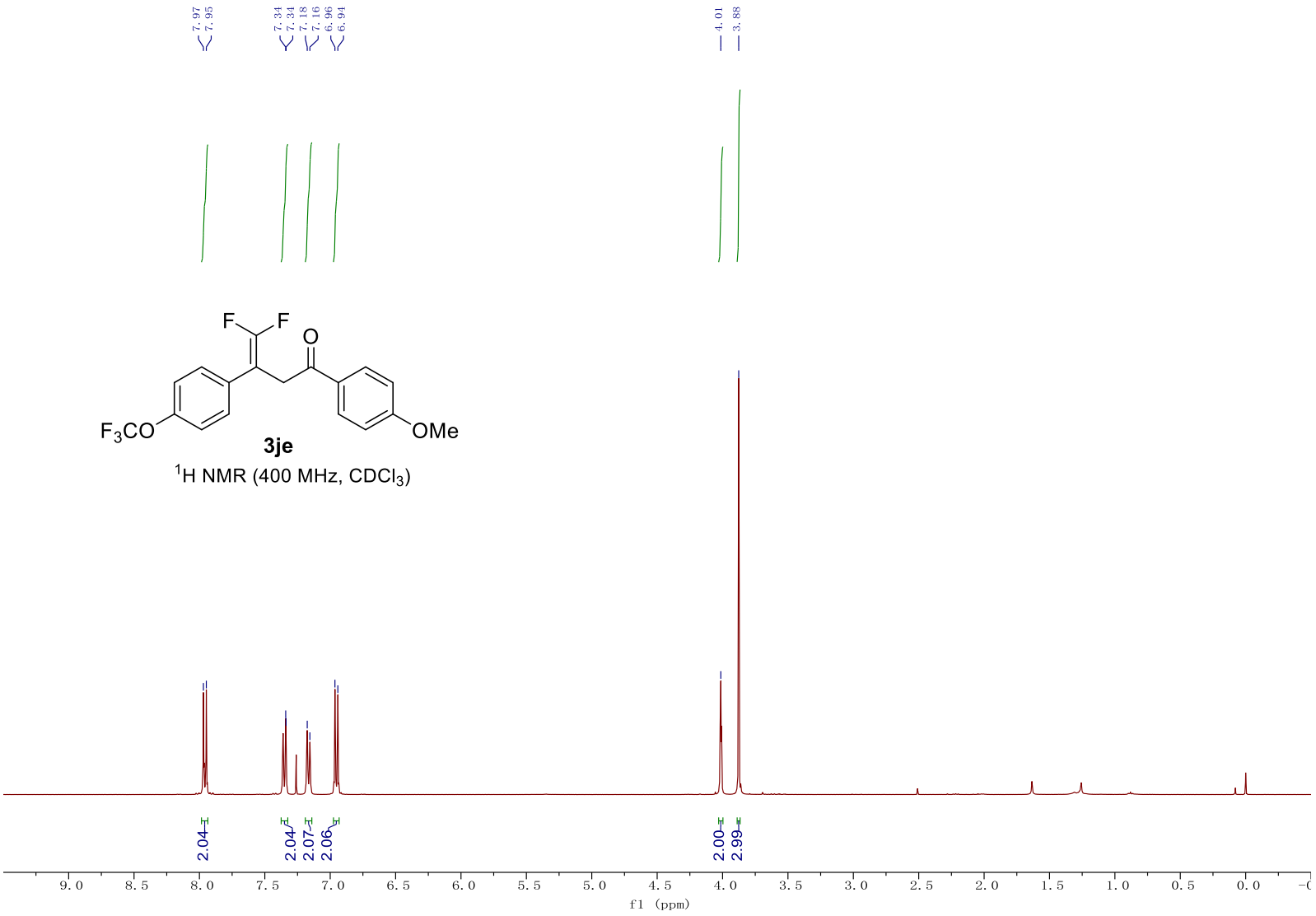
^{19}F NMR (376 MHz, $CDCl_3$)

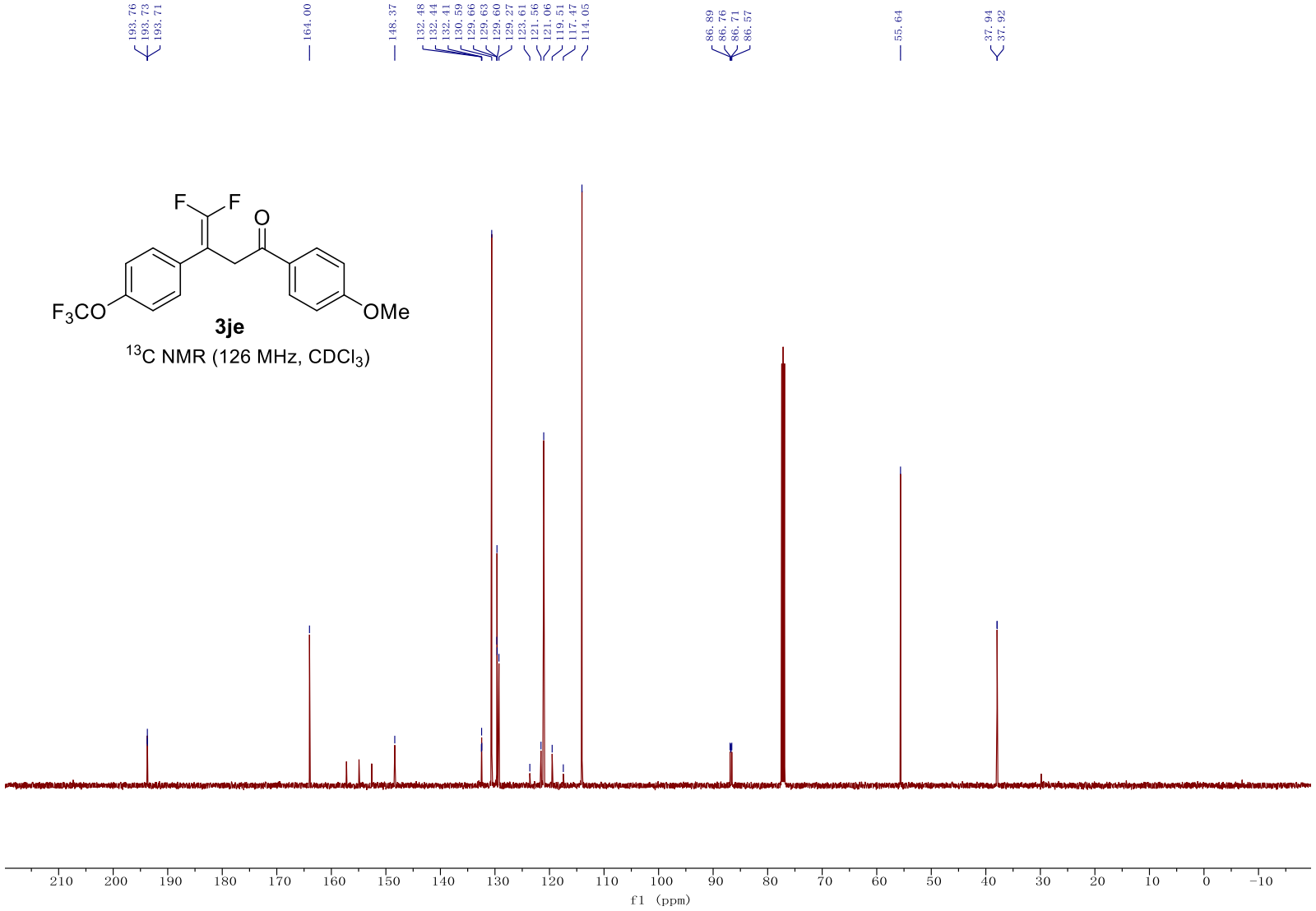


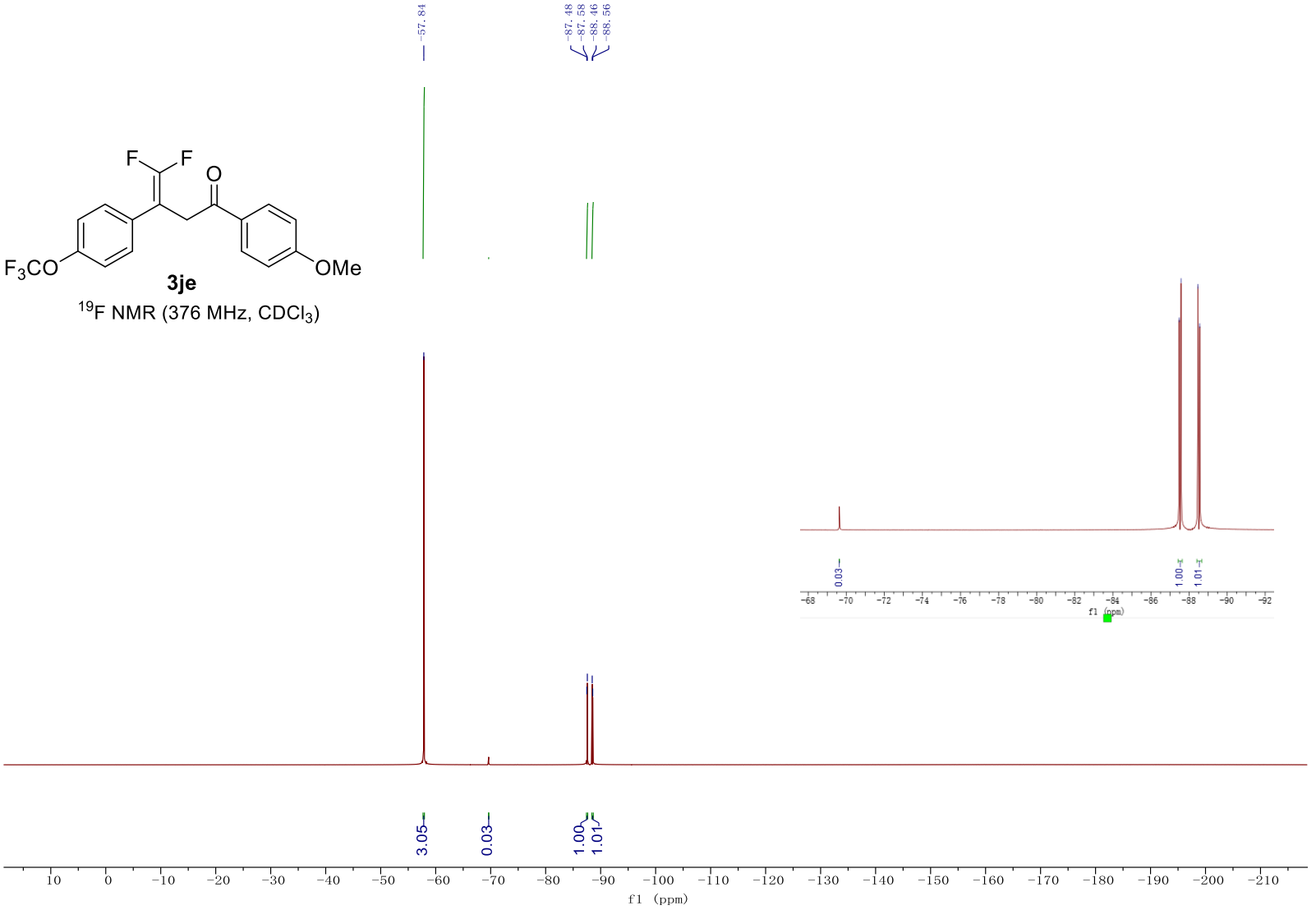

7.96
7.94
6.94
6.93
6.84
6.80
4.22
3.96
3.87
F
F
O
O
O
OMe
3ie
1H NMR (400 MHz, CDCl3)
1.99
1.99
0.98
1.95
4.02
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

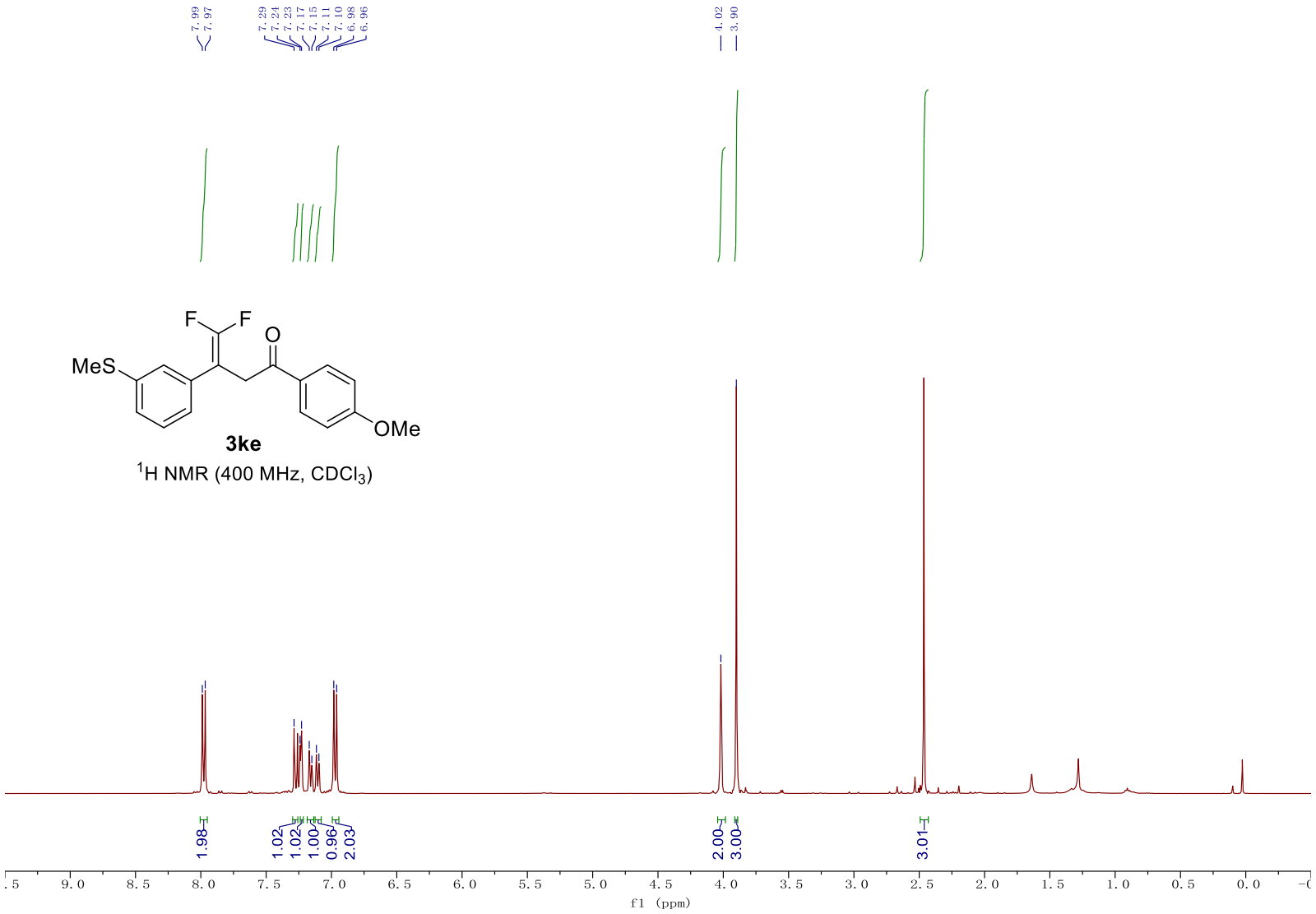

193.03
162.79
155.97
153.68
153.65
151.37
142.37
141.95
129.57
128.40
125.74
120.24
120.21
120.19
116.34
116.02
116.00
115.97
112.92
86.08
85.94
85.90
85.77
63.45
63.36
54.61
37.02
37.01
F
F
O
O
O
OMe
3ie
13C NMR (126 MHz, CDCl3)
f1 (ppm)

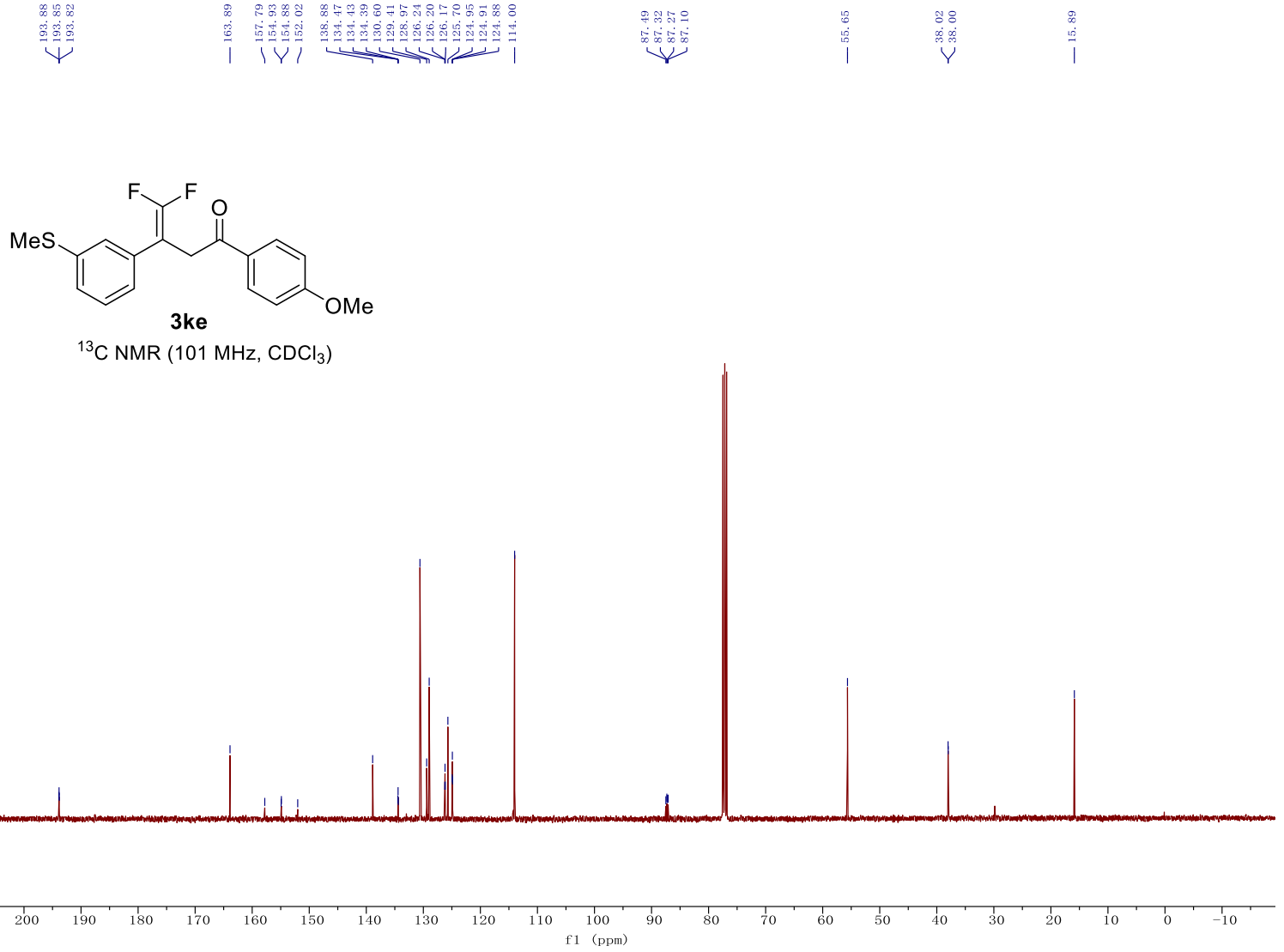

F
F
O
O
O
OMe
3ie
^{19}F NMR (376 MHz, $CDCl_3$)
-88.89
-88.97
-89.47
-89.56
0.02
0.99
1.00
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)
−66 −68 −70 −72 −74 −76 −78 −80 −82 −84 −86 −88 −90 −92 −94
f1 (ppm)

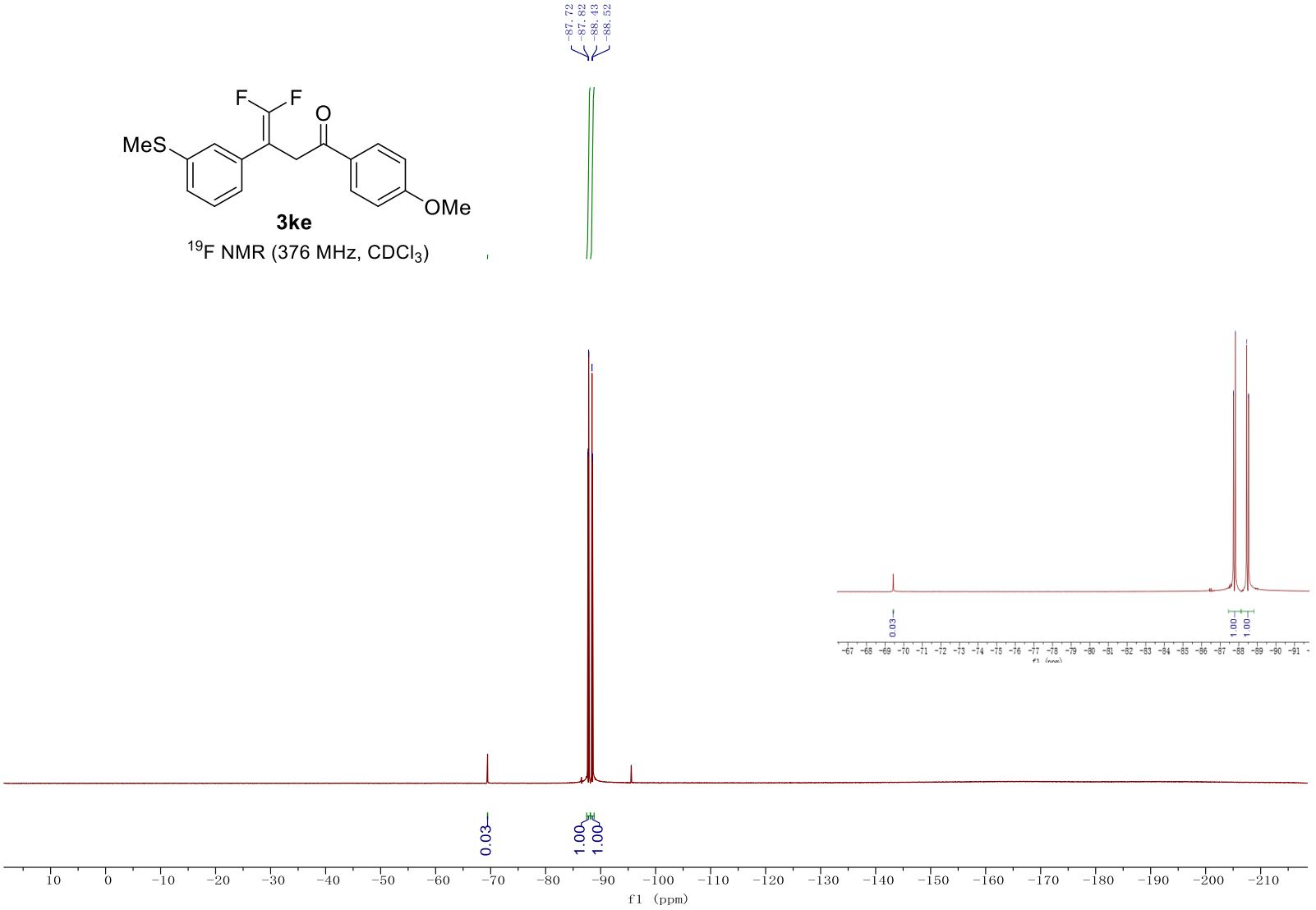

7.97
7.95
7.34
7.34
7.18
7.16
6.96
6.94
4.01
3.88
F
F
O
F3CO
OMe
3je
1H NMR (400 MHz, CDCl3)
2.04
2.04
2.07
2.06
2.00
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

