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Supplementary Materials for

A remote C–C bond cleavage–enabled skeletal reorganization: Access to medium-/large-sized cyclic alkenes

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The PDF file includes:

- scheme S1. Control experiments.
- fig. S1. Speculated energy profiles for carbonyl, aryl, and vinyl migration process.
- fig. S2. X-ray structures of **5I** and **6.**
- Experimental procedure
- Mechanistic study
- NMR spectra

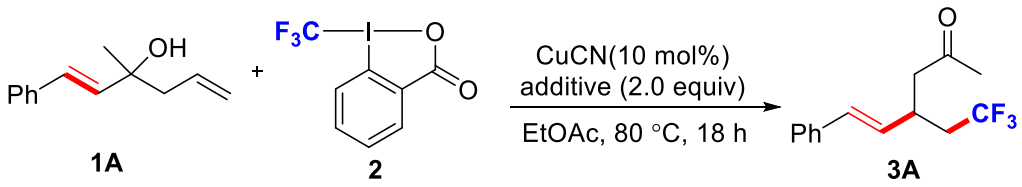
Other Supplementary Material for this manuscript includes the following:
(available at advances.sciencemag.org/cgi/content/full/3/11/e1701487/DC1)

- CIF Files 1 and 2

General Information

All reactions were carried out under argon using Schlenk techniques. Reagents were purchased from commercial sources and used as received. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on a Bruker DPX 400 or a Bruker DPX 500 spectrometers at 400 MHz or 500 MHz for ^{1}H NMR, 100 MHz or 125 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR, and 162 MHz for ^{31}P NMR in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard, [$CFCl_3$ as an external reference (0 ppm) for ^{19}F NMR]. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data was obtained using Bruker Apex IV RTMS.

scheme S1. Control experiments.



additive: TEMPO, **3A**, 13%
benzoquinone, **3A**, 10%

Figure S1 and S2

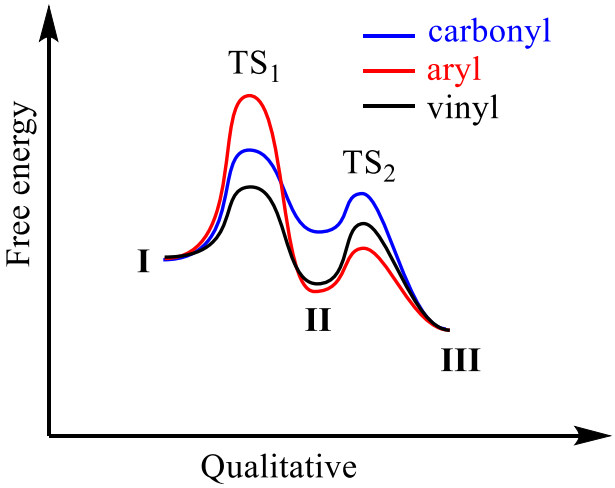
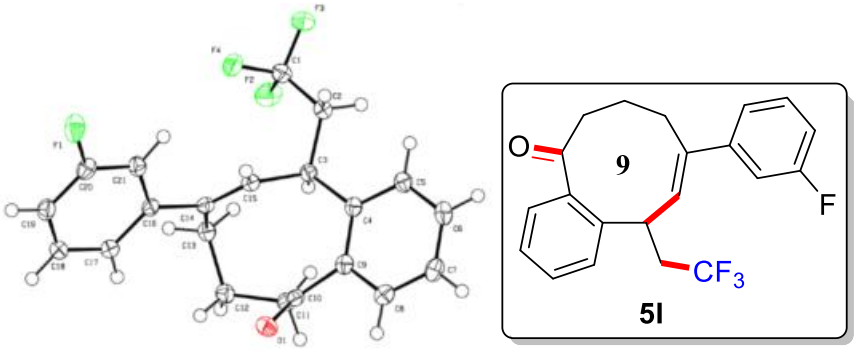


fig. S1. Speculated energy profiles for carbonyl, aryl, and vinyl migration process. The correlated free energy is shown for the proposed reaction pathway.



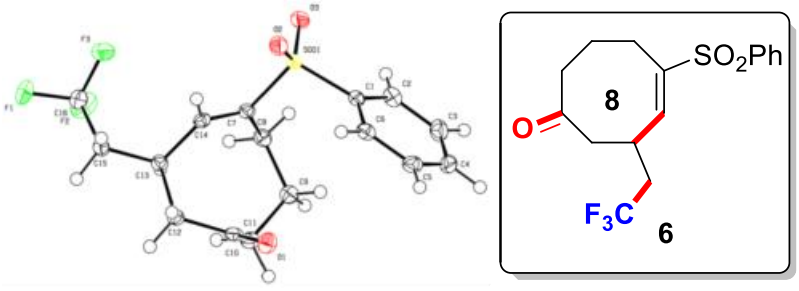
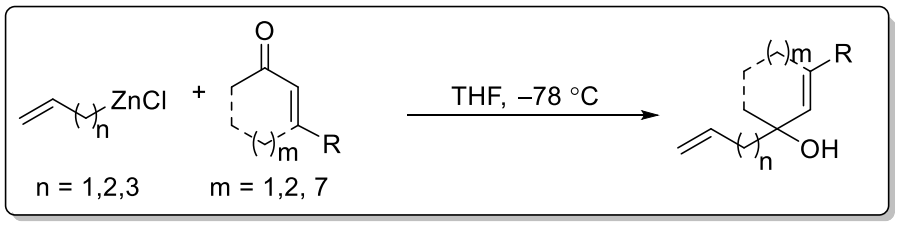


fig. S2. X-ray structures of 5I and 6. The structure of **5I** and **6** are confirmed by X-ray analysis.

Experimental procedure

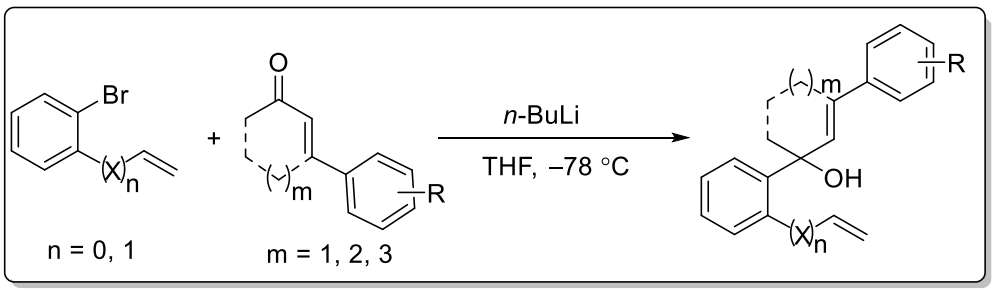
General procedure for synthesis of substrates

Method AA



The allylzinc chloride (0.50 M in THF, 3.0 mmol) was prepared as following: to a suspension of $ZnCl_2$ (409 mg, 3.0 mmol) and LiCl (254 mg, 6.0 mmol) in THF (3 mL) was added a solution of allylmagnesium bromide in diethyl ether (1.0 M, 3 mL, 3.0 mmol) at −78 °C under nitrogen, and the mixture was stirred at 0 ºC for 30 min.
To a solution of ketone (2.5 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added allylzinc chloride (3 mmol, 1.2 equiv) over 5 min at −78 °C. The reaction mixture was stirred for 30 min at 0 °C and then stirred at room temperature for 2 h. After completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl solution (10 mL). EtOAc was used to extract the product from the aqueous layer (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the desired products **1A-1L**, **1Q**, **4A-4E** and **4M-4O**.

Method AB

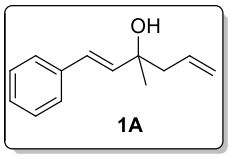


To a solution of 1-bromo-2-vinylbenzene (1.0 g, 5.5 mmol, 1.1 equiv) in anhydrous THF (10 mL) was added *n*-BuLi (2.3 mL, 2.4 M in *n*-hexane, 5.5 mmol, 1.1 equiv) over 10 min at −78 °C. The reaction mixture was stirred for 2 h at −78 °C and then to this solution was added a solution of (*E*)-4-phenylbut-3-en-2-one (0.73 g, 5.0 mmol, 1.0 equiv) in THF (10 mL) over 10 min. The reaction mixture was stirred for an additional 2 h, and quenched with saturated $NaHCO_3$ solution (10 mL). EtOAc was used to extract the product from the aqueous layer (3 × 30 mL). The combined organic layer was dried

over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the desired product **1M** (0.8 g, 64%).

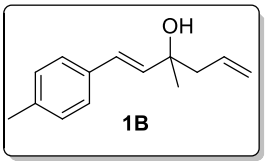
The synthesis of other substrates (**1N-1P**, **4G-4L**, **4P**) is similar to that of **1M**.

(*E*)-3-methyl-1-phenylhexa-1,5-dien-3-ol



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.37 (m, 2H), 7.35 - 7.30 (m, 2H), 7.26 - 7.21 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.92 - 5.79 (m, 1H), 5.21 - 5.14 (m, 2H), 2.46 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.37 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.87 (s, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.2, 133.5, 128.5, 127.39, 127.37, 126.4, 119.2, 72.3, 47.3, 27.9. HRMS (ESI) m/z calcd. for $C_{13}H_{17}O$ $[M+H]^+$ 189.1274, found 189.1272.

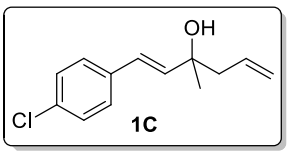
(*E*)-3-methyl-1-(p-tolyl)hexa-1,5-dien-3-ol



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.92 - 5.79 (m, 1H), 5.21 - 5.13 (m, 2H), 2.49 - 2.36 (m, 2H), 2.35 (s, 3H), 1.89 (s, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.2, 134.1, 133.6, 129.2, 127.2, 126.3, 119.1, 72.3, 47.3, 27.9, 21.1.

HRMS (ESI) m/z calcd. for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1431.

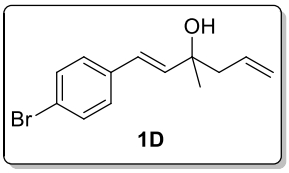
(*E*)-1-(4-chlorophenyl)-3-methylhexa-1,5-dien-3-ol



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.25 (m, 4H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 5.88 - 5.76 (m, 1H), 5.20 - 5.13 (m, 2H), 2.43 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.35 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.86 (s, 1H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

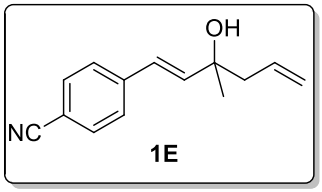
δ 136.9, 135.4, 133.4, 133.0, 128.7, 127.6, 126.3, 119.4, 72.3, 47.2, 27.9. HRMS (ESI) m/z calcd. for $C_{13}H_{16}OCl$ $[M+H]^+$ 223.0884, found 223.0878.

(*E*)-1-(4-bromophenyl)-3-methylhexa-1,5-dien-3-ol



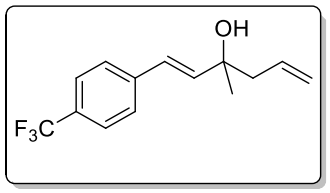
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.40 (m, 2H), 7.25 - 7.21 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 5.88 - 5.76 (m, 1H), 5.20 - 5.12 (m, 2H), 2.43 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.35 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.23 (s, 1H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 135.8, 133.3, 131.6, 127.9, 126.3, 121.1, 119.4, 72.3, 47.2, 27.8. HRMS (ESI) m/z calcd. for $C_{13}H_{14}Br$ $[M-OH]^+$ 249.0273, found 249.0270.

(*E*)-4-(3-hydroxy-3-methylhexa-1,5-dien-1-yl)benzonitrile



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.85 - 5.76 (m, 1H), 5.22 - 5.14 (m, 2H), 2.45 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.37 (dd, *J* = 13.5, 8.5 Hz, 1H), 1.99 (s, 1H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 133.0, 132.4, 129.0, 126.9, 126.4, 126.1, 119.9, 110.5, 72.4, 47.1, 27.9. HRMS (ESI) m/z calcd. for $C_{14}H_{16}ON$ $[M+H]^+$ 214.1226, found 214.1222.

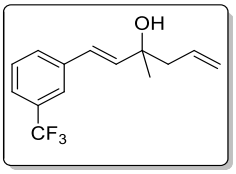
(*E*)-3-methyl-1-(4-(trifluoromethyl)phenyl)hexa-1,5-dien-3-ol



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.91 - 5.79 (m, 1H), 5.24 - 5.16 (m, 2H), 2.48 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.40 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.08 (s, 1H),

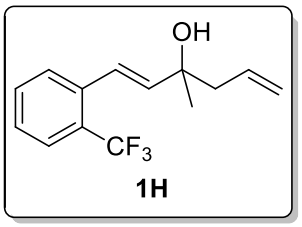
1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 138.9, 133.2, 129.2 (q, *J* = 32.2 Hz), 126.5, 126.3, 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.0 Hz), 119.5, 72.4, 47.2, 27.8. HRMS (ESI) m/z calcd. for $C_{14}H_{14}F_3$ $[M\text{-}OH]^+$ 239.1042, found 239.1039.

(*E*)-3-methyl-1-(3-(trifluoromethyl)phenyl)hexa-1,5-dien-3-ol



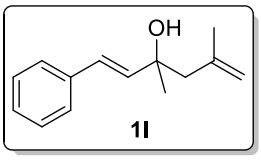
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 5.89 – 5.77 (m, 1H), 5.21 – 5.14 (m, 2H), 2.46 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.37 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.16 (s, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.7, 133.2, 131.9 (q, *J* = 31.9 Hz), 129.6, 129.0, 126.2, 124.1 (q, *J* = 270.6 Hz), 123.88 (q, *J* = 3.7 Hz), 122.91 (q, *J* = 3.9 Hz), 119.5, 72.4, 47.2, 27.9. HRMS (ESI) m/z calcd. for $C_{14}H_{14}F_3$ $[M\text{-}OH]^+$ 239.1042, found 239.1039.

(*E*)-3-methyl-1-(2-(trifluoromethyl)phenyl)hexa-1,5-dien-3-ol



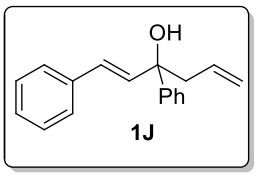
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 16.0, 2.4 Hz, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 5.90 – 5.78 (m, 1H), 5.21 – 5.13 (m, 2H), 2.46 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.38 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.33 (s, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 136.4, 133.2, 131.8, 127.5, 127.3 (q, *J* = 32.1 Hz), 127.0, 125.66 (q, *J* = 5.5 Hz), 124.3 (q, *J* = 272.6 Hz), 124.0, 119.3, 72.4, 47.1, 27.6. HRMS (ESI) m/z calcd. for $C_{14}H_{14}F_3$ $[M\text{-}OH]^+$ 239.1042, found 239.1040.

(*E*)-3,5-dimethyl-1-phenylhexa-1,5-dien-3-ol



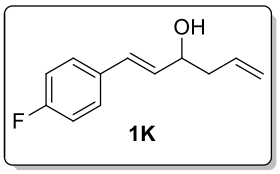
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.97 (s, 1H), 4.83 (s, 1H), 2.41 (s, 2H), 2.17 (s, 1H), 1.81 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 137.0, 136.8, 128.5, 127.2, 126.6, 126.3, 115.4, 72.1, 50.8, 28.6, 24.6. HRMS (ESI) m/z calcd. for $C_{14}H_{17}$ $[M\text{-}OH]^+$ 185.1325, found 185.1322.

(*E*)-1,3-diphenylhexa-1,5-dien-3-ol



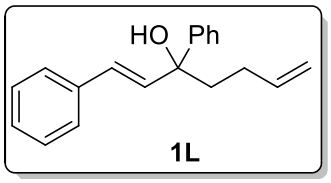
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.27 – 7.15 (m, 4H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 5.74 – 5.63 (m, 1H), 5.22 – 5.10 (m, 2H), 2.82 – 2.71 (m, 2H), 2.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 136.7, 135.1, 133.1, 128.5, 128.3, 127.5, 127.0, 126.5, 125.4, 120.1, 75.6, 47.0. HRMS (ESI) m/z calcd. for $C_{18}H_{17}$ $[M\text{-}OH]^+$ 233.1325, found 233.1322.

(*E*)-1-(4-fluorophenyl)hexa-1,5-dien-3-ol



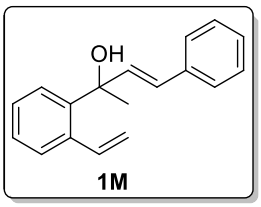
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.03 – 6.96 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.91 – 5.79 (m, 1H), 5.21 – 5.12 (m, 2H), 4.37 – 4.30 (m, 1H), 2.46 – 2.33 (m, 2H), 2.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.3 Hz), 133.9, 132.77 (d, *J* = 3.3 Hz), 131.27 (d, *J* = 2.1 Hz), 129.1, 127.89 (d, *J* = 7.9 Hz), 118.3, 115.4 (d, *J* = 21.5 Hz), 71.6, 41.9. HRMS (ESI) m/z calcd. for $C_{12}H_{12}F$ $[M\text{-}OH]^+$ 175.0918, found 175.0917.

(*E*)-1,3-diphenylhepta-1,6-dien-3-ol



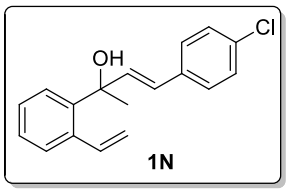
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.45 - 7.38 (m, 4H), 7.36 - 7.27 (m, 4H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 5.93 - 5.85 (m, 1H), 5.08 - 5.97 (m, 2H), 2.25 - 2.04 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 138.6, 135.6, 128.9, 128.5, 128.3, 128.0, 127.6, 126.9, 126.5, 125.4, 114.7, 77.3, 76.9, 41.4, 28.2. HRMS (ESI) m/z calcd. for $C_{19}H_{19}$ $[M\text{-}OH]^+$ 247.1481, found 247.1479.

(*E*)-4-phenyl-2-(2-vinylphenyl)but-3-en-2-ol



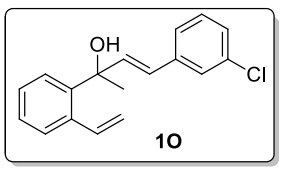
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.65 (m, 1H), 7.59 - 7.53 (m, 1H), 7.50 - 7.39 (m, 3H), 7.37 - 7.32 (m, 4H), 7.30 - 7.27 (m, 1H), 6.63 (dd, *J* = 16.0, 0.8 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 5.57 (d, *J* = 17.6 Hz, 1H), 5.26 (dd, *J* = 11.2, 1.2 Hz, 1H), 2.65 (s, 1H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.5, 136.9, 136.6, 136.3, 128.4, 127.9, 127.6, 127.5, 127.4, 126.4, 125.5, 115.1, 74.9, 29.4. HRMS (ESI) m/z calcd. for $C_{18}H_{17}$ $[M\text{-}OH]^+$ 233.1325, found 233.1322.

(*E*)-4-(4-chlorophenyl)-2-(2-vinylphenyl)but-3-en-2-ol



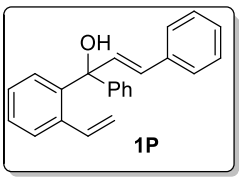
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 - 7.59 (m, 1H), 7.55 - 7.50 (m, 1H), 7.38 (dd, *J* = 17.0, 11.0 Hz, 1H), 7.35 - 7.30 (m, 2H), 7.30 - 7.25 (m, 4H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.55 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 2.56 (s, 1H), 1.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 137.3, 136.93, 136.91, 135.1, 133.1, 128.6, 128.1, 127.7, 127.6, 127.5, 127.3, 125.5, 115.4, 75.0, 29.4. HRMS (ESI) m/z calcd. for $C_{18}H_{16}Cl$ $[M\text{-}OH]^+$ 267.0935, found 267.0932.

(*E*)-4-(3-chlorophenyl)-2-(2-vinylphenyl)but-3-en-2-ol



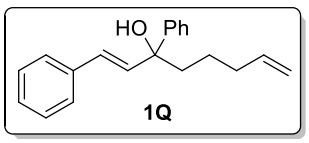
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 - 7.61 (m, 1H), 7.52 - 7.48 (m, 1H), 7.41 – 7.35 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.33 - 7.26 (m, 4H), 7.16 - 7.12 (m, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 5.53 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.22 (dd, *J* = 11.0, 1.0 Hz, 1H), 2.37 (s, 1H), 1.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 137.5, 137.0, 135.7, 135.3, 133.9, 129.24, 129.21, 128.6, 128.1, 127.7, 127.5, 126.4, 126.2, 125.6, 115.5, 75.2, 29.6. HRMS (ESI) m/z calcd. for $C_{18}H_{16}Cl$ $[M\text{-}OH]^+$ 267.0935, found 267.0931.

(*E*)-1,3-diphenyl-1-(2-vinylphenyl)prop-2-en-1-ol



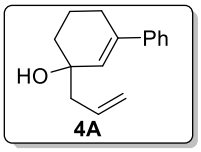
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 - 7.54 (m, 1H), 7.51 - 7.46 (m, 1H), 7.42 - 7.39 (m, 2H), 7.37 - 7.27 (m, 7H), 7.25 - 7.17 (s, 4H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 5.47 (d, *J* = 17.5 Hz, 1H), 5.06 (d, *J* = 11.0 Hz, 1H), 2.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 136.9, 135.0, 133.1, 129.0, 128.63, 128.61, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.4, 127.3, 126.9, 126.8, 126.7, 126.2, 116.7, 79.8. HRMS (ESI) m/z calcd. for $C_{23}H_{19}$ $[M\text{-}OH]^+$ 295.1481, found 295.1474.

(*E*)-1,3-diphenylocta-1,7-dien-3-ol



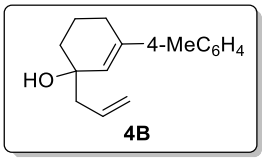
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 - 7.57 (m, 2H), 7.55 - 7.51 (m, 1H), 7.47 - 7.39 (m, 3H), 7.36 - 7.27 (m, 4H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 5.90 - 5.78 (m, 1H), 5.10 - 4.95 (m, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.20 - 2.15 (m, 2H), 2.12 - 2.02 (m, 3H), 1.89 - 1.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 138.5, 138.0, 130.4, 128.9, 128.5, 128.22, 128.21, 126.5, 126.2, 125.4, 115.3, 76.8, 41.9, 33.1, 23.3. HRMS (ESI) m/z calcd. for $C_{20}H_{21}$ $[M\text{-}OH]^+$ 261.1638, found 261.1636.

3-allyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 5.99 (s, 1H), 5.97 - 5.89 (m, 1H), 5.20 - 5.14 (m, 2H), 2.47 (dt, *J* = 17.0, 5.0 Hz, 1H), 2.43 - 2.32 (m, 3H), 1.93 - 1.76 (m, 4H), 1.74 - 1.67 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 139.8, 133.6, 128.9, 128.2, 127.4, 125.4, 118.7, 69.9, 46.9, 35.1, 27.7, 19.4. HRMS (ESI) m/z calcd. for $C_{15}H_{17}$ $[M\text{-}OH]^+$ 197.1325, found 197.1325.

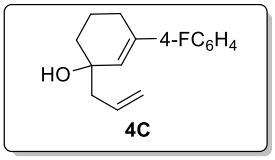
3-allyl-4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol



4B

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.00 - 5.86 (m, 2H), 5.21 - 5.13 (m, 2H), 2.50 - 2.40 (m, 3H), 2.39 - 2.30 (m, 4H), 1.95 - 1.66 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.5, 137.1, 133.7, 128.9, 128.0, 125.3, 118.6, 69.9, 46.9, 35.1, 27.7, 21.0, 19.4. HRMS (ESI) m/z calcd. for $C_{16}H_{19}$ $[M\text{-}OH]^+$ 211.1481, found 211.1480.

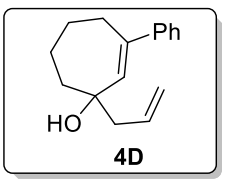
3-allyl-4'-fluoro-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol



4C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 - 7.33 (m, 2H), 7.04 - 6.98 (m, 2H), 5.97 - 5.87 (m, 2H), 5.20 - 5.13 (m, 2H), 2.46 - 2.38 (m, 3H), 2.35 - 2.27 (m, 1H), 1.91 - 1.75 (m, 4H), 1.72 - 1.65 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244.8 Hz), 138.9, 137.5 (d, *J* = 2.0 Hz), 133.5, 128.8, 127.0 (d, *J* = 7.9 Hz), 118.9, 115.1 (d, *J* = 21.3 Hz), 69.8, 46.9, 35.1, 27.8, 19.4. HRMS (ESI) m/z calcd. for $C_{15}H_{16}F$ $[M\text{-}OH]^+$ 215.1231, found 215.1229.

1-allyl-3-phenylcyclohept-2-enol

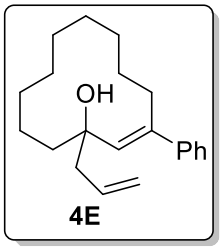


4D

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 - 1.49 (m, 1H), 7.37 - 7.33 (m, 1H), 7.32 - 7.29 (m,

3H), 5.98 - 5.88 (m, 2H), 5.82 (s, 1H), 5.22 - 5.16 (m, 2H), 2.75 - 2.69 (m, 1H), 2.63 - 2.56 (m, 1H), 2.53 - 2.48 (m, 1H), 2.45 - 2.39 (m, 1H), 2.26 - 2.22 (m, 2H), 1.80 - 1.73 (m, 3H), 1.66 - 1.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 137.5, 133.6, 128.2, 126.8, 126.2, 125.7, 118.8, 74.9, 46.4, 37.9, 31.7, 27.0, 24.2. HRMS (ESI) m/z calcd. for $C_{16}H_{19}$ $[M\text{-}OH]^+$ 211.1481, found 211.1480.

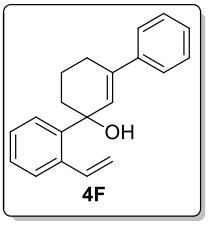
(*E*)-1-allyl-3-phenylcyclododec-2-enol



4E

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 5H), 5.93 – 5.81 (m, 1H), 5.49 (s, 1H), 5.23 – 5.13 (m, 2H), 3.48 – 3.37 (m, 1H), 2.60 – 2.48 (m, 2H), 2.28 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.97 – 1.87 (m, 2H), 1.82 – 1.70 (m, 2H), 1.70 – 1.59 (m, 1H), 1.58 – 1.25 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.7, 133.5, 133.2, 128.0, 126.9, 126.6, 119.6, 75.8, 48.3, 39.3, 28.3, 27.94, 27.90, 26.1, 24.9, 24.3, 23.1, 22.6. HRMS (ESI) m/z calcd. for $C_{21}H_{29}$ $[M\text{-}OH]^+$ 281.2264, found 281.2261.

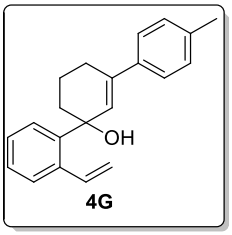
2-vinyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-1'-ol



4F

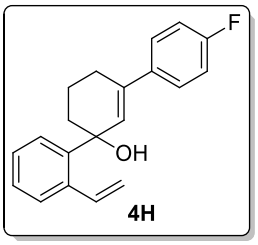
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 1H), 7.60 – 7.58 (m, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.40 – 7.34 (m, 3H), 6.26 (s, 1H), 5.62 (dd, J = 17.3, 1.4 Hz, 1H), 5.29 (dd, J = 10.9, 1.4 Hz, 1H), 2.70 (dt, J = 17.4, 4.6 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.33 (s, 1H), 2.28 – 2.18 (m, 1H), 2.11 – 2.02 (m, 2H), 1.90 – 1.84 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.3, 139.4, 137.2, 136.4, 129.8, 128.5, 128.0, 127.8, 127.5, 127.5, 126.6, 125.7, 115.1, 73.4, 36.9, 27.4, 19.8.

4''-methyl-2-vinyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-1'-ol



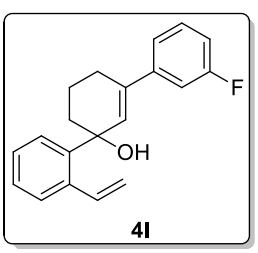
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 1H), 7.66 – 7.63 (m, 1H), 7.56 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 5.67 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.33 (dd, *J* = 11.0, 1.5 Hz, 1H), 2.73 (dt, *J* = 17.5, 5.0 Hz, 1H), 2.58 – 2.53 (m, 1H), 2.50 (s, 3H), 2.48 (s, 1H), 2.30 – 2.24 (m, 1H), 2.14 – 2.08 (m, 2H), 1.94 – 1.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 138.8, 138.1, 137.2, 137.0, 136.1, 128.9, 128.8, 127.7, 127.22, 127.16, 126.4, 125.2, 114.7, 73.0, 36.7, 27.1, 21.0, 19.5. HRMS (ESI) m/z calcd. for $C_{21}H_{21}$ $[M\text{-}OH]^+$ 273.1638, found 273.1636.

4''-fluoro-2-vinyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-1'-ol



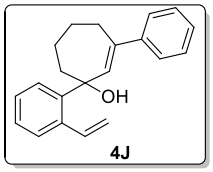
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.71 (m, 1H), 7.59 - 7.54 (m, 1H), 7.49 - 7.41 (m, 3H), 7.35 - 7.30 (m, 2H), 7.12 - 7.04 (m, 2H), 6.15 (s, 1H), 5.59 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.26 (dd, *J* = 10.8, 1.6 Hz, 1H), 2.60 (dt, *J* = 17.6, 4.8 Hz, 1H), 2.54 (s, 1H), 2.49 - 2.38 (m, 1H), 2.24 - 2.15 (m, 1H), 2.06 - 1.98 (m, 2H), 1.87 - 1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz), 143.9, 138.0, 137.1 (d, *J* = 3.3 Hz), 136.9, 136.1, 129.6, 127.8, 127.30 (d, *J* = 1.8 Hz), 127.0, 126.9, 126.3, 115.1 (d, *J* = 21.2 Hz), 114.9, 73.1, 36.5, 27.3, 19.5. HRMS (ESI) m/z calcd. for $C_{20}H_{20}OF$ $[M+H]^+$ 295.1493, found 295.1493.