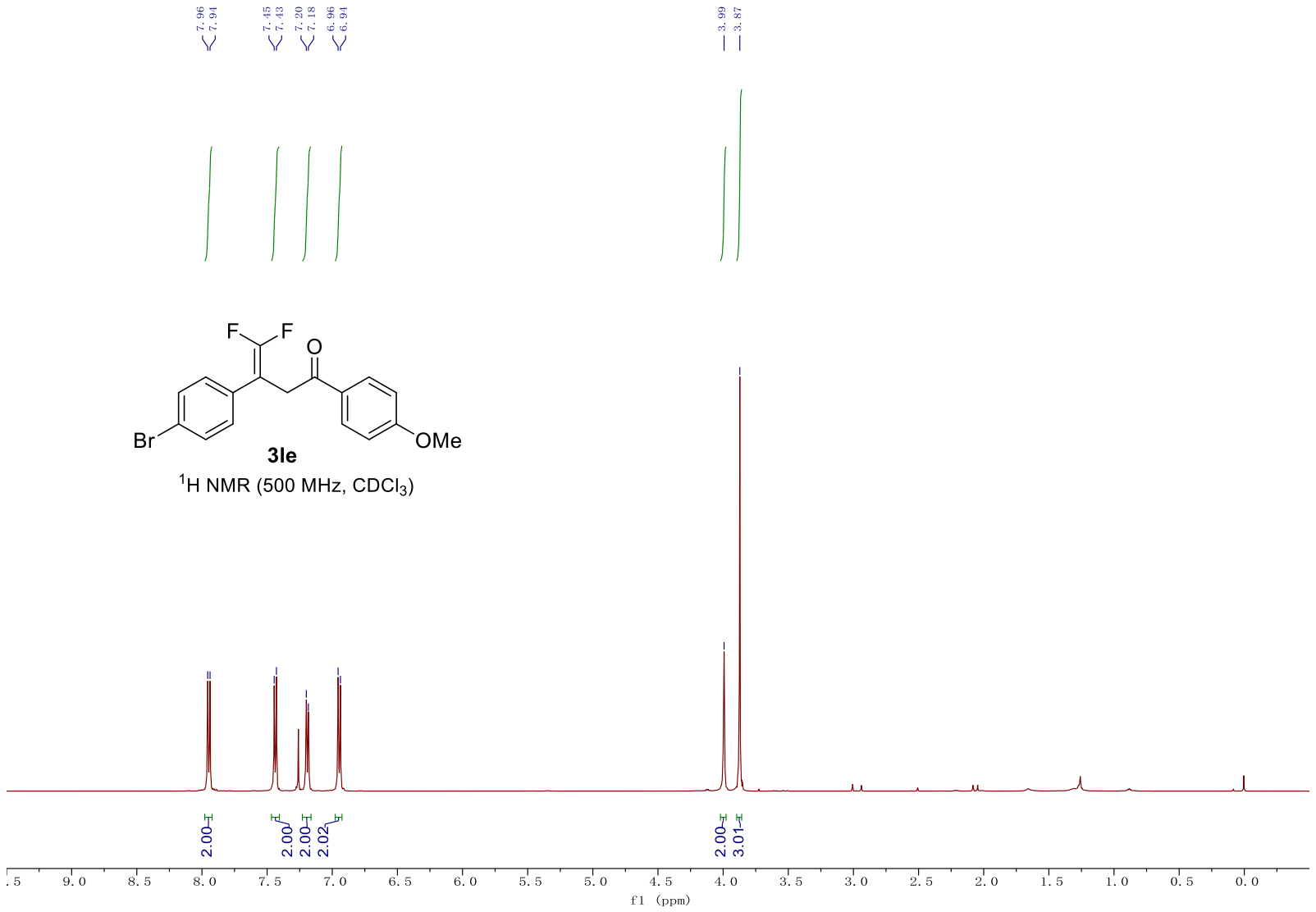

193.76
193.73
193.71
164.00
148.37
132.48
132.44
132.41
130.59
129.66
129.63
129.60
129.27
123.61
121.56
121.06
119.51
117.47
114.05
86.89
86.76
86.71
86.57
55.64
37.94
37.92
F
F
O
F3CO
OMe
3je
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

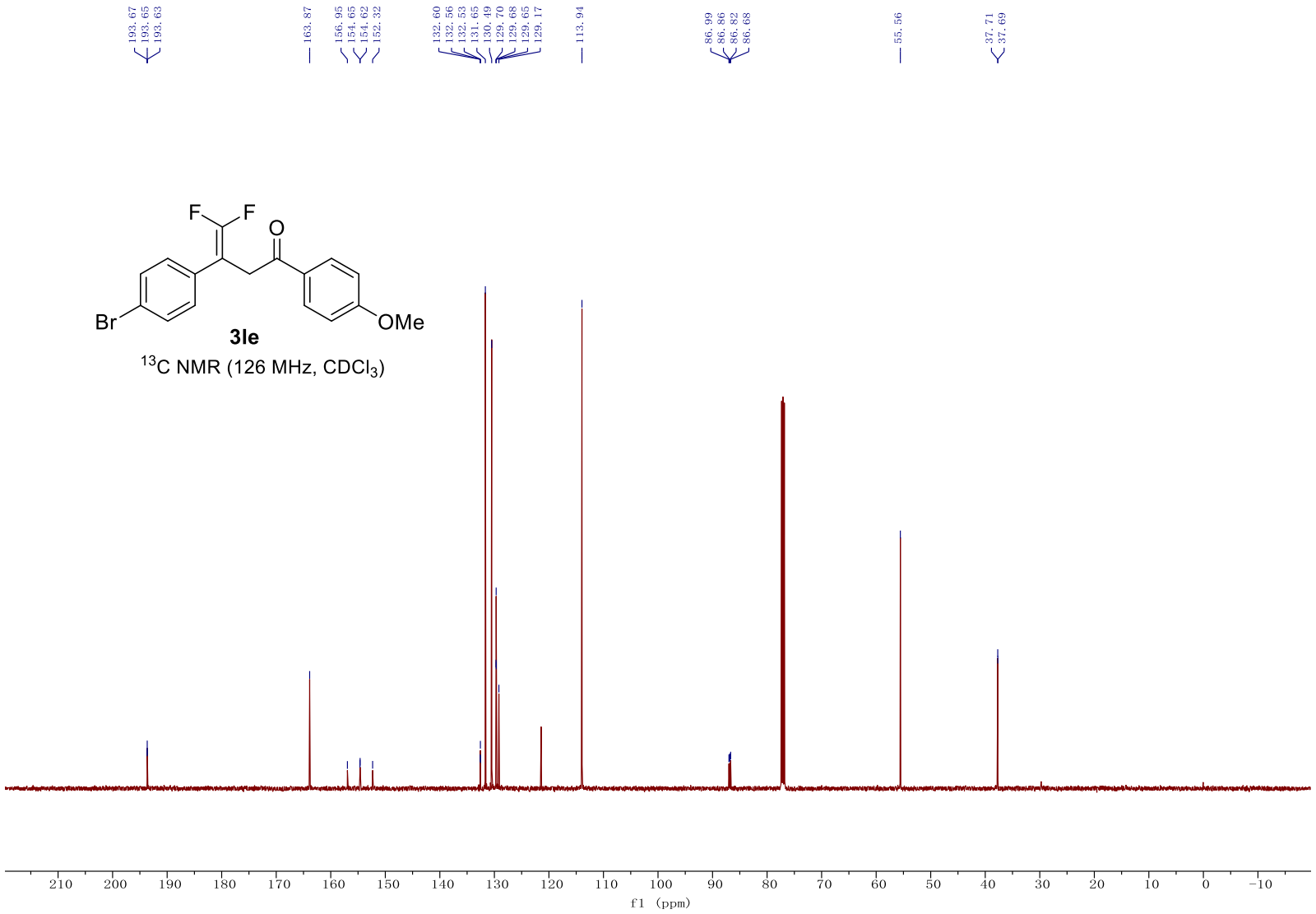

F
F
O
F3CO
OMe
3je
19F NMR (376 MHz, CDCl3)
-57.84
-87.48
-87.58
-88.46
-88.56
3.05
0.03
1.00
1.01
f1 (ppm)

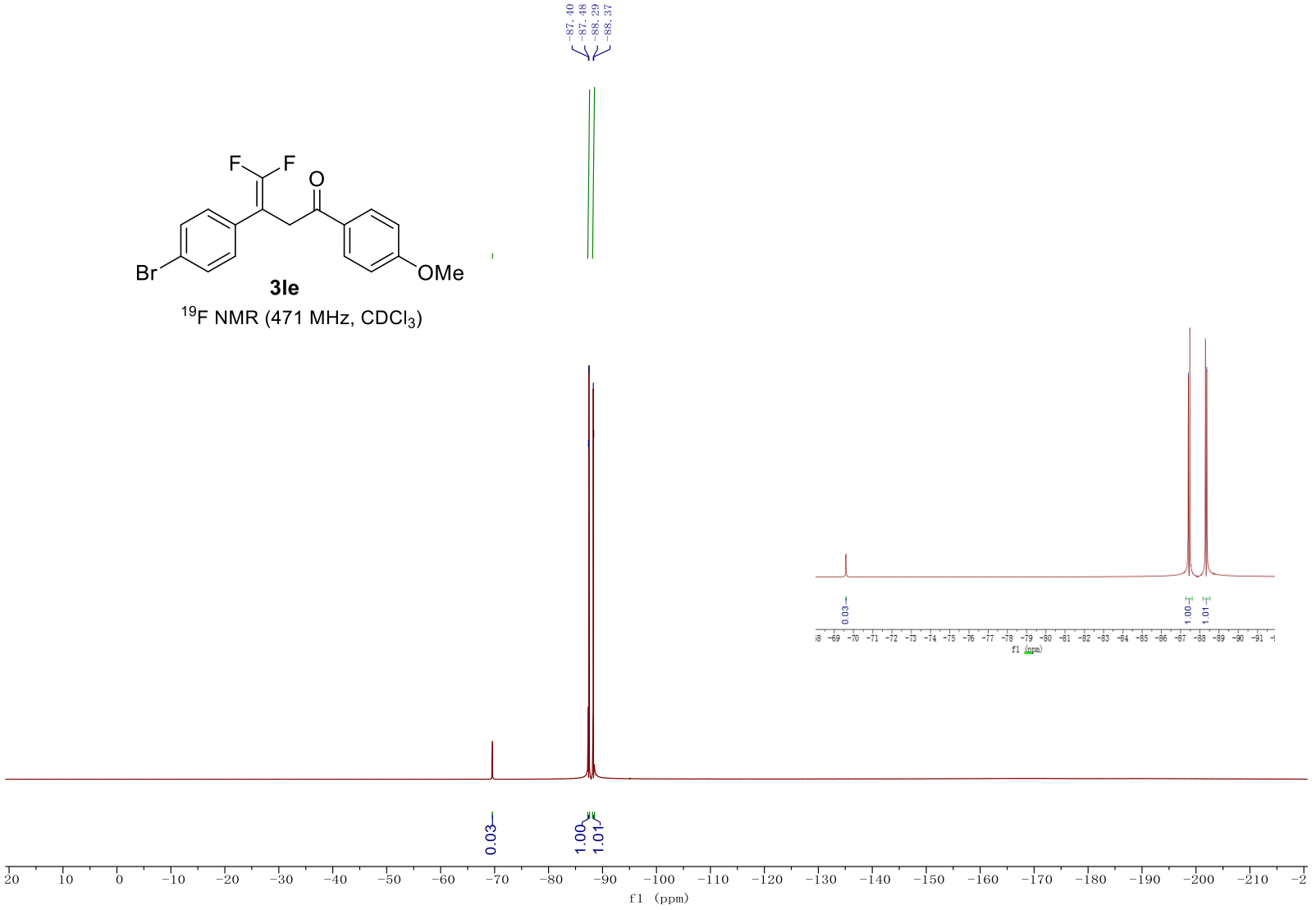

7.99
7.97
7.29
7.24
7.23
7.17
7.15
7.11
7.10
6.98
6.96
4.02
3.90
F
F
O
MeS
OMe
3ke
1H NMR (400 MHz, CDCl3)
1.98
1.02
1.02
1.00
0.96
2.03
2.00
3.00
3.01
f1 (ppm)

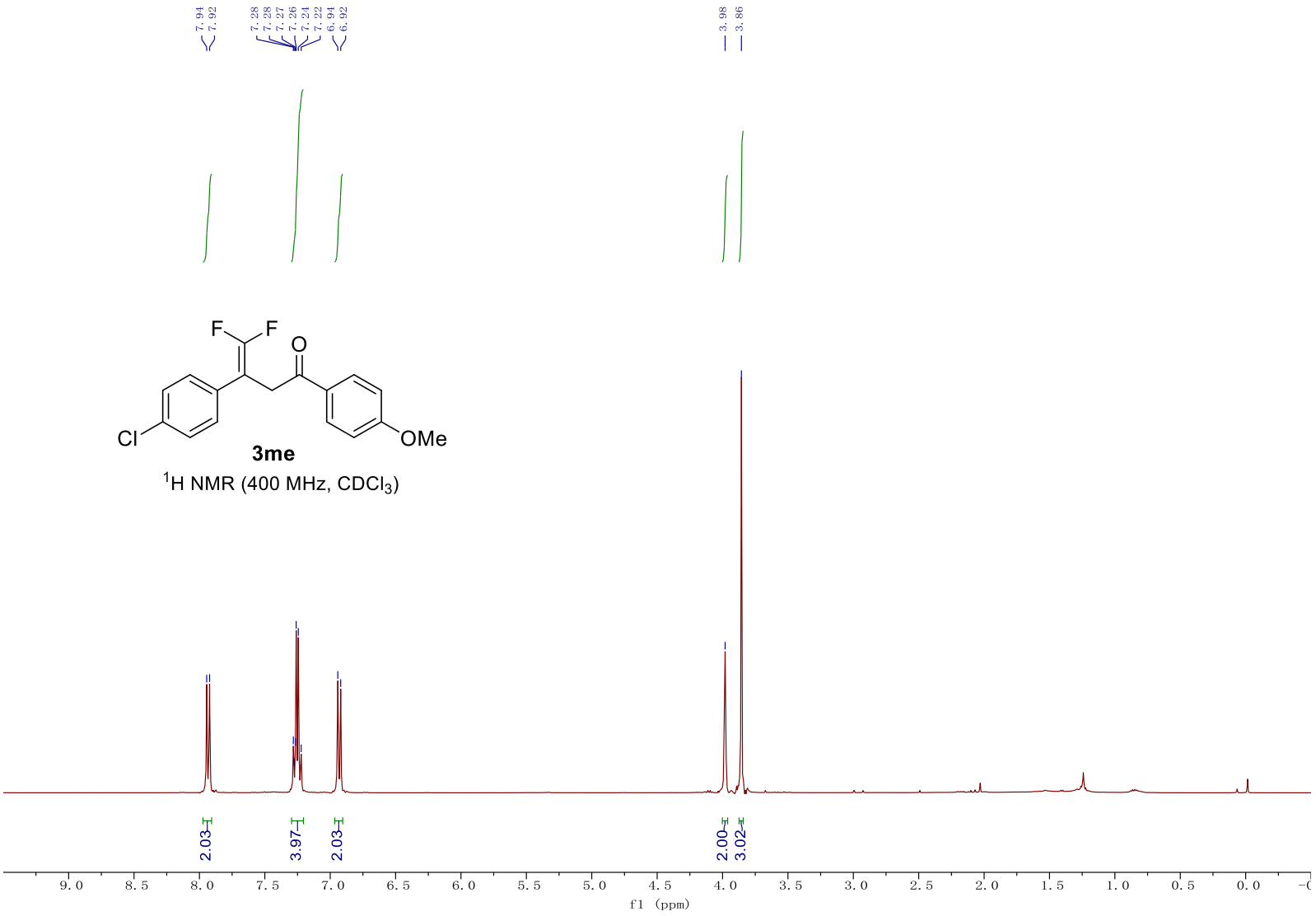

193.88
193.85
193.82
163.89
157.79
154.93
154.88
152.02
138.88
134.47
134.43
134.39
130.60
129.41
128.97
126.24
126.20
126.17
125.70
124.95
124.91
124.88
114.00
87.49
87.32
87.27
87.10
55.65
38.02
38.00
15.89
F
F
O
MeS
OMe
3ke
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

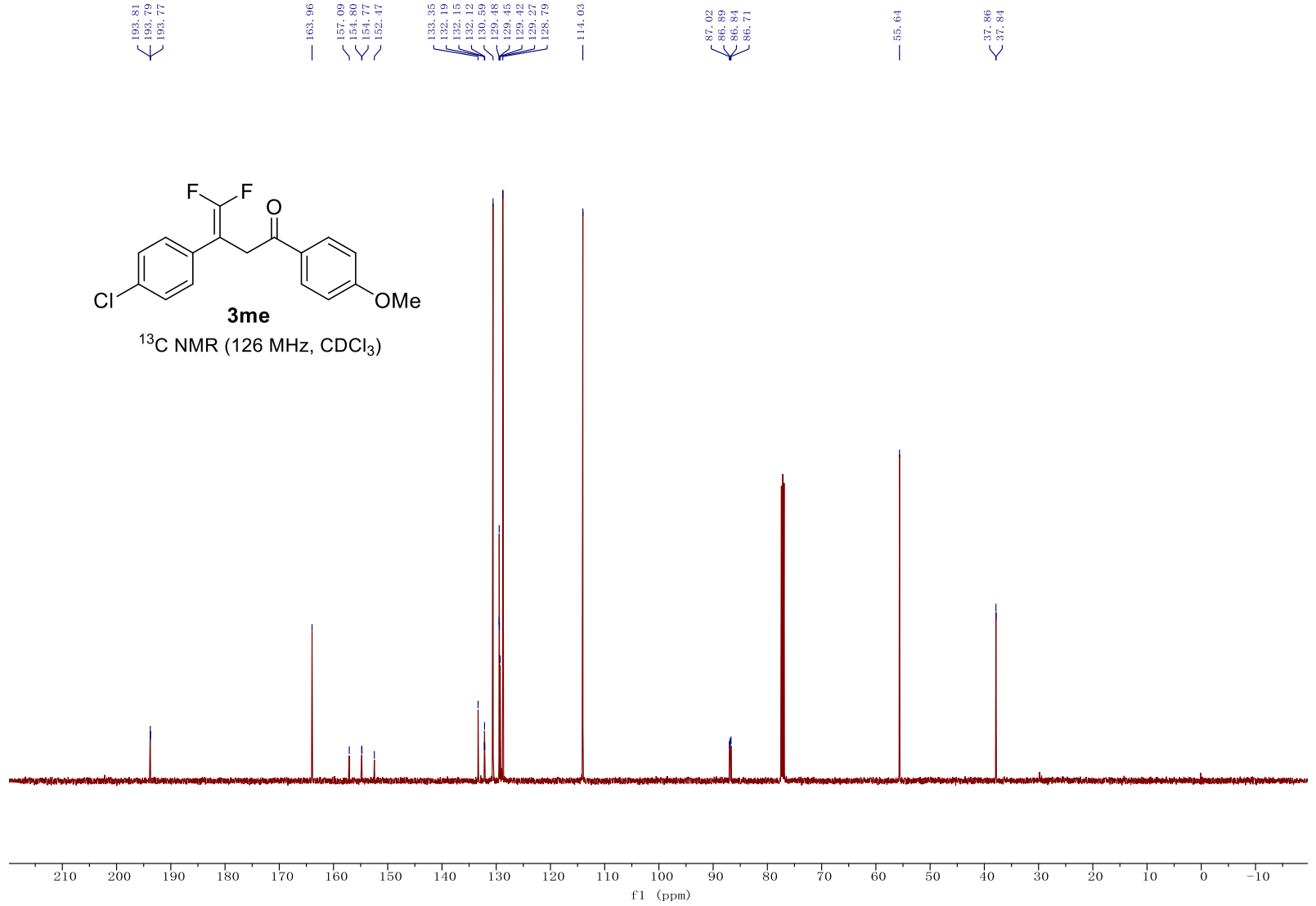

F
F
O
MeS
OMe
3ke
^{19}F NMR (376 MHz, $CDCl_3$)
-87.72
-87.82
-88.43
-88.52
0.03
1.00
1.00
f1 (ppm)