3''-fluoro-2-vinyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-1'-ol



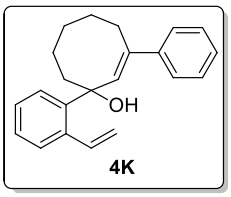
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 - 7.72 (m, 1H), 7.60 - 7.57 (m, 1H), 7.48 (dd, *J* = 17.0, 10.5 Hz, 1H), 7.37 - 7.28 (m, 4H), 7.26 - 7.22 (m, 1H), 7.06 (td, *J* = 8.5, 2.0 Hz, 1H), 6.25 (s, 1H), 5.61 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.29 (dd, *J* = 11.0, 1.5 Hz, 1H), 2.64 - 2.54 (m, 2H), 2.50 - 2.42 (m, 1H), 2.26 - 2.19 (m, 1H), 2.08 - 2.01 (m, 2H), 1.87 - 1.79 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (d, *J* = 243.6 Hz), 143.7, 143.35 (d, *J* = 7.3 Hz), 136.8, 136.1, 130.5, 129.62 (d, *J* = 8.4 Hz), 127.8, 127.27 (d, *J* = 7.9 Hz), 126.3, 120.94 (d, *J* = 2.8 Hz), 114.9, 114.1 (d, *J* = 21.0 Hz), 112.2 (d, *J* = 21.8 Hz), 73.0, 36.4, 27.0, 19.4. HRMS (ESI) m/z calcd. for $C_{20}H_{20}OF$ [M+H]+ 295.1493, found 295.1486

3-phenyl-1-(2-vinylphenyl)cyclohept-2-enol



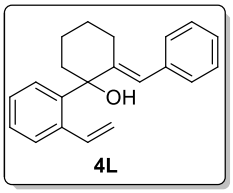
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 - 7.70 (m, 1H), 7.59 - 7.50 (m, 2H), 7.42 - 7.38 (m, 2H), 7.36 - 7.26 (m, 5H), 6.06 (s, 1H), 5.60 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.8, 1.6 Hz, 1H), 2.91 - 2.82 (m, 1H), 2.75 - 2.67 (m, 1H), 2.46 - 2.39 (m, 1H), 2.14 (s, 1H), 2.10 - 2.00 (m, 2H), 1.98 - 1.89 (m, 2H), 1.82 - 1.73 (m, 1H), 1.70 - 1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 145.1, 143.8, 137.4, 136.2, 136.0, 128.1, 128.0, 127.4, 127.3, 126.9, 126.1, 125.6, 115.0, 77.9, 38.9, 31.9, 26.4, 23.9.

(E)-3-phenyl-1-(2-vinylphenyl)cyclooct-2-enol



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 - 7.70 (m, 1H), 7.59 - 7.52 (m, 2H), 7.49 - 7.45 (m, 2H), 7.41 - 7.29 (m, 5H), 6.24 (s, 1H), 5.58 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.04 - 2.95 (m, 1H), 2.78 - 2.69 (m, 1H), 2.65 - 2.57 (m, 1H), 2.31 (s, 1H), 2.22 - 2.15 (m, 1H), 2.11 - 2.02 (m, 1H), 1.93 - 1.84 (m, 1H), 1.80 - 1.67 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 137.7, 136.8, 135.3, 128.4, 128.1, 128.0, 127.3, 127.2, 126.8, 126.1, 125.0, 124.9, 114.7, 77.7, 41.0, 28.2, 27.8, 23.8, 23.6. HRMS (ESI) m/z calcd. for $C_{22}H_{25}O$ $[M+H]^+$ 305.1900, found 305.1894 .

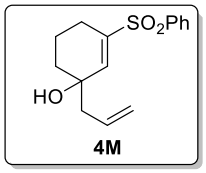
(*E*)-2-benzylidene-1-(2-vinylphenyl)cyclohexanol



4L

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.54 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.34 - 7.27 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.15 - 7.11 (m, 2H), 6.14 (s, 1H), 5.57 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.22 (dd, *J* = 11.0, 1.5 Hz, 1H), 2.76 - 2.58 (m, 2H), 2.46 - 2.39 (m, 1H), 2.00 - 1.88 (m, 3H), 1.83 - 1.77 (m, 1H), 1.73 - 1.69 (m, 1H), 1.53 - 1.48 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 142.6, 138.1, 137.5, 137.0, 128.7, 127.8, 127.7, 127.6, 127.4, 126.3, 125.3, 114.4, 77.9, 39.9, 26.6, 26.4, 22.2. HRMS (ESI) m/z calcd. for $C_{17}H_{14}F$ $[M\text{-}OH]^+$ 273.1638, found 273.1634.

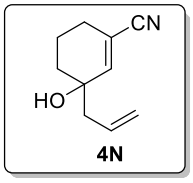
1-allyl-3-(phenylsulfonyl)cyclohex-2-enol



4M

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.63 – 7.58 (m, 1H), 7.54 – 7.49 (m, 2H), 6.84 (s, 1H), 5.86 – 5.76 (m, 1H), 5.21 – 5.10 (m, 2H), 2.40 – 2.31 (m, 2H), 2.28 (s, 1H), 2.23 – 2.15 (m, 1H), 2.12 – 2.03 (m, 1H), 1.75 – 1.62 (m, 3H), 1.61 – 1.55 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 140.0, 138.6, 133.4, 131.9, 129.2, 128.1, 120.0, 69.4, 45.7, 34.0, 23.0, 18.8. HRMS (ESI) m/z calcd. for $C_{15}H_{19}O_3S$ $[M+H]^+$ 279.1049, found 279.1048.

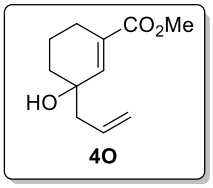
3-allyl-3-hydroxycyclohex-1-enecarbonitrile



4N

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (s, 1H), 5.86 - 5.76 (m, 1H), 5.24 - 5.14 (m, 2H), 2.32 (dd, *J* = 7.5, 0.5 Hz, 2H), 2.29 - 2.21 (m, 1H), 2.19 - 2.12 (m, 1H), 2.05 (s, 1H), 1.83 - 1.70 (m, 3H), 1.68 - 1.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 131.7, 120.3, 118.8, 114.4, 68.6, 45.6, 34.0, 26.8, 18.2. HRMS (ESI) m/z calcd. for $C_{10}H_{14}ON$ $[M+H]^+$ 164.1070 , found 164.1071.

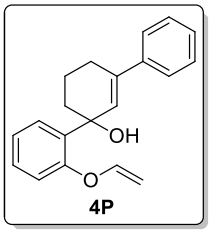
methyl 3-allyl-3-hydroxycyclohex-1-enecarboxylate



4O

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 5.89 - 5.77 (m, 1H), 5.18 - 5.08 (m, 2H), 3.71 (s, 3H), 2.38 - 2.26 (m, 3H), 2.18 - 2.06 (m, 2H), 1.74 - 1.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 141.4, 132.6, 131.9, 119.4, 69.3, 51.7, 45.9, 34.5, 24.3, 18.7. HRMS (ESI) m/z calcd. for $C_{11}H_{17}O_3$ $[M+H]^+$ 197.1172, found 197.1170.

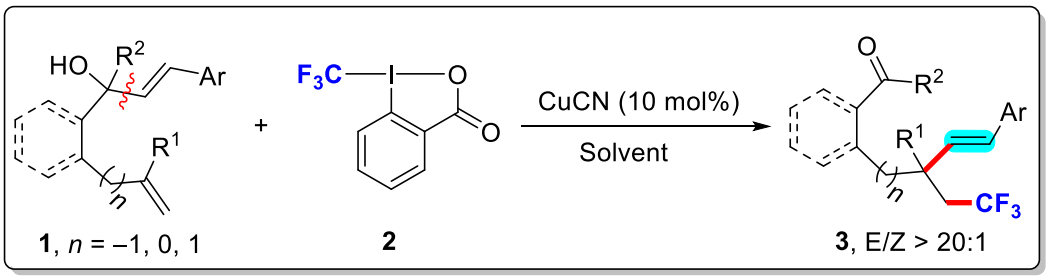
2-(vinyloxy)-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-1'-ol



4P

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.47 (m, 3H), 7.40 - 7.34 (m, 2H), 7.33 - 7.25 (m, 2H), 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 7.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.63 (dd, *J* = 13.6, 6.0 Hz, 1H), 6.22 (s, 1H), 4.85 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.53 (dd, *J* = 6.0, 2.0 Hz, 1H), 3.70 (s, 1H), 2.62 - 2.44 (m, 2H), 2.27 - 2.19 (m, 1H), 2.13 - 2.06 (m, 1H), 2.05 - 1.95 (m, 1H), 1.76 - 1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 147.7, 141.5, 139.9, 136.3, 128.4, 128.22, 128.19, 128.0, 127.4, 125.6, 123.1, 117.1, 96.3, 73.0, 36.7, 27.5, 19.7. HRMS (ESI) m/z calcd. for $C_{20}H_{21}O_2$ $[M+H]^+$ 293.1536, found 293.1532.

General procedures for trifluoromethylation reactions



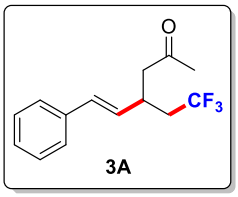
Method A: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv), **2** (94.5 mg, 0.3 mmol, 1.5 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), and EtOAc (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 80 °C for 18 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 × 5 mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **3A**, **3D**, **3E**, **3G**, **3I**.

The experimental procedure for performing the large-scale synthesis of **3A** is similar to that mentioned above in Method A.

Method B: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv), **2** (76 mg, 0.24 mmol, 1.2 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), and 1,4-dioxane (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 80 °C for 10 h. Then a second portion of **2** (76 mg, 0.24 mmol, 1.2 equiv) was added and the tube was stirred for an additional 10 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 × 5 mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **3A**–**3C**, **3F**, **3H**, **3J**, **3K**.

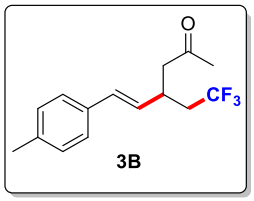
Method C: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv), **2** (94.5 mg, 0.3 mmol, 1.5 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), and EtOAc (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 60 °C for 24 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 × 5 mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **3L**–**3Q**.

(*E*)-6-phenyl-4-(2,2,2-trifluoroethyl)hex-5-en-2-one



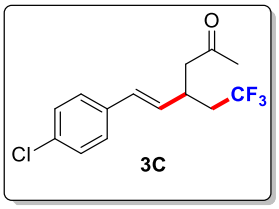
Compound **3A**, colorless oil, 69% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.18 – 3.09 (m, 1H), 2.68 (d, *J* = 6.5 Hz, 2H), 2.42 – 2.24 (m, 2H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 136.7, 131.3, 130.2, 128.5, 127.6, 126.5 (q, *J* = 276.0 Hz), 126.2, 47.8, 38.0 (q, *J* = 27.0 Hz), 32.9 (q, *J* = 2.6 Hz), 30.5. ^{19}F NMR (376MHz, $CDCl_3$) δ –63.0. HRMS (APCI) m/z calcd. for $C_{14}H_{16}OF_3$ $[M + H]^+$ 257.1148, found 257.1142.

(*E*)-6-(p-tolyl)-4-(2,2,2-trifluoroethyl)hex-5-en-2-one



Compound **3B**, colorless oil, 69% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 8.5 Hz, 1H), 3.16 – 3.07 (m, 1H), 2.67 (d, *J* = 6.5 Hz, 2H), 2.38 – 2.24 (m, 5H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 137.4, 133.9, 131.1, 129.2, 129.1, 126.5 (q, *J* = 275.9 Hz), 126.1, 47.9, 38.0 (q, *J* = 26.9 Hz), 32.9 (q, *J* = 2.5 Hz), 30.6, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.1. HRMS (APCI) m/z calcd. for $C_{15}H_{18}OF_3$ $[M + H]^+$ 271.1304, found 271.1297.

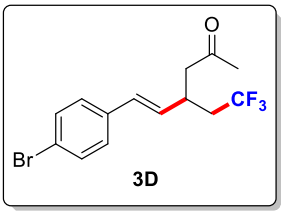
(*E*)-6-(4-chlorophenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-2-one



Compound **3C**, colorless oil, 77% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 4H), 6.41 (d, *J* = 15.5 Hz, 1H), 6.07 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.16 – 3.08 (m, 1H), 2.67 (d, *J* = 6.5 Hz, 2H), 2.40 – 2.24 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 135.2, 133.2, 130.9, 130.1, 128.7, 127.5, 126.5 (q, *J* = 275.9 Hz), 47.7, 37.9 (q, *J*

= 27.1 Hz), 32.8 (q, *J* = 2.5 Hz), 30.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.1. HRMS (APCI) m/z calcd. for $C_{14}H_{15}OClF_3$ $[M + H]^+$ 291.0758, found 291.0752.

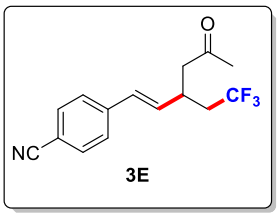
(*E*)-6-(4-bromophenyl)-4-(2,2,2-trifluoroethyl)hex-5-en-2-one



3D

Compound **3D**, colorless oil, 69% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.20 – 7.17 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 16.0, 8.5 Hz, 1H), 3.16 – 3.08 (m, 1H), 2.67 (d, *J* = 6.5 Hz, 2H), 2.41 – 2.23 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 135.6, 131.6, 131.0, 130.2, 127.8, 126.4 (q, *J* = 276.0 Hz), 121.3, 47.6, 37.9 (q, *J* = 27.1 Hz), 32.8 (q, *J* = 2.5 Hz), 30.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.1. HRMS (APCI) m/z calcd. for $C_{14}H_{15}OBrF_3$ $[M + H]^+$ 335.0253, found 335.0248.

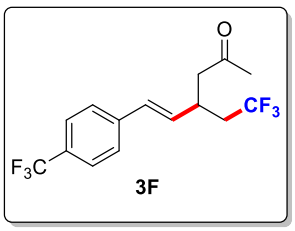
(*E*)-4-(5-oxo-3-(2,2,2-trifluoroethyl)hex-1-en-1-yl)benzonitrile



3E

Compound **3E**, colorless oil, 72% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.20 – 3.12 (m, 1H), 2.70 (d, *J* = 6.0 Hz, 2H), 2.44 – 2.24 (m, 2H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 141.2, 134.3, 132.4, 129.9, 126.8, 126.3 (q, *J* = 275.9 Hz), 118.9, 110.8, 47.5, 37.8 (q, *J* = 27.3 Hz), 32.8 (q, *J* = 2.4 Hz), 30.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.1. HRMS (APCI) m/z calcd. for $C_{15}H_{15}ONF_3$ $[M + H]^+$ 282.1100, found 282.1099.

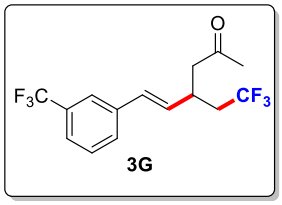
(*E*)-4-(2,2,2-trifluoroethyl)-6-(4-(trifluoromethyl)phenyl)hex-5-en-2-one



3F

Compound **3F**, colorless oil, 80% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.70 (d, *J* = 6.5 Hz, 2H), 2.44 – 2.24 (m, 2H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 140.2, 132.9, 130.1, 129.4 (q, *J* = 32.1 Hz), 126.4(2), 126.4(1) (q, *J* = 275.9 Hz), 125.5 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 270.3 Hz), 47.6, 38.2 (q, *J* = 27.1 Hz), 32.8 (q, *J* = 2.6 Hz), 30.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.5 (s, 3F), –63.1 (s, 3F). HRMS (APCI) m/z calcd. for $C_{15}H_{15}OF_6$ $[M + H]^+$ 325.1022, found 325.1016.

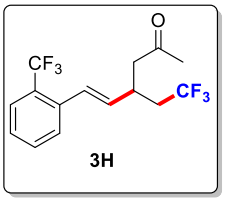
(*E*)-4-(2,2,2-trifluoroethyl)-6-(3-(trifluoromethyl)phenyl)hex-5-en-2-one



3G

Compound **3G**, colorless oil, 63% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.51 – 7.45 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.70 (d, *J* = 6.5 Hz, 2H), 2.43 – 2.25 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 137.5, 132.2, 131.0 (q, *J* = 31.9 Hz), 130.1, 129.5, 129.0, 126.4 (q, *J* = 275.9 Hz), 124.1(1) (q, *J* = 3.8 Hz), 124.0(5) (q, *J* = 270.6 Hz), 122.8 (q, *J* = 3.9 Hz), 47.6, 37.9 (q, *J* = 27.1 Hz), 32.8 (q, *J* = 2.5 Hz), 30.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8 (s, 3F), –63.1 (s, 3F). HRMS (APCI) m/z calcd. for $C_{15}H_{15}OF_6$ $[M + H]^+$ 325.1022, found 325.1014.

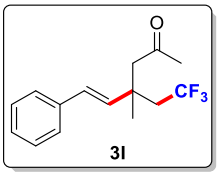
(*E*)-4-(2,2,2-trifluoroethyl)-6-(2-(trifluoromethyl)phenyl)hex-5-en-2-one



3H

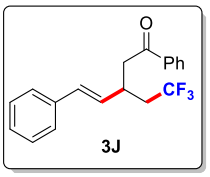
Compound **3H**, colorless oil, 81% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.82 (dd, *J* = 15.5, 2.0 Hz, 1H), 6.09 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.22 – 3.13 (m, 1H), 2.70 (d, *J* = 6.5 Hz, 2H), 2.43 – 2.26 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 136.0, 134.7, 131.9, 127.6, 127.5, 127.4 (q, *J* = 5.9 Hz), 127.3, 126.4 (q, *J* = 275.5 Hz), 125.7 (q, *J* = 5.6 Hz), 123.9 (d, *J* = 272.3 Hz), 47.6, 37.8 (q, *J* = 27.3 Hz), 32.9 (q, *J* = 2.6 Hz), 30.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –59.6 (s, 3F), –63.1 (s, 3F). HRMS (APCI) m/z calcd. for $C_{15}H_{15}OF_6$ $[M + H]^+$ 325.1022, found 325.1016.

(*E*)-4-methyl-6-phenyl-4-(2,2,2-trifluoroethyl)hex-5-en-2-one



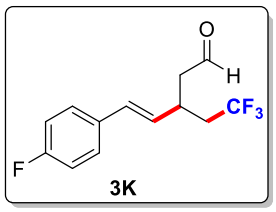
Compound **3I**, colorless oil, 65% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 6.37 (s, 2H), 2.72 (s, 2H), 2.64 – 2.52 (m, 2H), 2.13 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 137.0, 136.2, 128.6, 127.5, 127.4, 126.7 (q, *J* = 277.1 Hz), 126.3, 52.0, 41.6 (q, *J* = 25.9 Hz), 36.2 (q, *J* = 1.8 Hz), 31.5, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –59.8. HRMS (APCI) m/z calcd. for $C_{15}H_{18}OF_3$ $[M + H]^+$ 271.1304, found 271.1299.

(*E*)-1,5-diphenyl-3-(2,2,2-trifluoroethyl)pent-4-en-1-one



Compound **3J**, colorless oil, 58% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.60 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.34 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 6.19 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.27 – 3.17 (m, 2H), 2.56 – 2.44 (m, 1H), 2.42 – 2.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 136.8, 133.3, 131.3, 130.5, 128.7, 128.5, 128.0, 127.5, 126.6 (q, *J* = 276.0 Hz), 126.3, 43.1, 38.2 (q, *J* = 26.9 Hz), 33.2 (q, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0. HRMS (APCI) m/z calcd. for $C_{19}H_{18}OF_3$ $[M + H]^+$ 319.1304, found 319.1299.

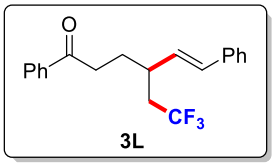
(*E*)-5-(4-fluorophenyl)-3-(2,2,2-trifluoroethyl)pent-4-enal



Compound **3K**, colorless oil, 44% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.33 – 7.27 (m, 2H), 7.03 – 6.95 (m, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.01 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.24 – 3.14 (m, 1H), 2.70 (d, *J* = 6.4 Hz, 2H), 2.42 – 2.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 162.4 (d, *J* = 247.1 Hz), 132.6 (d, *J* = 3.3 Hz), 130.6, 129.3 (d, *J* = 2.1 Hz), 127.8 (d, *J* = 8.1 Hz), 126.3 (q, *J* = 275.9 Hz), 115.5 (d, *J* = 21.5

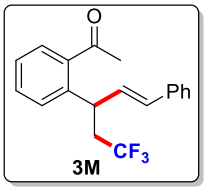
Hz), 48.0, 38.2 (q, J = 27.3 Hz), 31.9 (q, J = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2 (s, 3F), –114.2 (s, 1F). HRMS (APCI) m/z calcd. for $C_{13}H_{13}OF_4$ $[M + H]^+$ 261.0897, found 261.0890.

(*E*)-1,6-diphenyl-4-(2,2,2-trifluoroethyl)hex-5-en-1-one



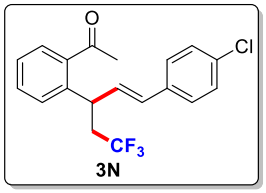
Compound **3L**, colorless oil, 55% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.43 (m, 2H), 7.39 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 6.46 (dd, J = 15.6, 3.6 Hz, 1H), 6.04 – 5.93 (m, 1H), 3.05 (td, J = 7.6, 2.0 Hz, 2H), 2.78 – 2.64 (m, 1H), 2.41 – 2.27 (m, 2H), 2.17 – 2.07 (m, 1H), 1.91 – 1.79 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 136.8, 136.8, 133.1, 132.0, 130.9, 128.6, 128.5, 127.6, 127.5, 126.5 (q, J = 275.8 Hz), 126.2, 39.6 (q, J = 26.8 Hz), 37.4 (q, J = 2.3 Hz), 35.8, 29.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0. HRMS (APCI) m/z calcd. for $C_{20}H_{20}OF_3$ $[M + H]^+$ 333.1461, found 333.1455.

(*E*)-1-(2-(5,5,5-trifluoro-1-phenylpent-1-en-3-yl)phenyl)ethanone



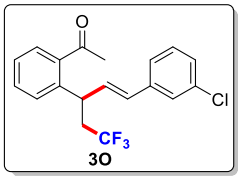
Compound **3M**, colorless oil, 68% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.0, 1.5 Hz, 1H), 7.47 (td, J = 8.0, 1.5 Hz, 1H), 7.40 (dd, J = 7.5, 1.0 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.29 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 6.45 (d, J = 16.0 Hz, 1H), 6.37 (dd, J = 16.0, 7.0 Hz, 1H), 4.70 – 4.64 (m, 1H), 2.71 – 2.62 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 141.5, 138.4, 136.8, 131.6, 130.9(9), 130.9(7), 128.8, 128.6, 128.5, 127.5, 126.6, 126.4 (q, J = 276.0 Hz), 126.3, 40.8 (q, J = 26.9 Hz), 37.6 (q, J = 2.6 Hz), 30.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.4. HRMS (APCI) m/z calcd. for $C_{19}H_{18}OF_3$ $[M + H]^+$ 319.1304, found 319.1297.

(*E*)-1-(2-(1-(4-chlorophenyl)-5,5,5-trifluoropent-1-en-3-yl)phenyl)ethanone



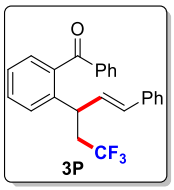
Compound **3N**, colorless oil, 72% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 – 7.21 (m, 4H), 6.45 – 6.31 (m, 2H), 4.68 (q, *J* = 7.2 Hz, 1H), 2.73 – 2.61 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 141.3, 138.3, 135.4, 133.1, 131.7, 131.6, 129.8, 128.9, 128.6(2), 128.5(8), 127.5, 126.7, 126.3 (q, *J* = 276.1 Hz), 39.7 (q, *J* = 26.9 Hz), 37.7 (q, *J* = 2.5 Hz), 30.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.4. HRMS (APCI) m/z calcd. for $C_{19}H_{17}OClF_3$ $[M + H]^+$ 353.0915, found 353.0905.

(*E*)-1-(2-(1-(3-chlorophenyl)-5,5,5-trifluoropent-1-en-3-yl)phenyl)ethanone



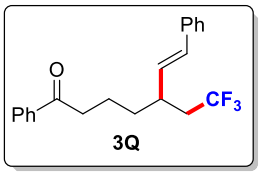
Compound **3O**, colorless oil, 65% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.36 – 7.31 (m, 2H), 7.21 – 7.15 (m, 3H), 6.40 (d, *J* = 2.8 Hz, 2H), 4.72 – 4.65 (m, 1H), 2.71 – 2.62 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 141.3, 138.8, 138.2, 134.5, 132.6, 131.7, 129.8, 129.7, 129.0, 128.6, 127.4, 126.7, 126.3 (q, *J* = 276.1 Hz), 126.1, 124.6, 39.7 (q, *J* = 27.0 Hz), 37.6 (q, *J* = 2.6 Hz), 30.0. ^{19}F NMR (376 MHz, DMSO) δ –64.1. HRMS (APCI) m/z calcd. for $C_{19}H_{17}OClF_3$ $[M + H]^+$ 353.0915, found 353.0904.

(*E*)-phenyl(2-(5,5,5-trifluoro-1-phenylpent-1-en-3-yl)phenyl)methanone



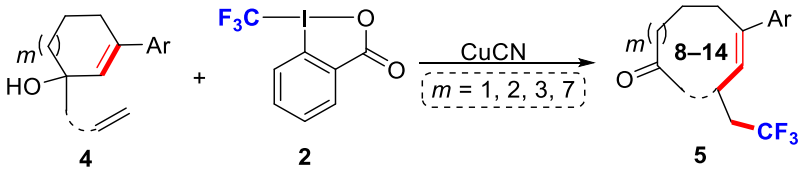
Compound **3P**, colorless oil, 78% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.49 – 7.41 (m, 3H), 7.34 – 7.30 (m, 2H), 7.28 – 7.18 (m, 5H), 6.39 – 6.23 (m, 2H), 4.23 (dd, *J* = 12.8, 6.4 Hz, 1H), 2.78 – 2.64 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 141.3, 138.4, 137.6, 136.7, 133.4, 131.2, 130.6, 130.5, 130.3, 128.9, 128.4(2), 128.3(7), 127.9, 127.5, 126.2(2), 126.1(8) (q, *J* = 276.3 Hz), 126.1, 39.7 (q, *J* = 27.0 Hz), 38.8 (q, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0. HRMS (APCI) m/z calcd. for $C_{24}H_{20}OF_3$ $[M + H]^+$ 381.1461, found 381.1451.

(*E*)-1,7-diphenyl-5-(2,2,2-trifluoroethyl)hept-6-en-1-one



Compound **3Q**, colorless oil, 30% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.99 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.05 – 2.93 (m, 2H), 2.68 – 2.57 (m, 1H), 2.32 – 2.19 (m, 2H), 1.88 – 1.74 (m, 2H), 1.71 – 1.64 (m, 1H), 1.56 – 1.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 137.0, 136.8, 133.0, 131.4, 131.3, 128.6, 128.5, 128.0, 126.6 (q, *J* = 275.8 Hz), 127.4, 126.2, 39.2 (q, *J* = 26.5 Hz), 38.2, 37.6 (q, *J* = 2.4 Hz), 34.5, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0. HRMS (APCI) m/z calcd. for $C_{21}H_{22}OF_3$ $[M + H]^+$ 347.1617, found 347.1609 .

General procedures for synthesis of medium- and large-sized alkenes (5A–5L)



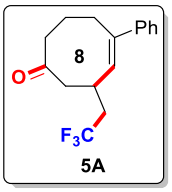
Method A: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **4** (0.2 mmol, 1.0 equiv), **2** (75 mg, 0.24 mmol, 1.2 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), and 1,4-dioxane (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 80 °C for 10 h. Then a second portion of **2** (75 mg, 0.24 mmol, 1.2 equiv) was added and the tube was stirred for an additional 10 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 × 5 mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **5A**–**5E**.

The experimental procedure for performing the large-scale synthesis of **5A** is similar to that mentioned above in Method A.

Method B: A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **4** (0.2 mmol, 1.0 equiv), **2** (94.5 mg, 0.3 mmol, 1.5 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), and EtOAc (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 60 °C for 24 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 × 5

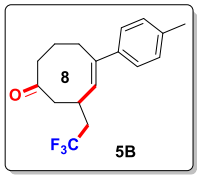
mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **5F**–**5L**.

(*E*)-5-phenyl-3-(2,2,2-trifluoroethyl)cyclooct-4-enone



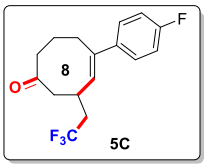
Compound **5A**, colorless oil, 65% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 5H), 5.60 (d, *J* = 9.5 Hz, 1H), 3.57 – 3.46 (m, 1H), 2.83 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.68 – 2.62 (m, 1H), 2.43 – 2.26 (m, 4H), 1.97 – 1.89 (m, 1H), 1.72 – 1.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.3, 142.4, 141.7, 129.9, 128.3, 127.3, 126.2(8) (q, *J* = 275.6 Hz), 126.2(5), 53.4, 41.1, 39.1 (q, *J* = 27.6 Hz), 31.5, 29.1 (q, *J* = 2.6 Hz), 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.0. HRMS (APCI) m/z calcd. for $C_{16}H_{18}OF_3$ $[M + H]^+$ 283.1304, found 283.1299.

(*E*)-5-(p-tolyl)-3-(2,2,2-trifluoroethyl)cyclooct-4-enone



Compound **5B**, colorless oil, 60% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.57 (d, *J* = 9.5 Hz, 1H), 3.55 – 3.44 (m, 1H), 2.82 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.76 – 2.61 (m, 3H), 2.42 – 2.26 (m, 7H), 1.96 – 1.89 (m, 1H), 1.70 – 1.63 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.4, 141.5, 139.4, 137.2, 129.2, 129.0, 126.3 (q, *J* = 275.8 Hz), 126.1, 53.5, 41.2, 39.2 (q, *J* = 27.5 Hz), 31.4, 29.1 (q, *J* = 2.6 Hz), 24.7, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.0. HRMS (APCI) m/z calcd. for $C_{17}H_{20}OF_3$ $[M + H]^+$ 297.1461, found 297.1454.

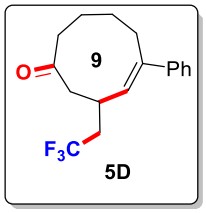
(*E*)-5-(4-fluorophenyl)-3-(2,2,2-trifluoroethyl)cyclooct-4-enone



Compound **5C**, colorless oil, 70% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.20 (m,

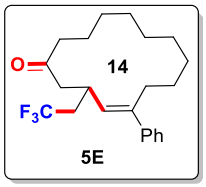
2H), 7.00 – 6.94 (m, 2H), 5.54 (d, *J* = 9.5 Hz, 1H), 3.56 – 3.47 (m, 1H), 2.84 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.78 – 2.69 (m, 2H), 2.59 (dq, *J* = 14.0, 2.5 Hz, 1H), 2.41 – 2.25 (m, 4H), 1.96 – 1.89 (m, 1H), 1.69 – 1.59 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 162.2 (d, *J* = 244.9 Hz), 140.8, 138.4 (d, *J* = 3.3 Hz), 130.0, 127.9 (d, *J* = 8.0 Hz), 126.2 (q, *J* = 275.8 Hz), 115.1 (q, *J* = 21.3 Hz), 53.4, 41.1, 39.1 (q, *J* = 27.6 Hz), 31.7, 29.1 (q, *J* = 2.6 Hz), 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.0 (s, 3F), –115.23 (s, 1F). HRMS (APCI) m/z calcd. for $C_{16}H_{17}OF_4$ $[M + H]^+$ 301.1210, found 301.1202.

(*E*)-5-phenyl-3-(2,2,2-trifluoroethyl)cyclonon-4-enone



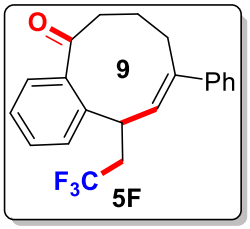
Compound **5D**, colorless oil,54% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 5.65 (d, *J* = 8.5 Hz, 1H), 3.43 – 3.35 (m, 1H), 2.67 (t, *J* = 12.0 Hz, 1H), 2.59 – 2.53 (m, 2H), 2.51 – 2.31 (m, 5H), 1.83 – 1.73 (m, 1H), 1.71 – 1.65 (m, 1H), 1.61 – 1.54 (m, 1H), 1.53 – 1.45 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.4, 141.3, 141.2, 130.6, 128.4, 127.4, 126.4, 126.3 (q, *J* = 277.8 Hz), 48.0, 42.0, 40.4 (q, *J* = 27.3 Hz), 31.3 (q, *J* = 2.6 Hz), 27.1, 25.9, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.5. HRMS (APCI) m/z calcd. for $C_{17}H_{20}OF_3$ $[M + H]^+$ 297.1461, found 297.1454.

(*E*)-5-phenyl-3-(2,2,2-trifluoroethyl)cyclotetradec-4-enone



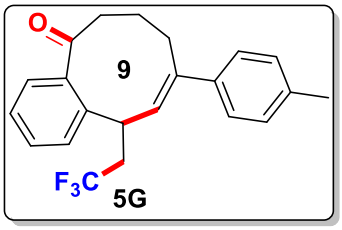
Compound **5E**, colorless oil, 46% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.26 – 7.22 (m, 1H), 5.44 (d, *J* = 10.5 Hz, 1H), 3.38 – 3.28 (m, 1H), 2.70 – 2.58 (m, 2H), 2.52 – 2.41 (m, 5H), 2.14 – 2.04 (m, 1H), 1.74 – 1.65 (m, 2H), 1.41 – 1.27 (m, 10H), 1.23 – 1.15 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.1, 142.6, 141.7, 129.7, 128.2, 127.0, 126.6, 126.5 (q, *J* = 276.0 Hz), 47.2, 42.1, 38.8 (q, *J* = 26.8 Hz), 29.2 (q, *J* = 2.5 Hz), 28.7, 26.9, 26.5, 25.9(9), 25.9(6), 25.2(5), 25.1(8), 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.5. HRMS (APCI) m/z calcd. for $C_{22}H_{30}OF_3$ $[M + H]^+$ 367.2243, found 367.2236.

(*E*)-9-phenyl-11-(2,2,2-trifluoroethyl)-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one



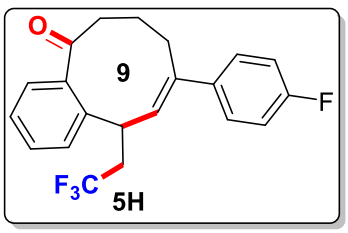
Compound **5F**, colorless oil, 46% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (td, *J* = 7.7, 1.5 Hz, 1H), 7.38 – 7.22 (m, 8H), 5.45 (d, *J* = 10.9 Hz, 1H), 4.67 (td, *J* = 10.8, 3.2 Hz, 1H), 3.06 – 2.89 (m, 3H), 2.72 (dt, *J* = 13.9, 3.7 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.15 – 2.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 144.4, 141.9, 139.2, 138.0, 131.6, 130.4, 128.3, 127.4, 127.3, 127.0, 126.8, 126.7 (q, *J* = 276 Hz), 124.3, 41.2, 36.6 (q, *J* = 27.0 Hz), 35.1 (q, *J* = 2.6 Hz), 29.6, 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8. HRMS (ESI) calcd. for $C_{21}H_{20}F_3O$ $[M + H]^+$ 345.1460, found 345.1457.

(*E*)-9-(p-tolyl)-11-(2,2,2-trifluoroethyl)-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one



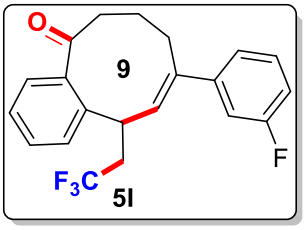
Compound **5G**, colorless oil, 52% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (td, *J* = 8.0, 1.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.08 (m, 4H), 5.41 (d, *J* = 11.0 Hz, 1H), 4.63 (td, *J* = 11.0, 3.0 Hz, 1H), 2.97 – 2.88 (m, 3H), 2.69 (dt, *J* = 13.5, 3.5 Hz, 1H), 2.58 – 2.51 (m, 2H), 2.32 (s, 3H), 2.09 – 2.03 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.1, 144.4, 139.0, 138.8, 138.0, 137.1, 130.9, 130.3, 128.9, 127.1, 126.8, 126.6(5) (q, *J* = 275.9 Hz), 126.5(8), 124.2, 41.1, 36.4 (q, *J* = 27.1 Hz), 35.0 (q, *J* = 2.6 Hz), 29.4, 24.3, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8. HRMS (APCI) m/z calcd. for $C_{22}H_{22}OF_3$ $[M + H]^+$ 359.1617, found 359.1607.

(*E*)-9-(4-fluorophenyl)-11-(2,2,2-trifluoroethyl)-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one



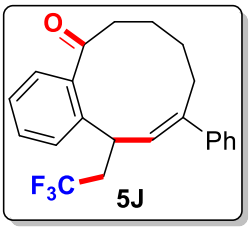
Compound **5H**, white solid, 41% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.23 – 7.16 (m, 3H), 6.99 – 6.93 (m, 2H), 5.36 (d, *J* = 11.0 Hz, 1H), 4.65 (td, *J* = 11.0, 3.0 Hz, 1H), 3.01 – 2.88 (m, 3H), 2.66 – 2.48 (m, 3H), 2.09 – 2.00 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.0, 162.3 (d, *J* = 244.6 Hz), 144.3, 138.3, 138.0, 137.9 (d, *J* = 3.3 Hz), 131.8, 130.5, 128.4 (d, *J* = 8.0 Hz), 127.3, 127.2, 126.7 (q, *J* = 275.8 Hz), 124.2, 115.1 (d, *J* = 21.1 Hz), 41.2, 36.5 (q, *J* = 27.0 Hz), 35.1 (q, *J* = 2.4 Hz), 29.9, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s, 3F), –115.3 (s, 1F). HRMS (APCI) m/z calcd. for $C_{21}H_{19}OF_4$ $[M + H]^+$ 363.1367, found 363.1362.

(*E*)-9-(3-fluorophenyl)-11-(2,2,2-trifluoroethyl)-6,7,8,11-tetrahydro-5H-benzo[9]annulen-5-one



Compound **5I**, white solid, 48% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (td, *J* = 8.0, 1.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.97 – 6.89 (m, 2H), 5.44 (d, *J* = 11.2 Hz, 1H), 4.64 (td, *J* = 11.2, 2.8 Hz, 1H), 3.02 – 2.87 (m, 3H), 2.67 – 2.50 (m, 3H), 2.11 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 162.7 (d, *J* = 243.8 Hz), 144.3, 144.1 (d, *J* = 7.4 Hz), 138.1, 137.5, 132.3, 130.4, 129.7 (d, *J* = 8.3 Hz), 127.3, 127.0, 126.6 (q, *J* = 275.8 Hz), 124.2, 122.4 (d, *J* = 2.6 Hz), 114.2 (d, *J* = 21.1 Hz), 113.6 (d, *J* = 21.7 Hz), 41.1, 36.4 (q, *J* = 27.1 Hz), 35.0 (q, *J* = 2.6 Hz), 29.5, 24.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8 (s, 3F), –113.4 (s, 1F). HRMS (APCI) m/z calcd. for $C_{21}H_{19}OF_4$ $[M + H]^+$ 363.1367, found 363.1363.

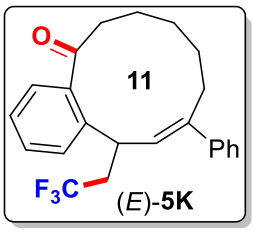
(*E*)-10-phenyl-12-(2,2,2-trifluoroethyl)-6,7,8,9-tetrahydrobenzo[10]annulen-5(12H)-one



Compound **5J**, colorless oil, 50% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 1H), 7.35 – 7.31 (m, 1H), 7.29 – 7.20 (m, 5H), 7.13 (M, 2H), 5.51 (d, *J* = 10.5 Hz, 1H), 4.74 – 4.66 (m, 1H), 3.25 – 3.17 (m, 1H), 2.90 – 2.82 (m, 1H), 2.73 – 2.63 (m, 2H), 2.60 – 2.48 (m, 2H), 1.64 – 1.58 (m, 1H), 1.55 – 1.46 (m, 2H), 1.39 – 1.29 (m, 1H). ^{13}C NMR

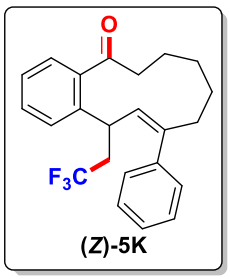
(125 MHz, $CDCl_3$) δ 211.6, 141.6, 140.6, 140.1, 138.9, 132.7, 130.6, 128.2, 127.1, 126.6, 126.4 (q, *J* = 276.0 Hz), 126.2(1), 126.1(8), 125.8, 45.7, 38.1 (q, *J* = 27.3 Hz), 33.2 (q, *J* = 3.1 Hz), 27.9, 27.2, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.9. HRMS (APCI) m/z calcd. for $C_{22}H_{22}OF_3$ $[M + H]^+$ 359.1617, found 359.1612.

(*E*)-11-phenyl-13-(2,2,2-trifluoroethyl)-6,7,8,9,10,13-hexahydro-5H-benzo[11]annulen-5-one



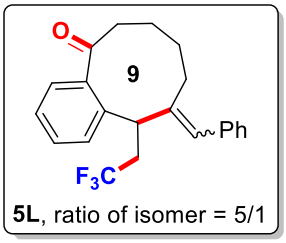
Compound (*E*)-**5K**, colorless oil, 25% yield, ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.38 (m, 1H), 7.32 – 7.20 (m, 6H), 5.77 (d, *J* = 10.0 Hz, 1H), 4.67 (td, *J* = 10.0, 5.0 Hz, 1H), 3.03 – 2.95 (m, 1H), 2.75 – 2.55 (m, 4H), 2.28 – 2.20 (m, 1H), 2.11 – 1.96 (m, 2H), 1.48 – 1.40 (m, 1H), 1.37 – 1.27 (m, 2H), 0.97 – 0.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.2, 142.5, 141.6, 141.3, 141.0, 131.0, 130.2, 128.2, 127.8, 127.1, 126.6, 126.4, 126.3 (q, *J* = 276.3 Hz), 126.1, 41.8, 40.3 (q, *J* = 21.4 Hz), 33.2 (q, *J* = 2.8 Hz), 28.3, 26.8, 25.6, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.8. HRMS (APCI) m/z calcd. for $C_{23}H_{24}OF_3$ $[M + H]^+$ 373.1774 , found 373.1770.

(*Z*)-11-phenyl-13-(2,2,2-trifluoroethyl)-6,7,8,9,10,13-hexahydro-5H-benzo[11]annulen-5-one



Compound (*Z*)-**5K**, colorless oil, 6% yield, ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.13 (m, 3H), 6.99 – 6.87 (m, 1H), 6.73 (d, *J* = 6.9 Hz, 2H), 5.77 (d, *J* = 8.7 Hz, 1H), 3.62 (dd, *J* = 13.5, 8.8 Hz, 1H), 3.19 (t, *J* = 11.3 Hz, 1H), 3.07 – 2.92 (m, 1H), 2.70 – 2.48 (m, 2H), 2.41 (qd, *J* = 12.9, 3.4 Hz, 2H), 1.93 (dt, *J* = 12.1, 7.5 Hz, 1H), 1.70 – 1.55 (m, 2H), 1.46 (dd, *J* = 10.5, 4.9 Hz, 2H), 1.21 – 1.05 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9, 144.8, 141.6, 141.1, 139.9, 131.6, 130.6, 129.6, 127.8, 127.7, 127.6, 126.8, 126.5 (q, *J* = 276.1 Hz), 126.3, 42.1, 42.0 (q, *J* = 26.6 Hz), 40.2, 37.7, 25.4, 23.8, 23.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.2. HRMS (APCI) m/z calcd. for $C_{23}H_{24}OF_3$ $[M + H]^+$ 373.1774, found 373.1771.

10-benzylidene-11-(2,2,2-trifluoroethyl)-6,7,8,9,10,11-hexahydro-5H-benzo[9]annulen-5-one

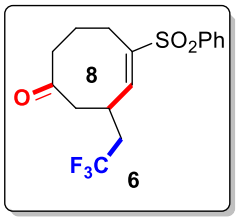


Compound (*Z*)-**5L**, colorless oil, (major isomer, 50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 5H), 7.11 – 7.00 (m, 3H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 4.42 (t, *J* = 7.2 Hz, 1H), 2.98 (dd, *J* = 14.5, 8.3 Hz, 1H), 2.78 – 2.58 (m, 3H), 2.52 – 2.41 (m, 1H), 2.20 (t, *J* = 13.7 Hz, 1H), 1.98 – 1.70 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 141.4, 140.5, 137.6, 137.5, 131.3, 130.3, 129.3, 128.5, 128.2, 126.8, 126.6, 126.5 (q, *J* = 276 Hz), 124.8, 45.6, 41.5, 37.6 (q, *J* = 27.2 Hz), 30.1, 28.6, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.2. HRMS (ESI) calcd. for $C_{22}H_{22}F_3O$ $[M + H]^+$ 359.1617, found 359.1613.

General procedures for the synthesis of medium-sized cyclic alkenes 6–9

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv), **2** (94.5 mg, 0.3 mmol, 1.5 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), and EtOAc or 1,4-dioxane (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 80 °C for 20 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2 × 5 mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **6**–**9**.

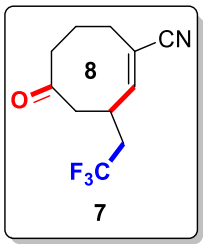
(*E*)-5-(phenylsulfonyl)-3-(2,2,2-trifluoroethyl)cyclooct-4-enone



Compound **6**, white solid, (70% conversion, 79% yield based on recovery of starting material), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 9.5 Hz, 1H), 3.39 – 3.30 (m, 1H), 2.82 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.64 – 2.52 (m, 2H), 2.46 – 2.33 (m, 4H), 2.28 – 2.22 (m, 1H), 1.74

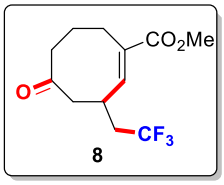
– 1.67 (m, 1H), 1.20 – 1.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 142.6, 141.4, 138.5, 133.7, 129.3, 128.4, 125.8 (d, *J* = 275.6 Hz), 52.1, 40.2, 38.4 (d, *J* = 28.4 Hz), 29.0 (d, *J* = 2.8 Hz), 26.5, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.3. HRMS (APCI) m/z calcd. for $C_{16}H_{18}O_3F_3S$ $[M + H]^+$ 347.0923, found 347.0916.

(*E*)-5-oxo-3-(2,2,2-trifluoroethyl)cyclooct-1-enecarbonitrile



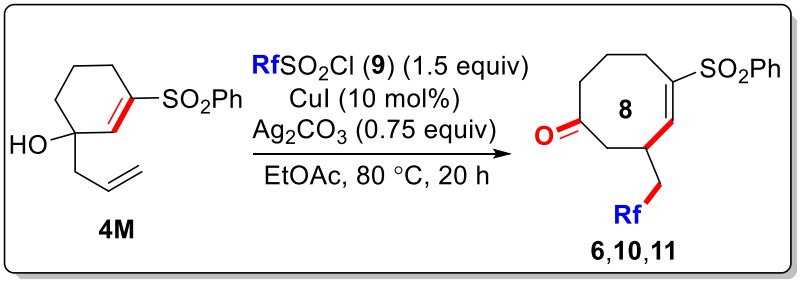
Compound **7**, colorless oil, (65% conversion, 58% yield based on recovery of starting material), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (d, *J* = 9.6 Hz, 1H), 3.50 – 3.38 (m, 1H), 2.81 (dd, *J* = 12.8, 4.0 Hz, 1H), 2.67 (td, *J* = 11.2, 3.6 Hz, 1H), 2.56 – 2.39 (m, 4H), 2.36 – 2.26 (m, 2H), 1.97 – 1.90 (m, 1H), 1.78 – 1.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 148.2, 125.6 (q, *J* = 275.7 Hz), 118.7, 116.2, 52.4, 40.3, 38.2 (q, *J* = 28.4 Hz), 29.9, 29.4 (q, *J* = 2.8 Hz), 23.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.3. HRMS (APCI) m/z calcd. for $C_{11}H_{13}ONF_3$ $[M + H]^+$ 232.0944, found 232.0939.

(*E*)-methyl 5-oxo-3-(2,2,2-trifluoroethyl)cyclooct-1-enecarboxylate



Compound **8**, colorless oil, (60% conversion, 60% yield based on recovery of starting material), ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (d, *J* = 9.5 Hz, 1H), 3.72 (s, 3H), 3.51 – 3.41 (m, 1H), 2.87 – 2.78 (m, 2H), 2.67 (td, *J* = 11.5, 3.0 Hz, 1H), 2.39 – 2.23 (m, 5H), 1.94 – 1.86 (m, 1H), 1.62 – 1.52 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.5, 166.8, 142.6, 133.5, 126.0 (q, *J* = 275.6 Hz), 52.7, 52.1, 41.0, 38.6 (q, *J* = 28.1 Hz), 29.3 (q, *J* = 2.8 Hz), 26.8, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.3. HRMS (APCI) m/z calcd. for $C_{12}H_{16}O_3F_3$ $[M + H]^+$ 265.1046, found 265.1041.

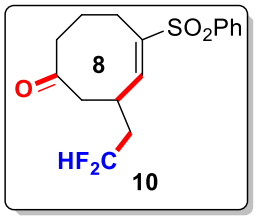
General procedures for synthesis of medium-sized cyclic alkenes 6, 10, 11



Under argon, a 25mL Schlenk tube equipped with a magnetic stir bar was charged with **4M**

(0.2 mmol, 55.6 mg, 1.0 equiv), **9** (0.3 mmol, 1.5equiv), CuI (1.8 mg, 0.02mmol, 0.1equiv), Ag_2CO_3 (42 mg, 0.15 mmol, 0.75 equiv) and EtOAc (2.0 mL). The sealed tube was then stirred at 80 °C for 20 h. After completion of the reaction as monitored by TLC, EtOAc (30 mL) was added and the reaction mixture was washed with brine (2 ×5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column chromatography to afford products **6**, **10** and **11**.

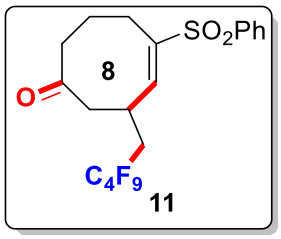
(*E*)-3-(2,2-difluoroethyl)-5-(phenylsulfonyl)cyclooct-4-enone



10

Compound **10**, colorless oil, (68% conversion, 65% yield based on recovery of starting material), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.67 – 7.61 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.52 (m, 2H), 6.90 (d, *J* = 9.2 Hz, 1H), 6.04 – 5.70 (m, 1H), 3.35 – 3.24 (m, 1H), 2.80 (dd, *J* = 12.8, 4.0 Hz, 1H), 2.64 – 2.53 (m, 2H), 2.47 – 2.37 (m, 2H), 2.24 – 2.05 (m, 3H), 1.70 – 1.61 (m, 1H), 1.09 – 0.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 142.5, 142.2, 138.6, 133.7, 129.3, 128.4, 115.4 (t, *J* = 238.7 Hz), 52.4, 40.1, 38.7 (t, *J* = 21.2 Hz), 28.8 (t, *J* = 5.5 Hz), 26.5, 24.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.2 - –117.4 (m, 1F). HRMS (APCI) m/z calcd. for $C_{16}H_{19}O_3F_2S$ $[M + H]^+$ 329.1017, found 329.1011.

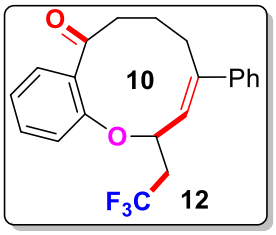
(*E*)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(phenylsulfonyl)cyclooct-4-enone



11

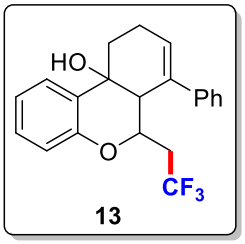
Compound **11**, colorless oil, 45% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.66 – 7.61 (m, 1H), 7.58 – 7.52 (m, 2H), 6.92 (d, *J* = 9.4 Hz, 1H), 3.55 – 3.43 (m, 1H), 2.83 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.67 – 2.53 (m, 2H), 2.50 – 2.30 (m, 4H), 2.28 – 2.21 (m, 1H), 1.74 – 1.65 (m, 1H), 1.20 – 1.07 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 142.3, 141.7, 138.5, 133.7, 129.3, 128.4, 119.3-106.3 (m), 52.5, 40.2, 35.3 (t, *J* = 20.9 Hz), 27.9, 26.5, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –80.9 - –81.0 (m), –112.9 - –113.05 (m), –124.3 - –124.5 (m), –125.8 - –126.0 (m). HRMS (APCI) m/z calcd. for $C_{19}H_{18}O_3F_9S$ $[M + H]^+$ 497.0827, found 497.0818.

(*E*)-4-phenyl-2-(2,2,2-trifluoroethyl)-6,7-dihydro-2H-benzo[b]oxecin-8(5H)-one



Compound **12**, colorless oil, 12% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.48 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 – 7.29 (m, 5H), 7.21 (td, *J* = 7.6, 0.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 8.8 Hz, 1H), 4.87 – 4.80 (m, 1H), 3.61 – 3.52 (m, 1H), 2.81 – 2.65 (m, 3H), 2.59 – 2.46 (m, 2H), 2.37 – 2.26 (m, 1H), 1.81 – 1.70 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 156.4, 147.0, 141.1, 134.0, 133.0, 130.4, 128.4, 128.1, 126.7, 125.9, 125.2 (q, *J* = 275.5 Hz), 124.5, 122.9, 38.6 (q, *J* = 27.1 Hz), 38.4, 29.2, 23.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.6. HRMS (APCI) m/z calcd. for $C_{21}H_{20}O_2F_3$ $[M + H]^+$ 361.1410, found 361.1398.

8-phenyl-6-(2,2,2-trifluoroethyl)-6a,7,10,10a-tetrahydro-6H-benzo[c]chromen-10a-ol



Compound **13**, colorless oil, 43% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.26 – 7.21 (m, 1H), 7.08 – 7.03 (m, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.11 (s, 1H), 4.59 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.50 (s, 1H), 2.60 – 2.49 (m, 1H), 2.30 – 2.08 (m, 5H), 1.79 – 1.70 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 140.5, 134.7, 129.7, 128.9, 128.8, 127.9, 127.7, 126.9, 126.5, 126.0 (q, *J* = 275.9 Hz), 122.1, 118.1, 69.9 (q, *J* = 2.8 Hz), 67.4, 47.2, 34.0 (q, *J* = 27.8 Hz), 32.8, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.8. HRMS (APCI) m/z calcd. for $C_{21}H_{20}O_2F_3$ $[M + H]^+$ 361.1410, found 361.1401.

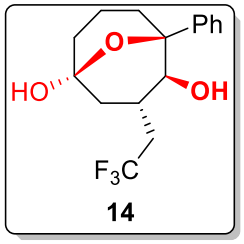
Procedures for Synthetic Applications

Experimental procedure for dihydroxylation of 5A

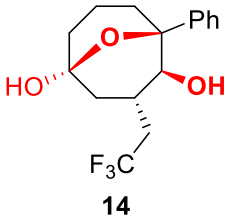
To a solution of **5A** (50 mg, 0.16 mmol) in acetone (3 mL) and water (1 mL) were added OsO_4 (0.5 mL, 2 mg/mL in *t*-BuOH) and *N*-methylmorpholine *N*-oxide (NMO) monohydrate (25 mg, 0.19 mmol) sequentially. Upon completion, the reaction mixture was stirred at room temperature for 4 days. Saturated Na_2SO_3 solution (2 mL) was then added. Dichloromethane was used to extract the product from the aqueous layer (3 ×15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford a crude product, which was purified by flash column

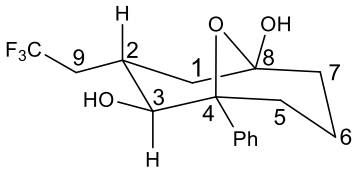
chromatography to afford the product **14** (37 mg, 62%).

5-phenyl-3-(2,2,2-trifluoroethyl)-9-oxabicyclo[3.3.1]nonane-1,4-diol



Compound **14** colorless oil, 62% yield, ^{1}H NMR (500 MHz, CD_3OD) δ 7.55 – 7.45 (m, 2H), 7.29 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.23 – 7.17 (m, 1H), 3.49 (d, *J* = 10.9 Hz, 1H), 2.73 – 2.57 (m, 1H), 2.31 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.25 – 2.15 (m, 2H), 2.08 – 1.90 (m, 2H), 1.85 (dqd, *J* = 14.6, 5.0, 2.5 Hz, 1H), 1.77 – 1.63 (m, 2H), 1.56 (td, *J* = 13.2, 5.1 Hz, 1H), 1.47 (td, *J* = 13.0, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 128.6, 128.1, 127.3 (q, *J* = 275 Hz), 125.8, 95.7, 80.8, 74.7, 38.4, 37.6, 35.4 (q, *J* = 27 Hz), 33.5, 32.4 (q, *J* = 2.7 Hz), 18.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7. HMRS (APCI) m/z calcd. for $C_{16}H_{18}O_2F_3$ $[M - H_2O + H]^+$ 299.1253, found 299.1248.



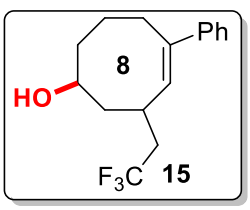


For a typical 9-oxabicyclo[3.3.1]nonane ring system, a boat-chair conformation is predominant. In CD_3OD, the coupling constant for the protons on C2 and C3 is 11.0 Hz, which is in accord with two *trans* axial protons, as shown above.

Experimental procedure for reduction of 5A

To a solution of **5A** (28 mg, 0.1 mmol) in THF was added $LiAlH_4$ (7 mg, 0.2 mmol) at 0 °C under argon atmosphere. Upon completion, the reaction mixture was stirred under the same conditions for 10 min. Na_2SO_4•xH_2O was then added and the solution was stirred for an additional 10 min and filtered. The solvent was evaporated to afford a crude product, which was purified by flash column chromatography to afford product **15** (23 mg, 82%, *E*/*Z* = 15:1).

(E)-5-phenyl-3-(2,2,2-trifluoroethyl)cyclooct-4-en-1-ol



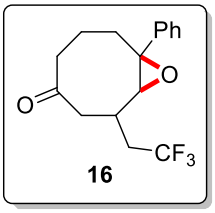
Compound **15**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.27 (m, 1H), 5.61 (d, *J* = 9.5 Hz, 1H), 3.89 – 3.85 (m, 1H), 3.21 – 3.09 (m, 1H), 2.71 – 2.56 (m, 2H), 2.33 – 2.19 (m, 2H), 2.08 – 1.96 (m, 2H), 1.96 – 1.82 (m, 2H), 1.76 (ddd, *J* = 12.7, 9.8, 5.1 Hz, 1H), 1.68 – 1.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 140.8, 129.4, 128.3, 127.1, 126.6 (q, *J* = 278 Hz), 125.9, 71.5, 44.8, 39.9 (q, *J* = 27.0 Hz), 39.0, 31.5, 29.6 (q, *J* = 2.7 Hz), 26.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.8. HMRS (APCI) m/z calcd. for $C_{16}H_{20}OF_3$ $[M + H]^+$ 285.1461, found 285.1456.

Experimental procedure for transformation of 5A to 16

To a solution of **5A** (0.10 mmol, 28.2 mg, 1.0 equiv) in dichloromethane (2 mL) was added *m*-CPBA (0.30 mmol, 73.7 mg, 70% purity) at 0 °C under nitrogen. The reaction flask was sealed under nitrogen and was allowed to warm to room temperature. Upon completion, the stirring was continued for 16 h. The reaction was then quenched with saturated $NaHCO_3$ solution and extracted with dichloromethane. The combined organic phase was collected and dried with Na_2SO_4. After filtration and evaporation, the residue thus obtained was purified by silica gel chromatography to afford product **16**.

The procedure for synthesis of **17** and **18** is similar to that of **16**.

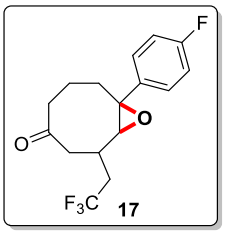
8-phenyl-2-(2,2,2-trifluoroethyl)-9-oxabicyclo[6.1.0]nonan-4-one



16

Compound **16**, colorless oil, 84% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 3H), 3.00 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.87 (d, *J* = 10.0 Hz, 1H), 2.70 – 2.51 (m, 3H), 2.49 – 2.42 (m, 2H), 2.41 – 2.36 (m, 1H), 2.27 – 2.15 (m, 1H), 1.95 – 1.75 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 139.8, 128.3, 128.1, 127.3, 126.2 (q, *J* = 275.5 Hz), 65.4, 64.3, 48.2, 40.8, 36.6 (q, *J* = 28.6 Hz), 35.4, 30.0 (q, *J* = 2.5 Hz), 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2. HRMS (APCI) m/z calcd. for $C_{16}H_{18}O_2F_3$ $[M + H]^+$ 299.1253, found 299.1248.