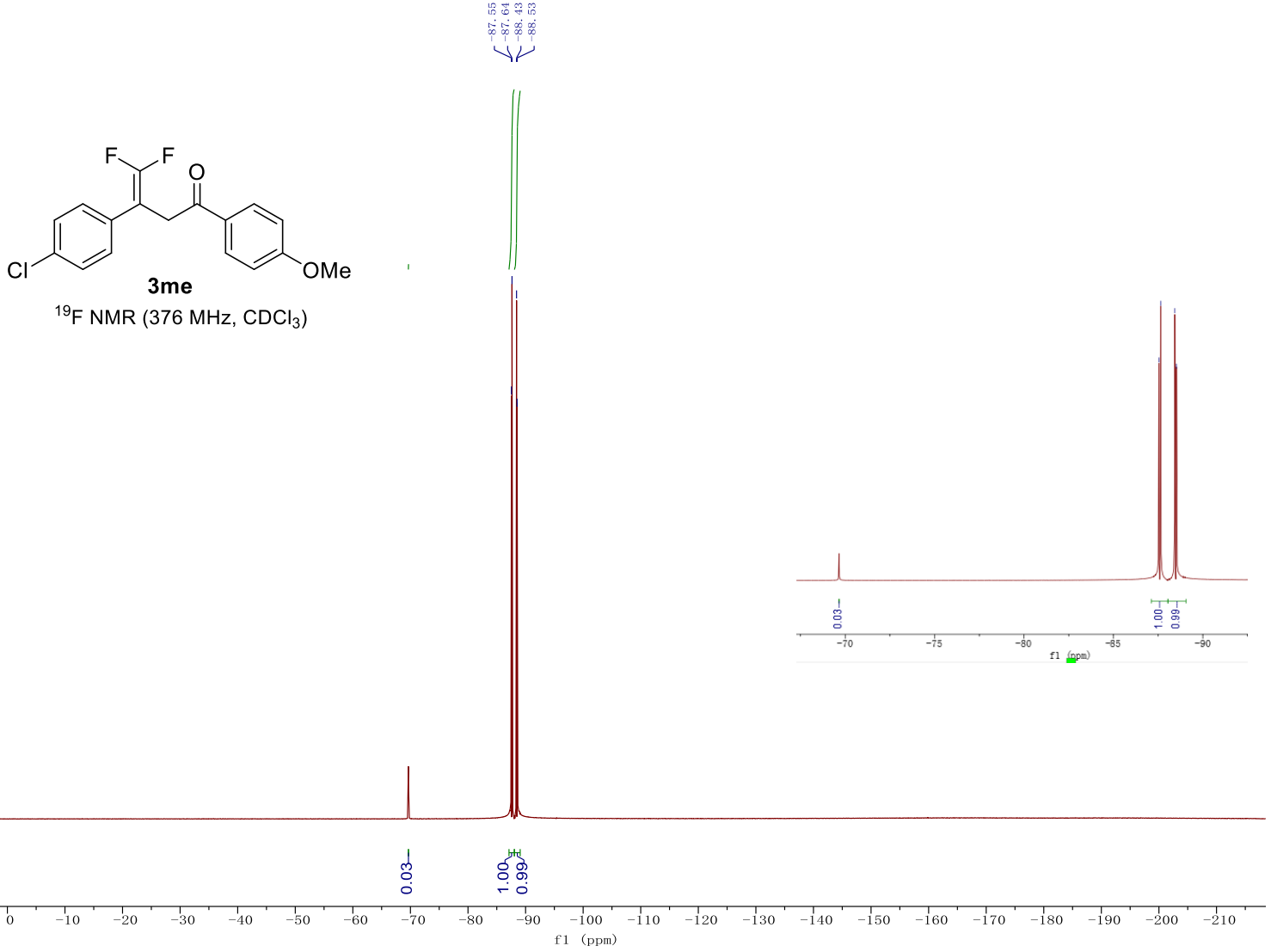

7.96
7.94
7.45
7.43
7.20
7.18
6.96
6.94
3.99
3.87
F
F
O
Br
OMe
3Ie
1H NMR (500 MHz, CDCl3)
2.00
2.00
2.00
2.02
2.00
3.01
f1 (ppm)

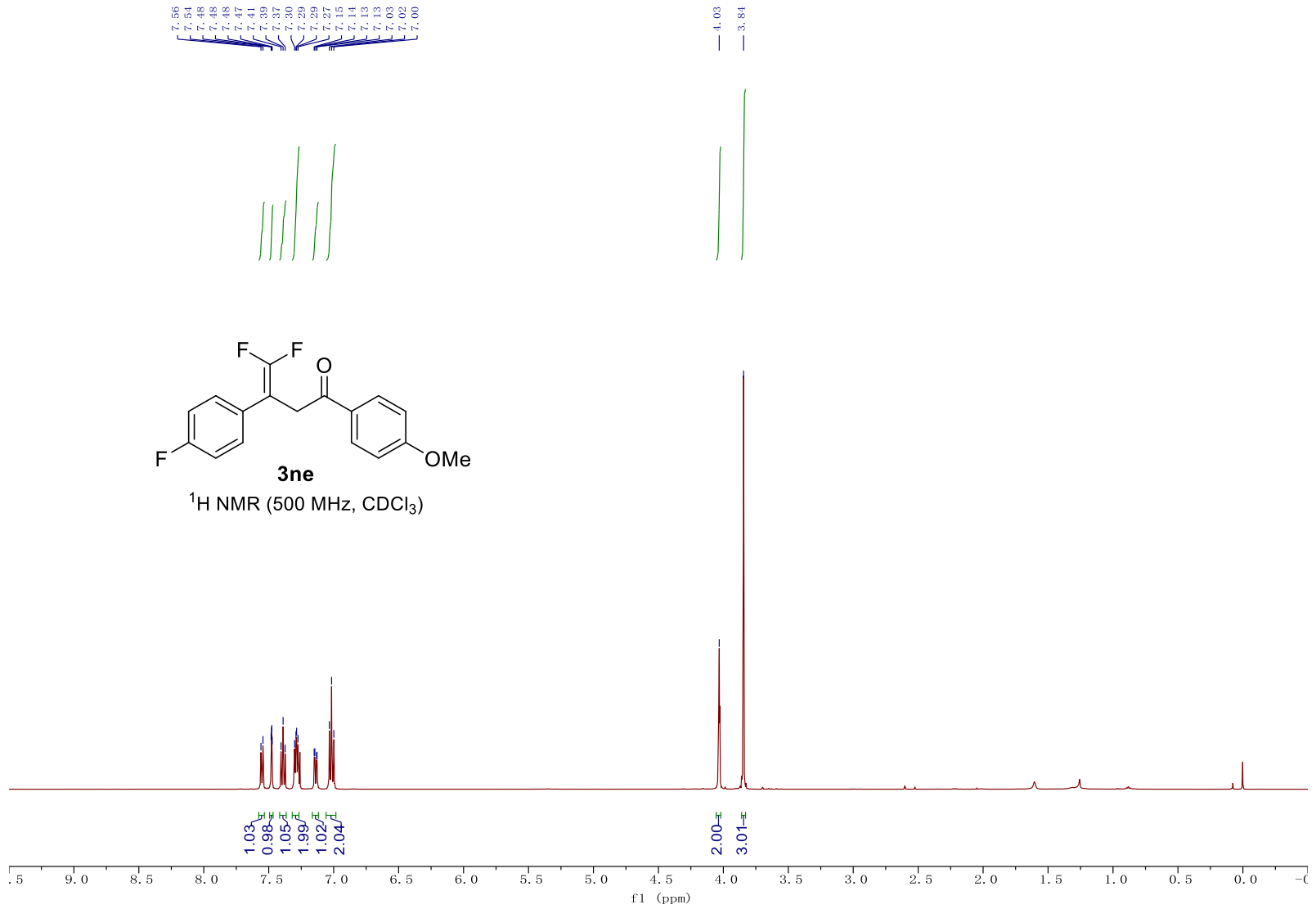

193.67
193.65
193.63
163.87
156.95
154.65
154.62
152.32
132.60
132.56
132.53
131.65
130.49
129.70
129.68
129.65
129.17
113.94
86.99
86.86
86.82
86.68
55.56
37.71
37.69
F
F
O
Br
OMe
3Ie
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


F
F
O
Br
OMe
3le
^{19}F NMR (471 MHz, $CDCl_3$)
-87.40
-87.48
-88.29
-88.37
0.03
1.00
1.01
f1 (ppm)


7.94
7.92
7.28
7.28
7.27
7.26
7.24
7.22
6.94
6.92
3.98
3.86
F
F
O
Cl
OMe
3me
1H NMR (400 MHz, CDCl3)
2.03
3.97
2.03
2.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

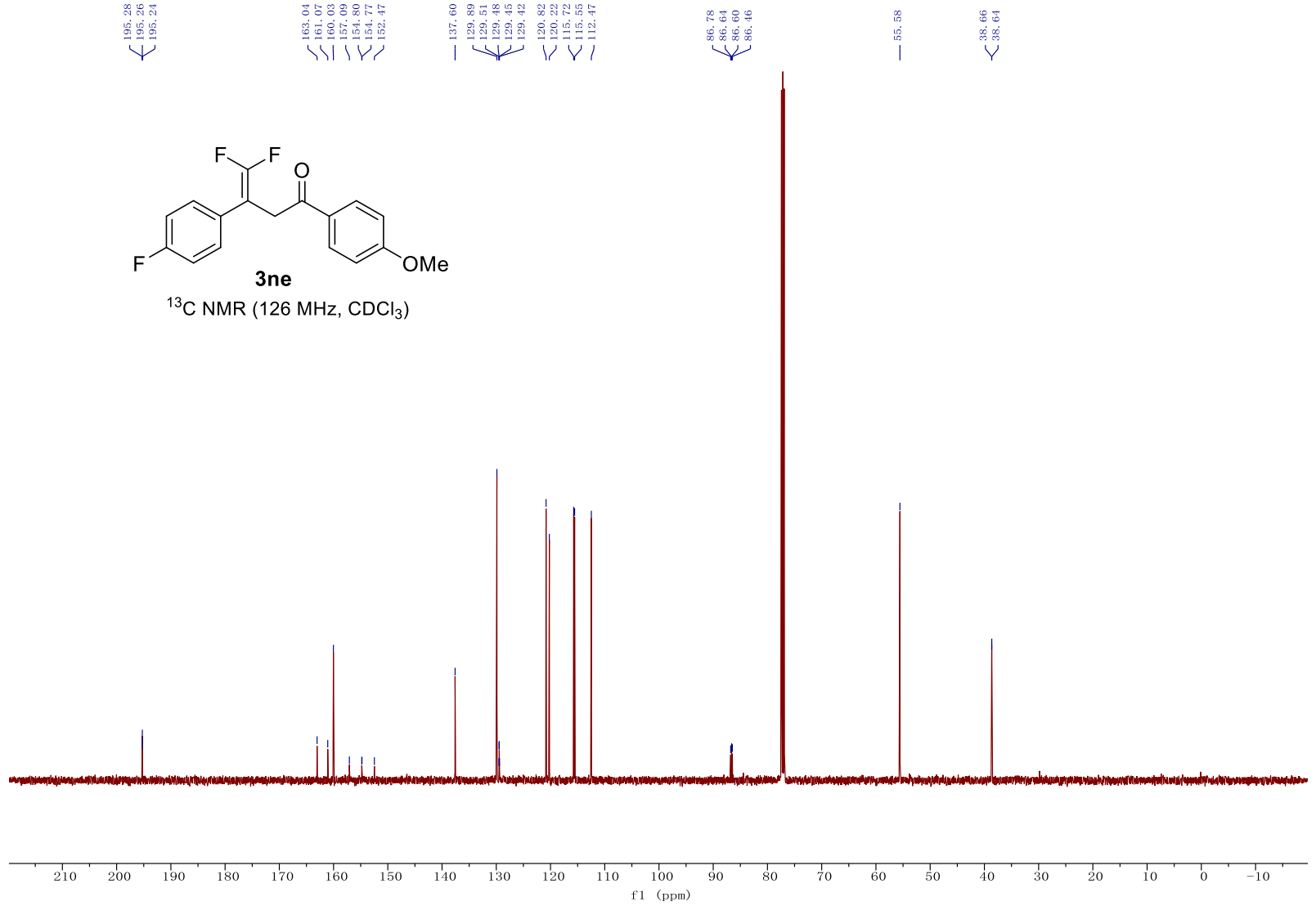

193.81
193.79
193.77
163.96
157.09
154.80
154.77
152.47
133.35
132.19
132.15
132.12
130.59
129.48
129.45
129.42
129.27
128.79
114.03
87.02
86.89
86.84
86.71
55.64
37.86
37.84
F
F
O
Cl
OMe
3me
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

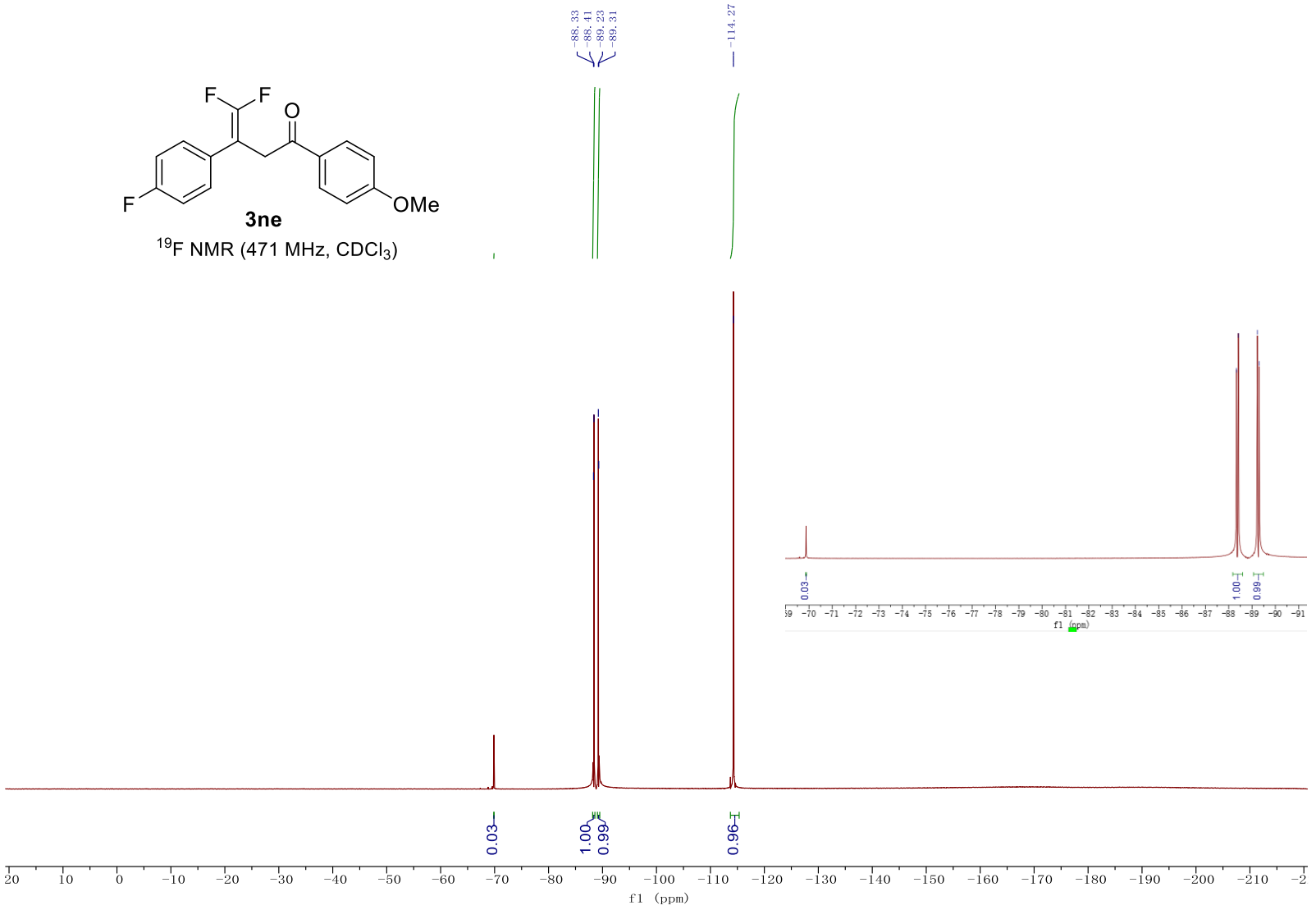

F
F
O
Cl
OMe
3me
^{19}F NMR (376 MHz, $CDCl_3$)
-87.55
-87.64
-88.43
-88.53
0.03
1.00
0.99
f1 (ppm)

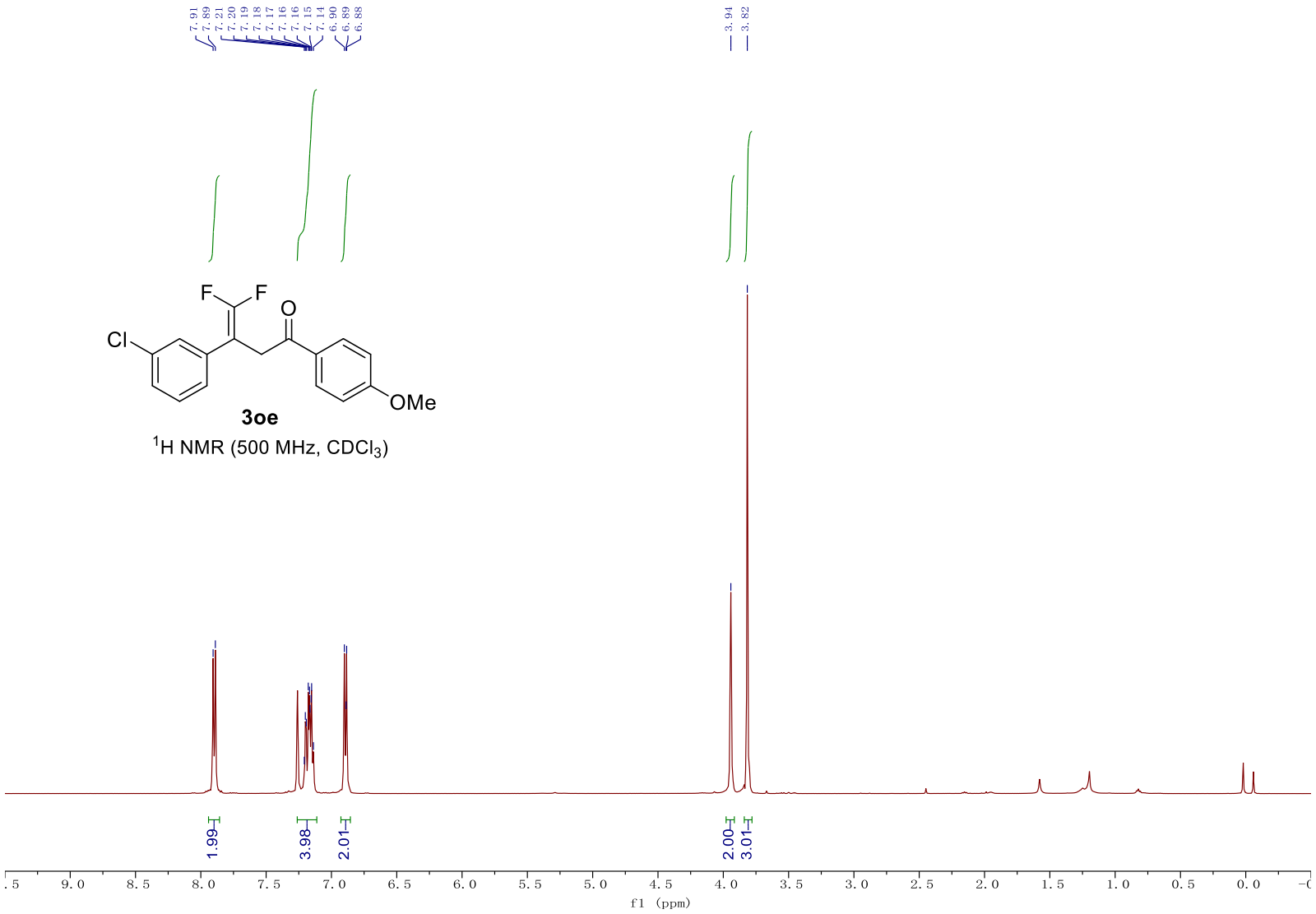


3ne

^{1}H NMR (500 MHz, $CDCl_3$)

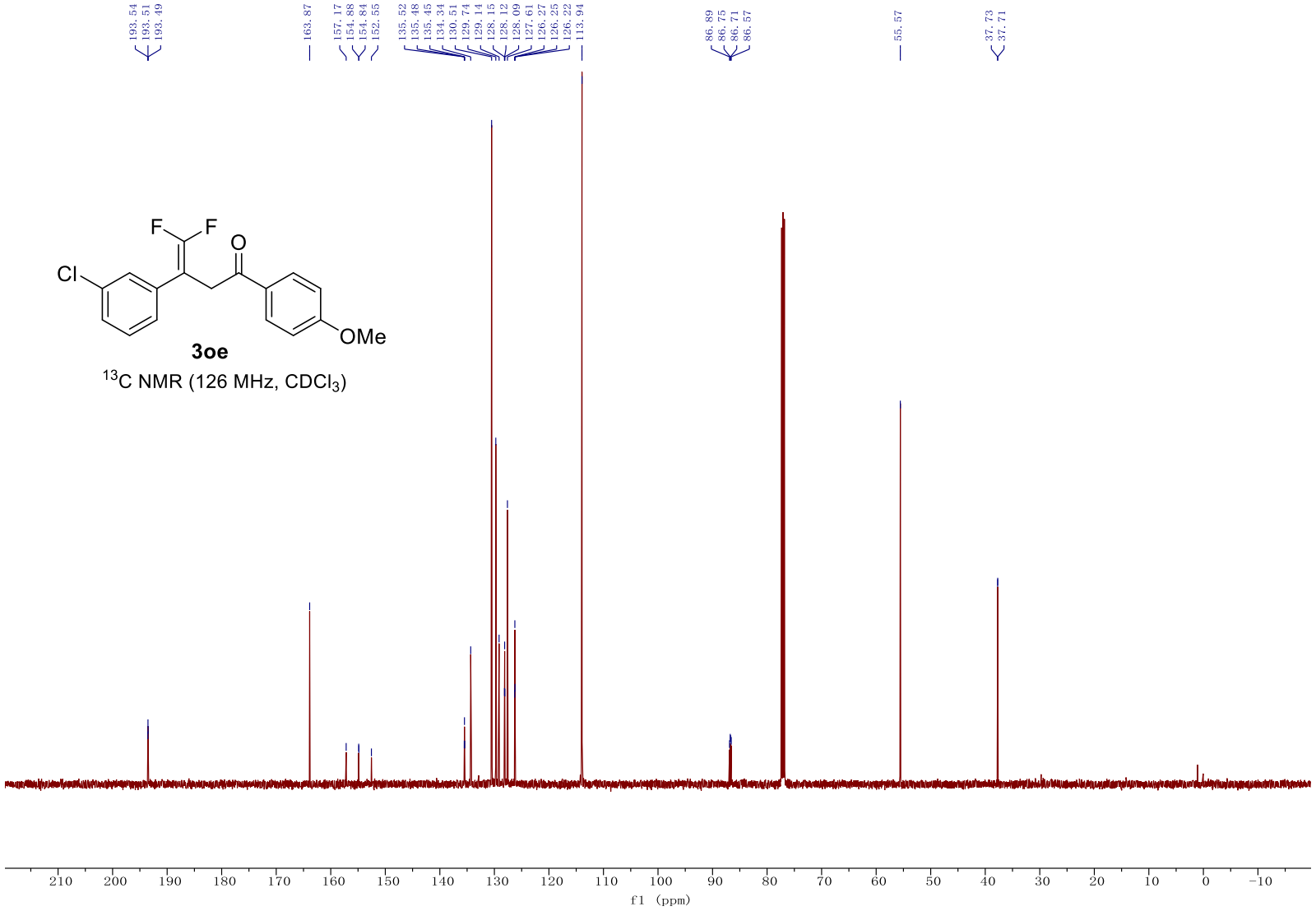

195.28
195.26
195.24
163.04
161.07
160.03
157.09
154.80
154.77
152.47
137.60
129.89
129.51
129.48
129.45
129.42
120.82
120.22
115.72
115.55
112.47
86.78
86.64
86.60
86.46
55.58
38.66
38.64
F
F
O
F
OMe
3ne
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

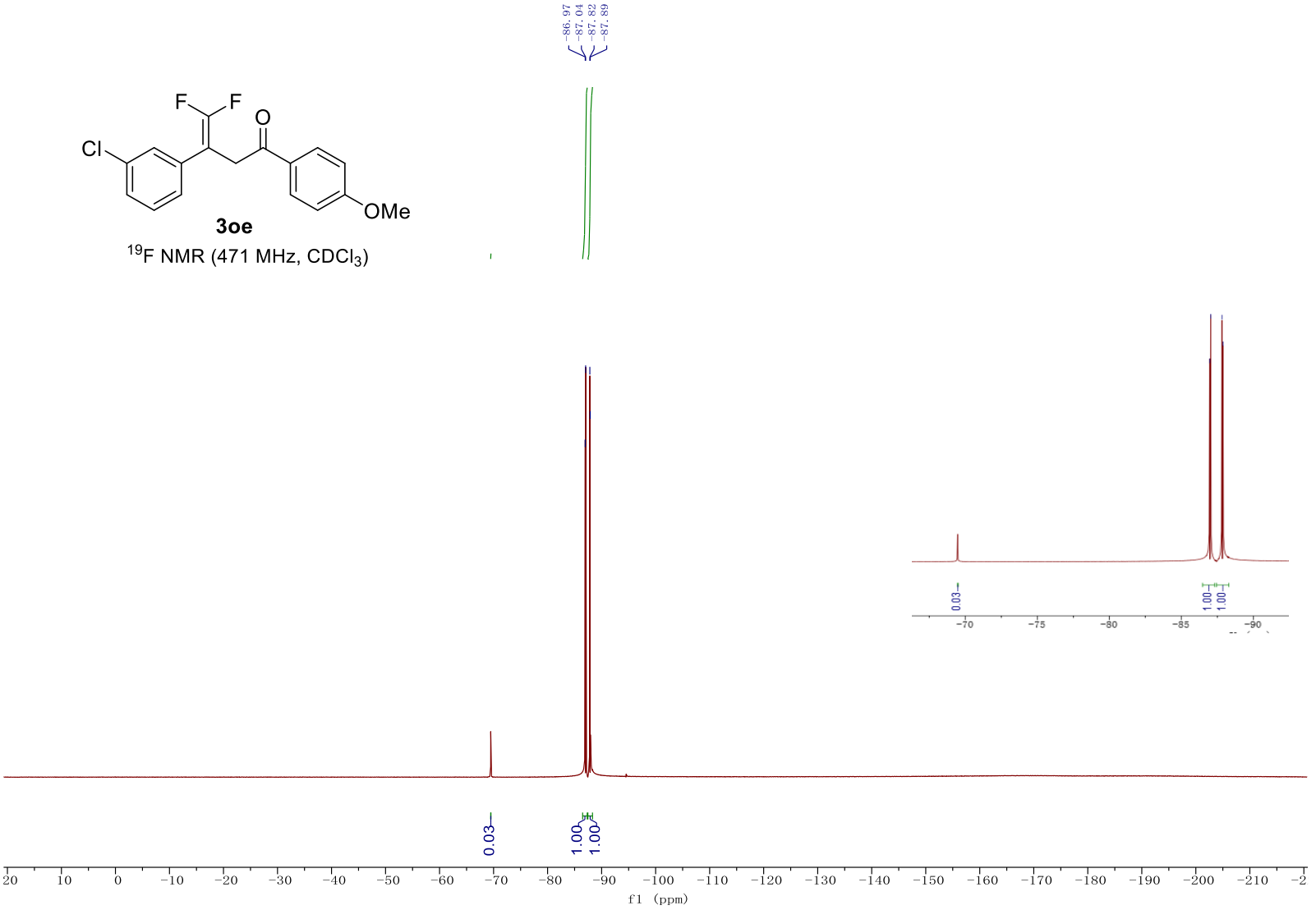

F
F
O
F
OMe
3ne
19F NMR (471 MHz, CDCl3)
-88.33
-88.41
-89.23
-89.31
-114.27
0.03
1.00
0.99
0.96
f1 (ppm)

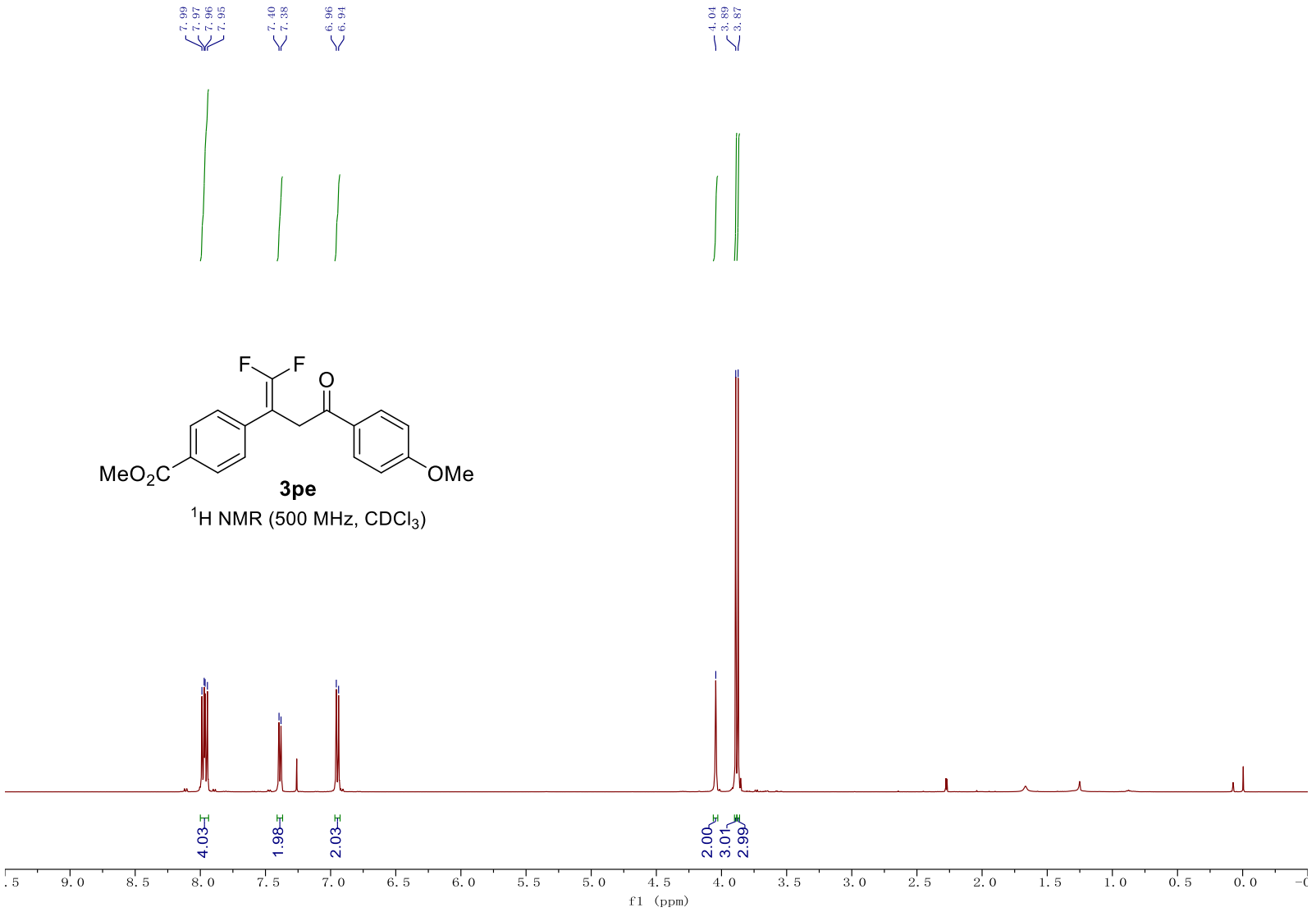


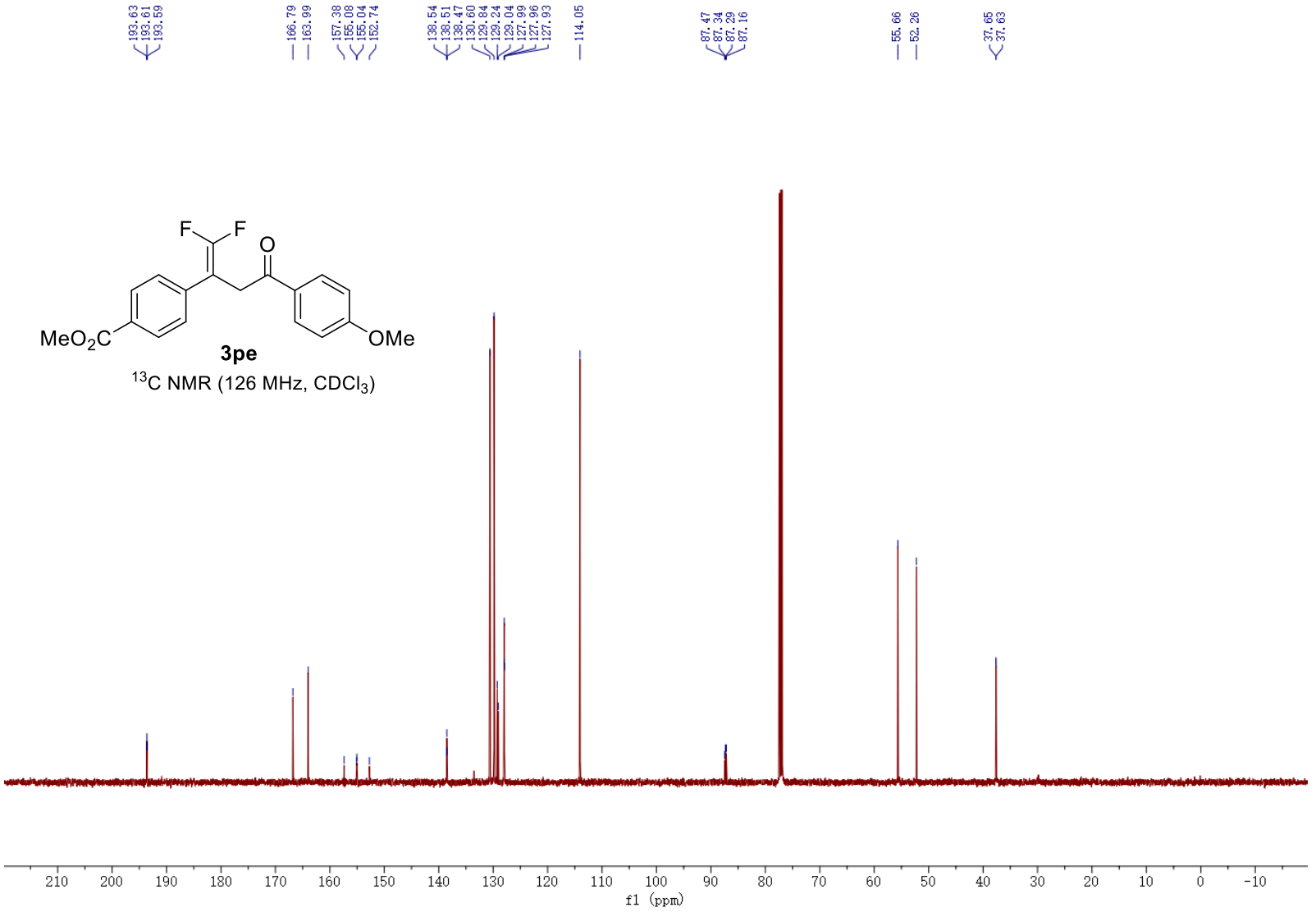
3oe

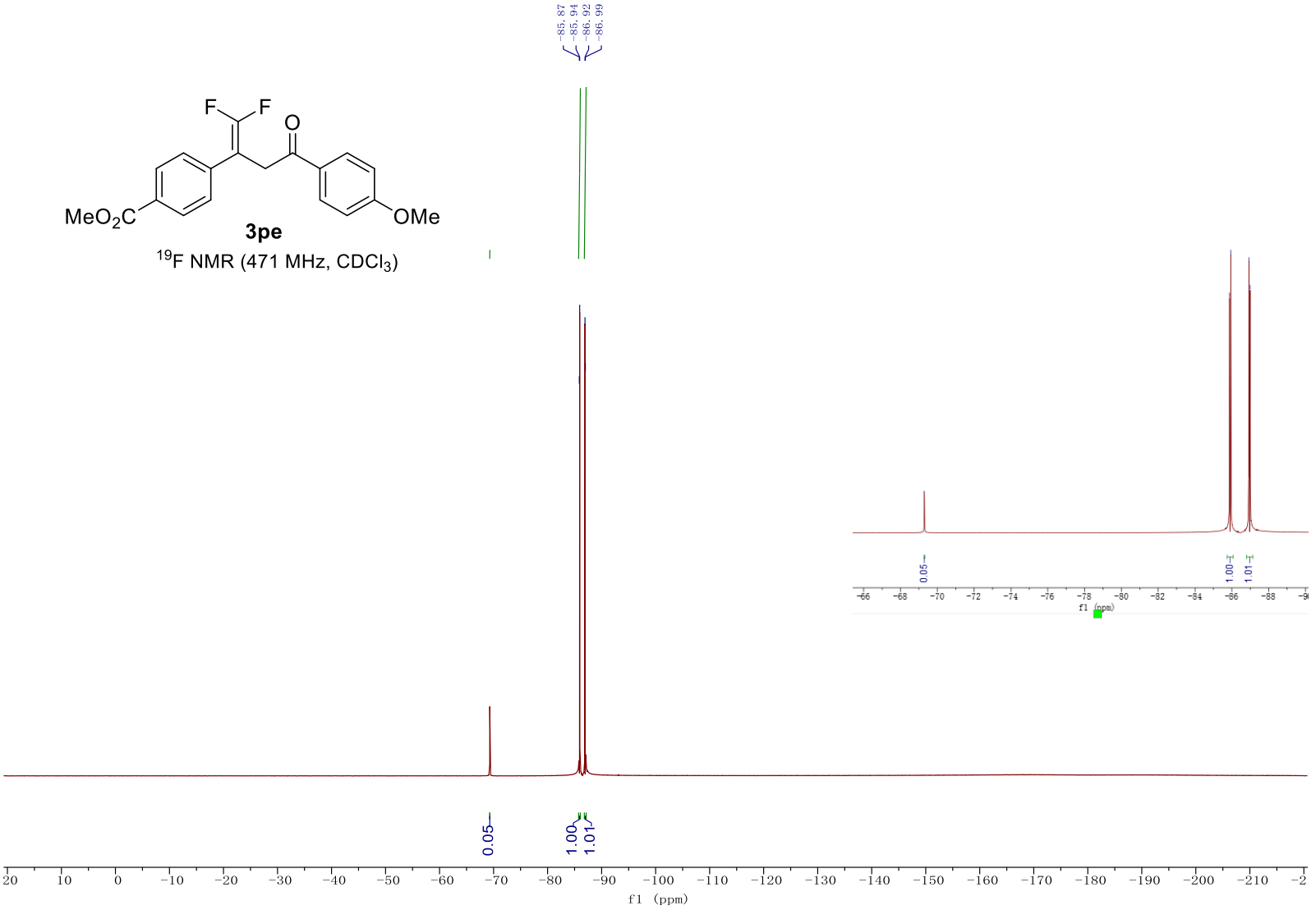
^{1}H NMR (500 MHz, $CDCl_3$)

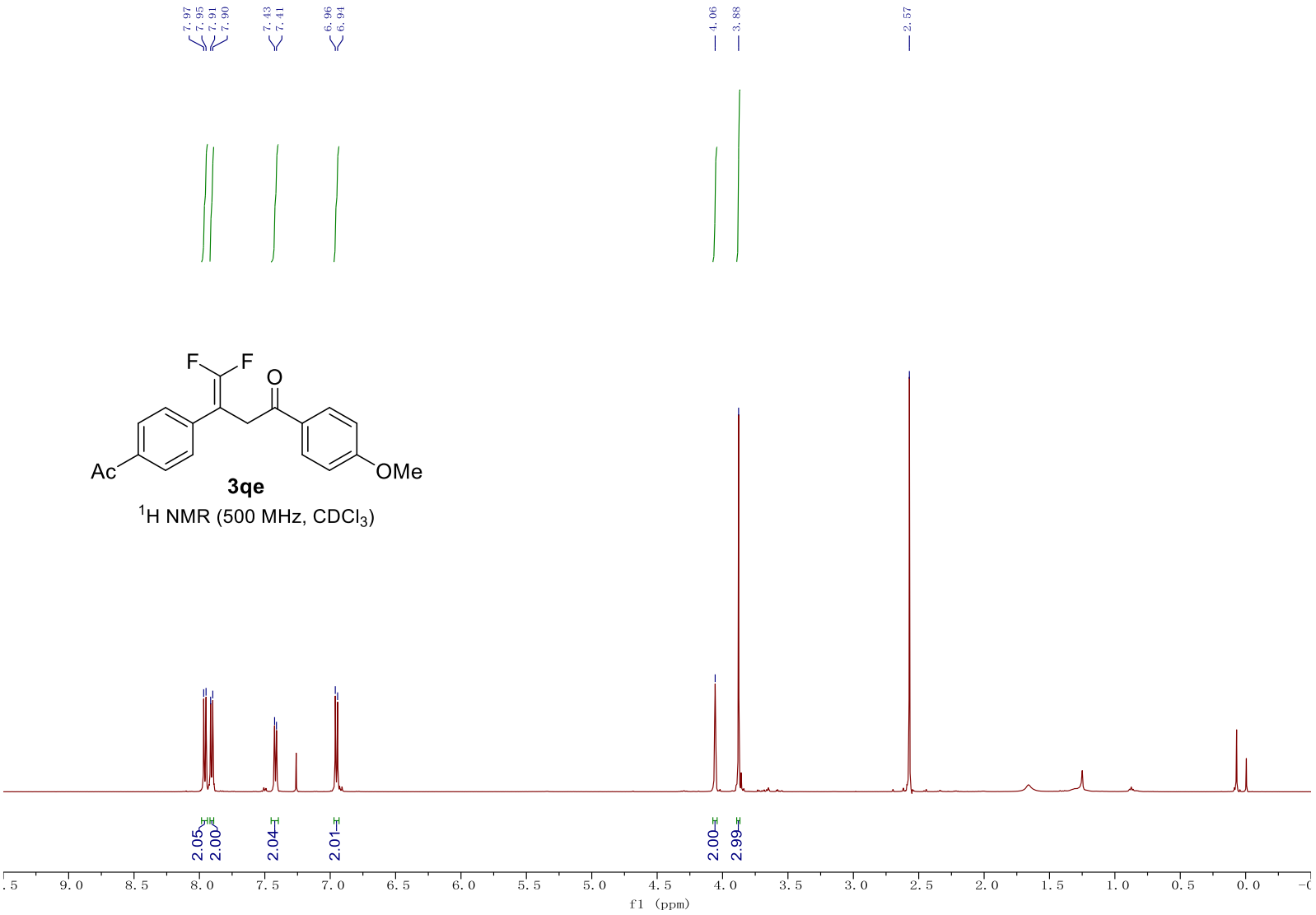

193.54
193.51
193.49
163.87
157.17
154.88
154.84
152.55
135.52
135.48
135.45
134.34
130.51
129.74
129.14
128.15
128.12
128.09
127.61
126.27
126.25
126.22
113.94
86.89
86.75
86.71
86.57
55.57
37.73
37.71
F
F
O
Cl
OMe
3oe
^{13}C NMR (126 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