8-(4-fluorophenyl)-2-(2,2,2-trifluoroethyl)-9-oxabicyclo[6.1.0]nonan-4-one

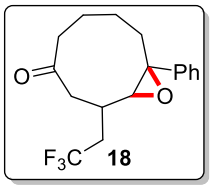


17

Compound **17**, colorless oil, 74% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 3.03 (dd, *J* = 12.9, 4.3 Hz, 1H), 2.85 (d, *J* = 9.7 Hz, 1H),

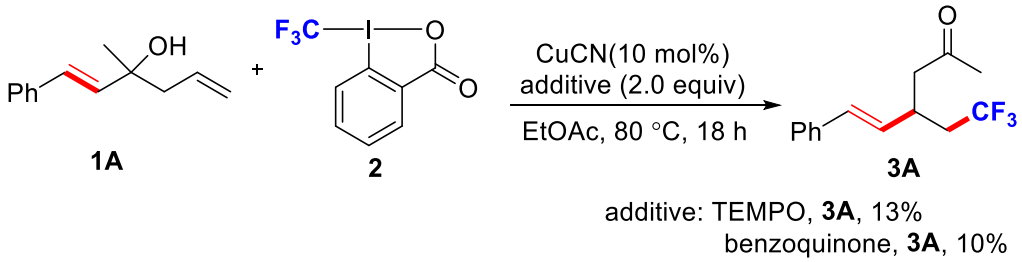
2.72 – 2.52 (m, 3H), 2.49 – 2.36 (m, 3H), 2.30 – 2.19 (m, 1H), 1.91 – 1.75 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.7, 162.4 (d, *J* = 246 Hz), 135.8 (d, *J* = 3.2 Hz), 129.2 (d, *J* = 8.2 Hz), 126.2 (q, *J* = 276 Hz), 115.2 (d, *J* = 21.4 Hz), 64.8, 64.5, 48.3, 40.7, 36.6 (q, *J* = 28.7 Hz), 35.5, 30.0 (q, *J* = 2.4 Hz), 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2, –113.5. HRMS (APCI) m/z calcd. for $C_{16}H_{17}O_2F_4$ $[M + H]^+$ 317.1159, found 317.1154.

9-phenyl-2-(2,2,2-trifluoroethyl)-10-oxabicyclo[7.1.0]decan-4-one



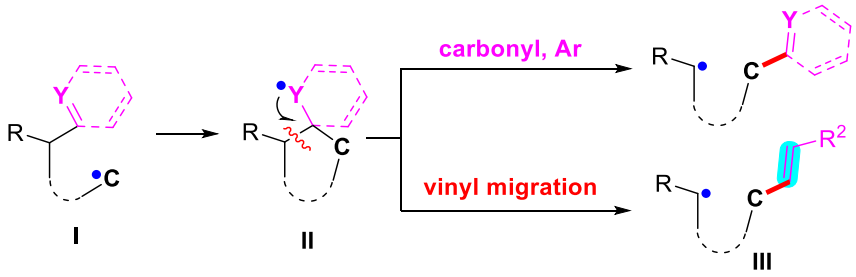
Compound **18**: colorless oil, 78% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 3.16 (d, *J* = 9.4 Hz, 1H), 2.83 (dd, *J* = 13.1, 3.7 Hz, 1H), 2.75 – 2.65 (m, 2H), 2.65 – 2.54 (m, 1H), 2.54 – 2.44 (m, 1H), 2.44 – 2.36 (m, 2H), 2.34 – 2.22 (m, 1H), 2.09 – 1.96 (m, 1H), 1.79 – 1.68 (m, 1H), 1.59 (dt, *J* = 15.0, 3.9 Hz, 1H), 1.57 – 1.50 (m, 1H), 1.37 – 1.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.1, 139.3, 128.4, 128.3, 127.5, 126.4 (q, *J* = 276 Hz), 66.7, 65.0, 45.2, 39.5, 37.6 (q, *J* = 27.8 Hz), 32.1 (q, *J* = 2.4 Hz), 28.7, 22.0, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9. HRMS (APCI) m/z calcd. for $C_{17}H_{20}O_2F_3$ $[M + H]^+$ 313.1410, found 313.1402.

Mechanistic study



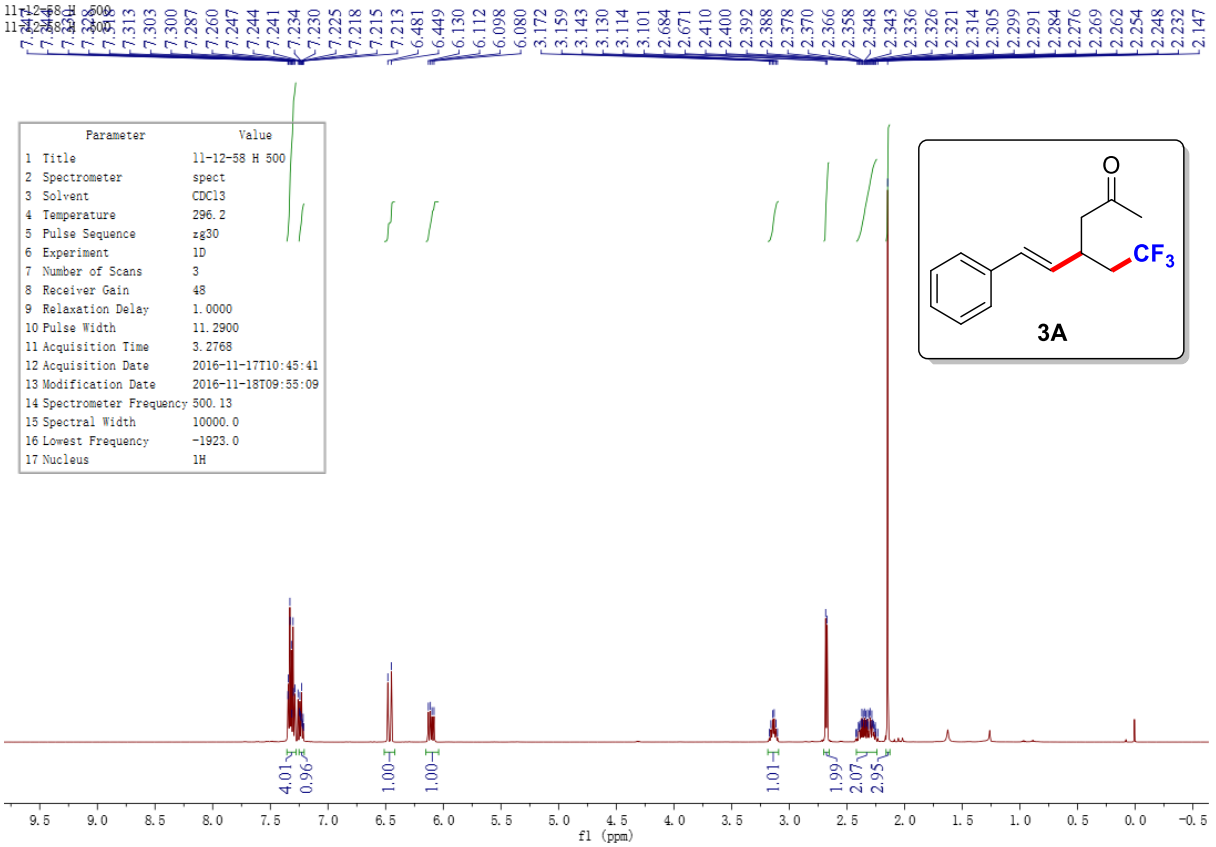
A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1A** (37.6 mg, 0.2 mmol, 1.0 equiv), **2** (94.5 mg, 0.3 mmol, 1.5 equiv), CuCN (1.8 mg, 0.02 mmol, 0.1 equiv), 2,2,6,6-tetramethylpiperidinooxy (47.3 mg, 0.3 mmol, 1.5 equiv) or benzoquinone (32 mg, 0.3 mmol, 1.5 equiv), and EtOAc (2.0 mL) under argon atmosphere. The sealed tube was then stirred at 80 °C for 18 h. Upon completion, the reaction solution was added with EtOAc (30 mL), followed by washing with saturated $NaHCO_3$ (2 × 5 mL) solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product. $PhCF_3$ (29.2 mg, 0.2 mmol) was added as an internal standard. ^{19}F NMR analysis of this reaction mixture indicated that **3A** was formed in 13% and 10% yield, respectively.

We have qualitatively compared the energy profiles for the corresponding 1,3-carbonyl, aryl, and vinyl migration reactions, as shown in fig. S1 below. We have tentatively assumed that the incipient radicals **I** all go through strained 4-membered transition states $\mathbf{TS_1}$ leading to the formation of the corresponding radical intermediates **II**. The final radical intermediates **III** are all relatively stable than both **I** and **II** and thus, we speculate that the second step, i.e., from **II** to **III**, should be of lower activation energy ($\mathbf{TS_2}$) than the first step (**I** to **II**, $\mathbf{TS_1}$). In this sense, we consider the different activation energies $\mathbf{TS_1}$ for the first step as the reason for different reactivity. Specifically, compared with vinyl migration, the formation of transition states $\mathbf{TS_1}$ during envisioned carbonyl and aryl migration involves breaking a relatively high-energy C=O bond (BDE of C=O to C–O is 88 kcal/mol, while that of C=C to C–C is 84 kcal/mol) and dearomatization, respectively, which we speculate might have disfavored these two process. However, this is a rather qualitative and rough speculation and we need more theoretical study for further demonstration of the detailed mechanism.

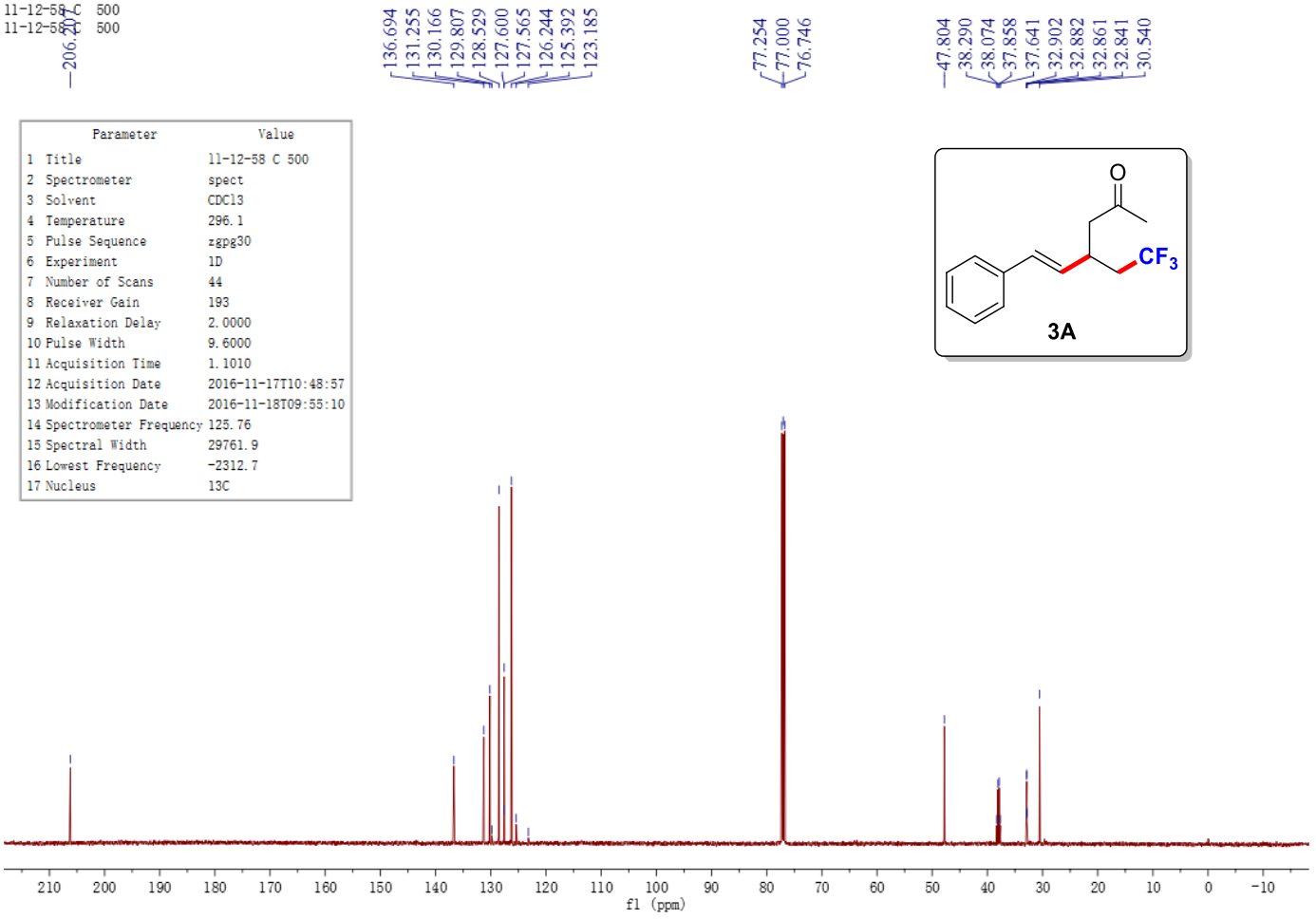

Y
R
C
I
Y
R
C
II
carbonyl, Ar
vinyl migration
R
C
Y
R
C
R2
III

NMR spectra

^{1}H NMR Spectrum of Compound **3A**



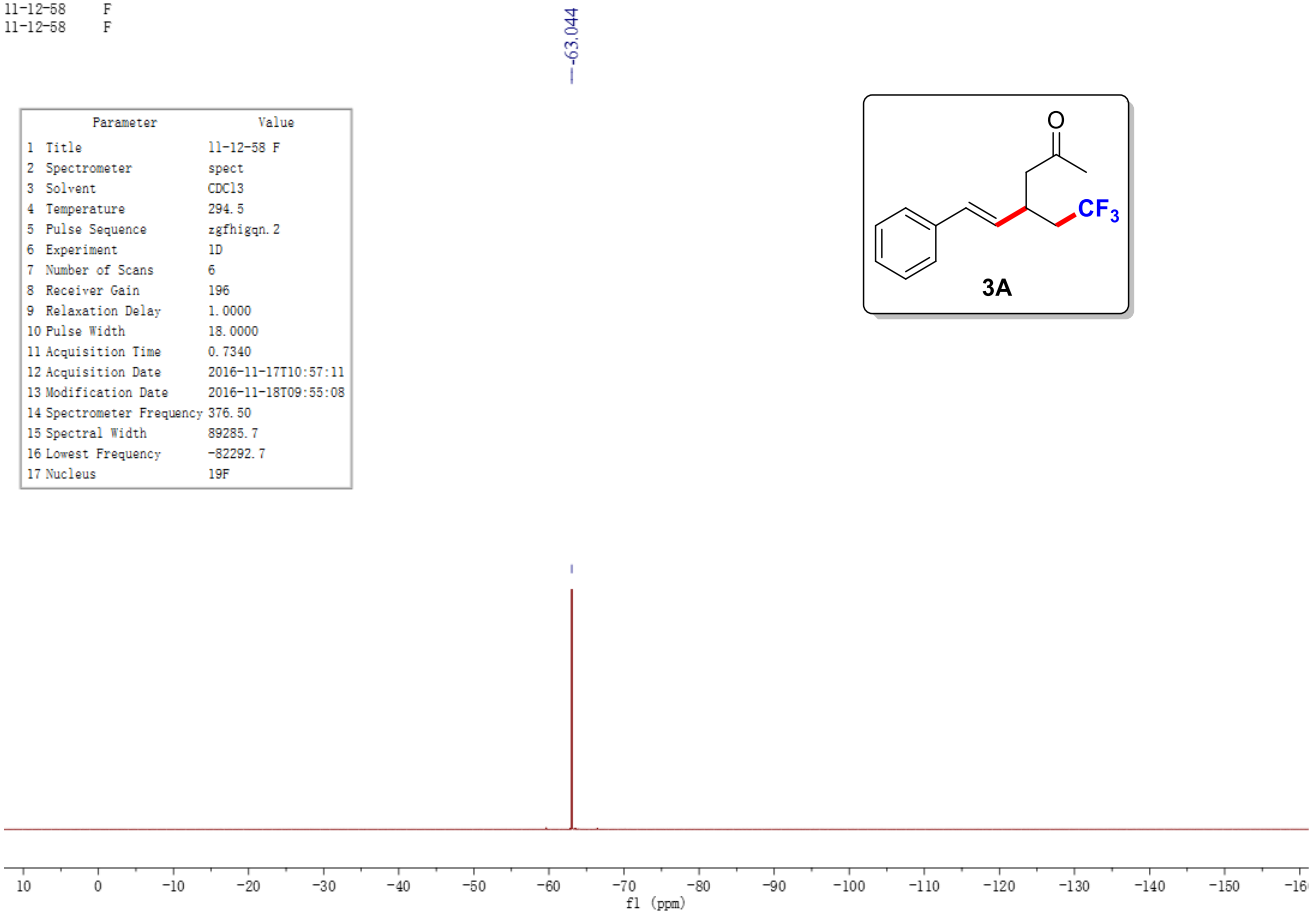
^{13}C NMR Spectrum of Compound **3A**



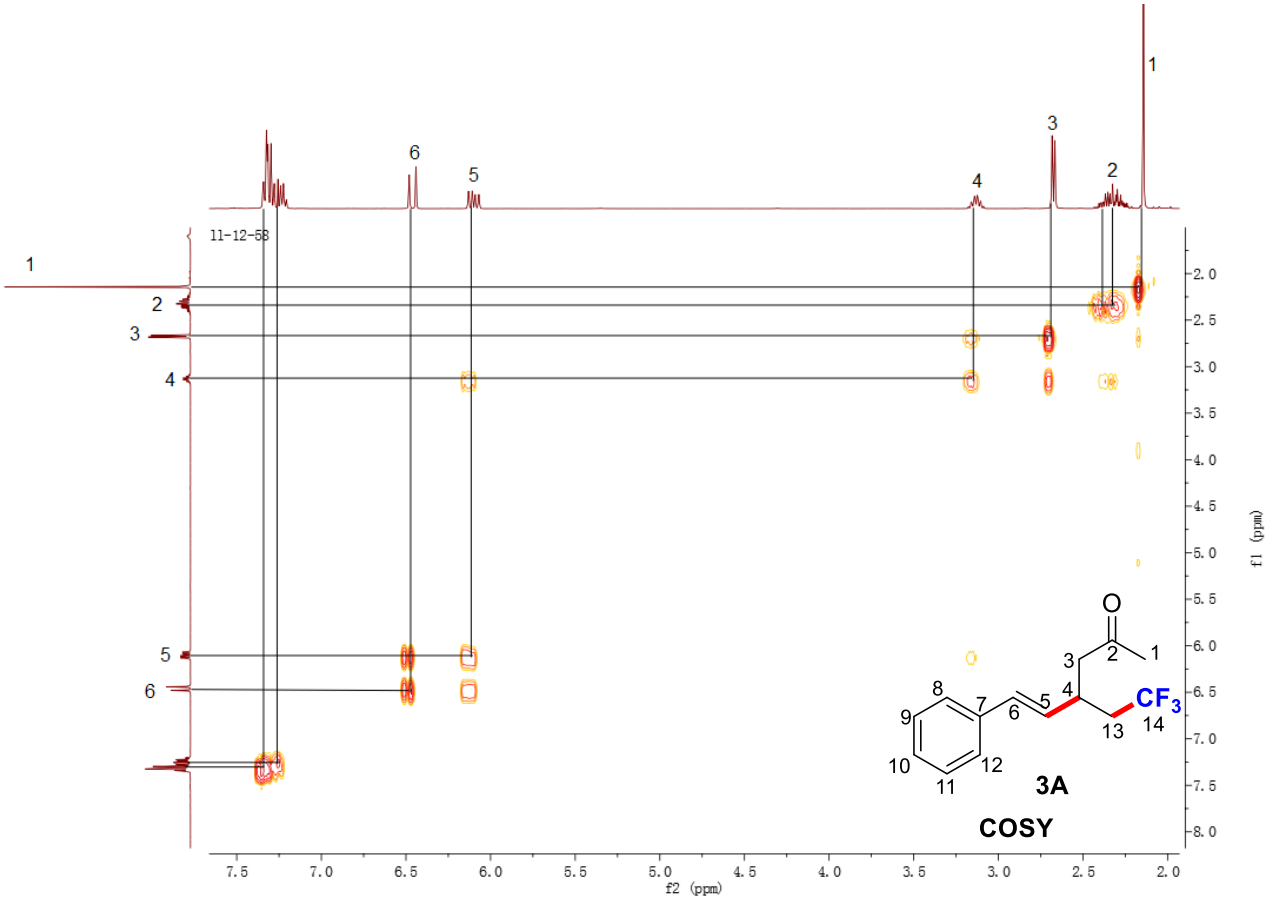
^{19}F NMR Spectrum of Compound **3A**

11-12-58 F
11-12-58 F

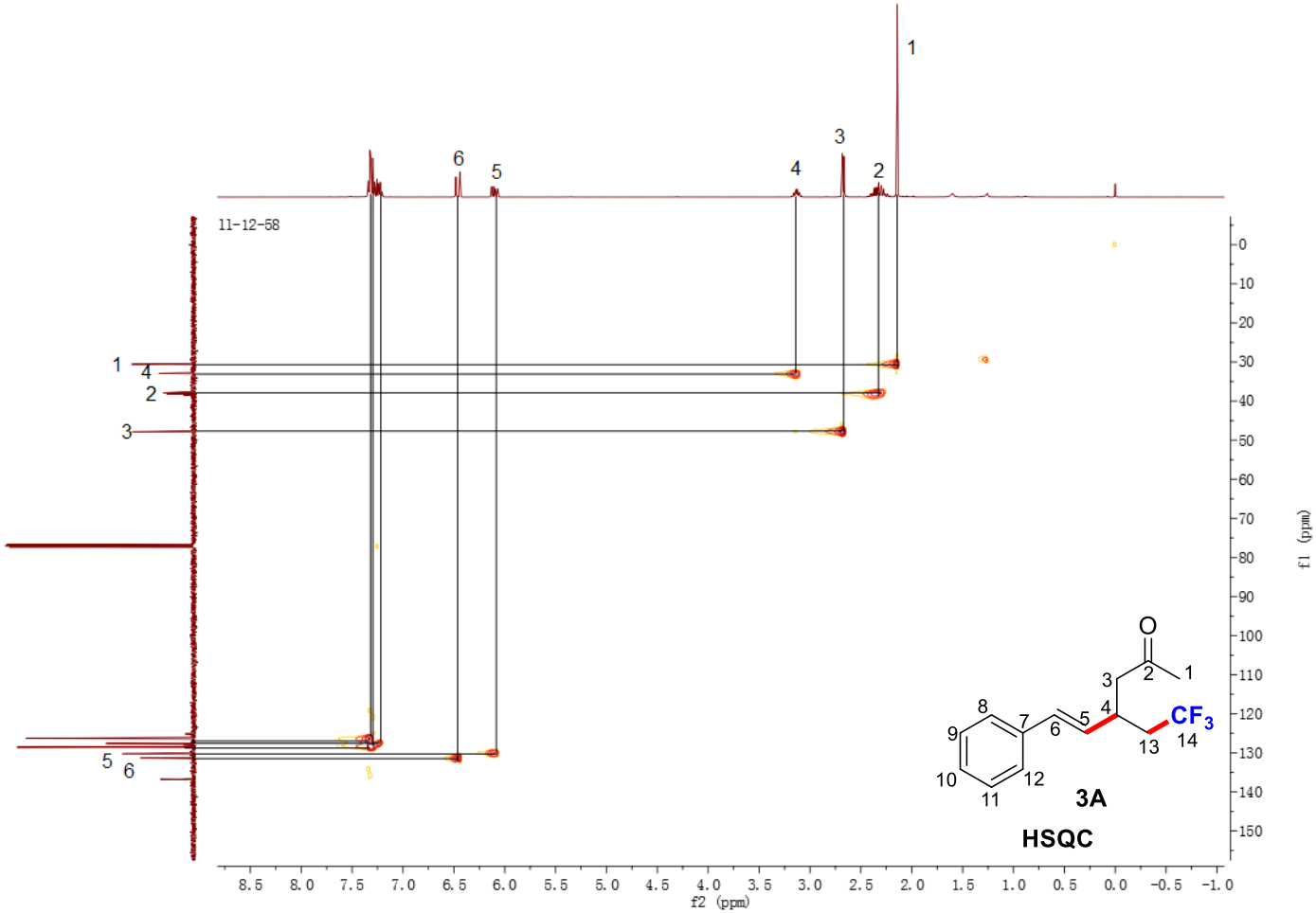
Parameter	Value
1 Title	11-12-58 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.5
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	6
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-17T10:57:11
13 Modification Date	2016-11-18T09:55:08
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



COSY of compound **3A**



HSQC of compound **3A**



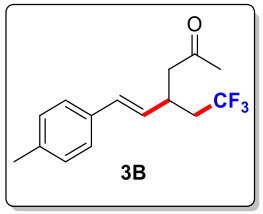
^{1}H NMR Spectrum of Compound **3B**

11-12-74 H 500
11-12-74 H 500

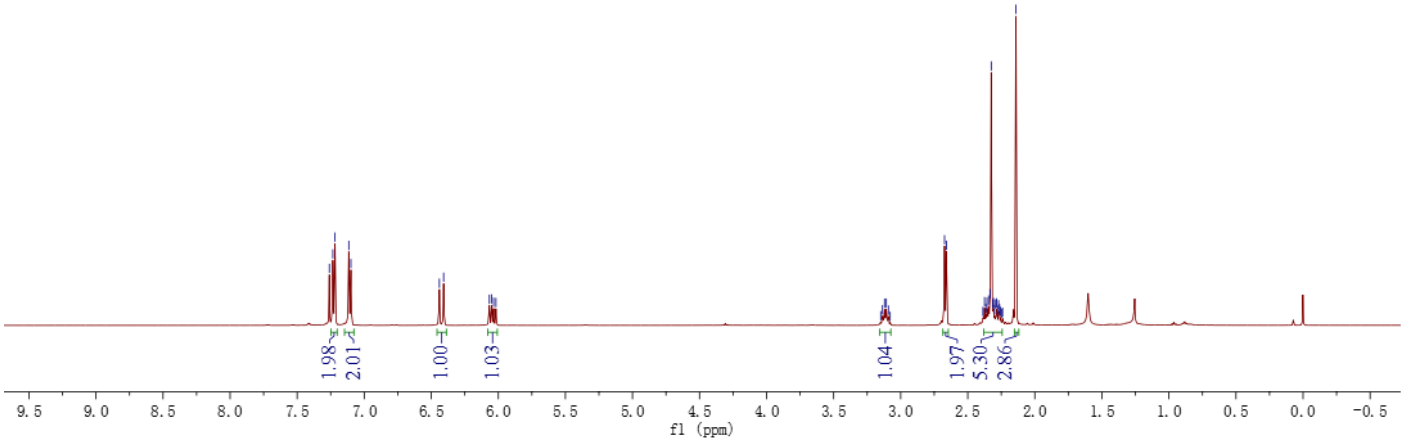
7.260 7.234 7.218 7.115 7.099 6.440 6.408 6.067 6.050 6.035 6.018

3.149 3.136 3.121 3.107 3.092 3.078 2.673 2.660 2.387 2.375 2.365 2.357 2.345 2.334 2.325 2.314 2.308 2.301 2.292 2.286 2.278 2.270 2.263 2.256 2.240

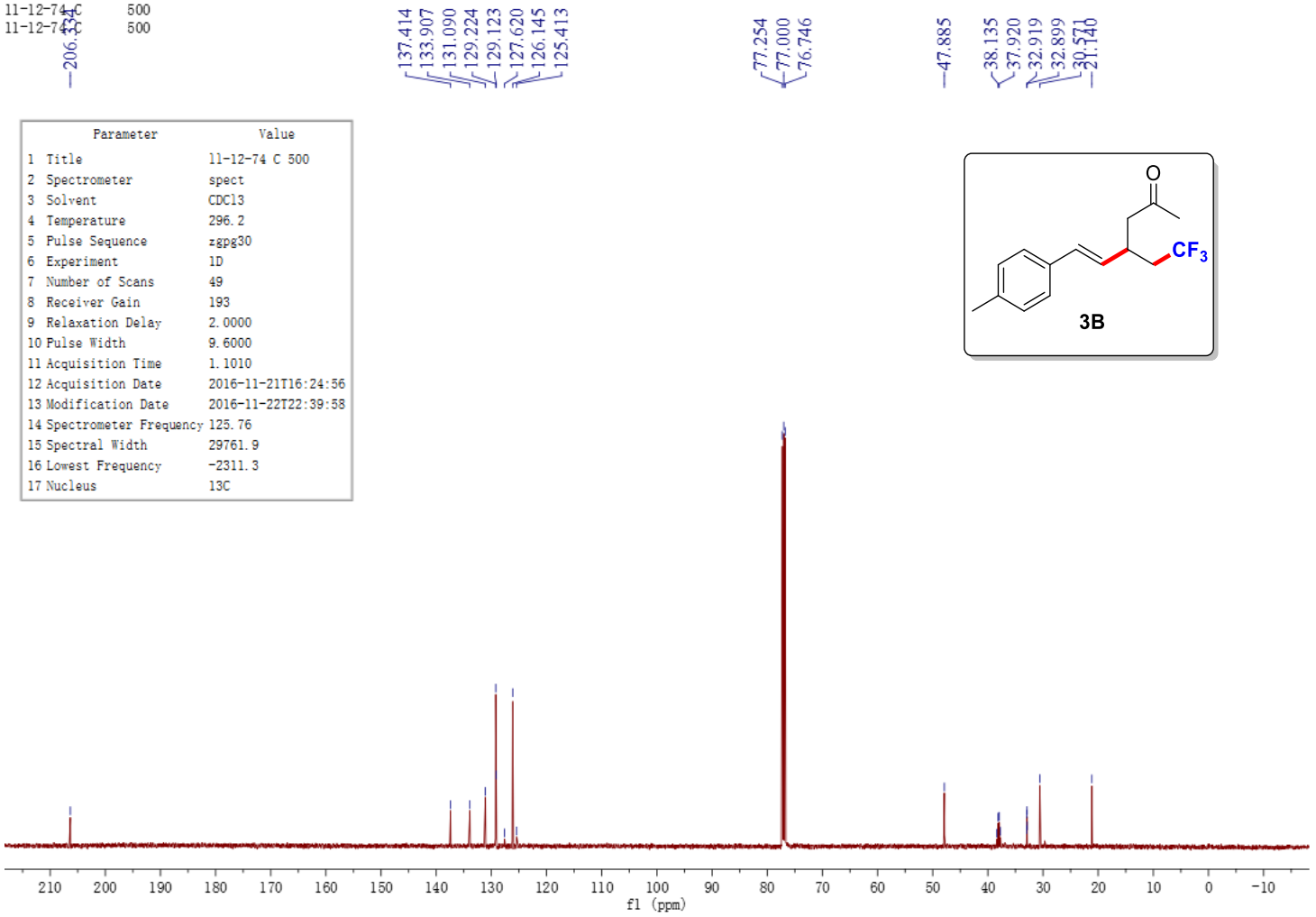
Parameter	Value
1 Title	11-12-74 H 500
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	3
8 Receiver Gain	71
9 Relaxation Delay	1.0000
10 Pulse Width	11.2900
11 Acquisition Time	3.2768
12 Acquisition Date	2016-11-21T16:23:00
13 Modification Date	2016-11-22T22:39:55
14 Spectrometer Frequency	500.13
15 Spectral Width	10000.0
16 Lowest Frequency	-1924.0
17 Nucleus	1H