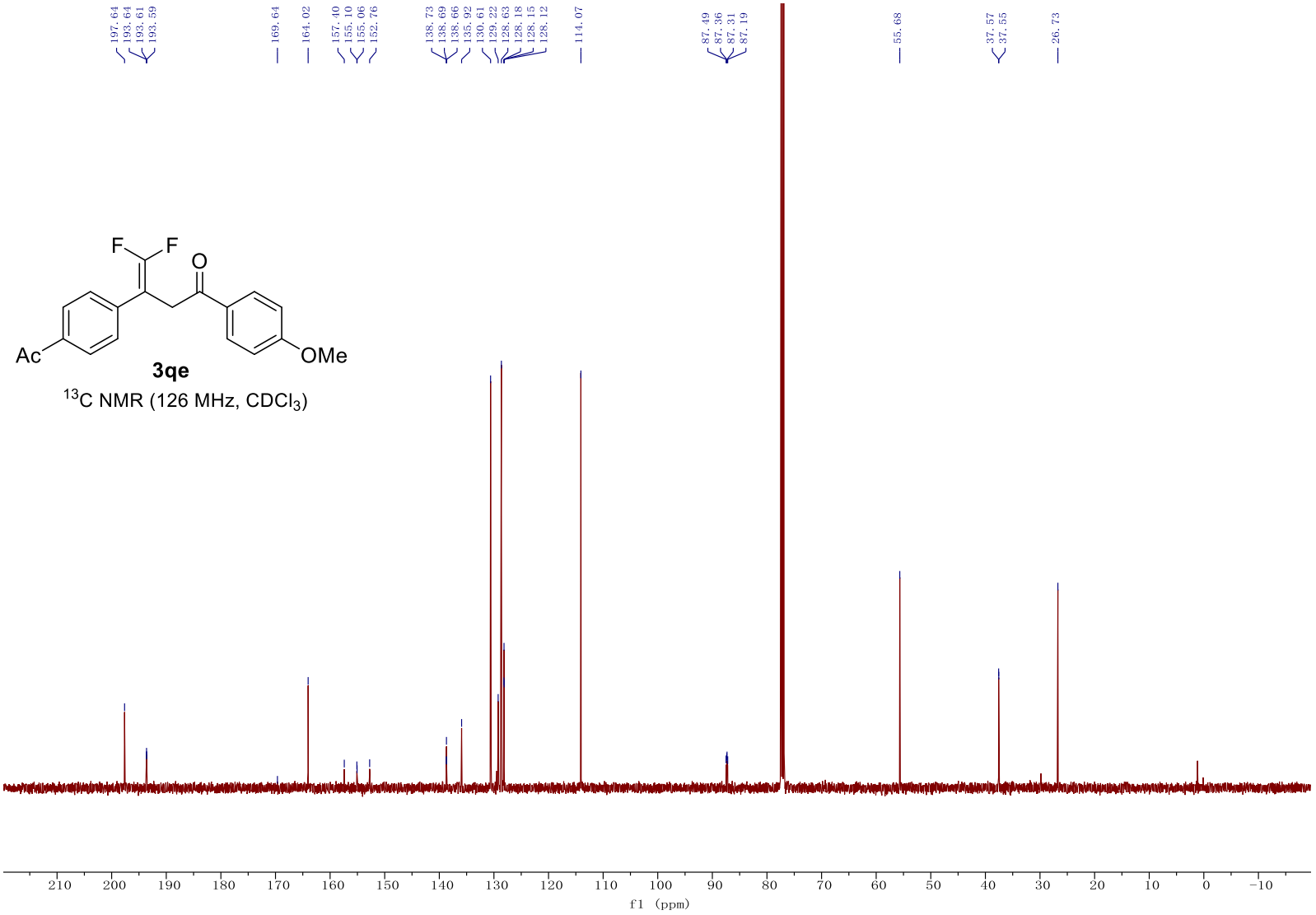

F
F
O
Cl
OMe
3oe
^{19}F NMR (471 MHz, $CDCl_3$)
-86.97
-87.04
-87.82
-87.89
0.03
1.00
1.00
f1 (ppm)

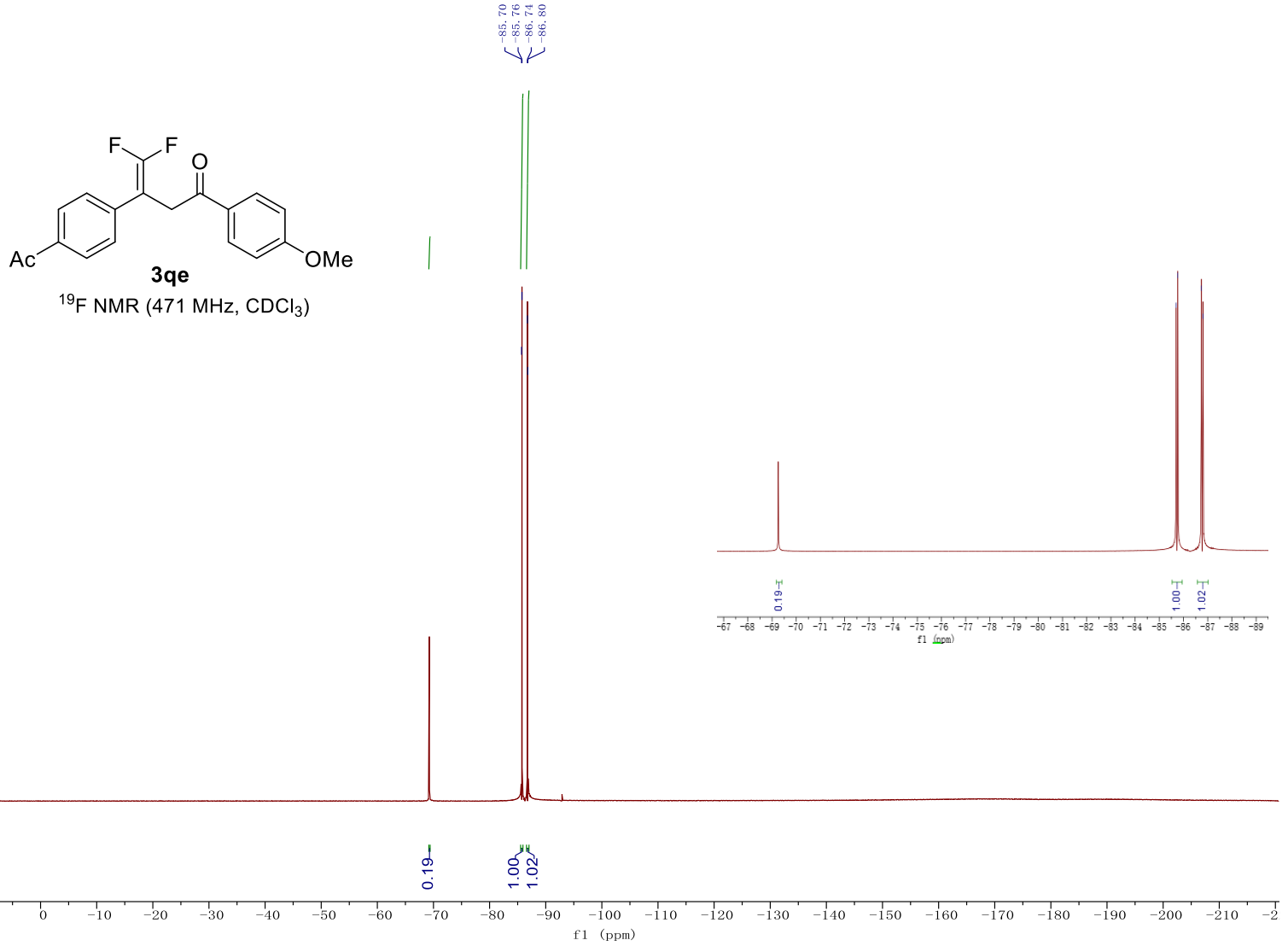

7.99
7.97
7.96
7.95
7.40
7.38
6.96
6.94
4.04
3.89
3.87
F
F
O
MeO2C
OMe
3pe
1H NMR (500 MHz, CDCl3)
4.03
1.98
2.03
2.00
3.01
2.99
f1 (ppm)

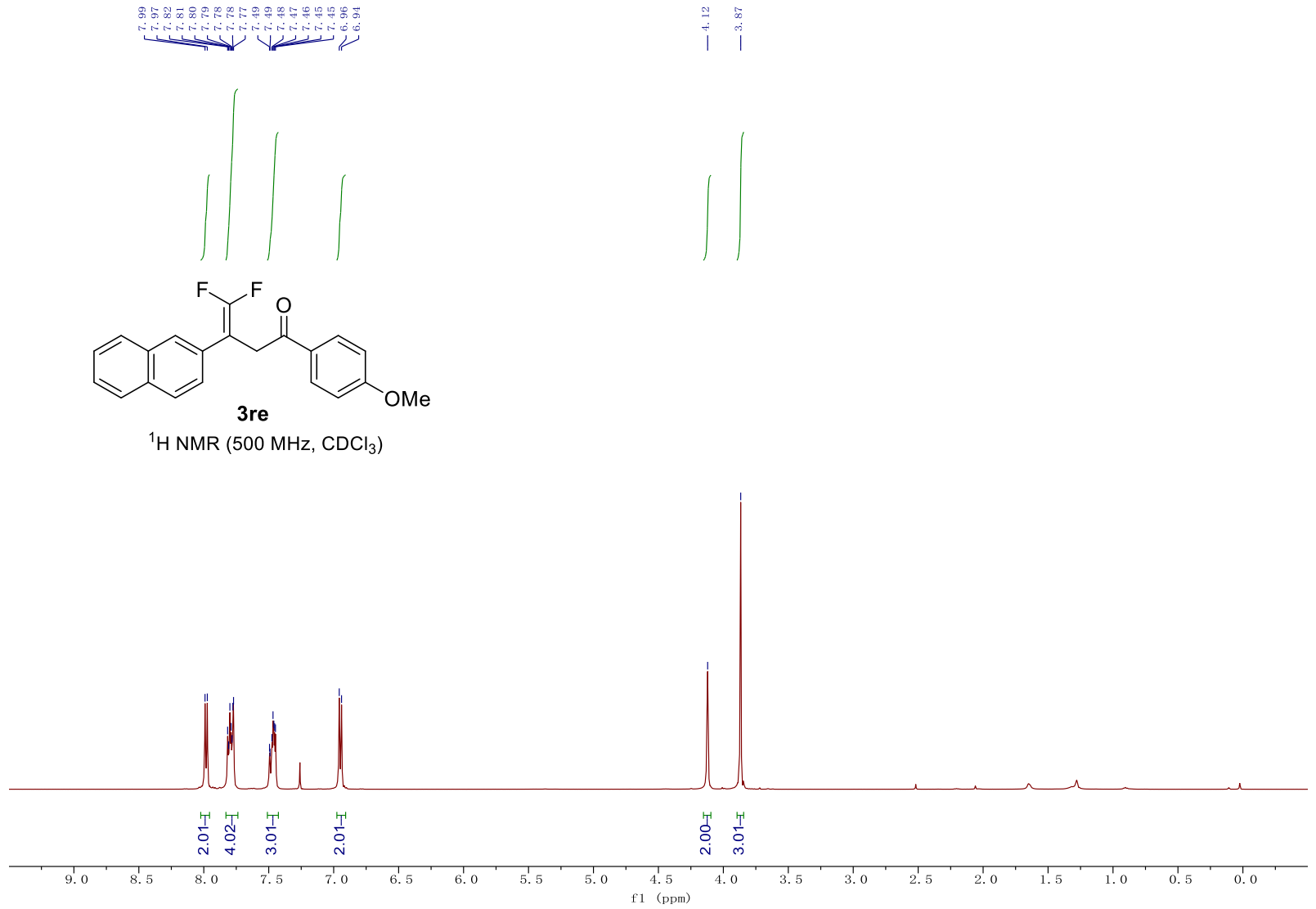

193.63
193.61
193.59
166.79
163.99
157.38
155.08
155.04
152.74
138.54
138.51
138.47
130.60
129.84
129.24
129.04
127.99
127.96
127.93
114.05
87.47
87.34
87.29
87.16
55.66
52.26
37.65
37.63
F
F
O
MeO2C
OMe
3pe
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

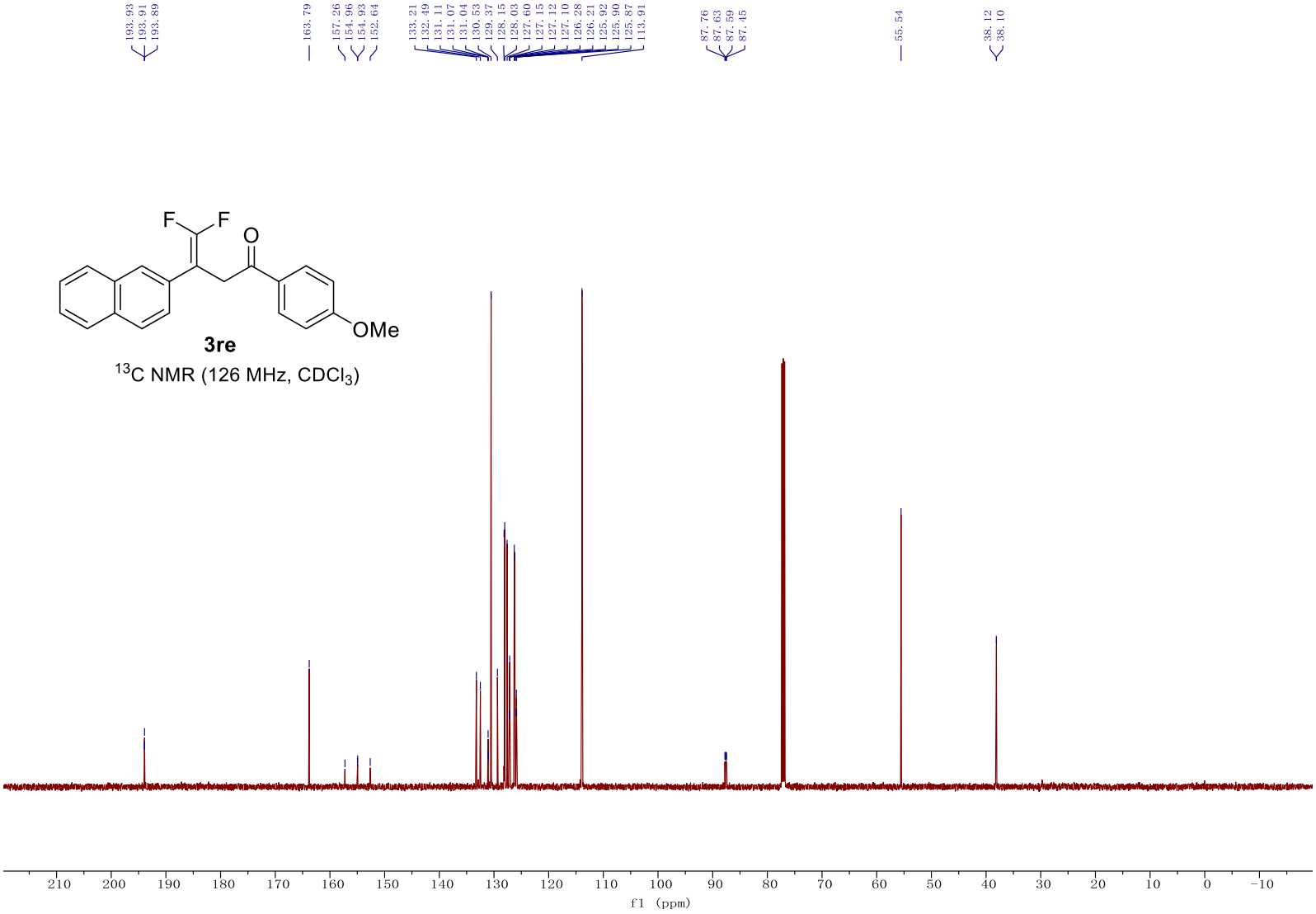

F
F
O
MeO2C
OMe
3pe
19F NMR (471 MHz, CDCl3)
-85.87
-85.94
-86.92
-86.99
0.05
1.00
1.01
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


7.97
7.95
7.91
7.90
7.43
7.41
6.96
6.94
4.06
3.88
2.57
F
F
O
Ac
OMe
3qe
^{1}H NMR (500 MHz, CDCl$_3$)
2.05
2.00
2.04
2.01
2.00
2.99
f1 (ppm)


197.64
193.64
193.61
193.59
169.64
164.02
157.40
155.10
155.06
152.76
138.73
138.69
138.66
135.92
130.61
129.22
128.63
128.18
128.15
128.12
114.07
87.49
87.36
87.31
87.19
55.68
37.57
37.55
26.73
F
F
O
Ac
OMe
3qe
13C NMR (126 MHz, CDCl3)
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)

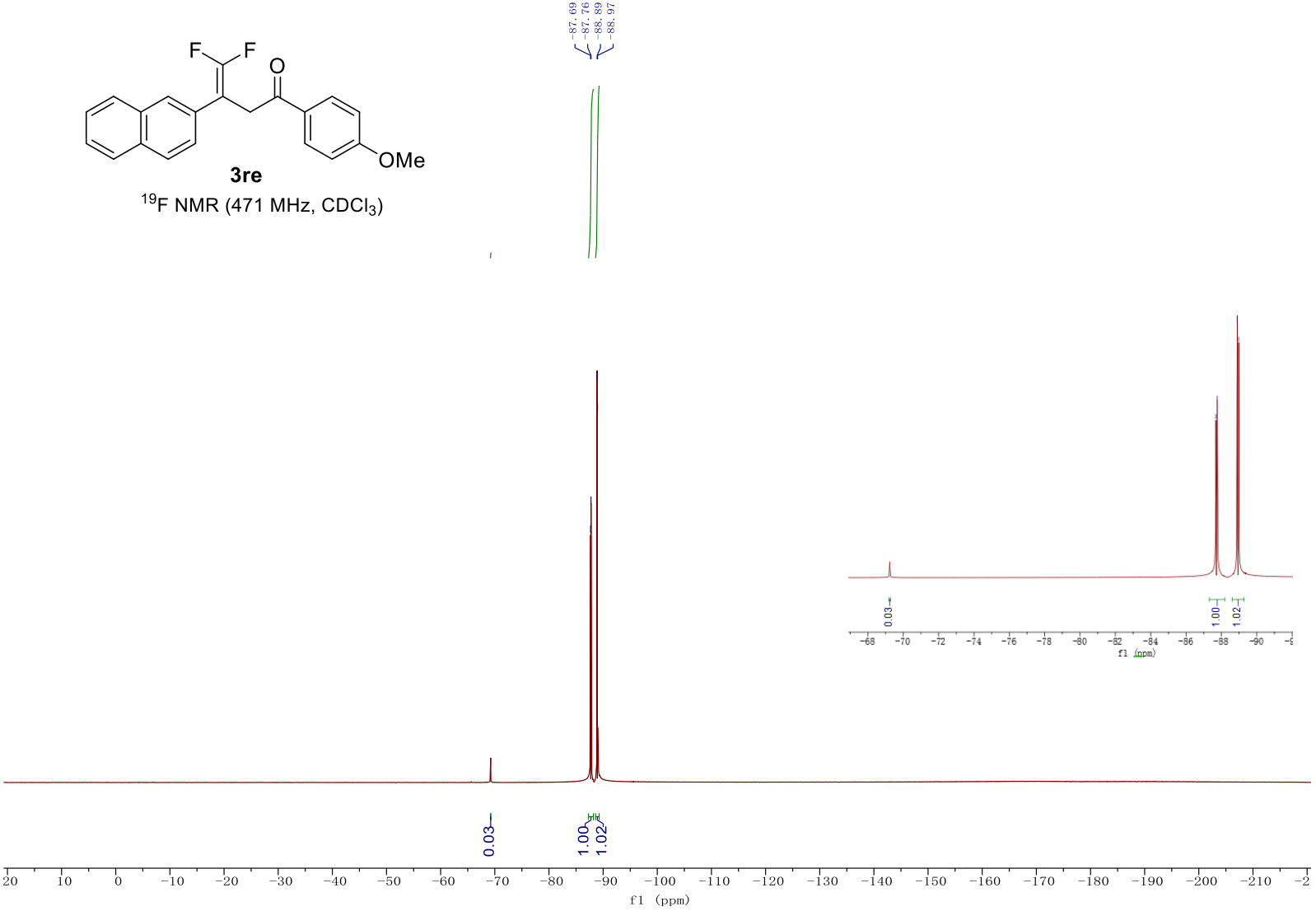

F
F
O
Ac
OMe
3qe
^{19}F NMR (471 MHz, $CDCl_3$)
-85.70
-85.76
-86.74
-86.80
0.19
1.00
1.02
f1 (ppm)

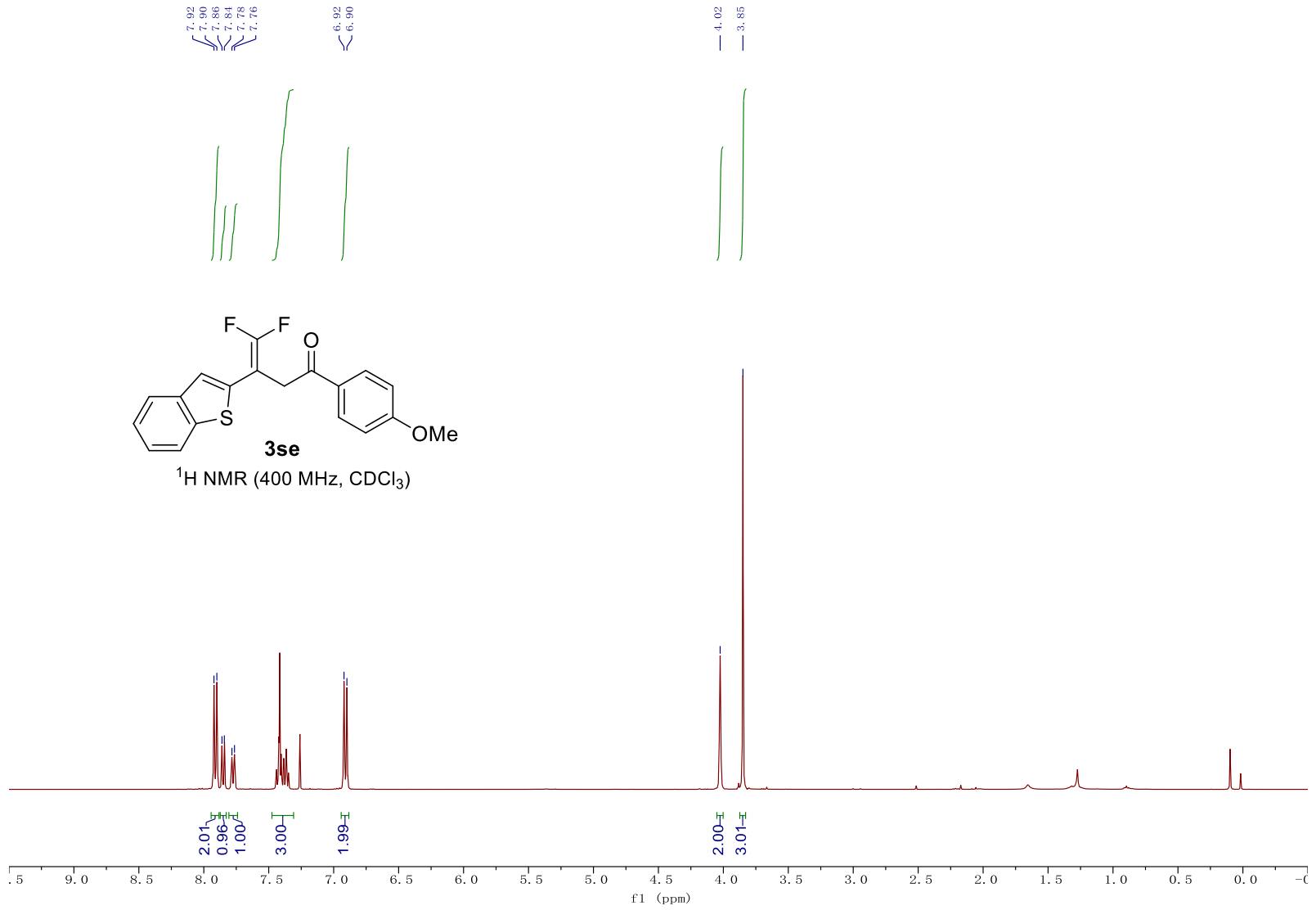

7.99
7.97
7.82
7.81
7.80
7.79
7.78
7.78
7.77
7.49
7.49
7.48
7.47
7.46
7.45
7.45
6.96
6.94
4.12
3.87
F
F
O
OMe
3re
1H NMR (500 MHz, CDCl3)
2.01
4.02
3.01
2.01
2.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

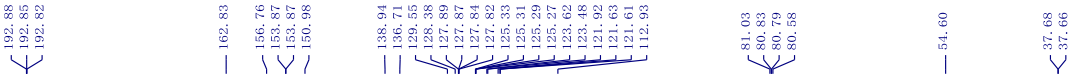

193.93
193.91
193.89
163.79
157.26
154.96
154.93
152.64
133.21
132.49
131.11
131.07
131.04
130.53
129.37
128.15
128.03
127.60
127.15
127.12
127.10
126.28
126.21
125.92
125.90
125.87
113.91
87.76
87.63
87.59
87.45
55.54
38.12
38.10
F
F
O
OMe
3re
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

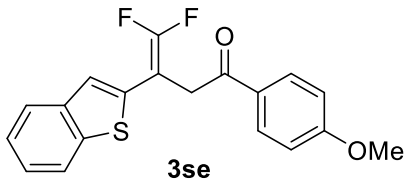
3re

^{19}F NMR (471 MHz, $CDCl_3$)



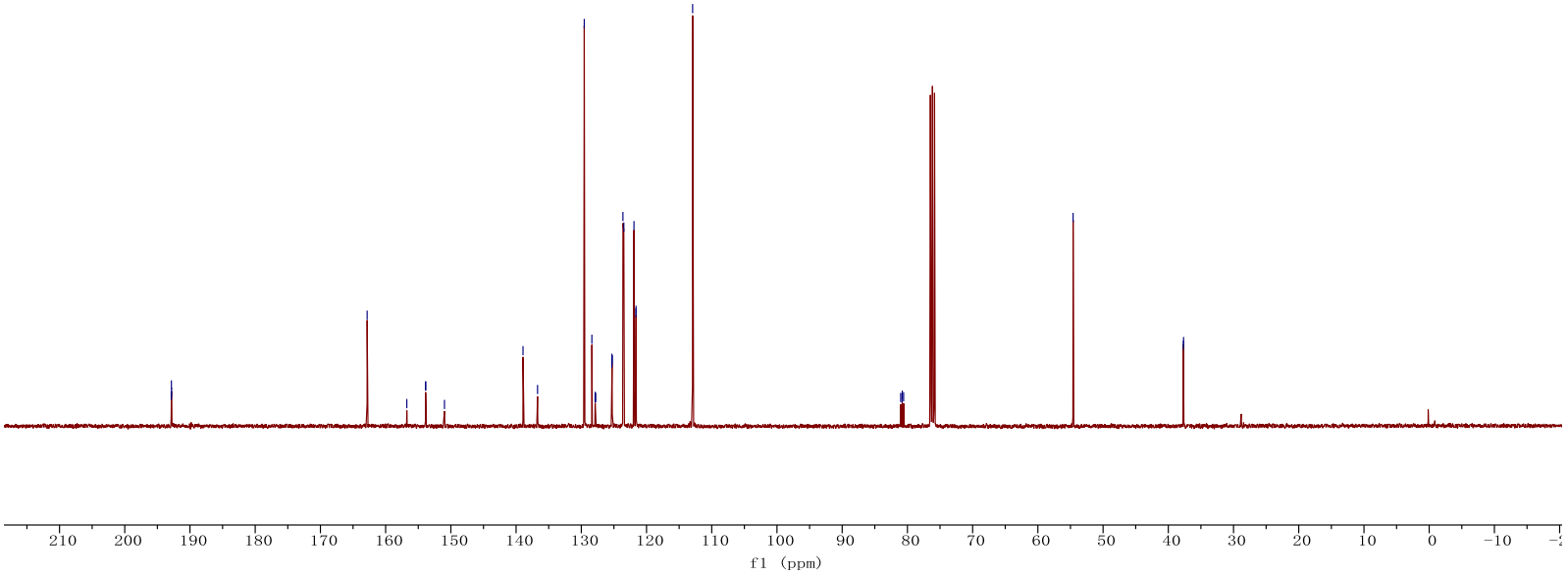

7.92
7.90
7.86
7.84
7.78
7.76
6.92
6.90
4.02
3.85
F
F
O
S
OMe
3se
1H NMR (400 MHz, CDCl3)
2.01
0.96
1.00
3.00
1.99
2.00
3.01
f1 (ppm)

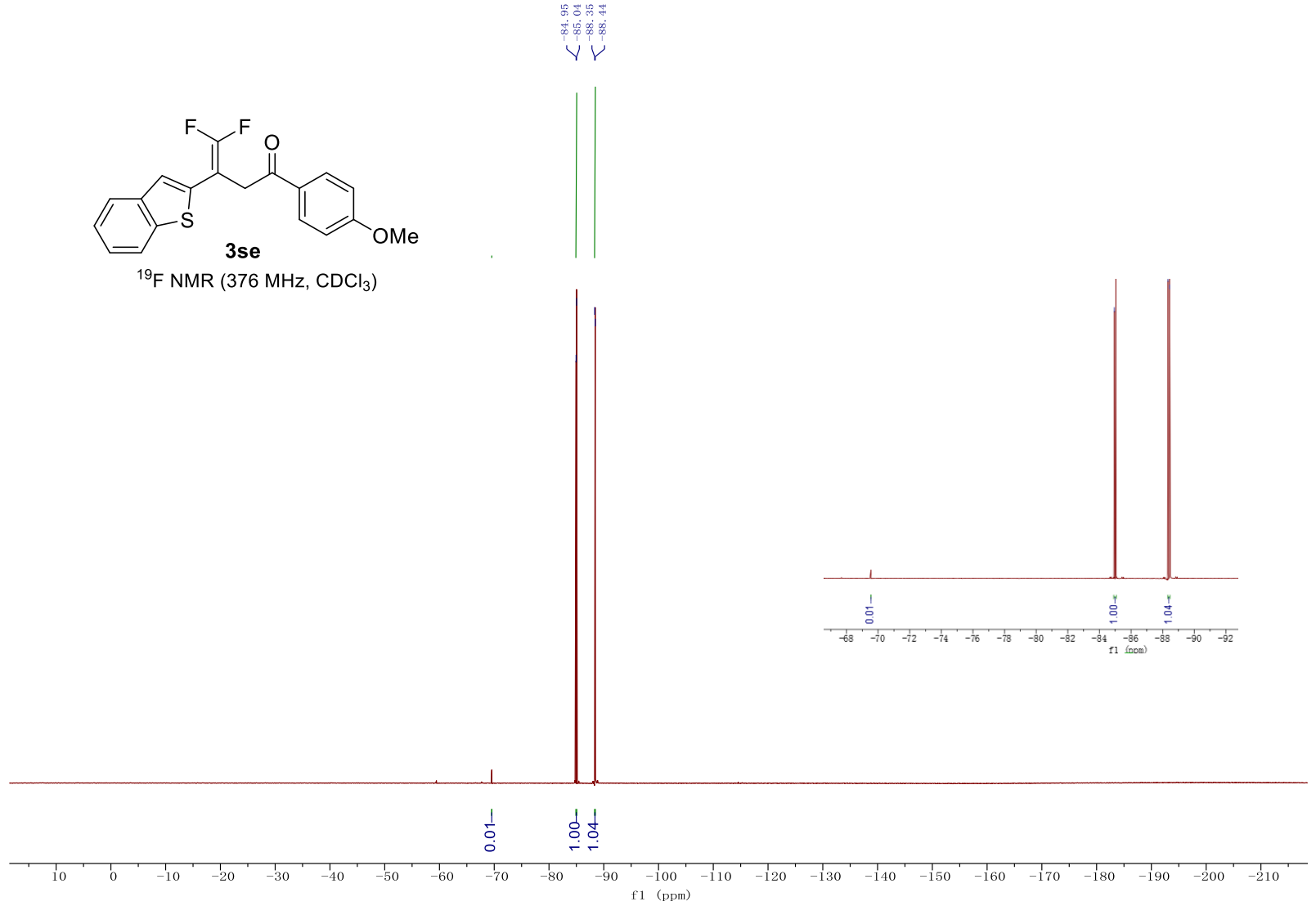


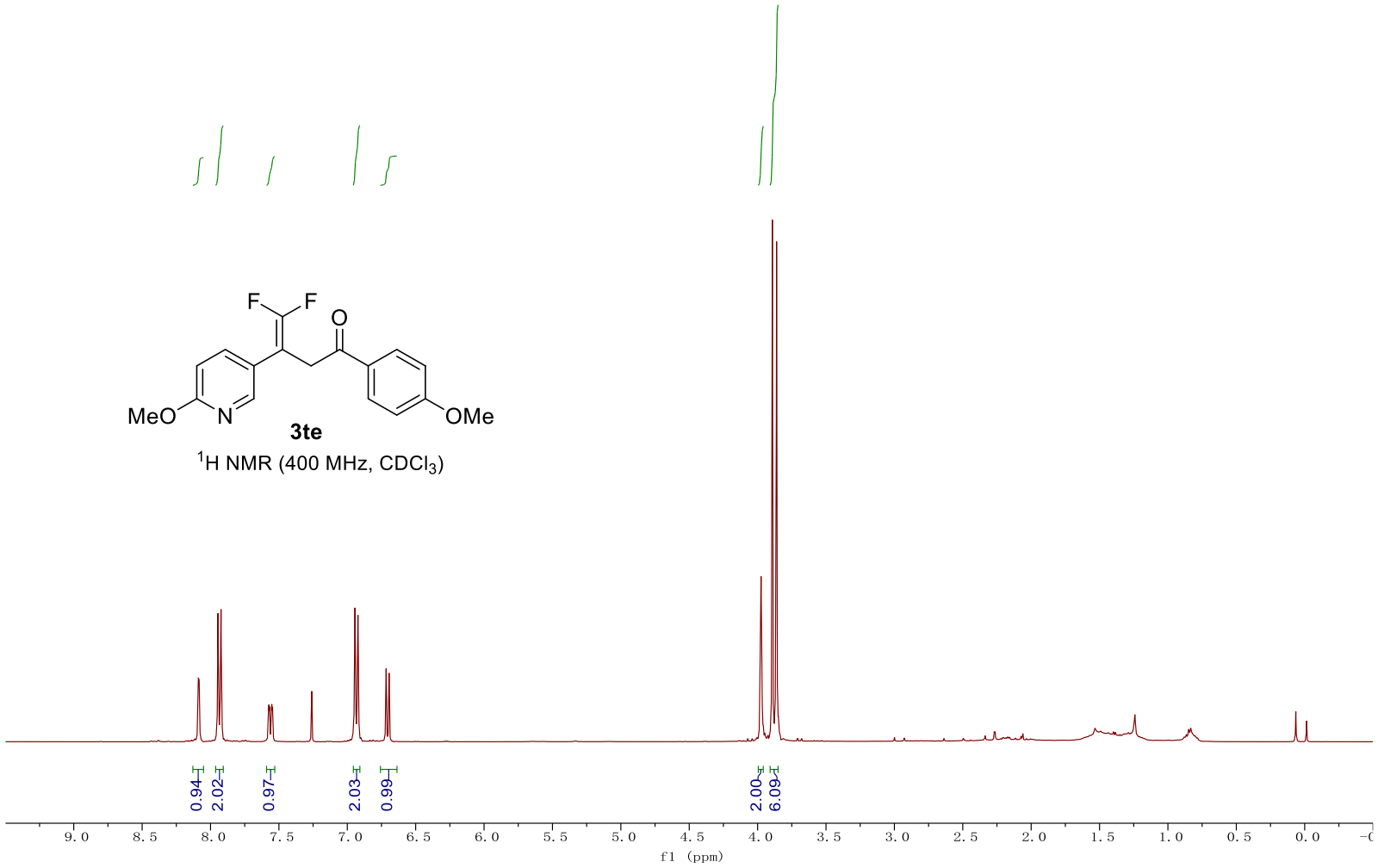


3se

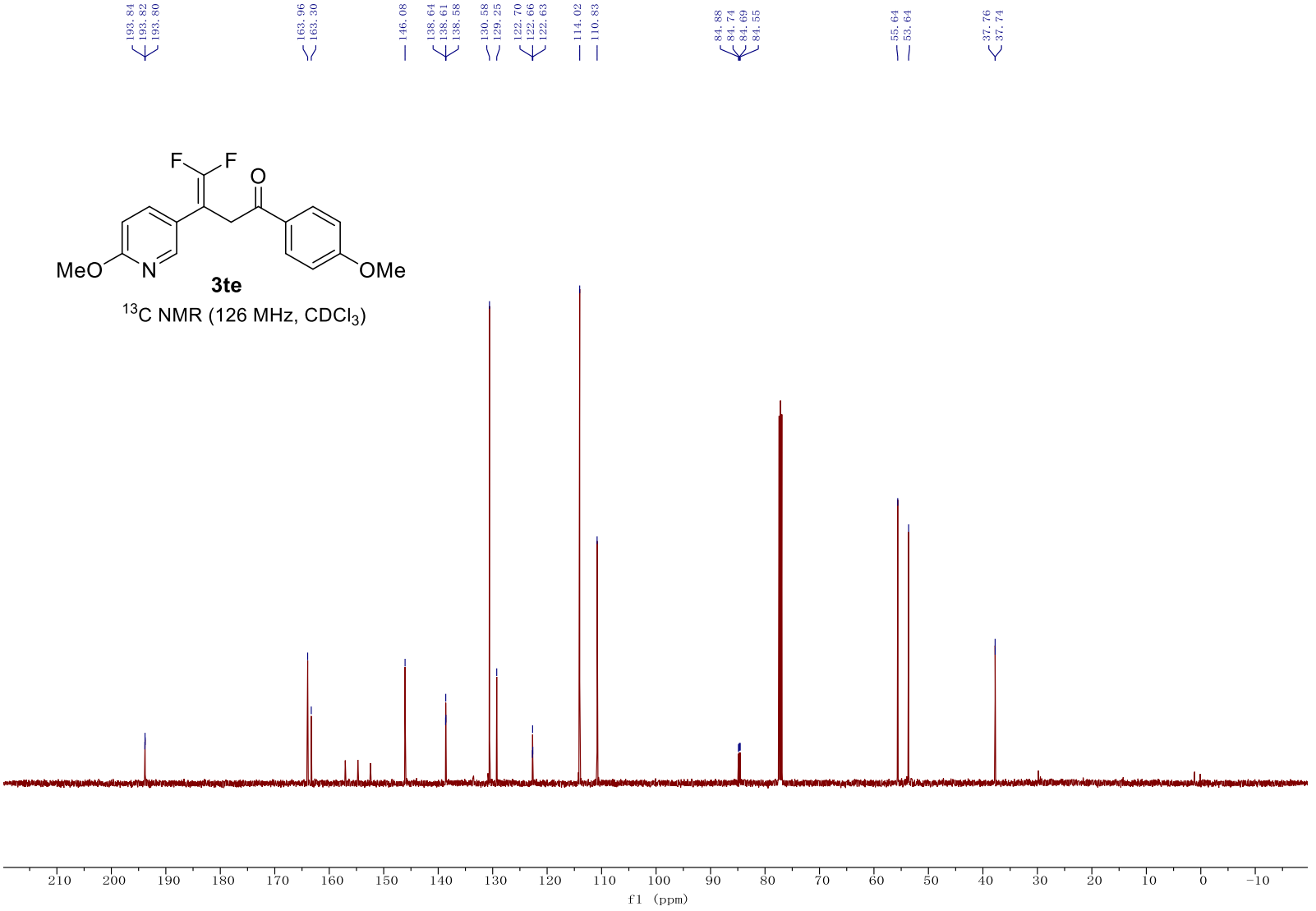
^{13}C NMR (101 MHz, $CDCl_3$)

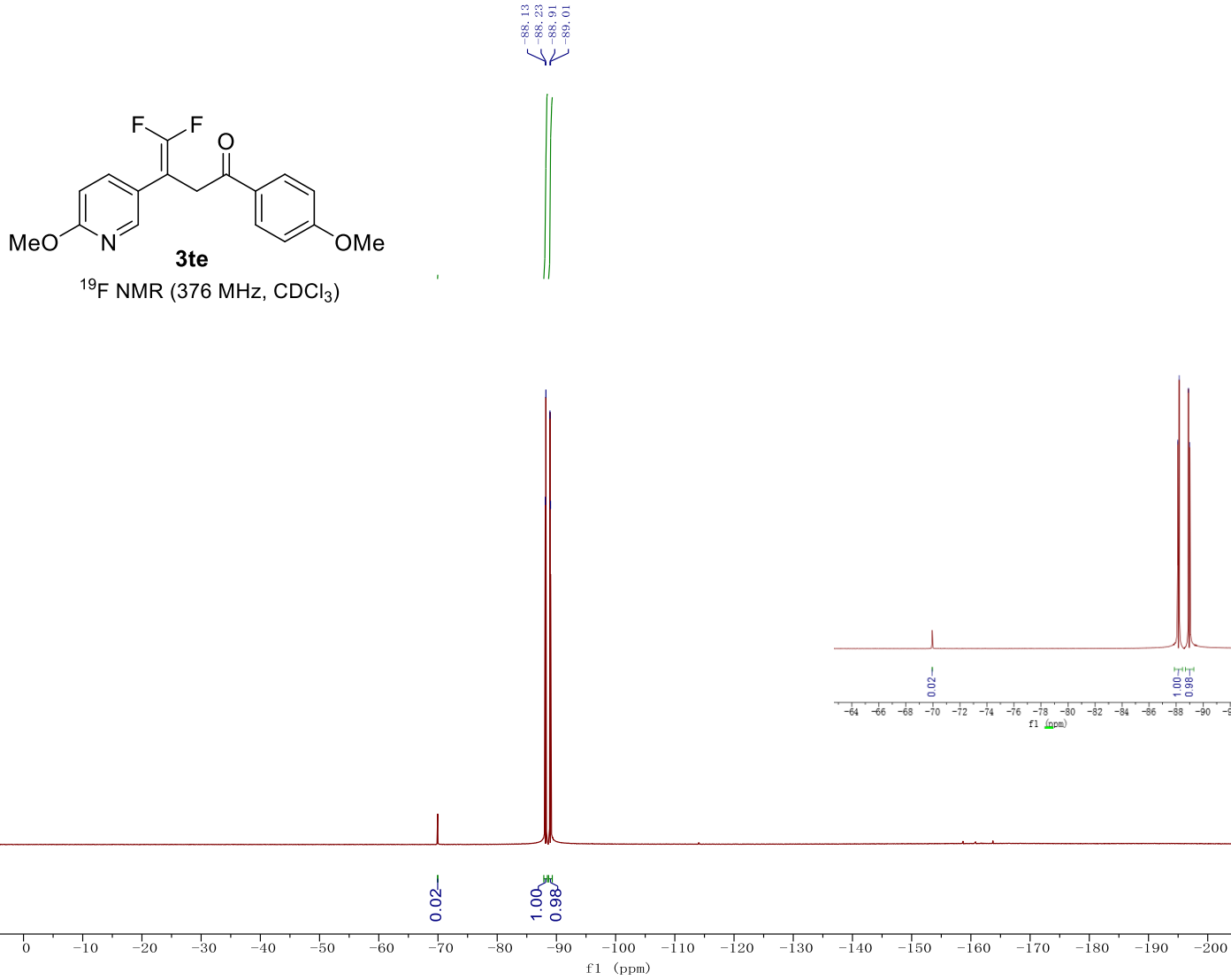


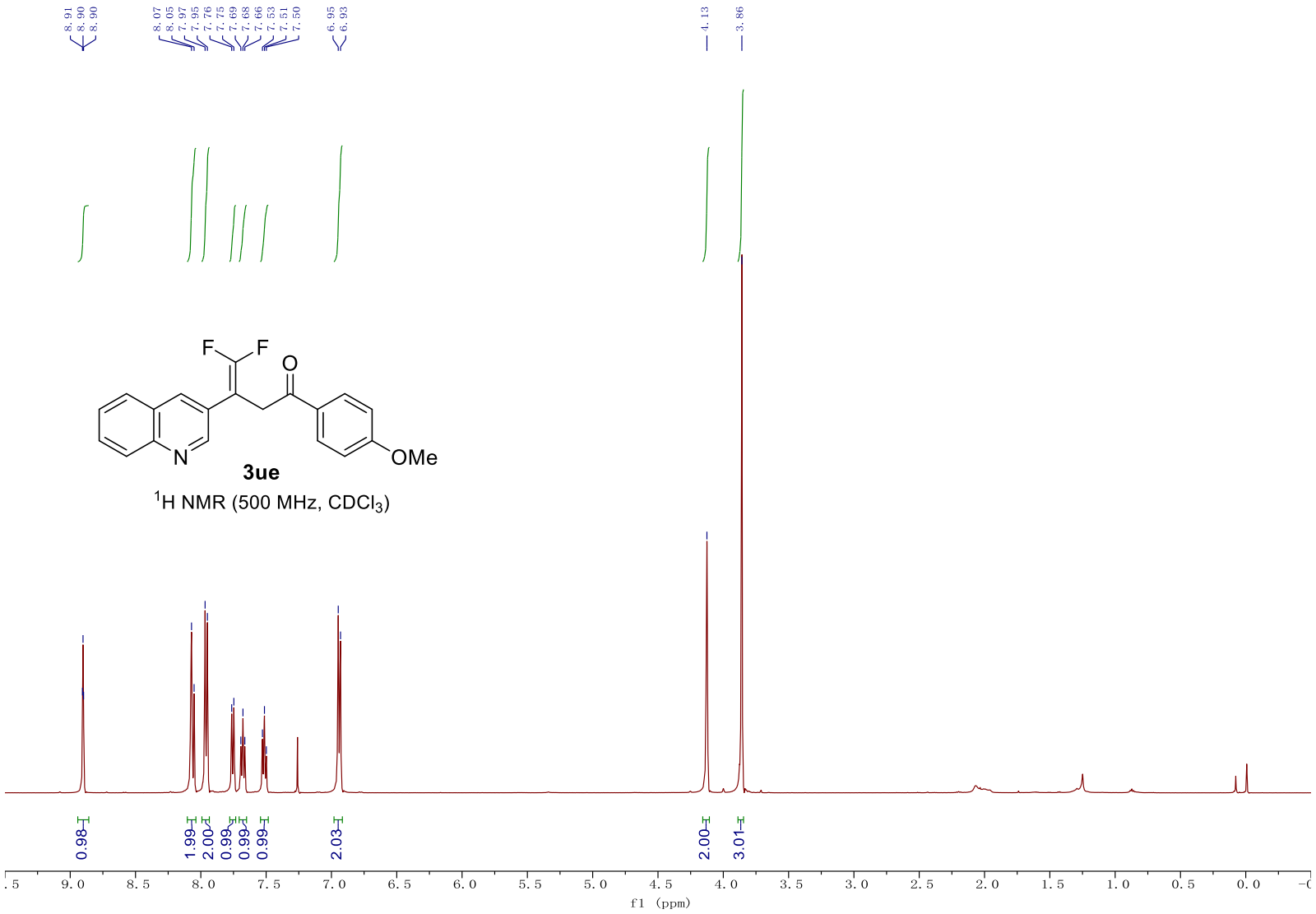

F
F
O
S
OMe
3se
^{19}F NMR (376 MHz, $CDCl_3$)
-84.95
-85.04
-88.35
-88.44
0.01
1.00
1.04
f1 (ppm)