3B



^{13}C NMR Spectrum of Compound **3B**

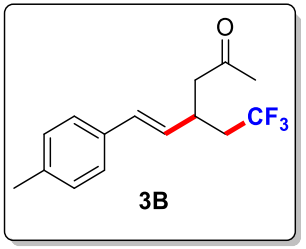


	Parameter	Value
1	Title	11-12-74 C 500
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	49
8	Receiver Gain	193
9	Relaxation Delay	2.0000
10	Pulse Width	9.6000
11	Acquisition Time	1.1010
12	Acquisition Date	2016-11-21T16:24:56
13	Modification Date	2016-11-22T22:39:58
14	Spectrometer Frequency	125.76
15	Spectral Width	29761.9
16	Lowest Frequency	-2311.3
17	Nucleus	13C

^{19}F NMR Spectrum of Compound **3B**

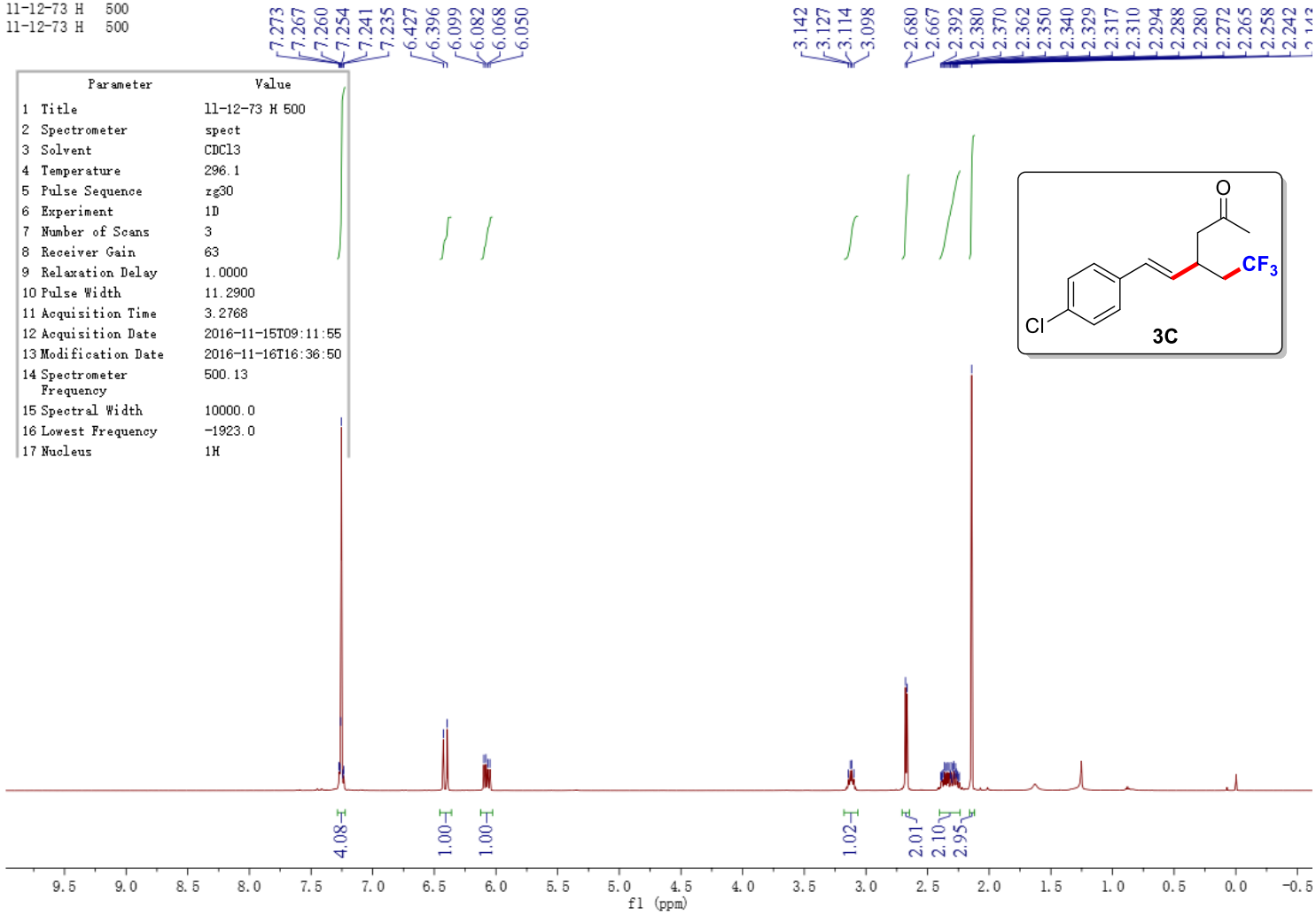
11-12-74 F
11-12-74 F

Parameter	Value
1 Title	11-12-74 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	295.0
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	2
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-22T15:45:13
13 Modification Date	2016-11-22T22:40:36
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F

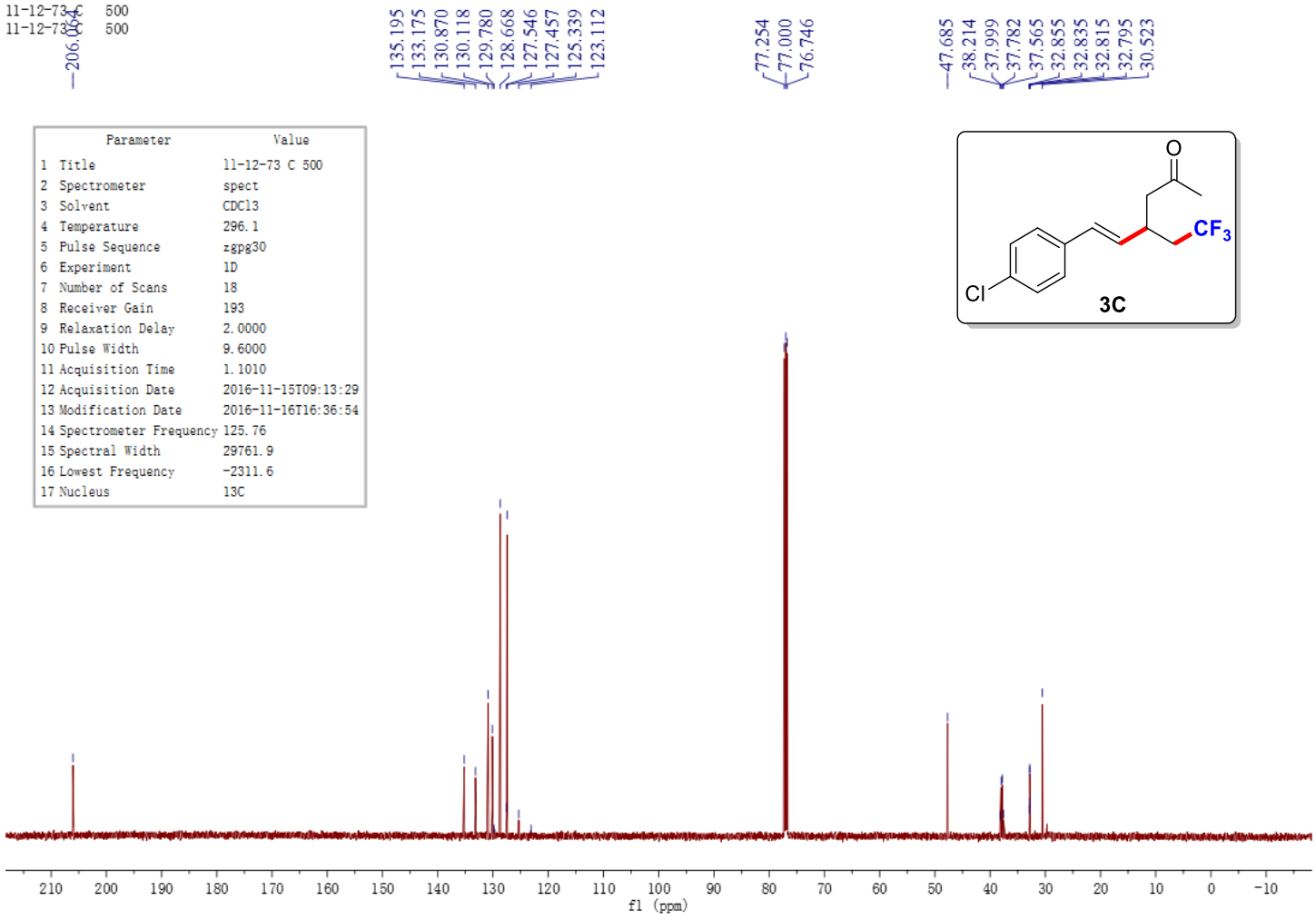


3B

^{1}H NMR Spectrum of Compound **3C**



^{13}C NMR Spectrum of Compound **3C**

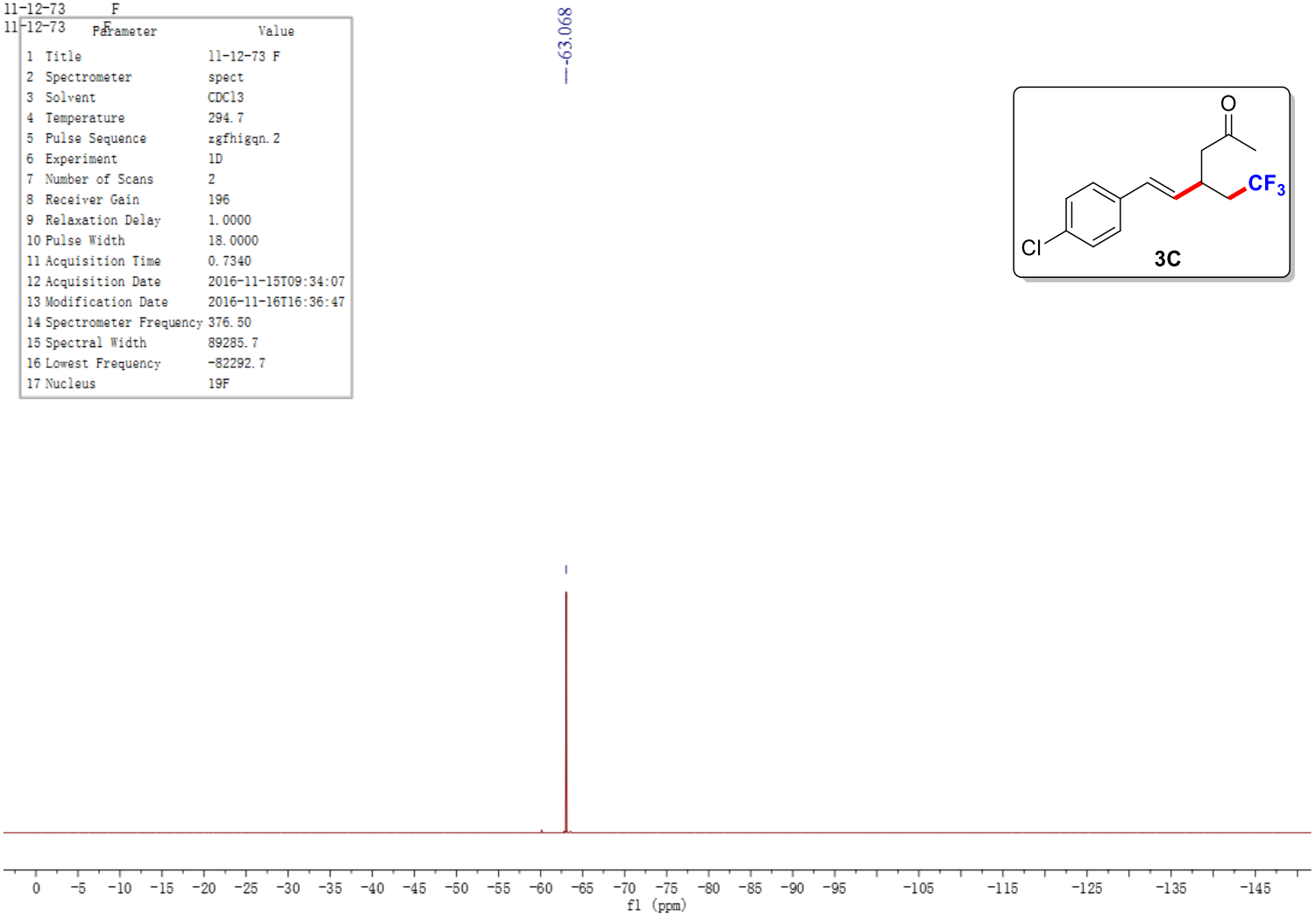


^{19}F NMR Spectrum of Compound **3C**

11-12-73 F

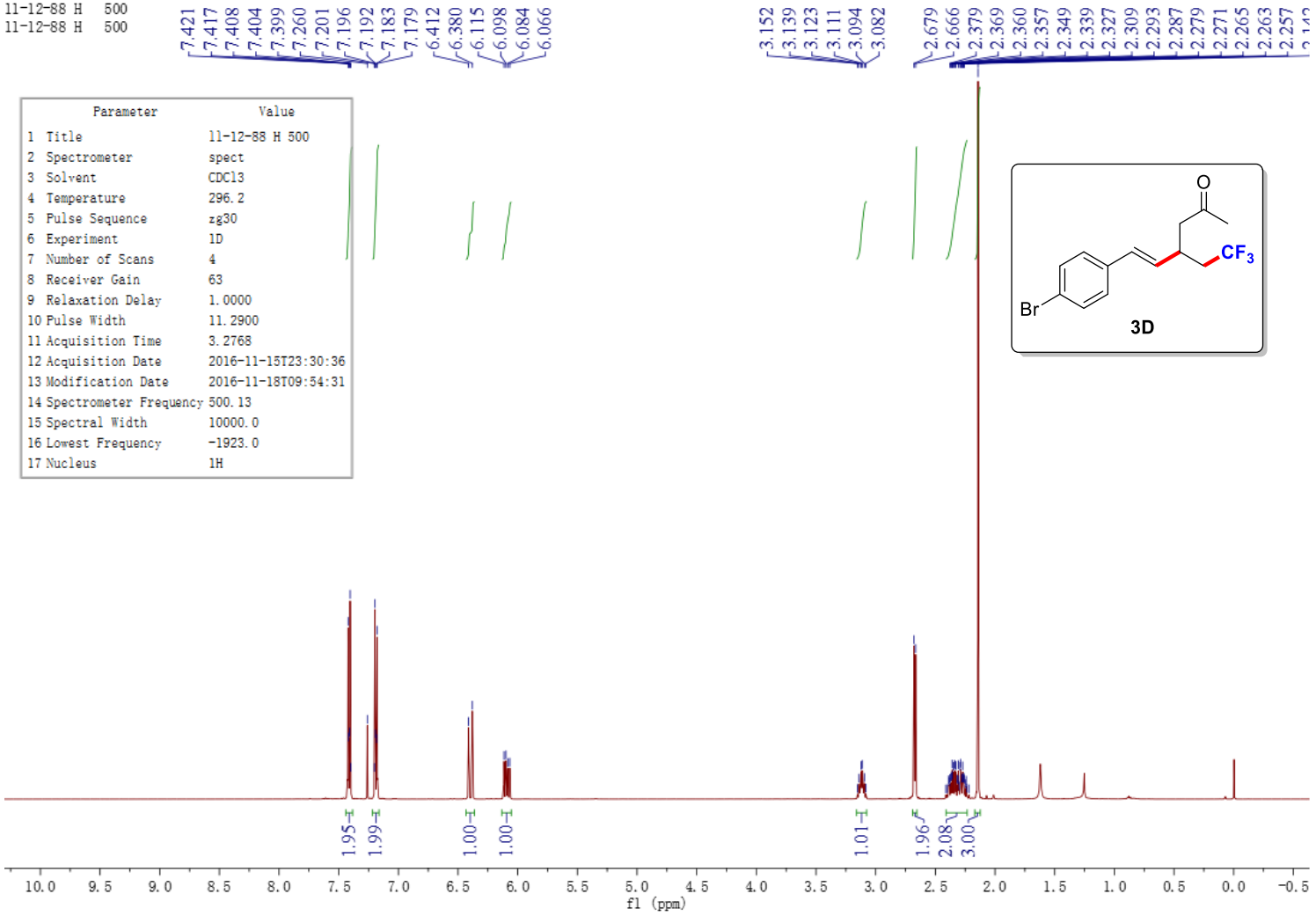
11-12-73 F

Parameter	Value
1 Title	11-12-73 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.7
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	2
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-15T09:34:07
13 Modification Date	2016-11-16T16:36:47
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F

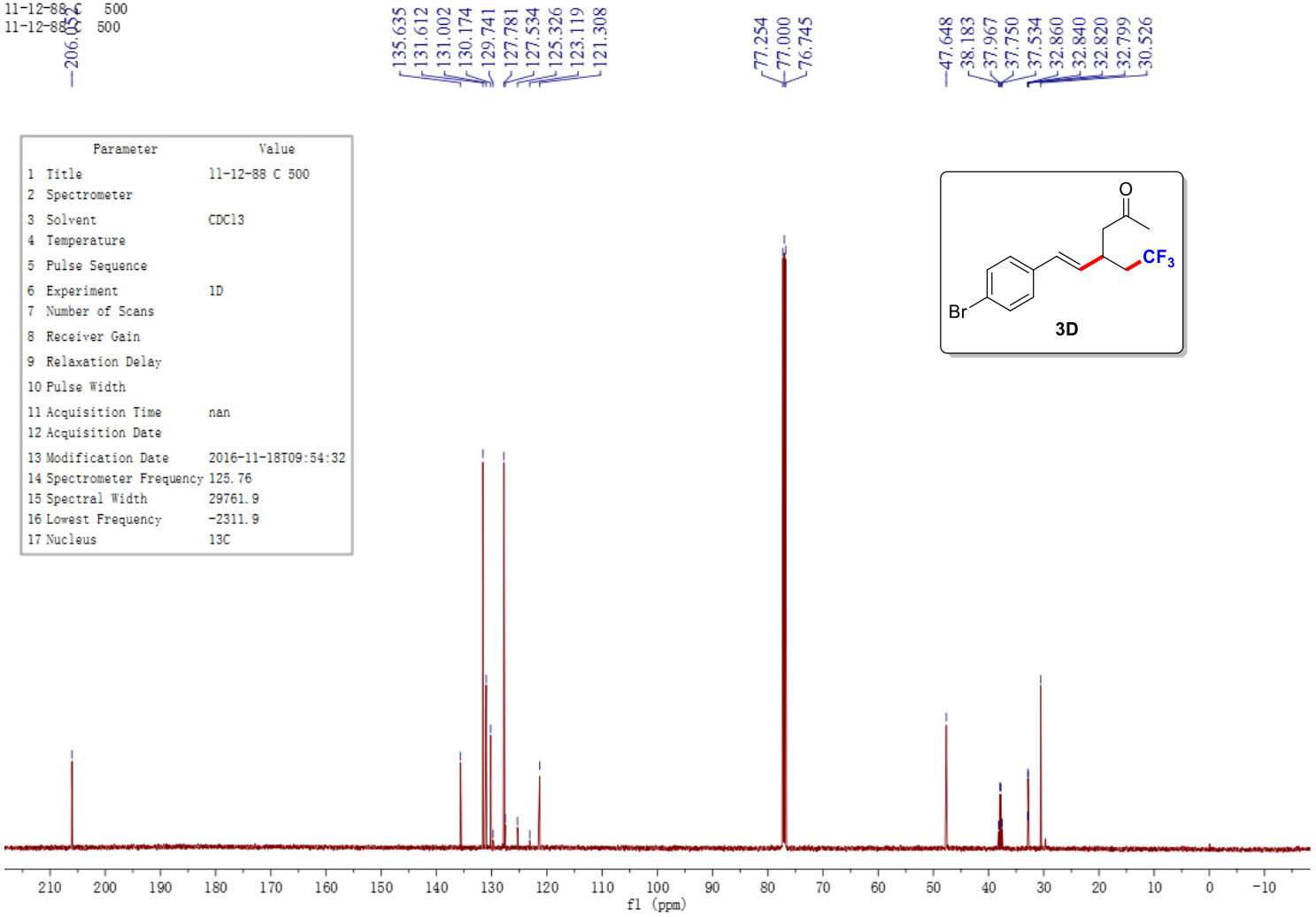


3C

^{1}H NMR Spectrum of Compound **3D**



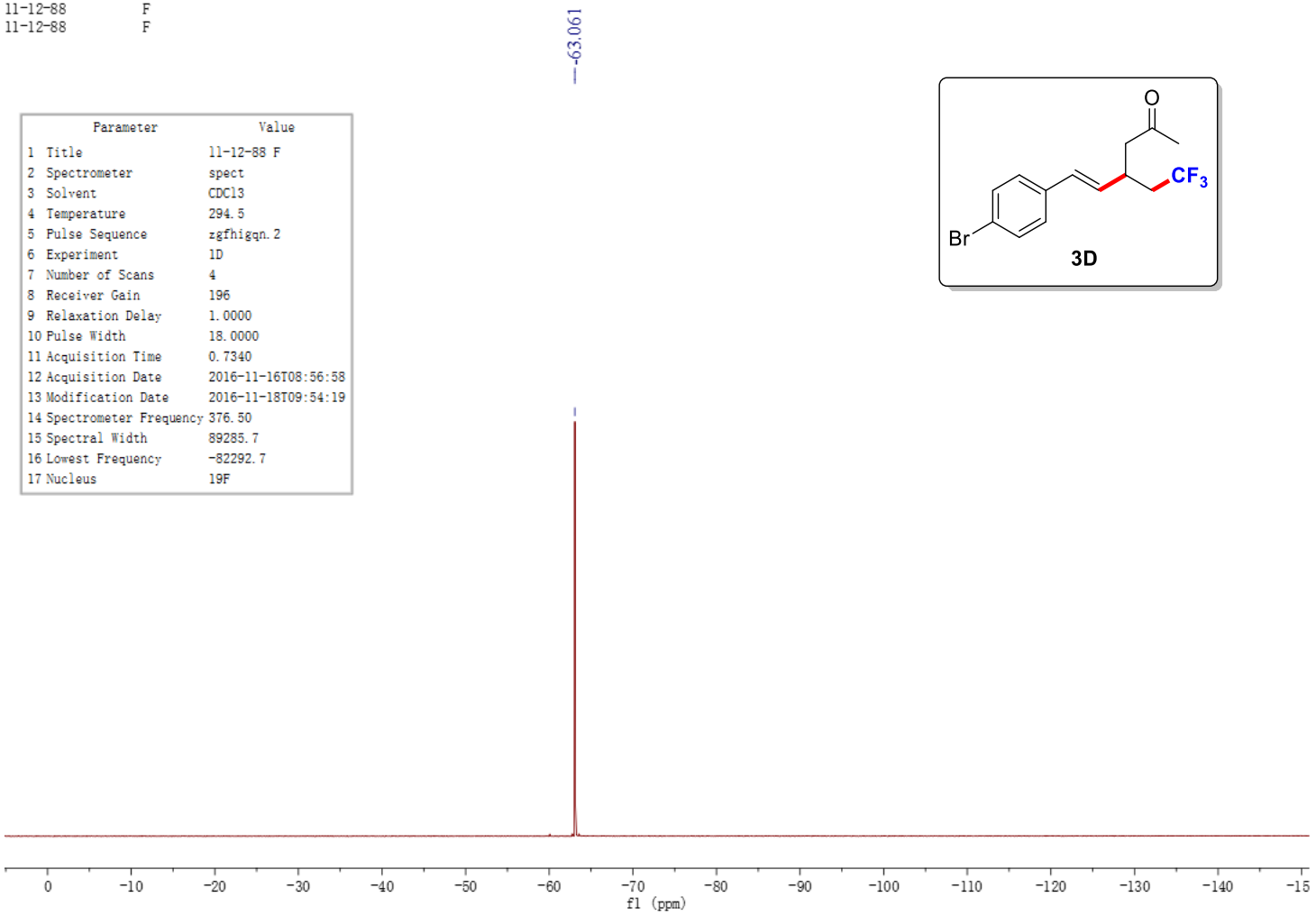
^{13}C NMR Spectrum of Compound **3D**



^{19}F NMR Spectrum of Compound **3D**

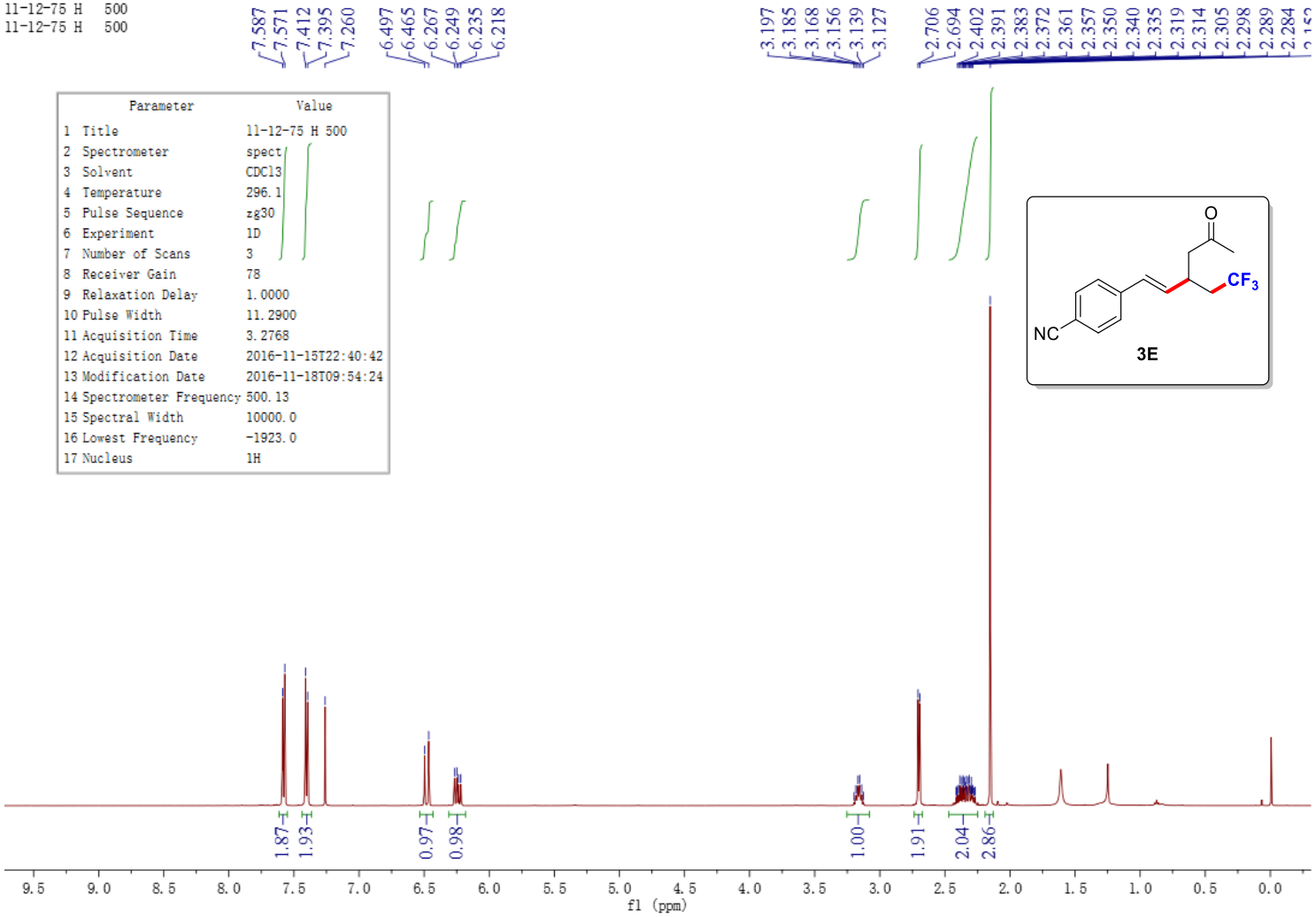
11-12-88 F
11-12-88 F

	Parameter	Value
1	Title	11-12-88 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.5
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	4
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-16T08:56:58
13	Modification Date	2016-11-18T09:54:19
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

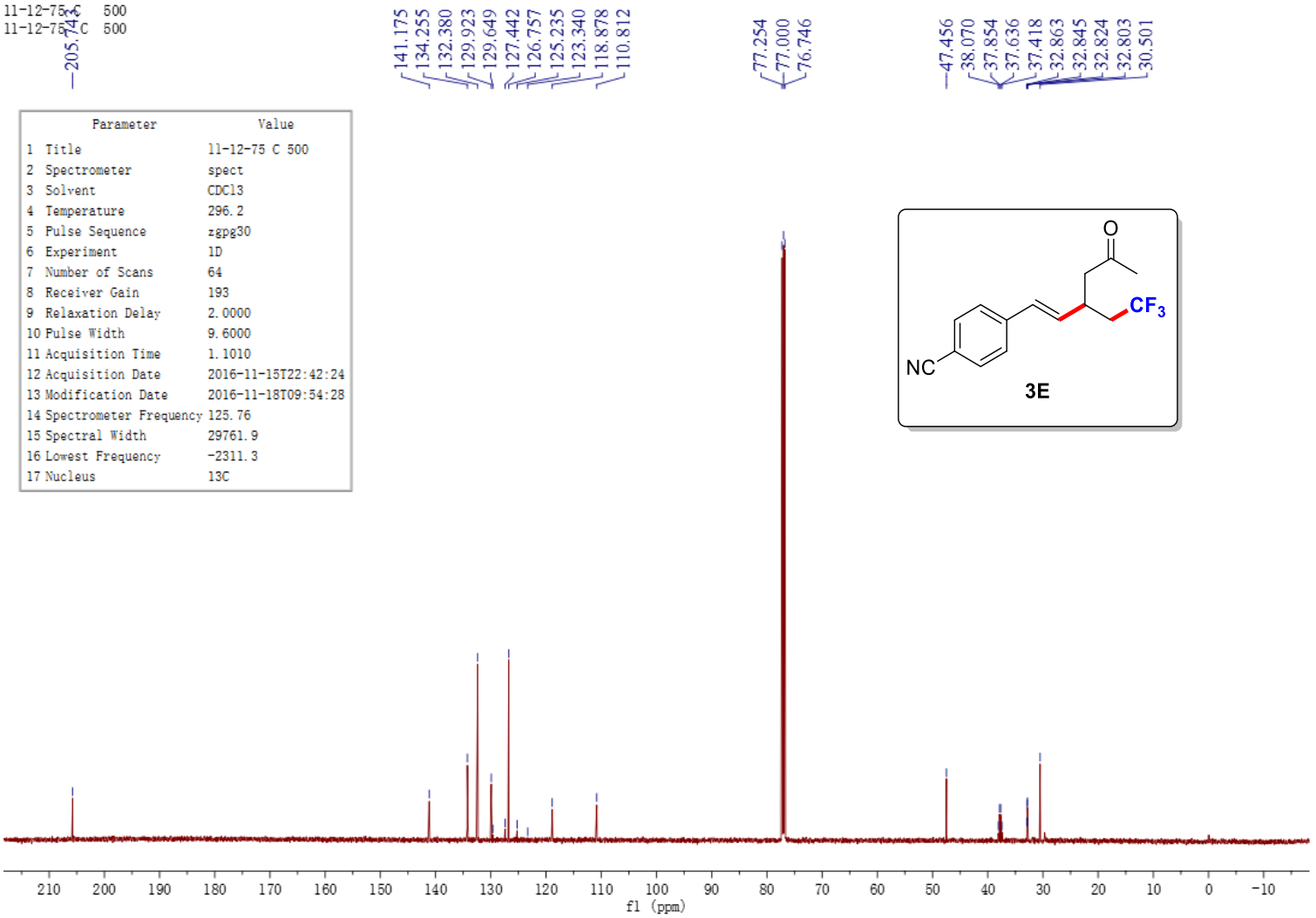


3D

^{1}H NMR Spectrum of Compound **3E**



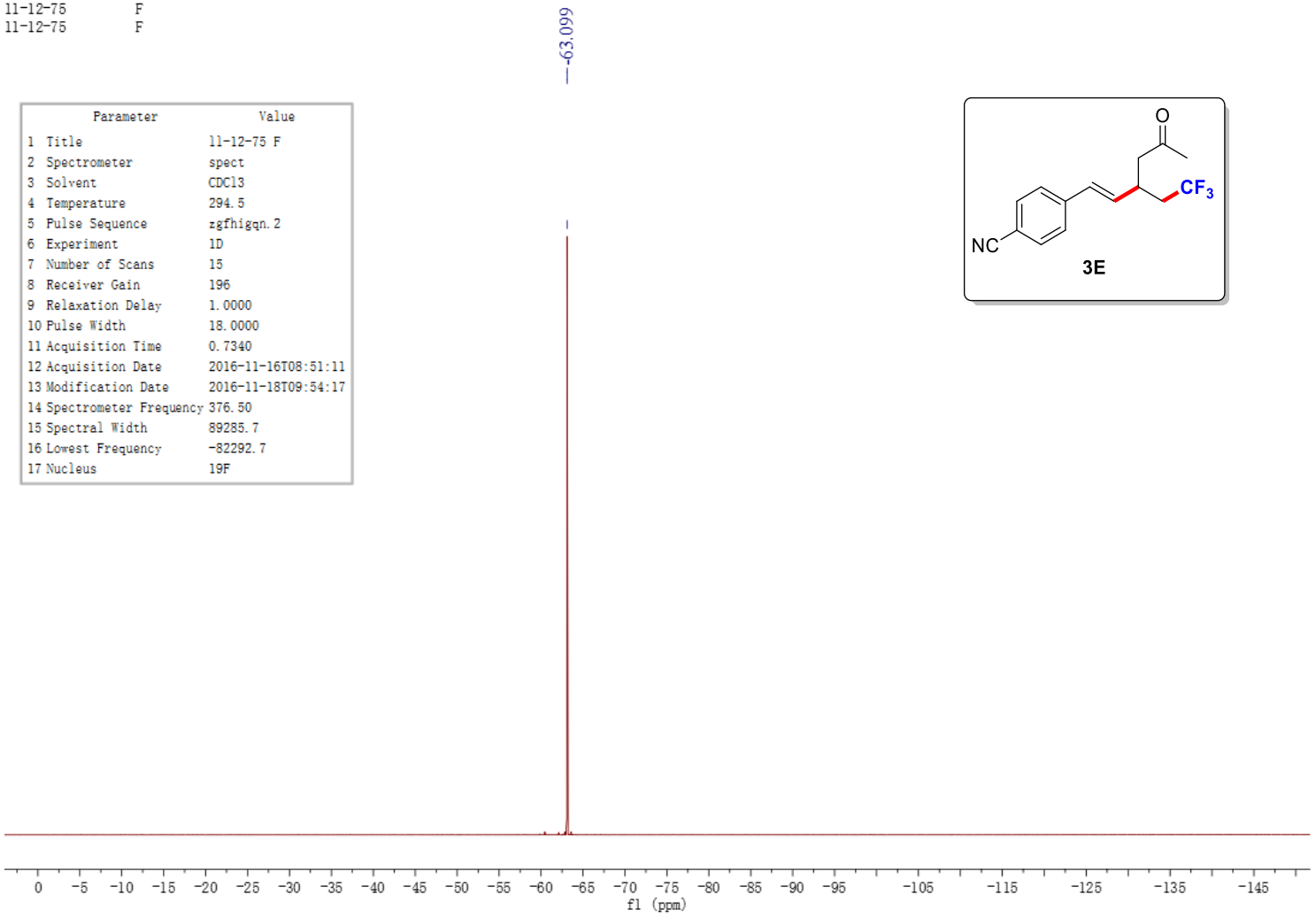
^{13}C NMR Spectrum of Compound **3E**



^{19}F NMR Spectrum of Compound **3E**

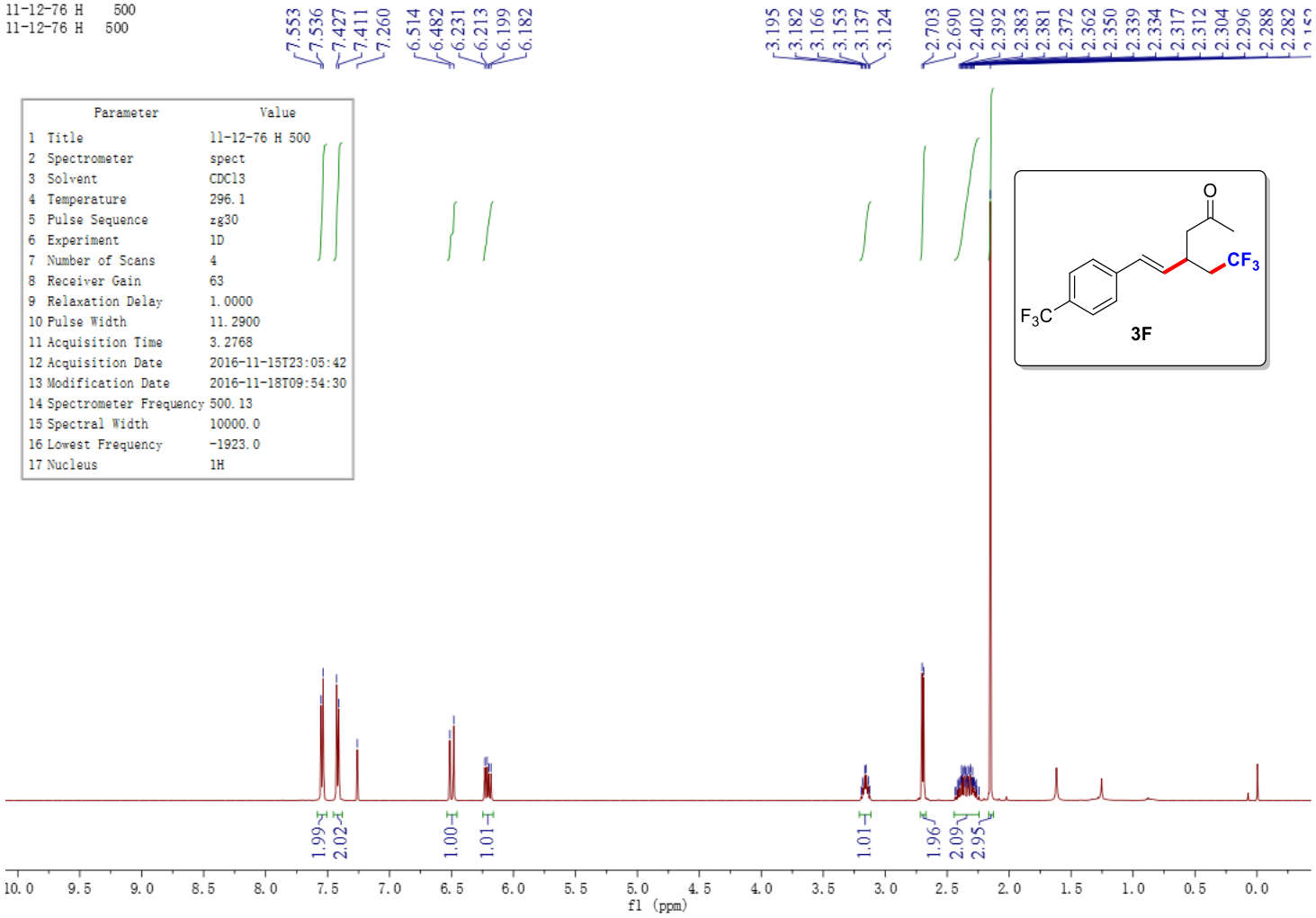
11-12-75 F
11-12-75 F

Parameter	Value
1 Title	11-12-75 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.5
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	15
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-16T08:51:11
13 Modification Date	2016-11-18T09:54:17
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F

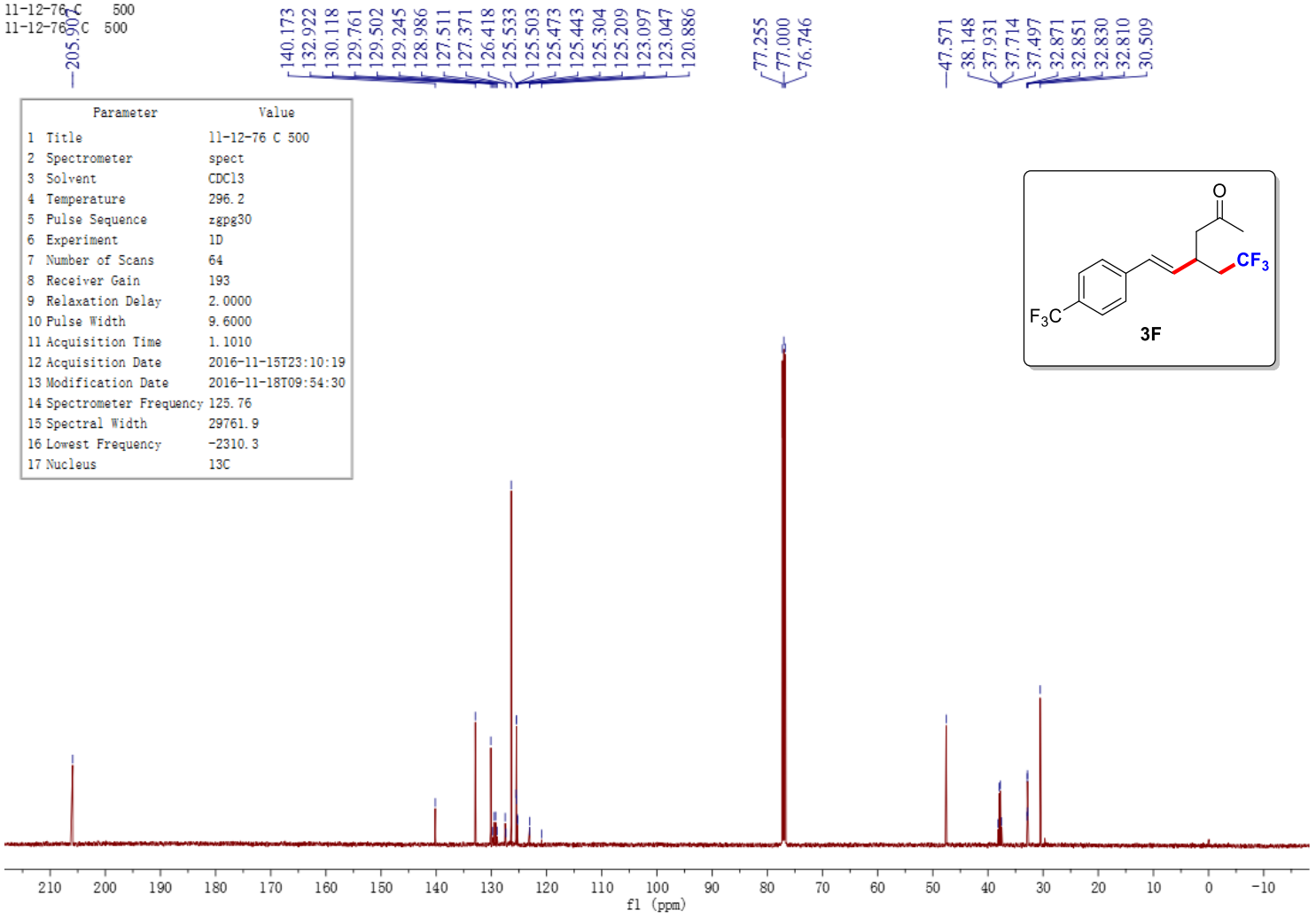


3E

^{1}H NMR Spectrum of Compound **3F**



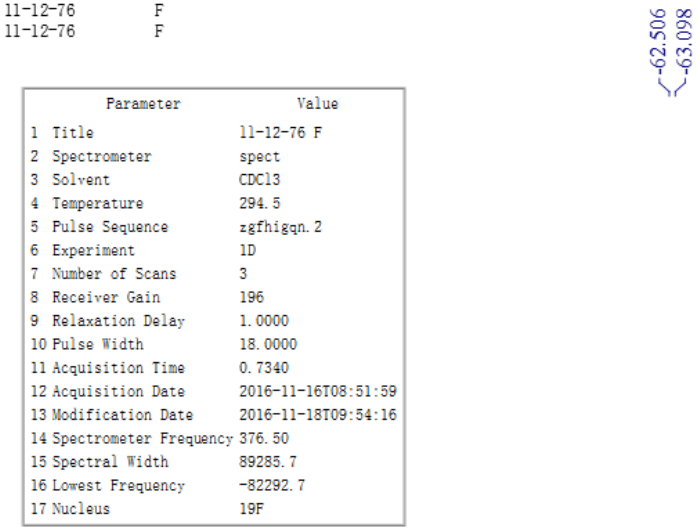
^{13}C NMR Spectrum of Compound **3F**

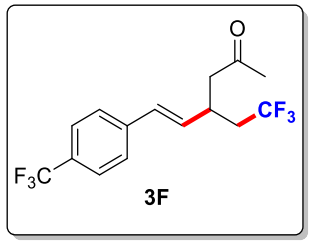


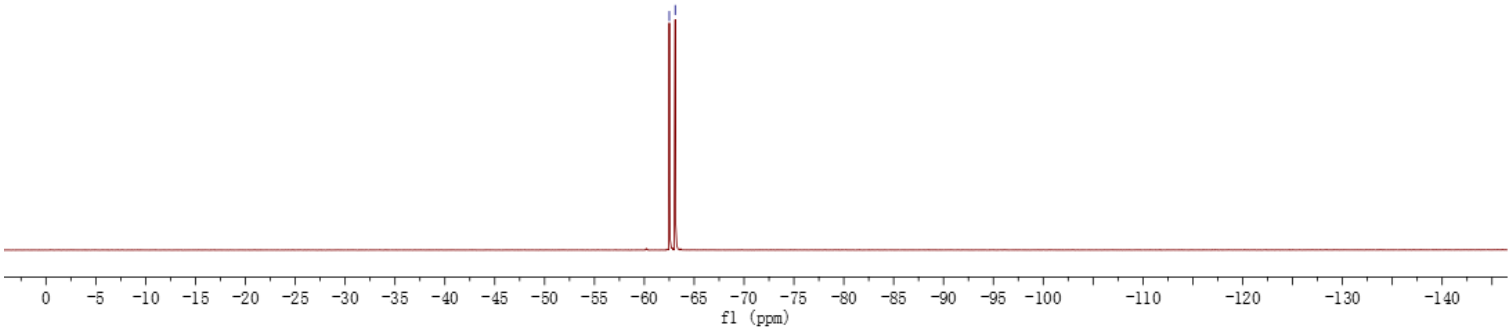
^{19}F NMR Spectrum of Compound **3F**

11-12-76 F
11-12-76 F

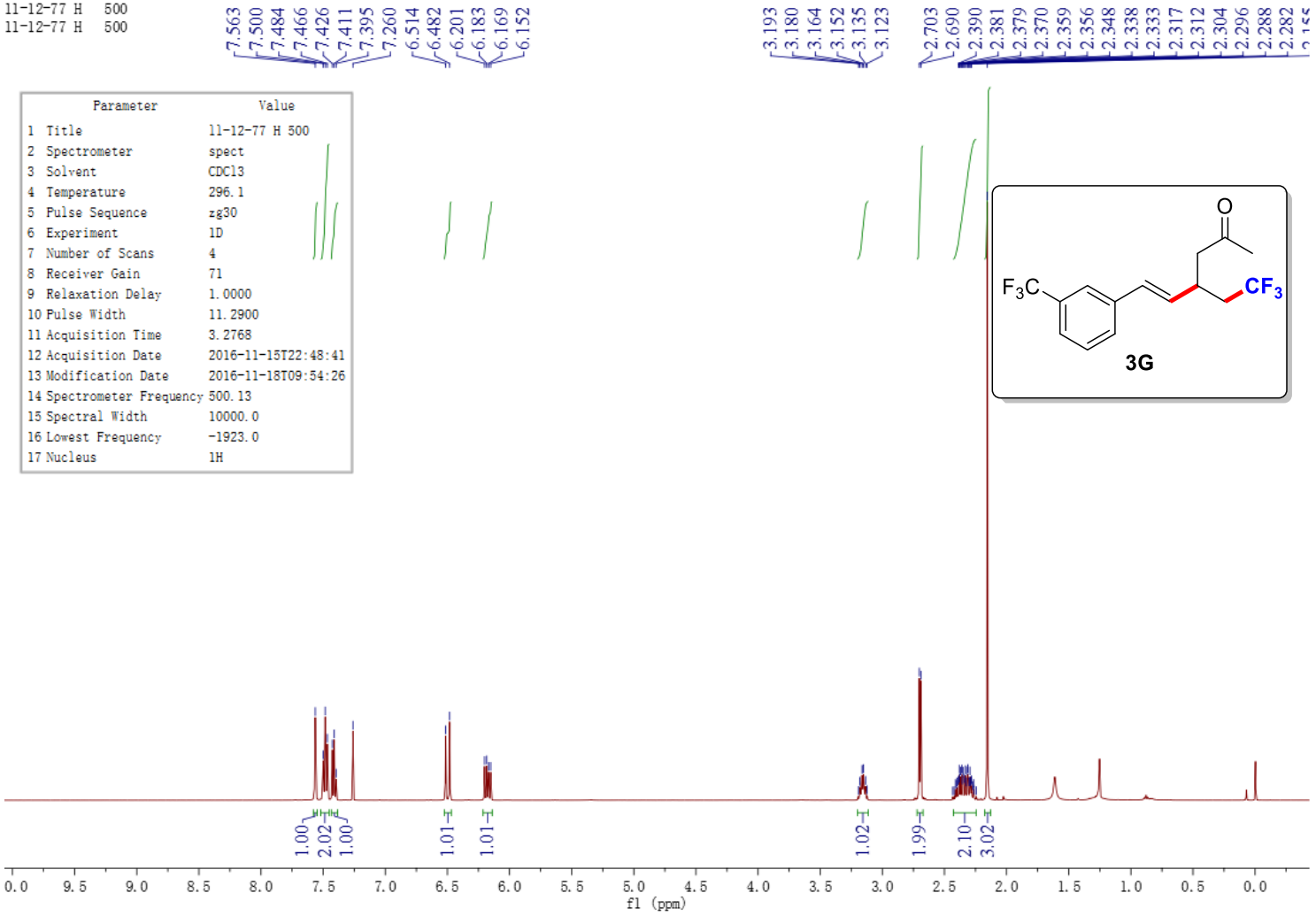
	Parameter	Value
1	Title	11-12-76 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.5
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	3
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-16T08:51:59
13	Modification Date	2016-11-18T09:54:16
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



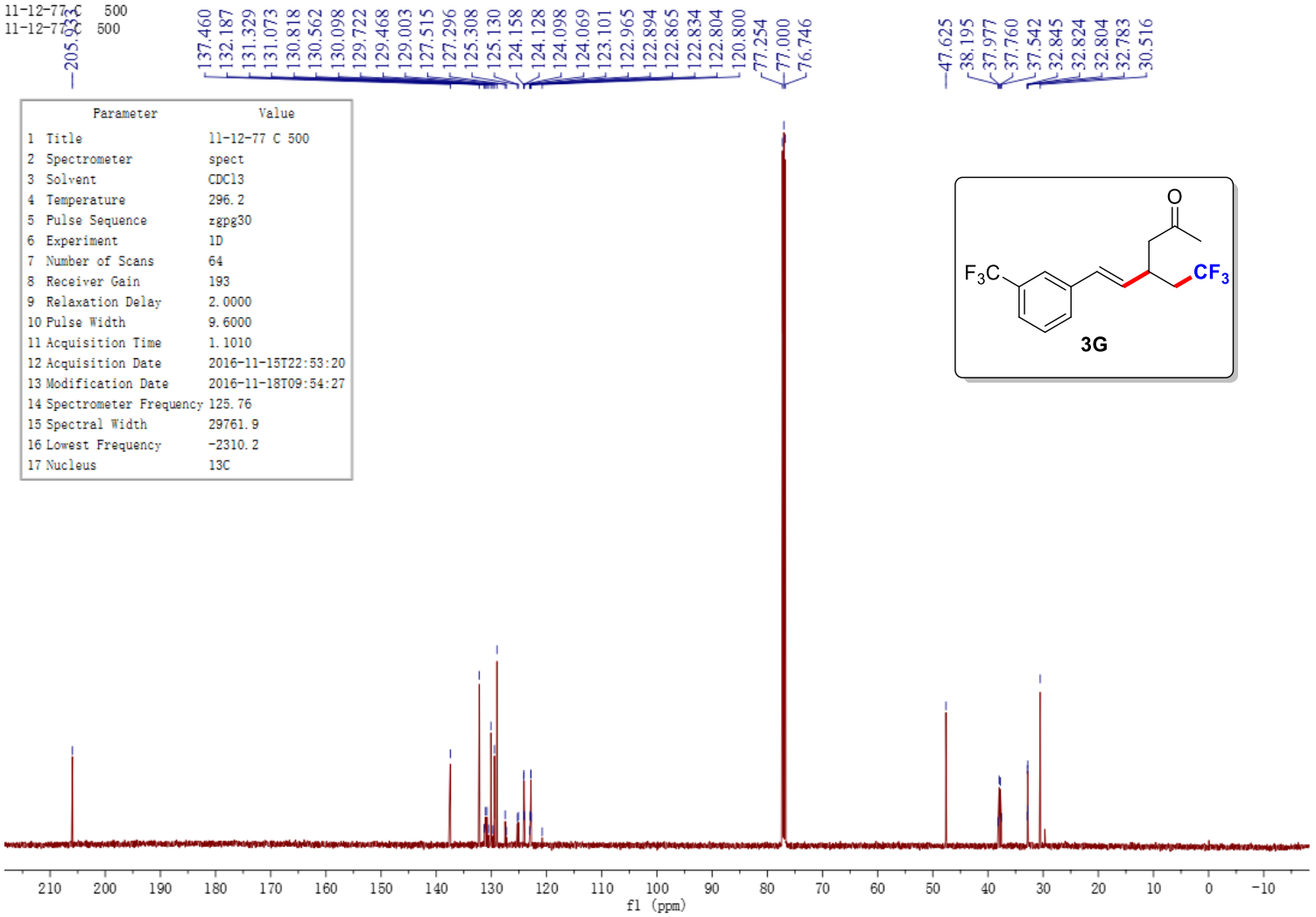




^{1}H NMR Spectrum of Compound **3G**



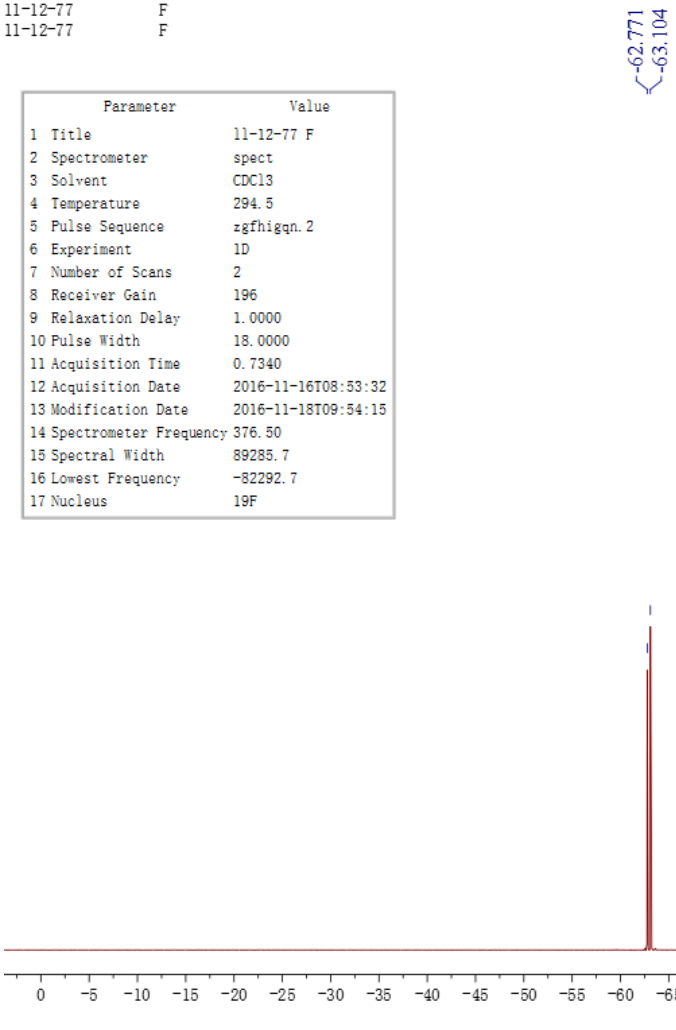
^{13}C NMR Spectrum of Compound **3G**

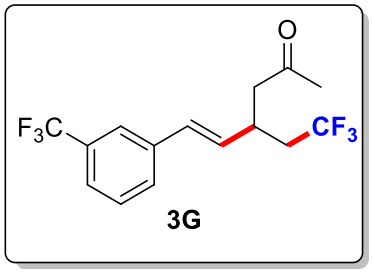


^{19}F NMR Spectrum of Compound **3G**

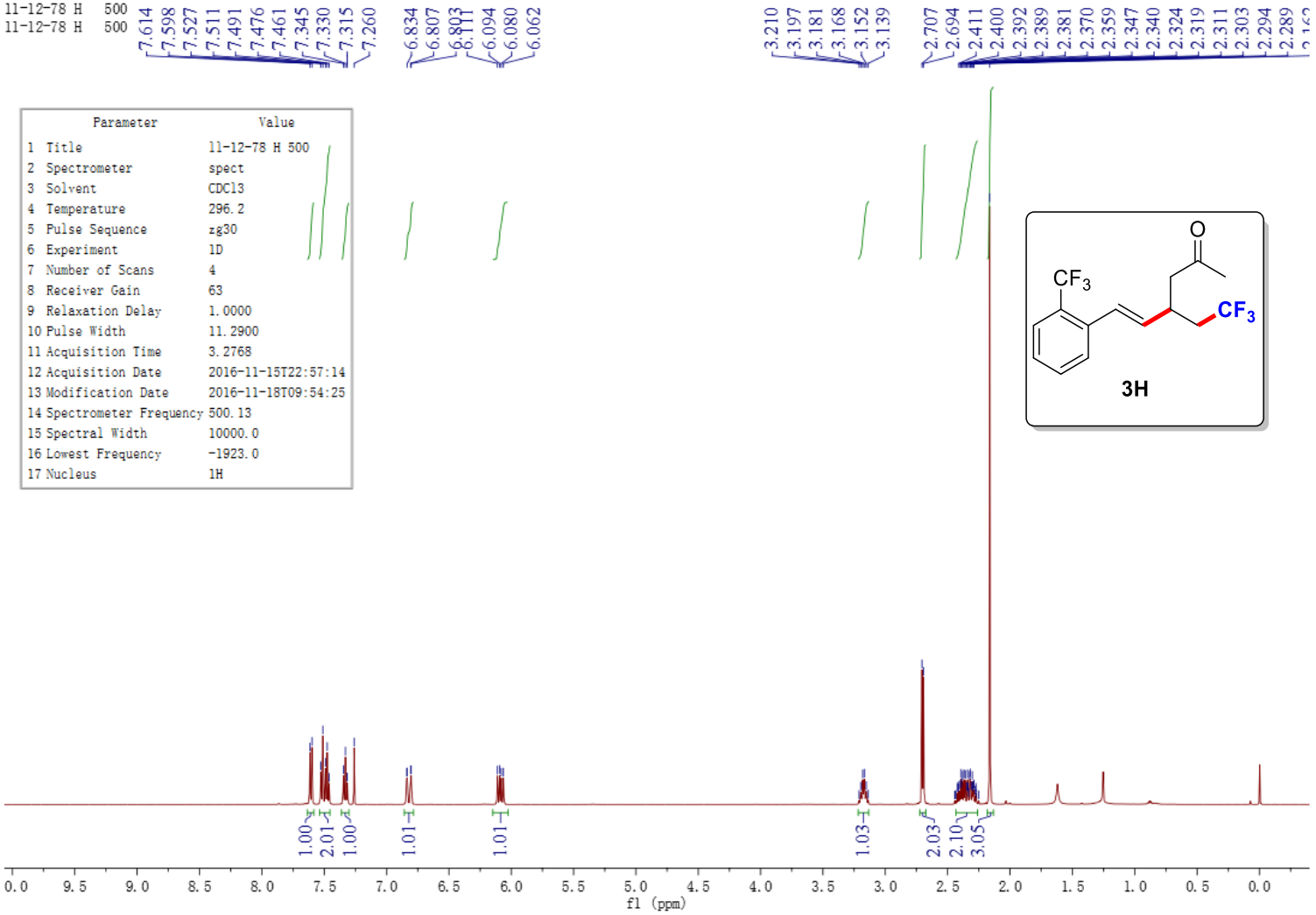
11-12-77 F
11-12-77 F

Parameter	Value
1 Title	11-12-77 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.5
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	2
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-16T08:53:32
13 Modification Date	2016-11-18T09:54:15
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F