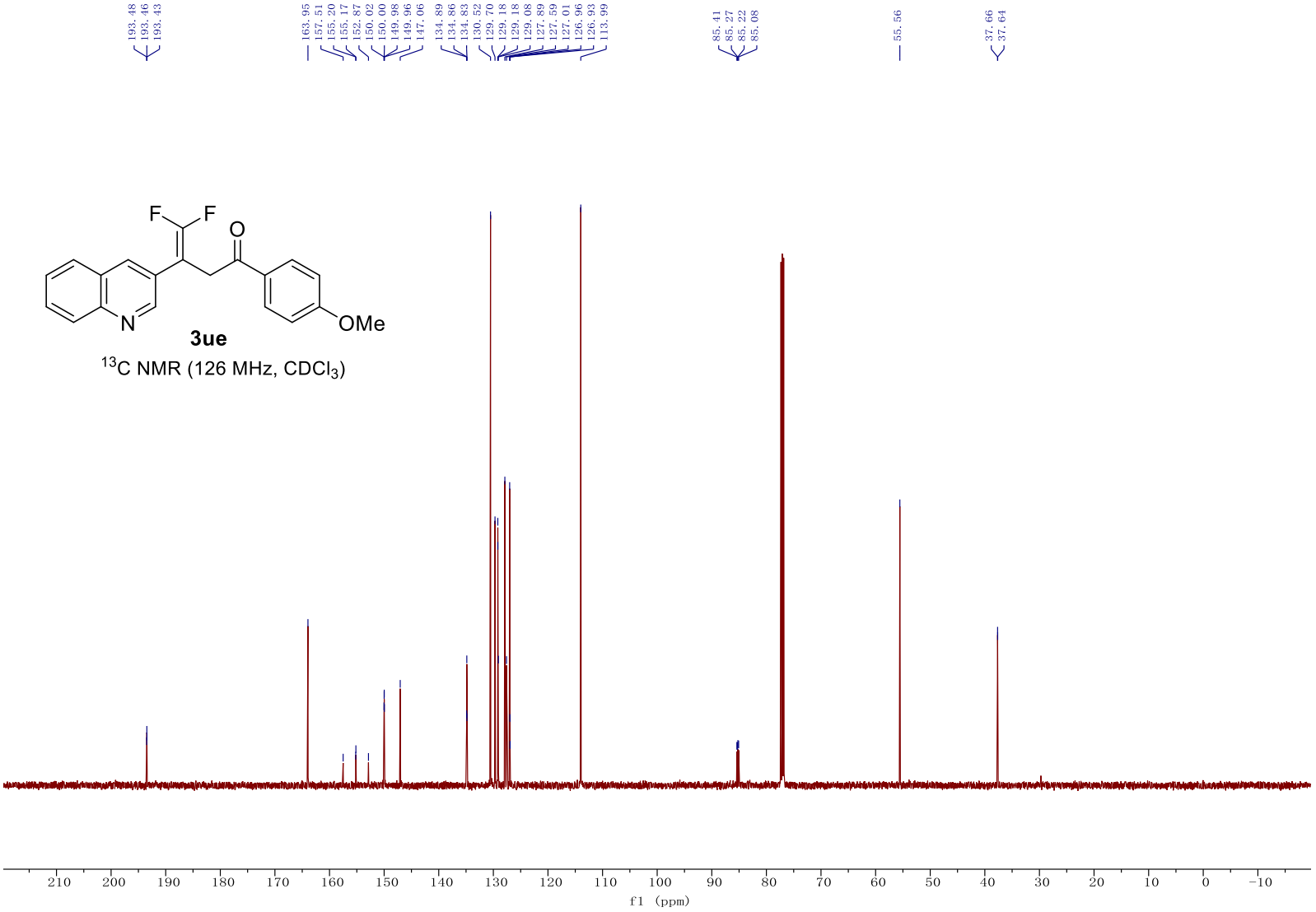


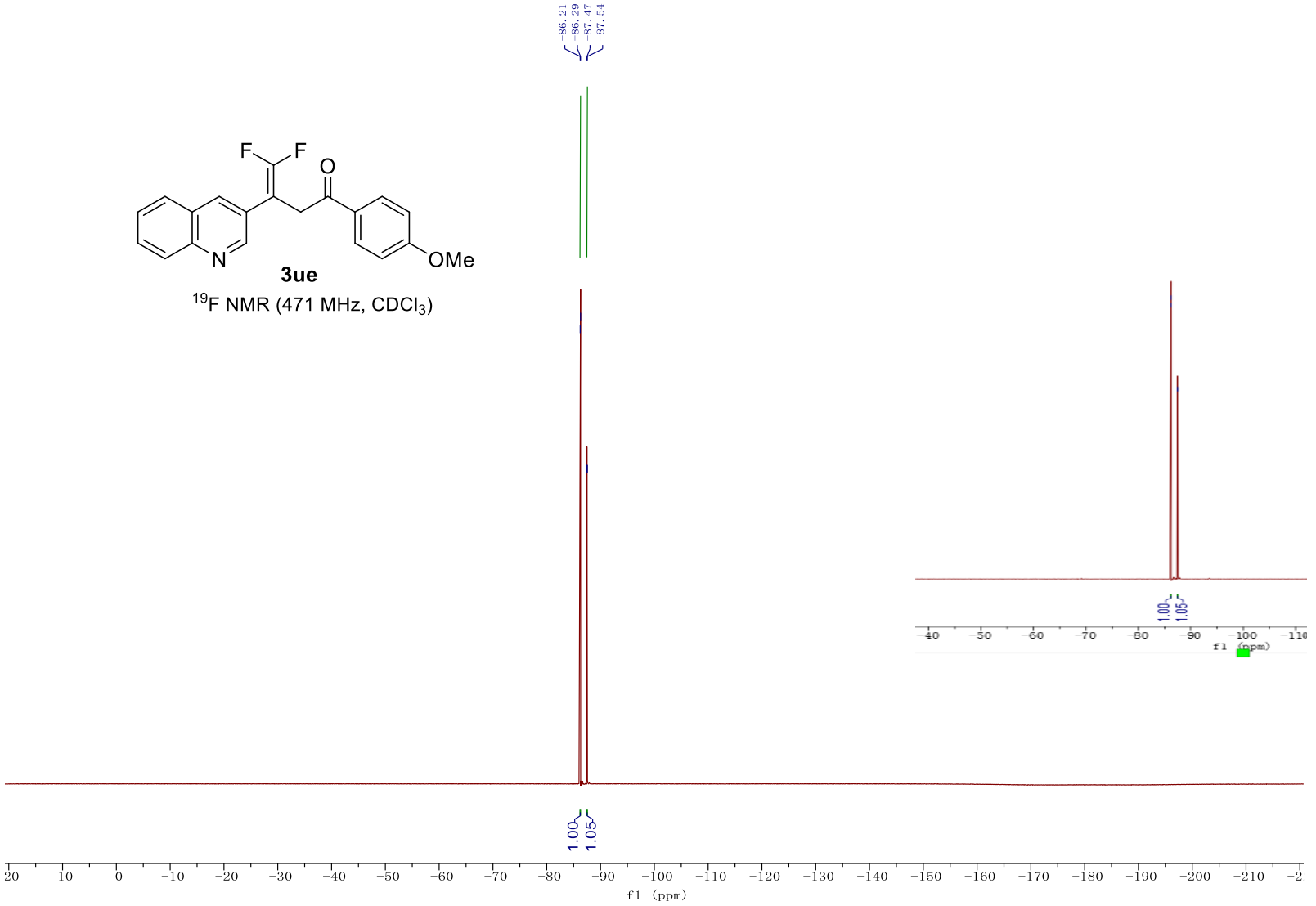
^{1}H NMR (400 MHz, $CDCl_3$)


193.84
193.82
193.80
163.96
163.30
146.08
138.64
138.61
138.58
130.58
129.25
122.70
122.66
122.63
114.02
110.83
84.88
84.74
84.69
84.55
55.64
53.64
37.76
37.74
F
F
O
MeO
N
OMe
3te
13C NMR (126 MHz, CDCl3)
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
MeO
N
OMe
3te
19F NMR (376 MHz, CDCl3)
-88.13
-88.23
-88.91
-89.01
0.02
1.00
0.98
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)
-64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96
f1 (ppm)

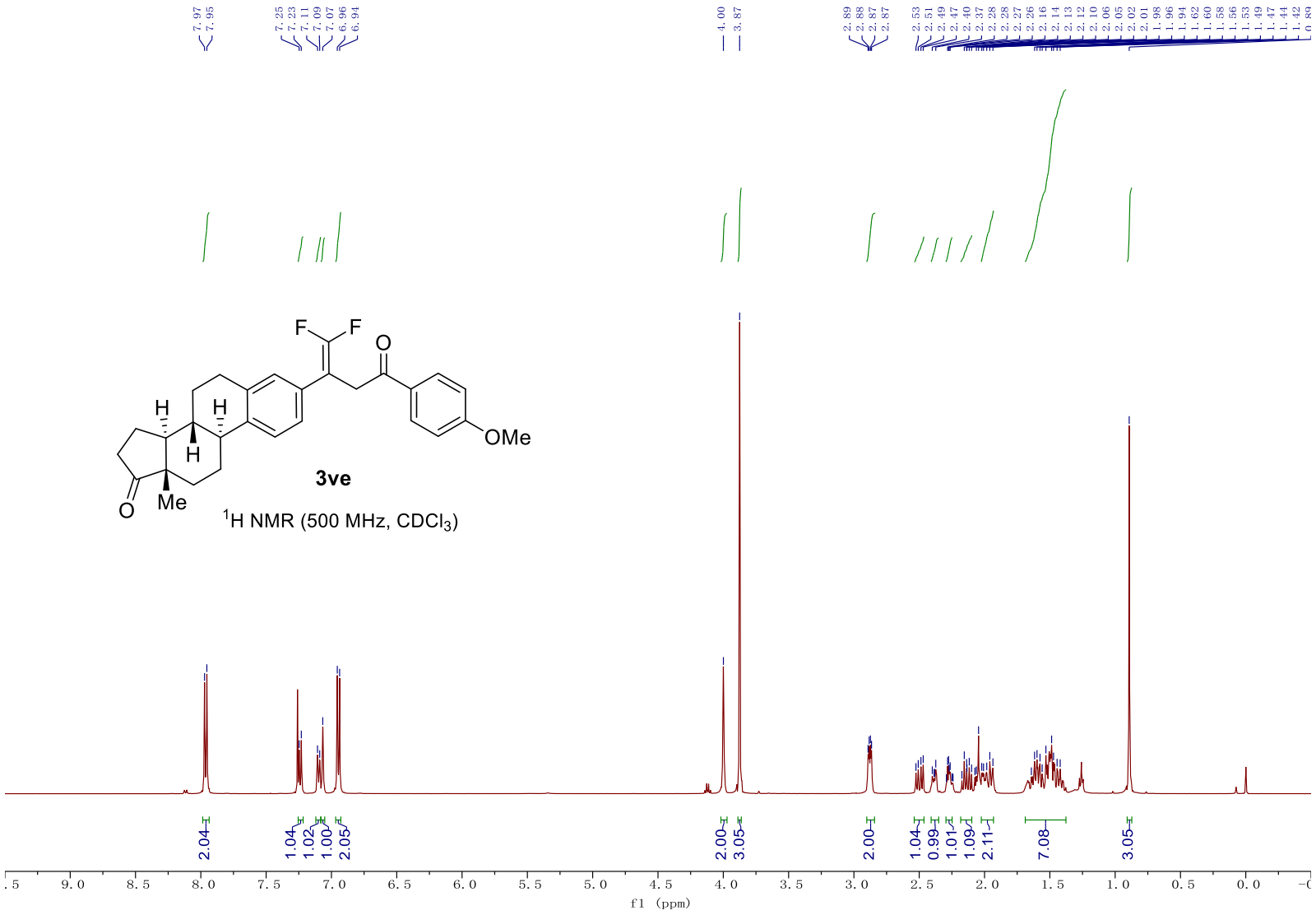

8.91
8.90
8.90
8.07
8.05
7.97
7.95
7.76
7.75
7.69
7.68
7.66
7.53
7.51
7.50
6.95
6.93
4.13
3.86
F
F
O
N
OMe
3ue
^{1}H NMR (500 MHz, $CDCl_3$)
0.98
1.99
2.00
0.99
0.99
2.03
2.00
3.01
f1 (ppm)

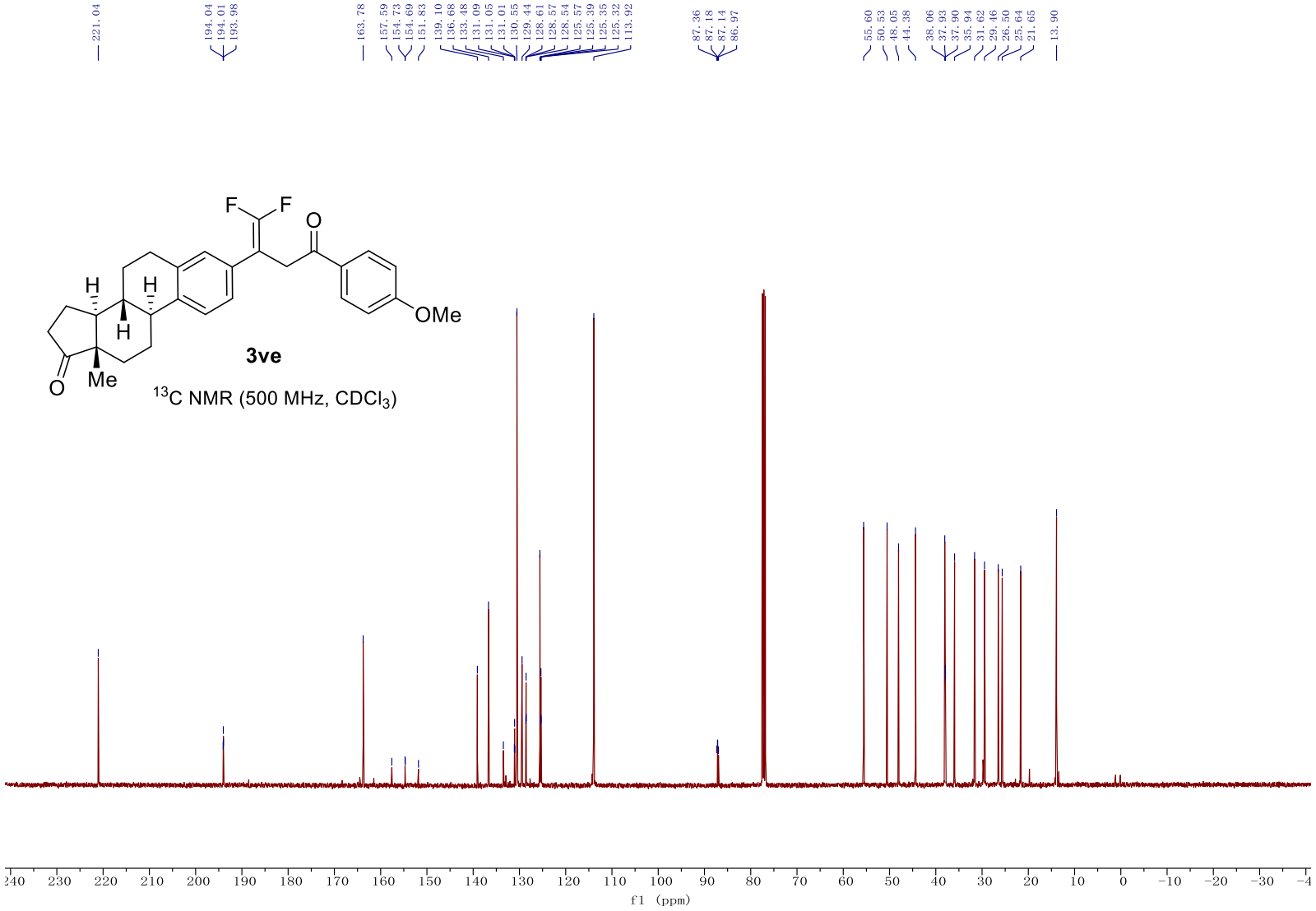

193.48
193.46
193.43
163.95
157.51
155.20
155.17
152.87
150.02
150.00
149.98
149.96
147.06
134.89
134.86
134.83
130.52
129.70
129.18
129.18
129.08
127.89
127.59
127.01
126.96
126.93
113.99
85.41
85.27
85.22
85.08
55.56
37.66
37.64
F
F
O
N
OMe
3ue
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