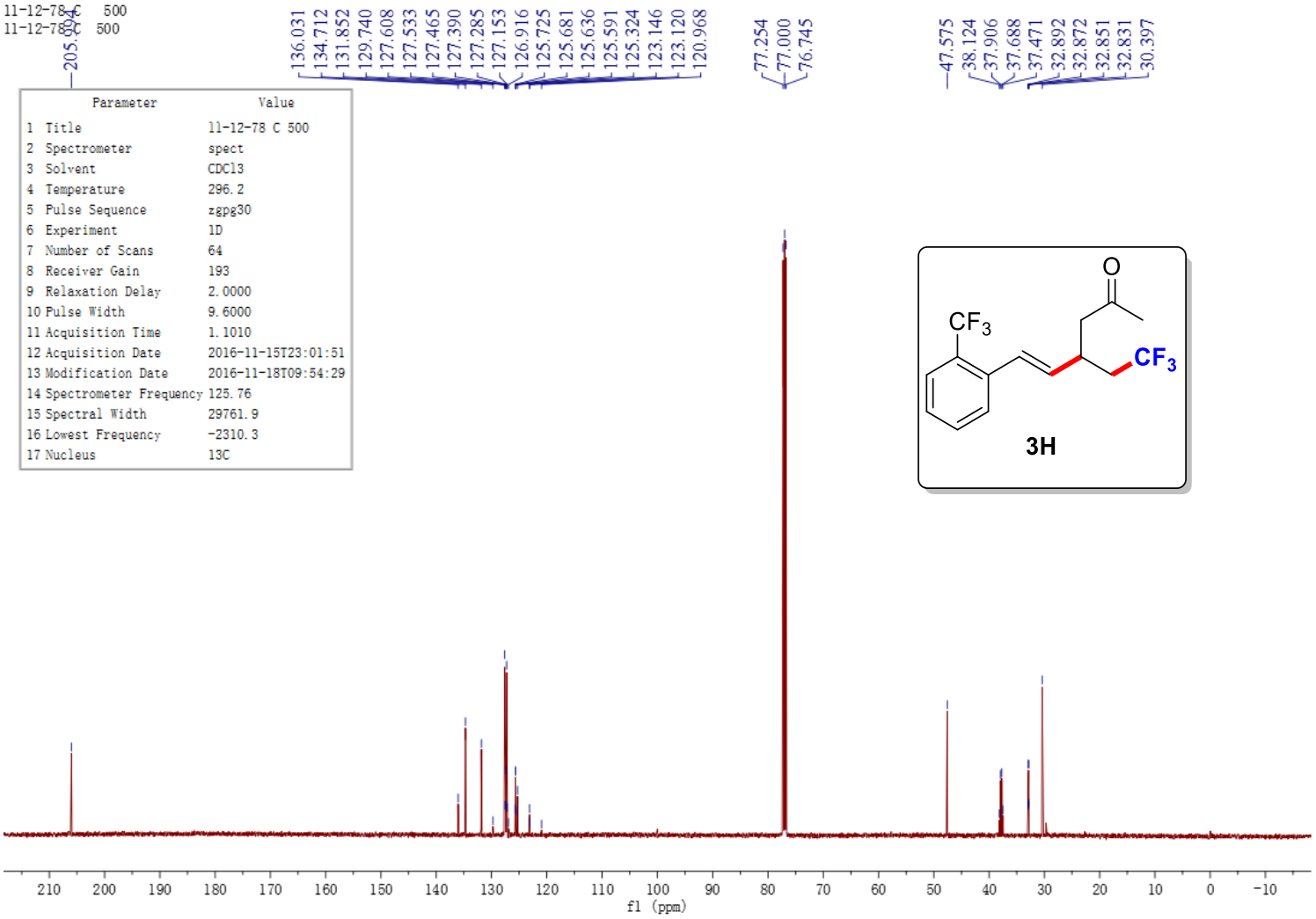




^{1}H NMR Spectrum of Compound **3H**



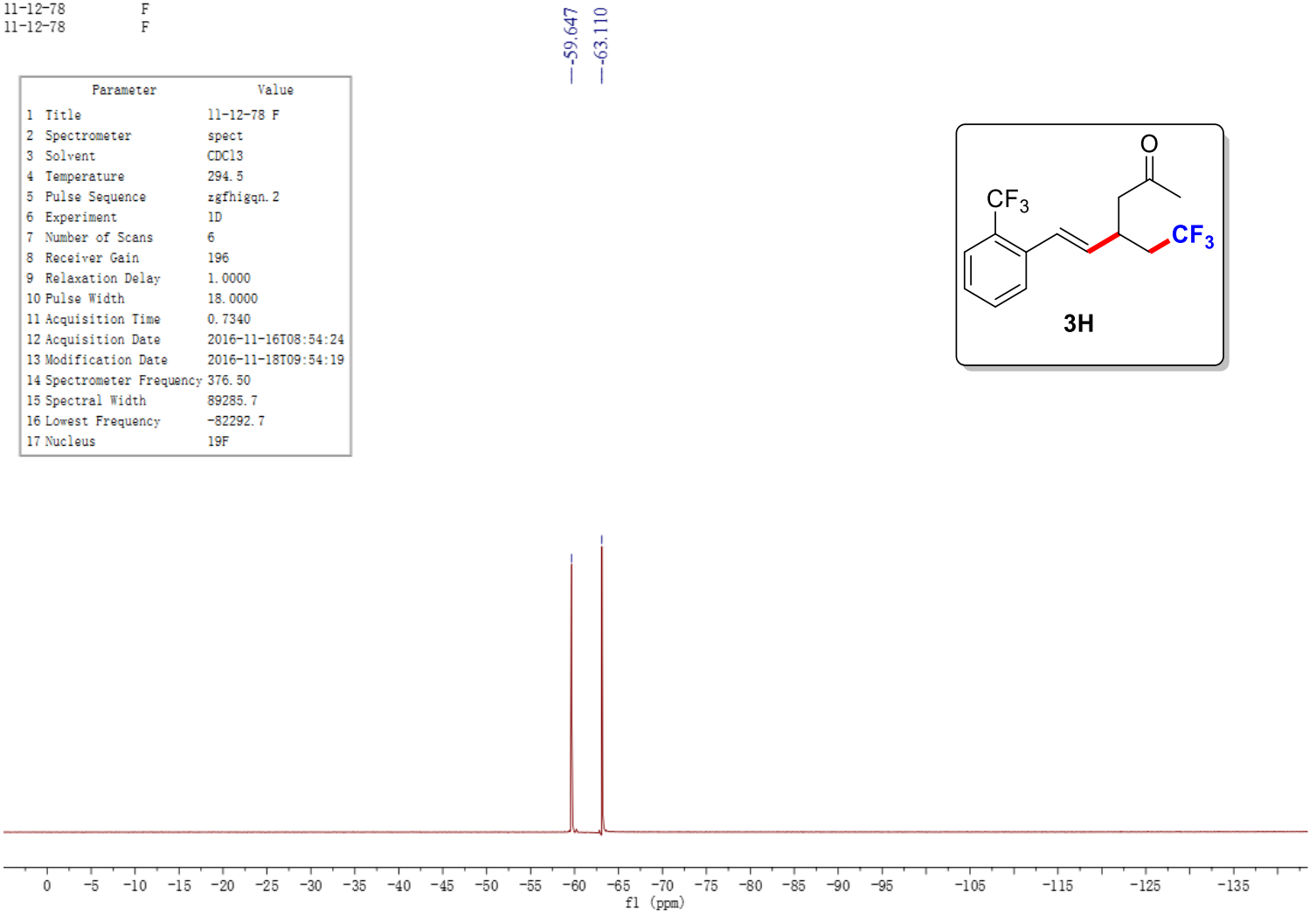
^{13}C NMR Spectrum of Compound **3H**



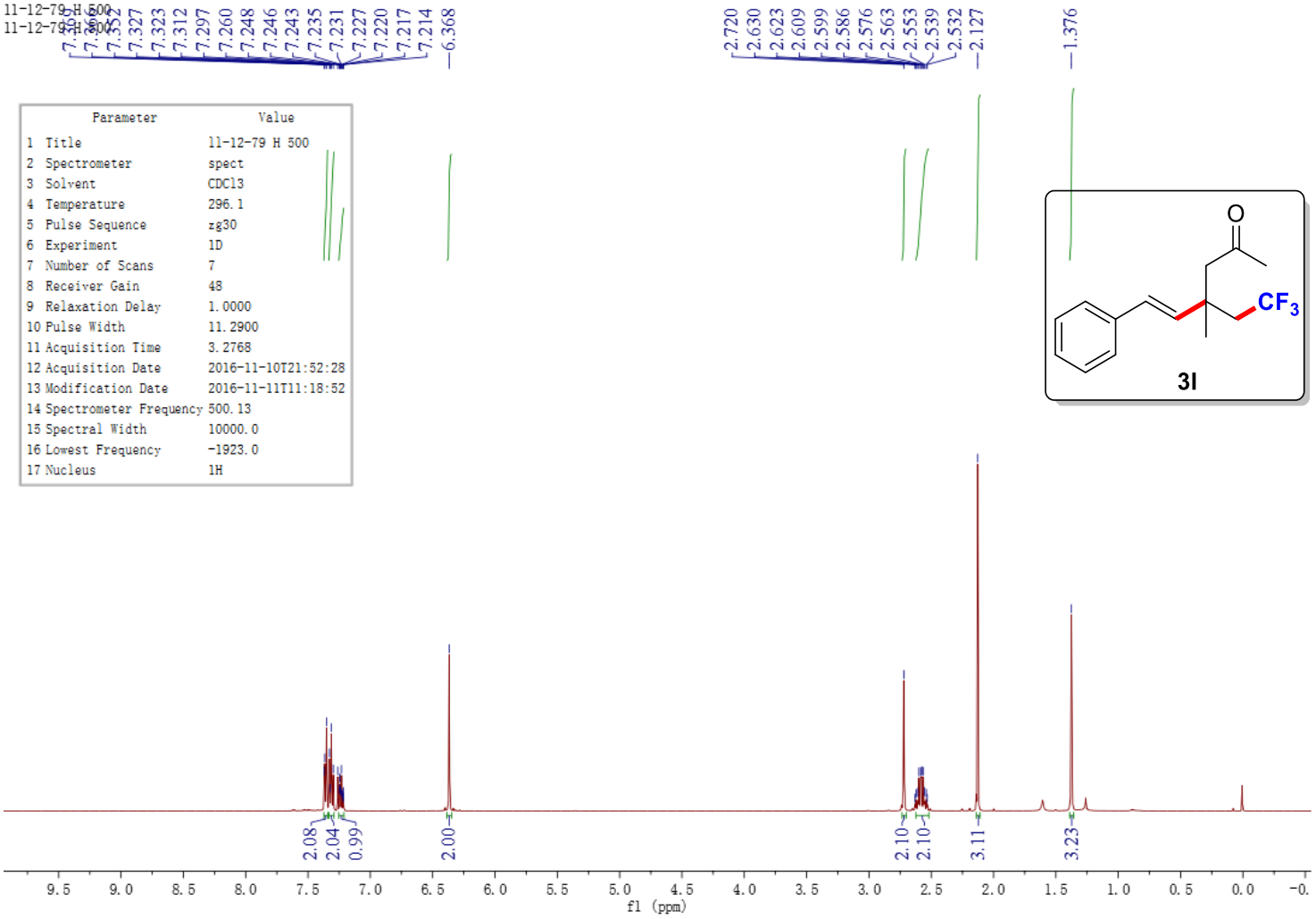
^{19}F NMR Spectrum of Compound **3H**

11-12-78 F
11-12-78 F

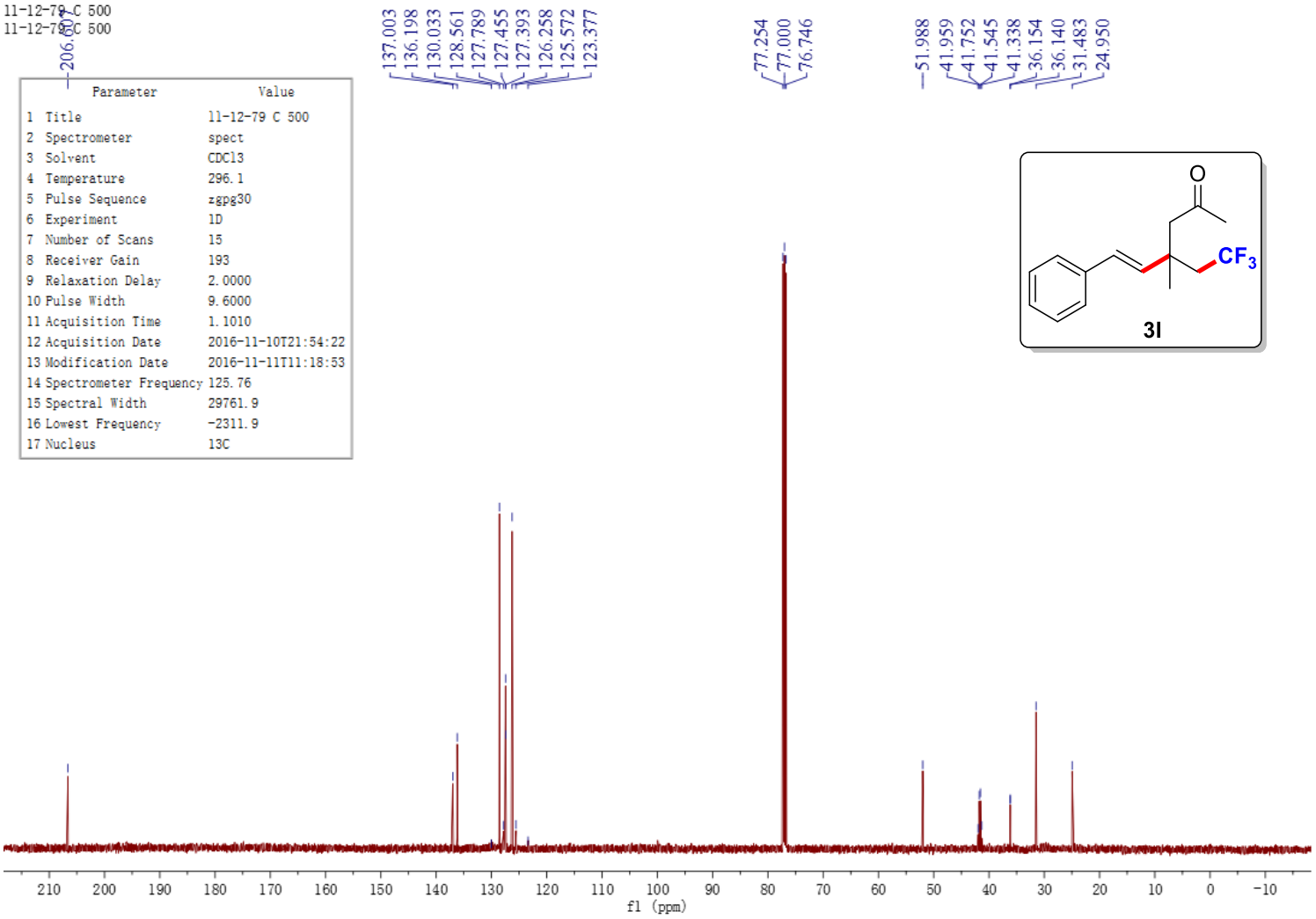
Parameter	Value
1 Title	11-12-78 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.5
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	6
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-16T08:54:24
13 Modification Date	2016-11-18T09:54:19
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



^{1}H NMR Spectrum of Compound **3I**



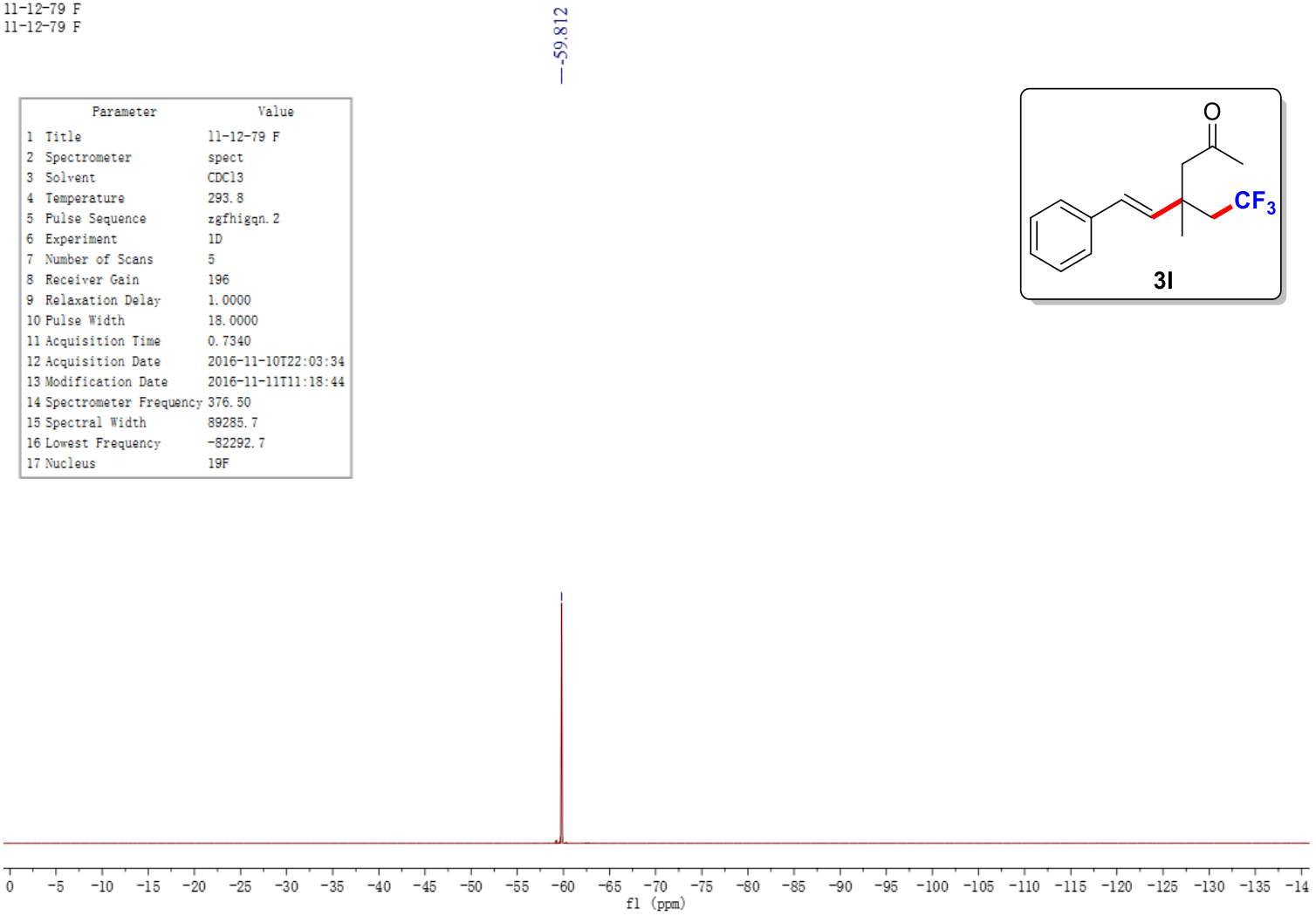
^{13}C NMR Spectrum of Compound **3I**



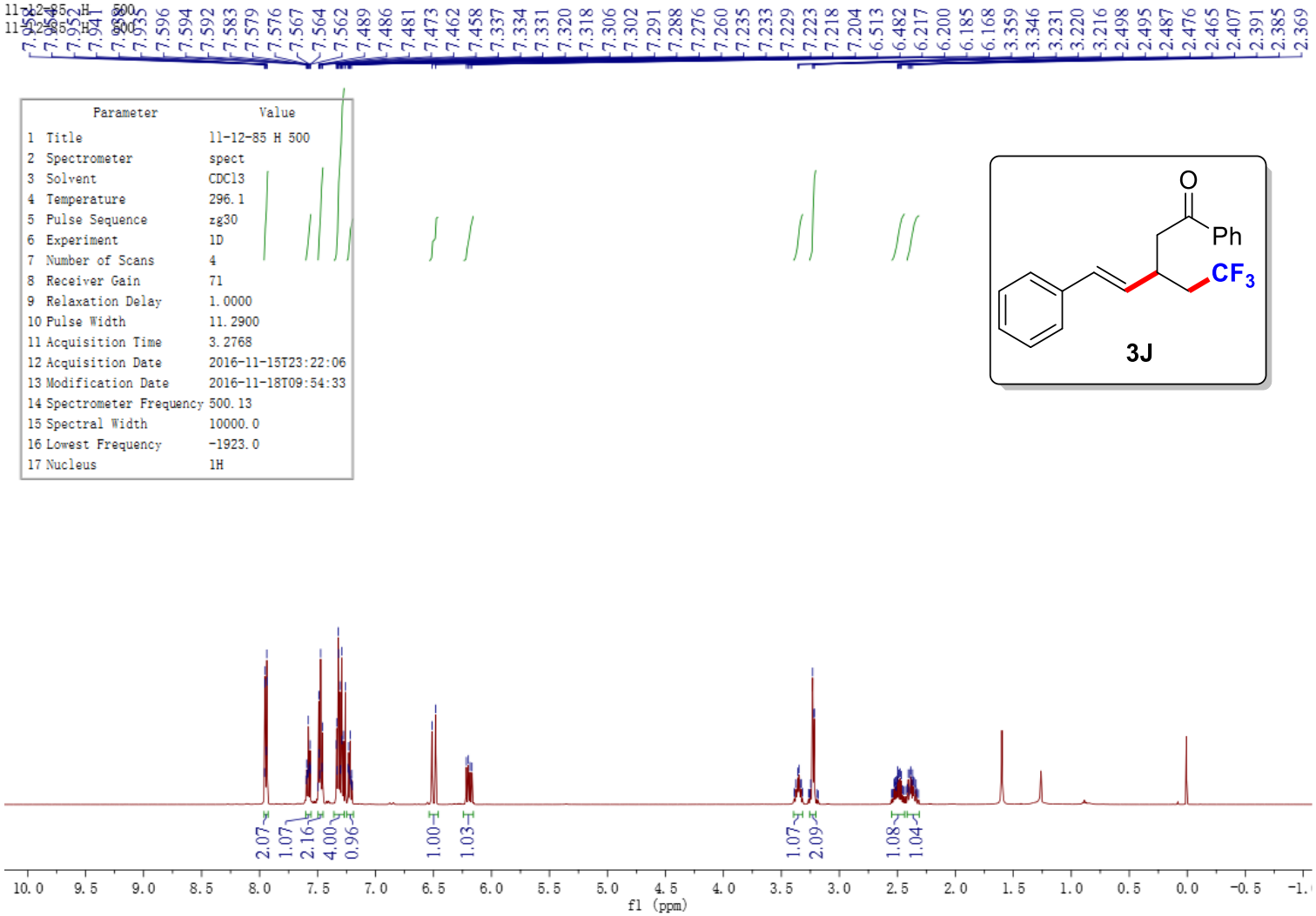
^{19}F NMR Spectrum of Compound **3I**

11-12-79 F
11-12-79 F

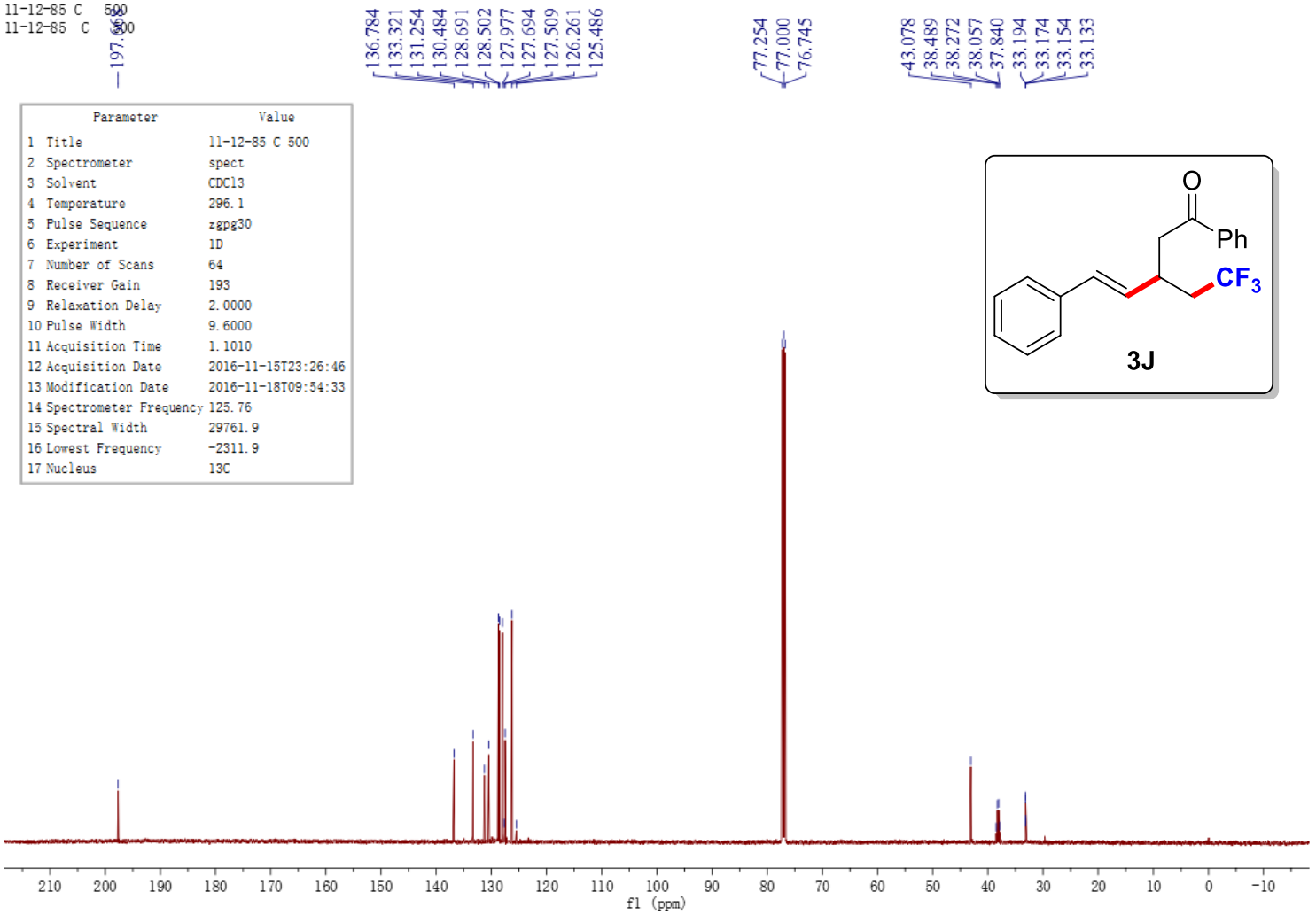
Parameter	Value
1 Title	11-12-79 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	293.8
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	5
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-11-10T22:03:34
13 Modification Date	2016-11-11T11:18:44
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