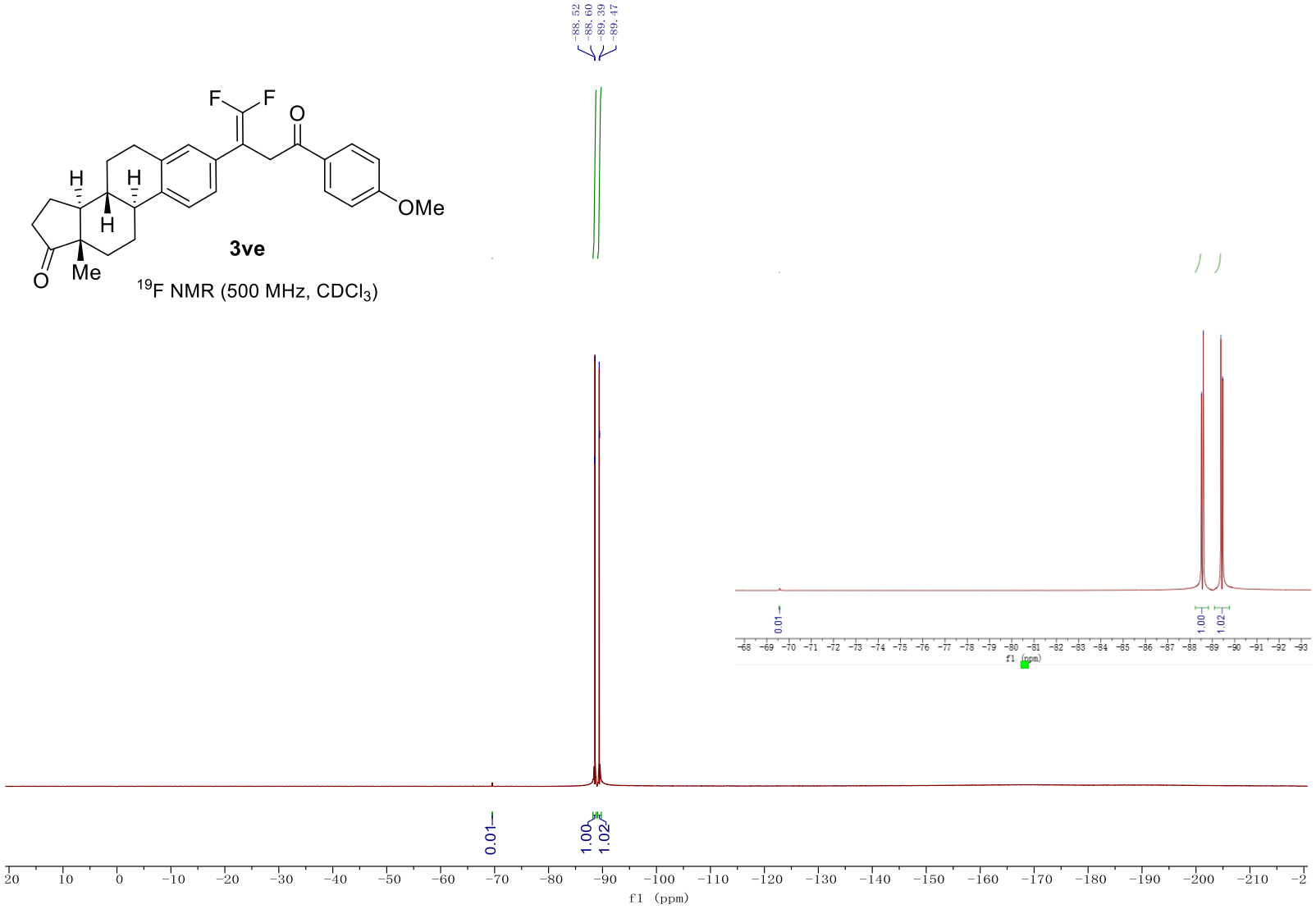


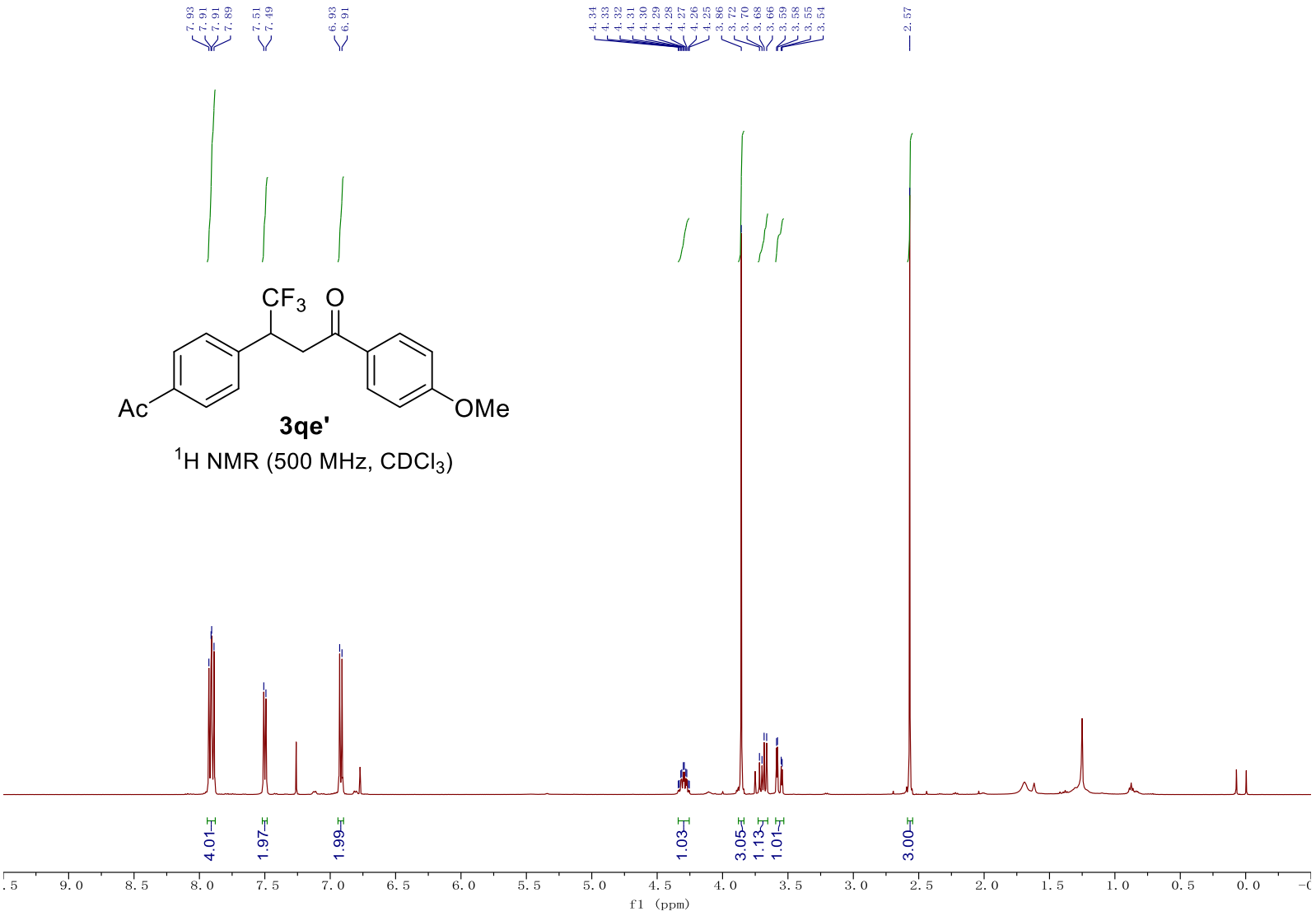
3ue

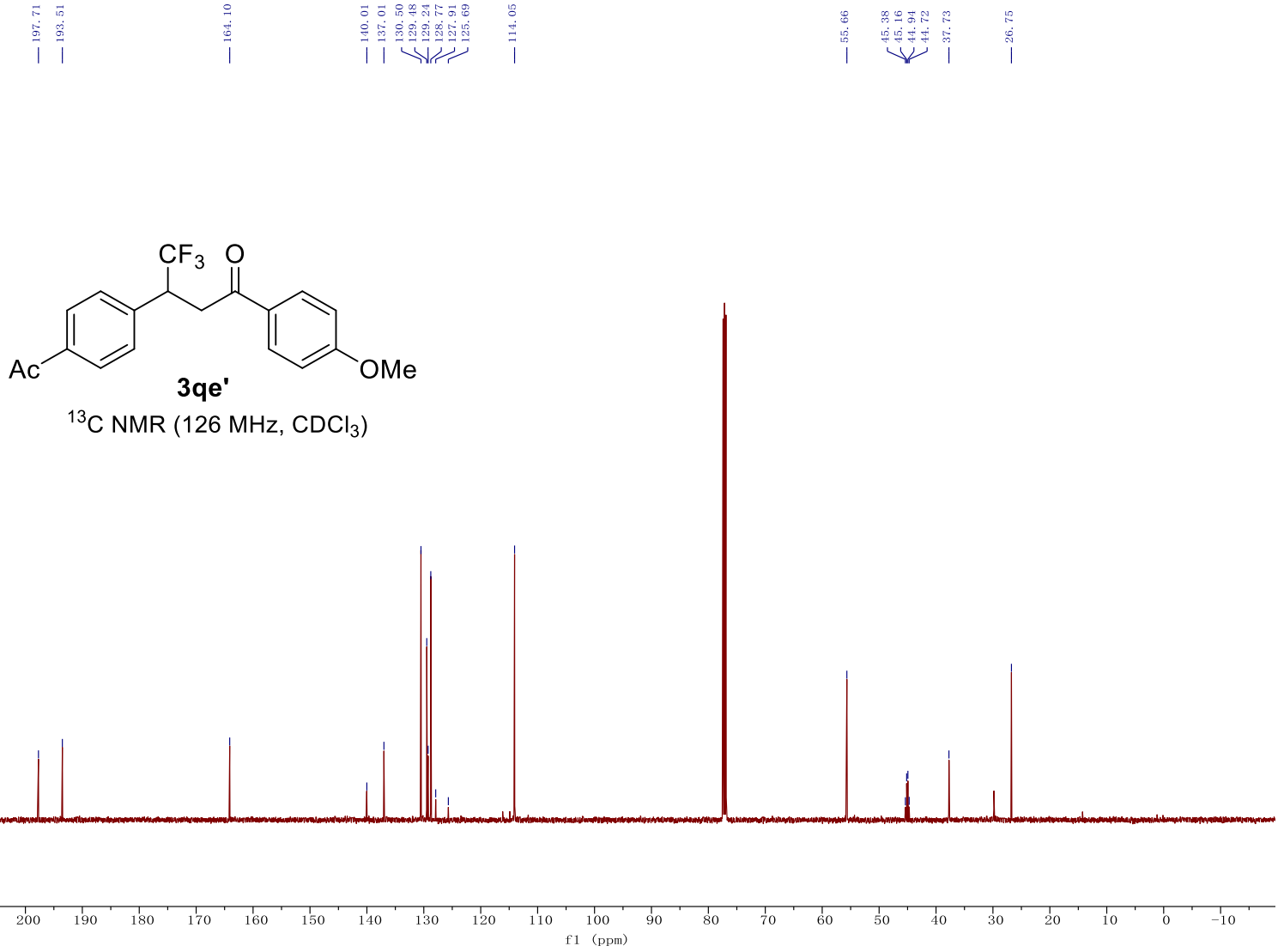
^{19}F NMR (471 MHz, $CDCl_3$)

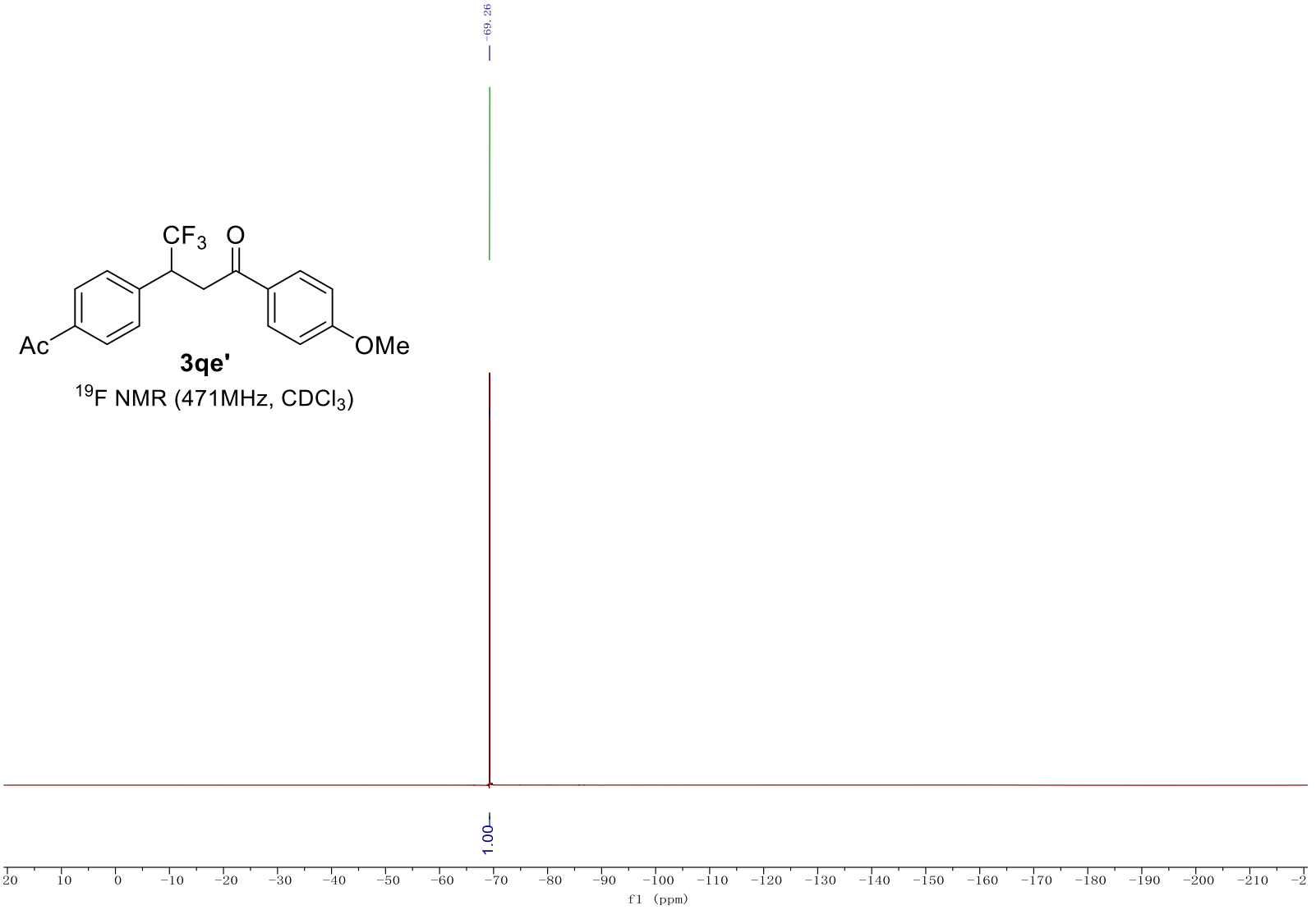

F
F
O
H
H
H
OMe
O
Me
3ve
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

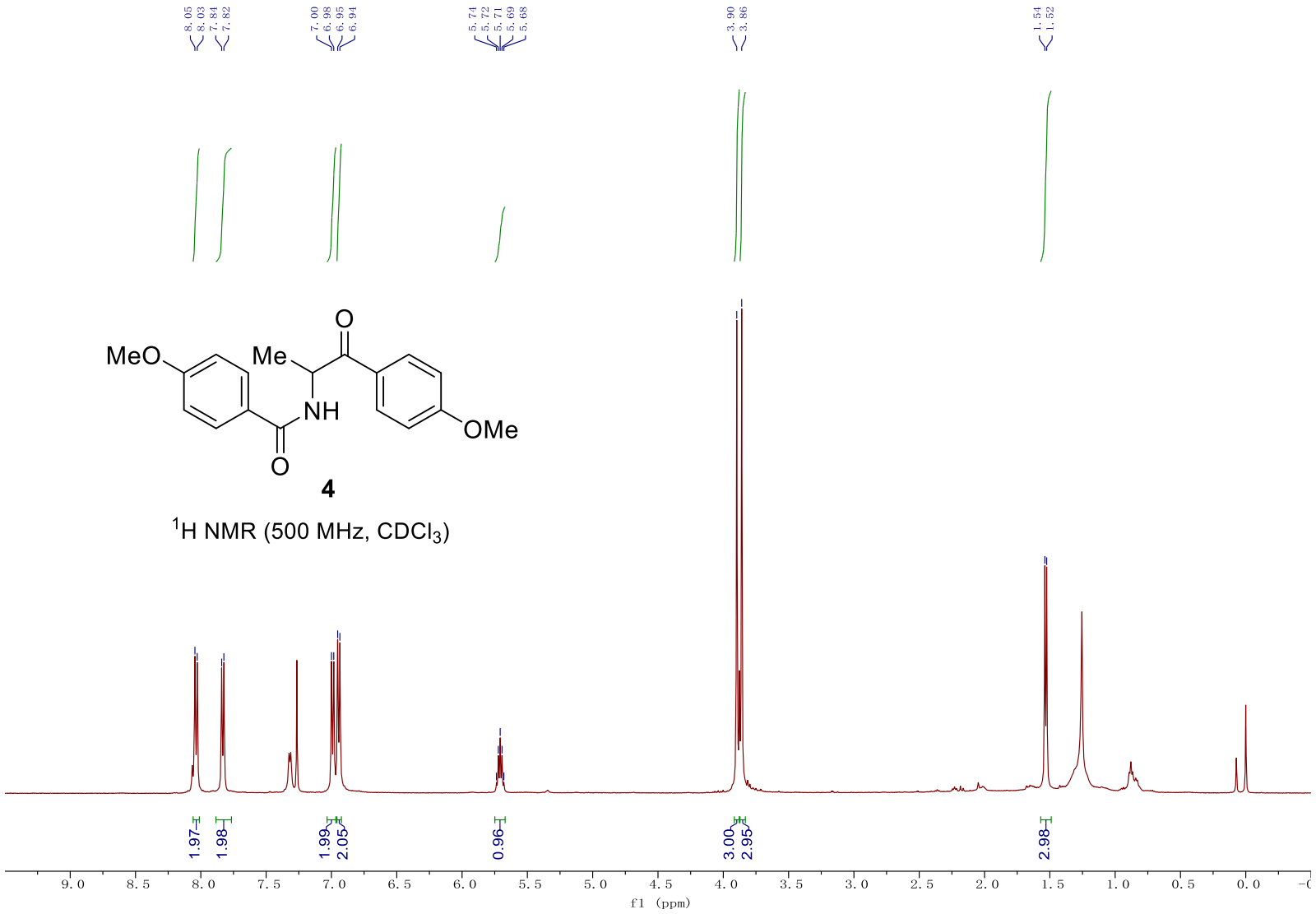

221.04
194.04
194.01
193.98
163.78
157.59
154.73
154.69
151.83
139.10
136.68
133.48
131.09
131.05
131.01
130.55
129.44
128.61
128.57
128.54
125.57
125.39
125.35
125.32
113.92
87.36
87.18
87.14
86.97
55.60
50.53
48.05
44.38
38.06
37.93
37.90
35.94
31.62
29.46
26.50
25.64
21.65
13.90
F
F
O
H
H
H
OMe
Me
O
3ve
13C NMR (500 MHz, CDCl3)
f1 (ppm)

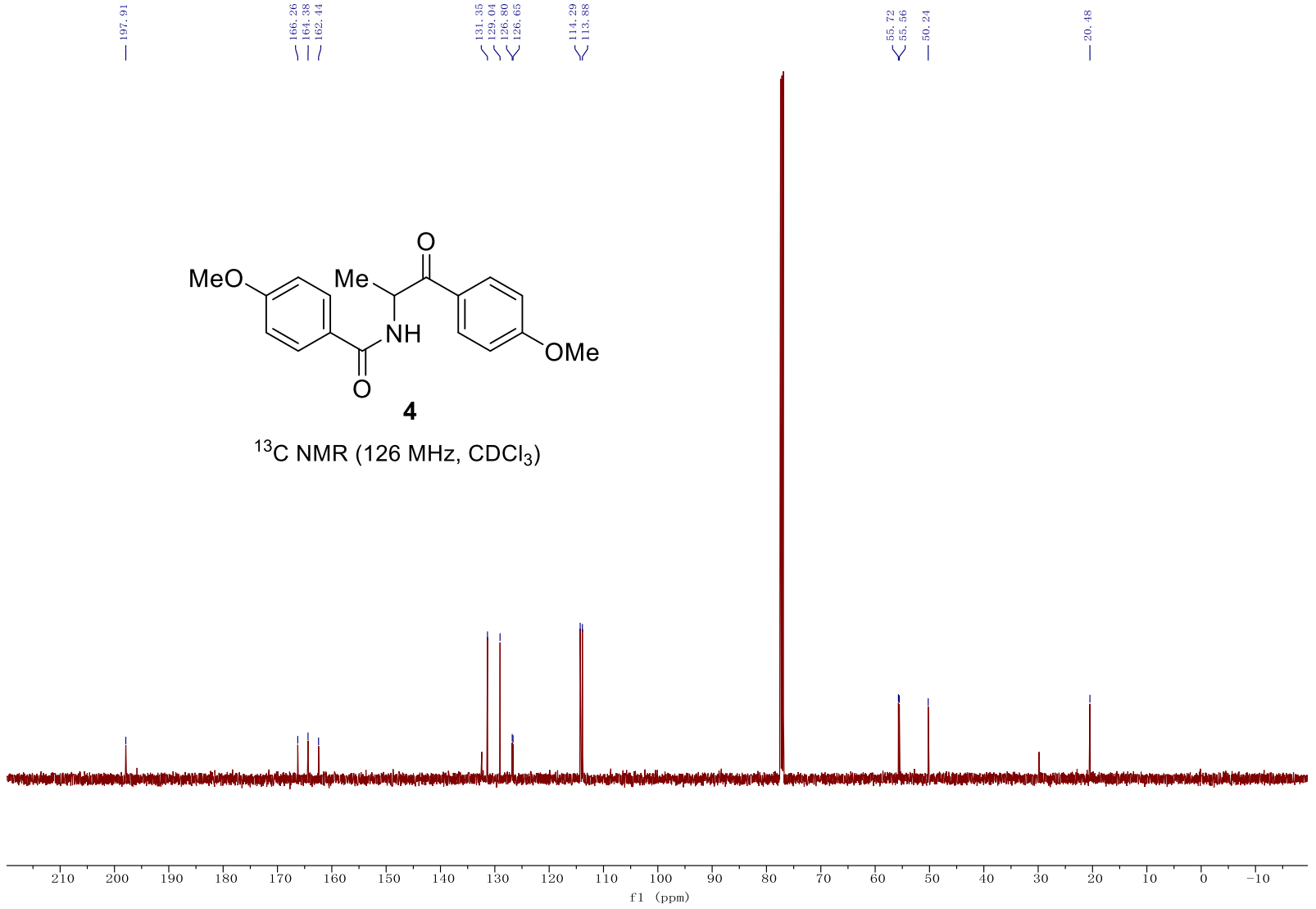

F
F
O
H
H
H
OMe
O
Me
3ve
19F NMR (500 MHz, CDCl3)
-88.52
-88.60
-89.39
-89.47
0.01
1.00
1.02
f1 (ppm)


7.93
7.91
7.91
7.89
7.51
7.49
6.93
6.91
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.25
3.86
3.72
3.70
3.68
3.66
3.59
3.58
3.55
3.54
2.57
CF3
O
Ac
OMe
3qe'
1H NMR (500 MHz, CDCl3)
4.01
1.97
1.99
1.03
3.05
1.13
1.01
3.00
f1 (ppm)


197.71
193.51
164.10
140.01
137.01
130.50
129.48
129.24
128.77
127.91
125.69
114.05
55.66
45.38
45.16
44.94
44.72
37.73
26.75
CF3
O
Ac
OMe
3qe'
13C NMR (126 MHz, CDCl3)
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)


CF3
O
Ac
OMe
3qe'
19F NMR (471MHz, CDCl3)
-69.26
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)


8.05
8.03
7.84
7.82
7.00
6.98
6.95
6.94
5.74
5.72
5.71
5.69
5.68
3.90
3.86
1.54
1.52
MeO
Me
NH
O
O
OMe
4
1H NMR (500 MHz, CDCl3)
1.97
1.98
1.99
2.05
0.96
3.00
2.95
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.91
166.26
164.38
162.44
131.35
129.04
126.80
126.65
114.29
113.88
55.72
55.56
50.24
20.48
MeO
Me
O
NH
O
OMe
4
13C NMR (126 MHz, CDCl3)
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)