^{1}H NMR Spectrum of Compound **3J**



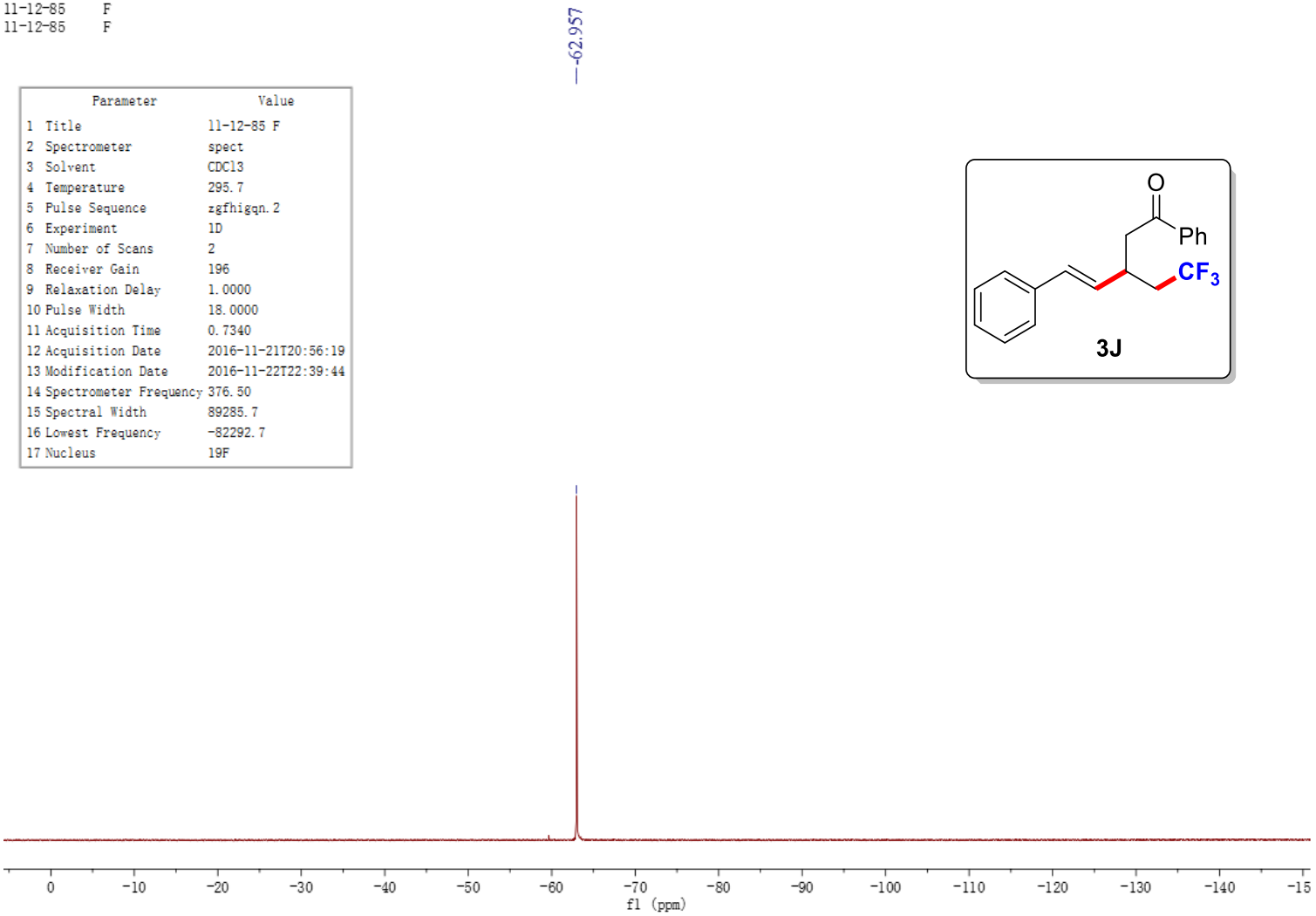
^{13}C NMR Spectrum of Compound **3J**



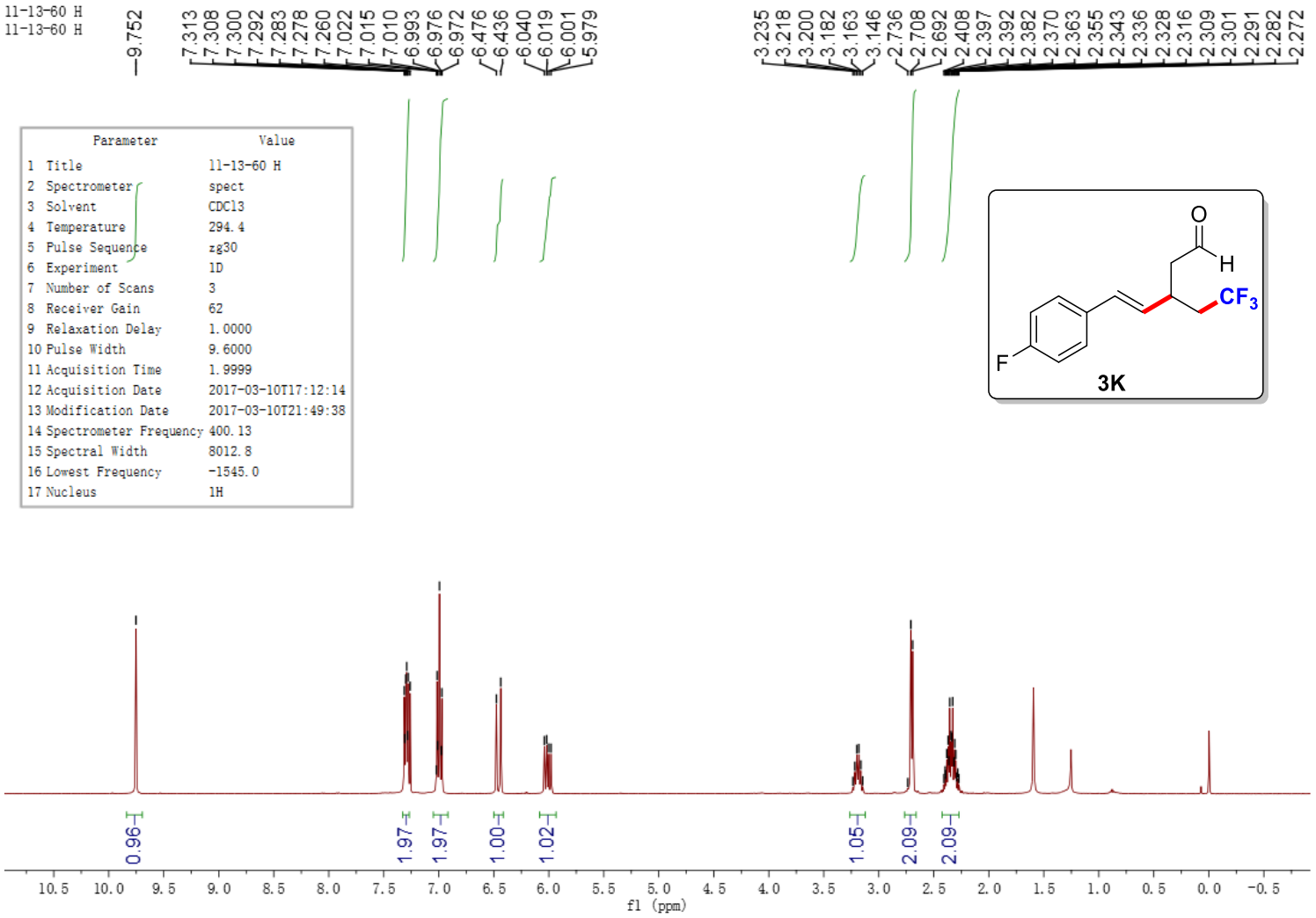
^{19}F NMR Spectrum of Compound **3J**

11-12-85 F
11-12-85 F

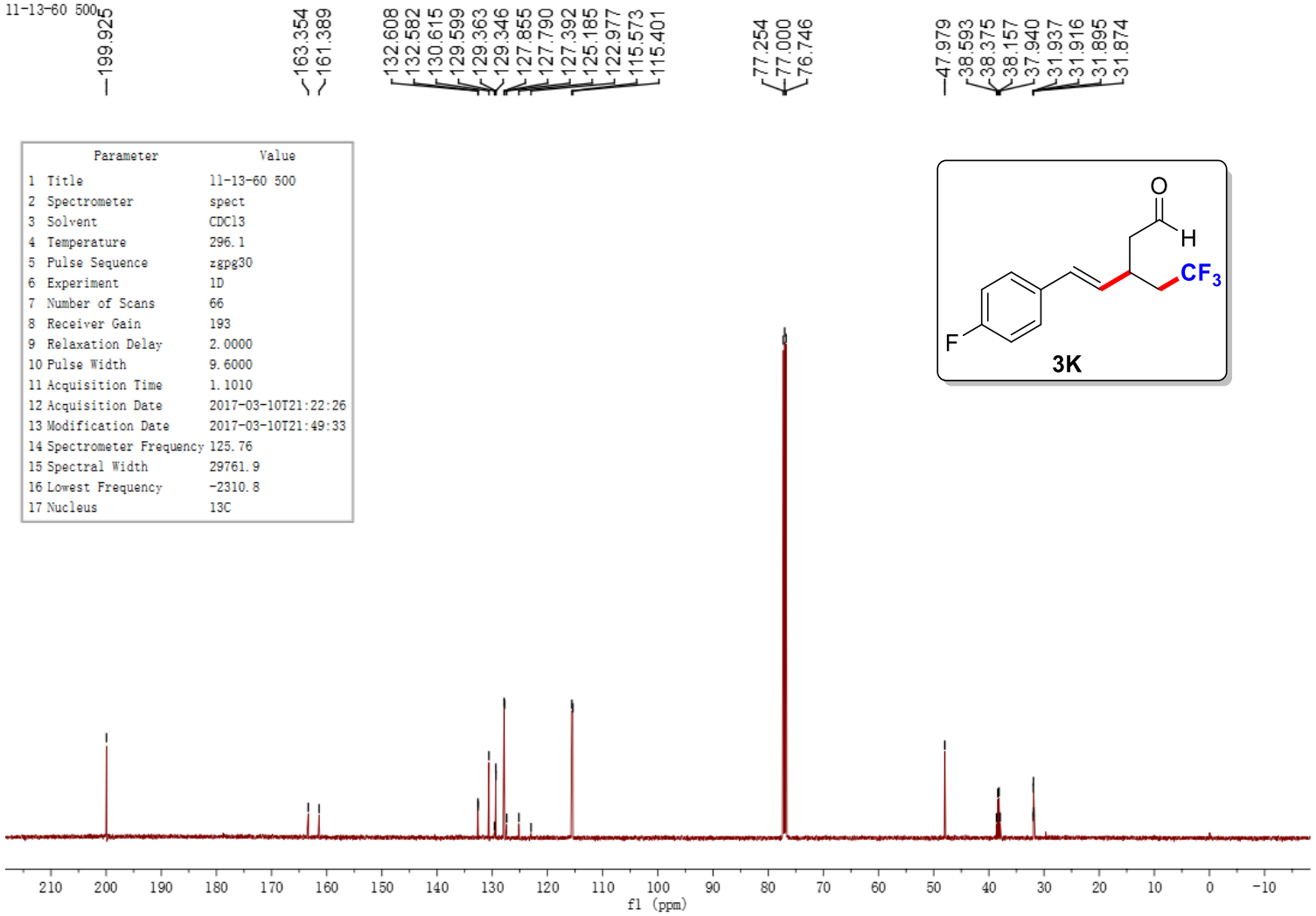
	Parameter	Value
1	Title	11-12-85 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	295.7
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	2
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-21T20:56:19
13	Modification Date	2016-11-22T22:39:44
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



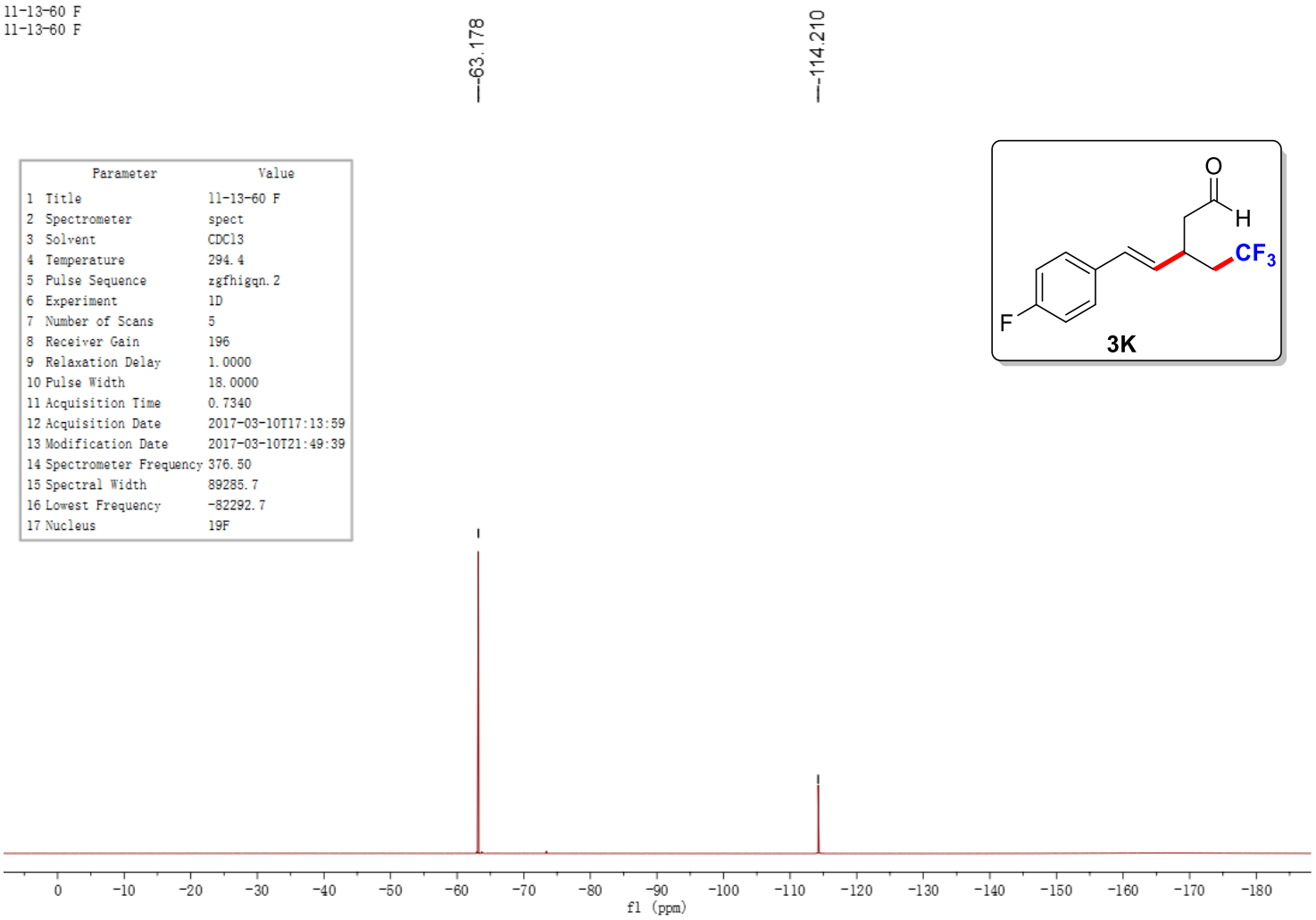
^{1}H NMR Spectrum of Compound **3K**



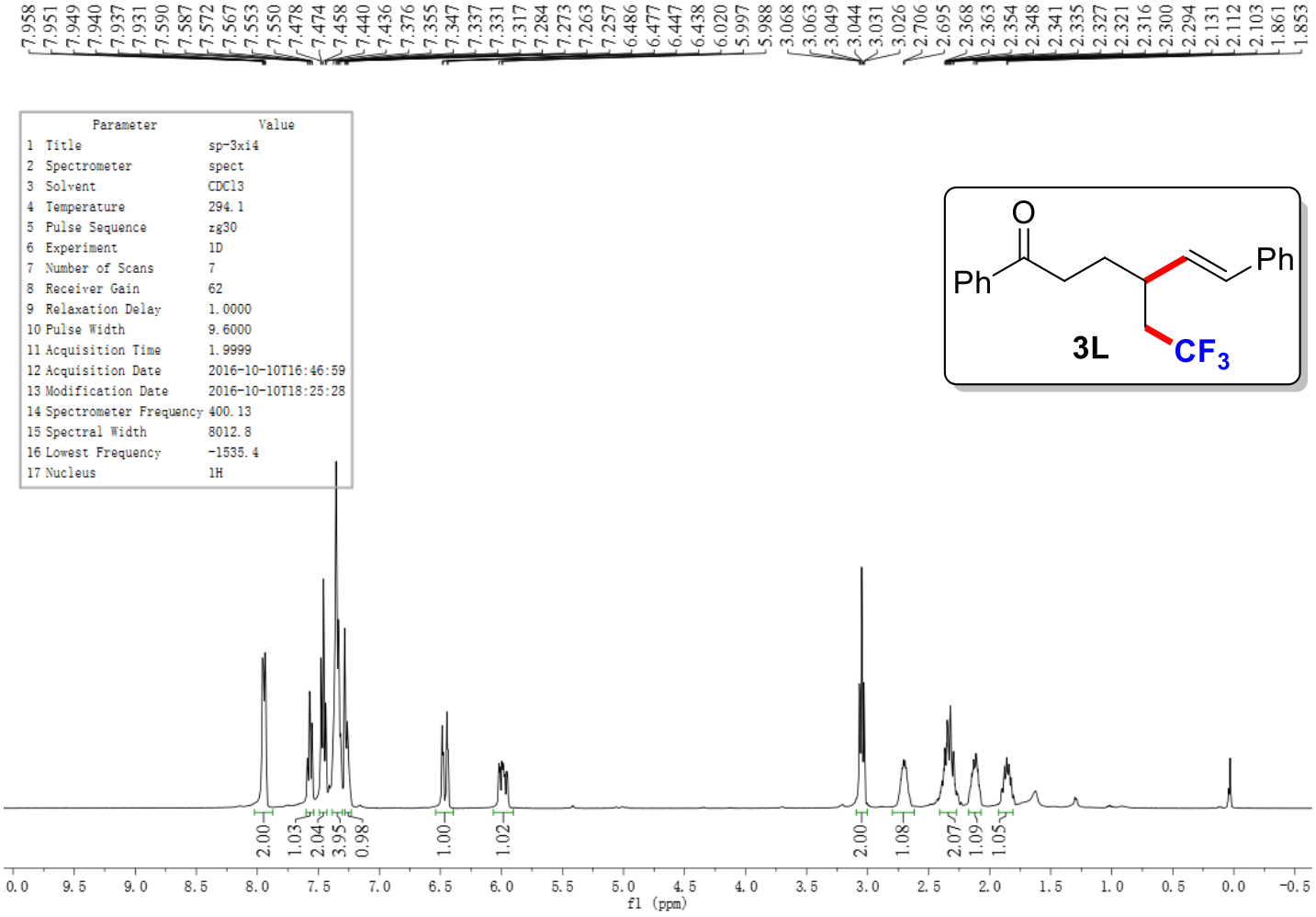
^{13}C NMR Spectrum of Compound **3K**



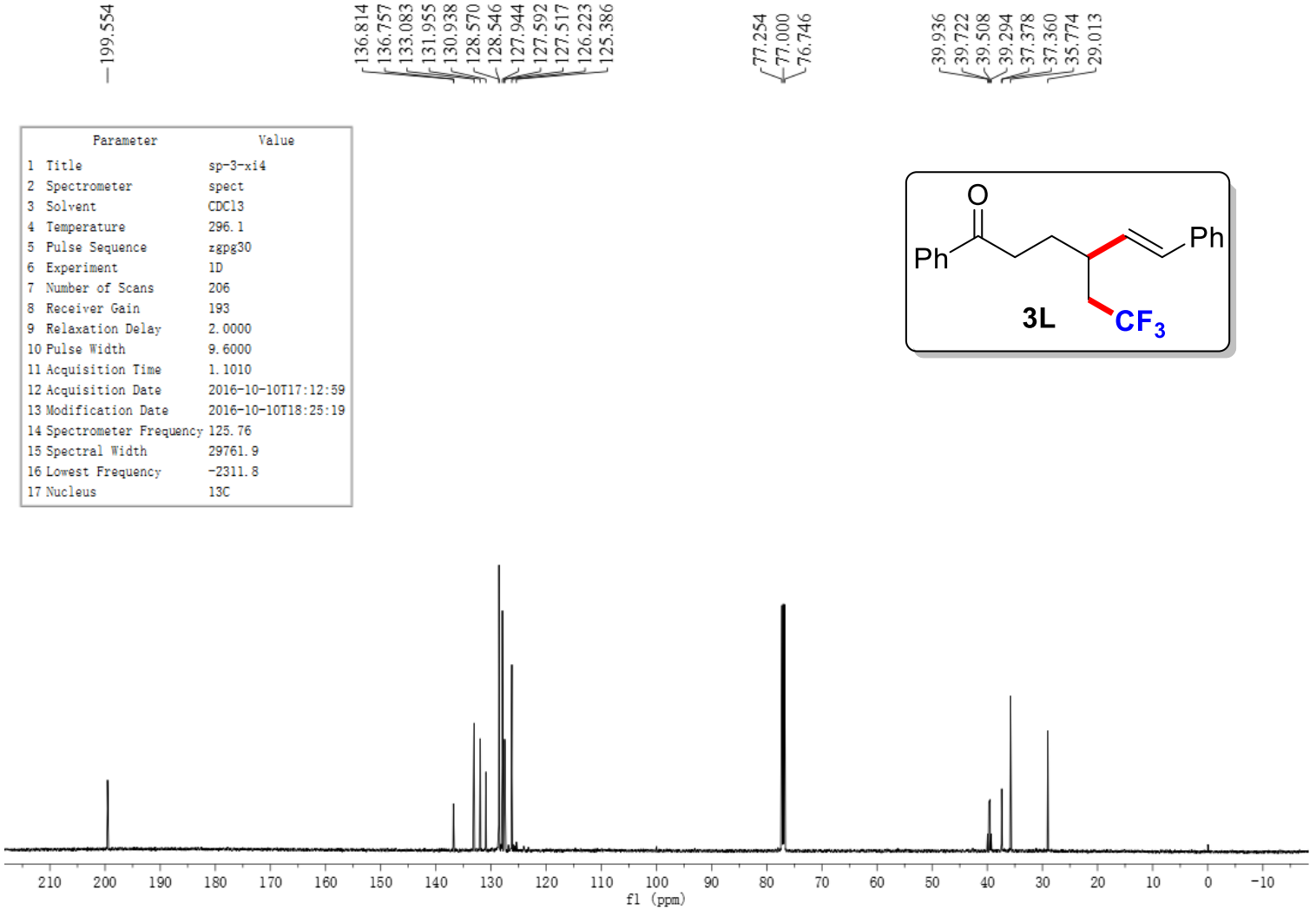
^{19}F NMR Spectrum of Compound **3K**



^{1}H NMR Spectrum of Compound **3L**

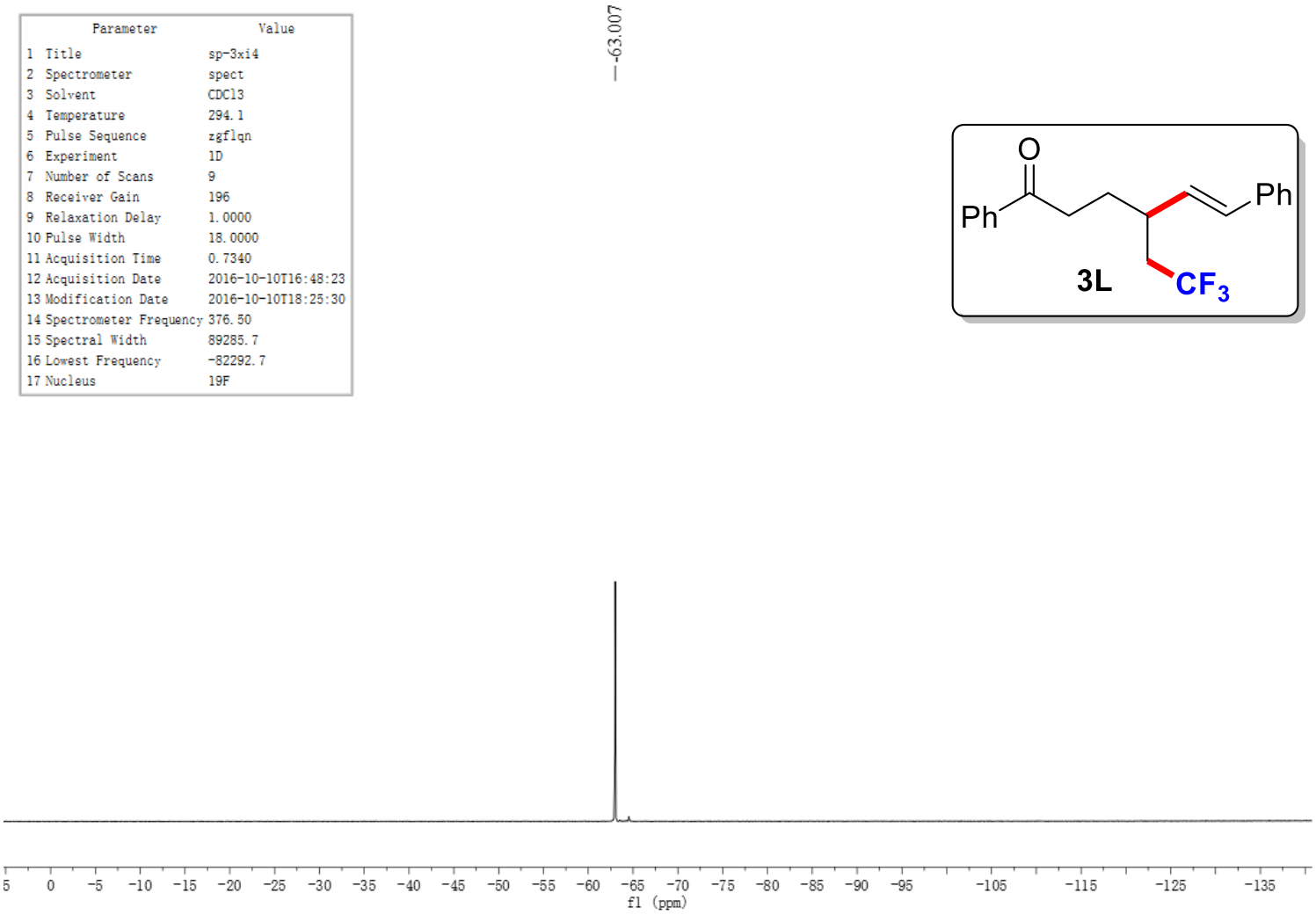


^{13}C NMR Spectrum of Compound **3L**

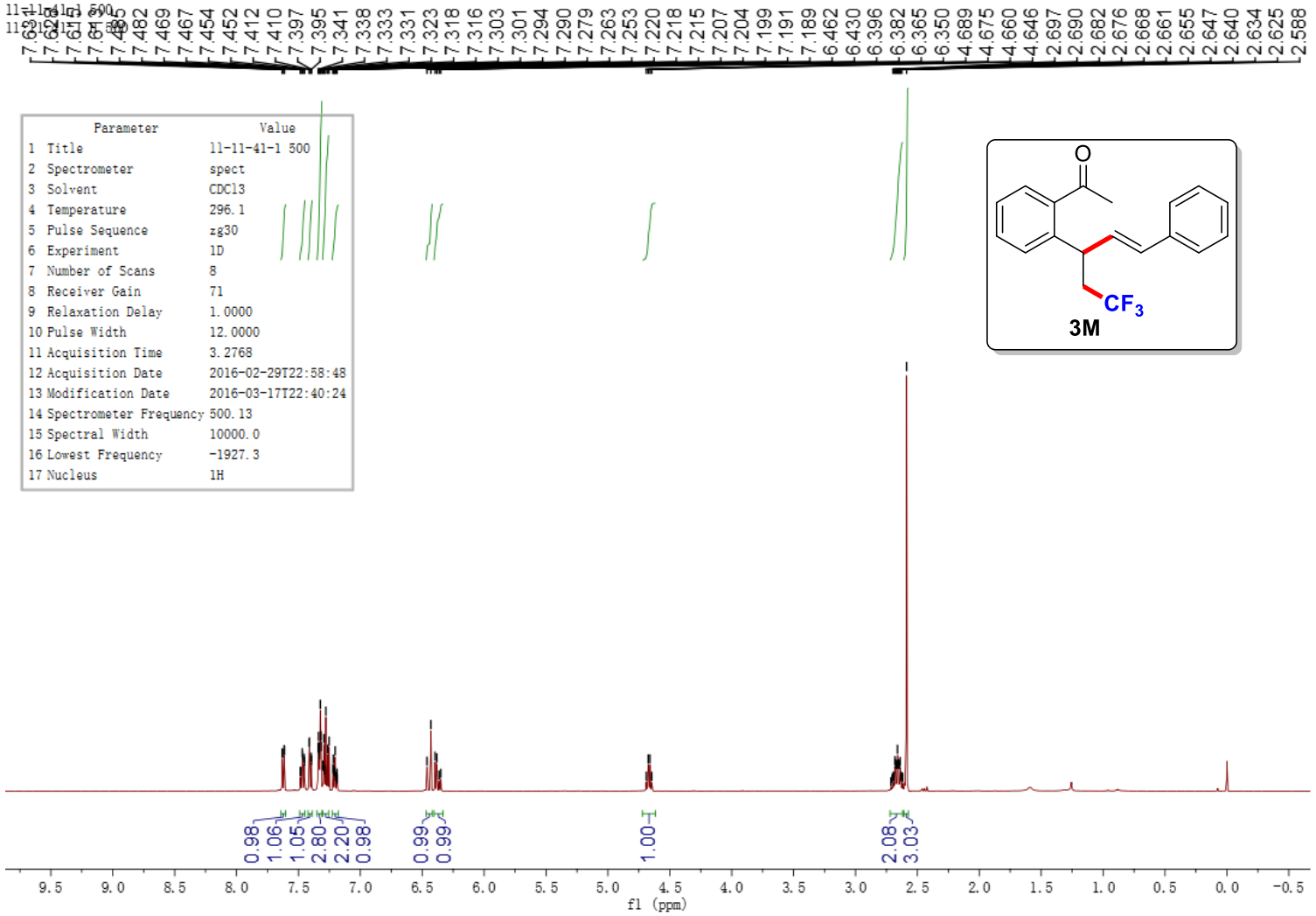


^{19}F NMR Spectrum of Compound **3L**

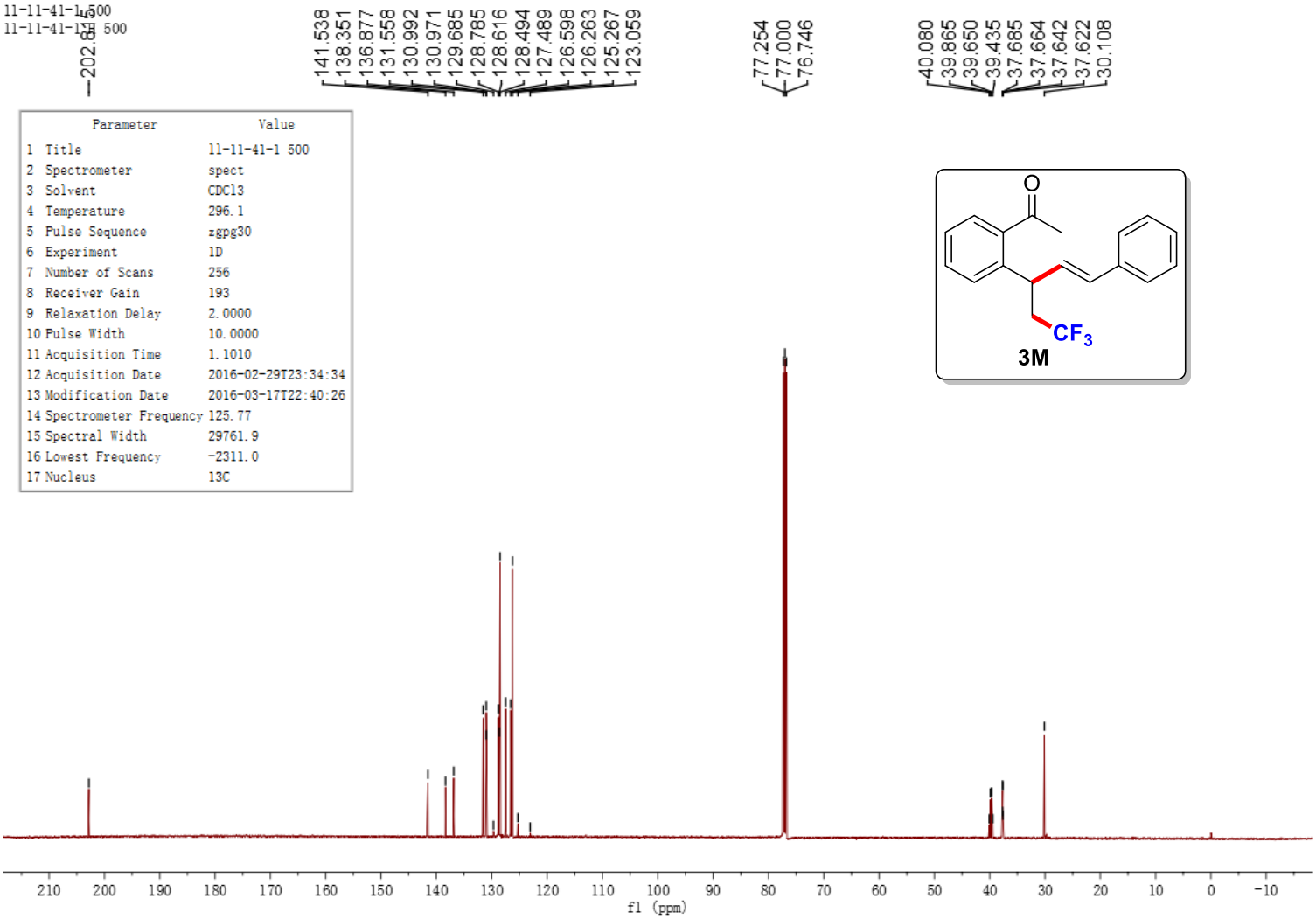
	Parameter	Value
1	Title	sp-3xi4
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.1
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	9
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-10-10T16:48:23
13	Modification Date	2016-10-10T18:25:30
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **3M**



^{13}C NMR Spectrum of Compound **3M**

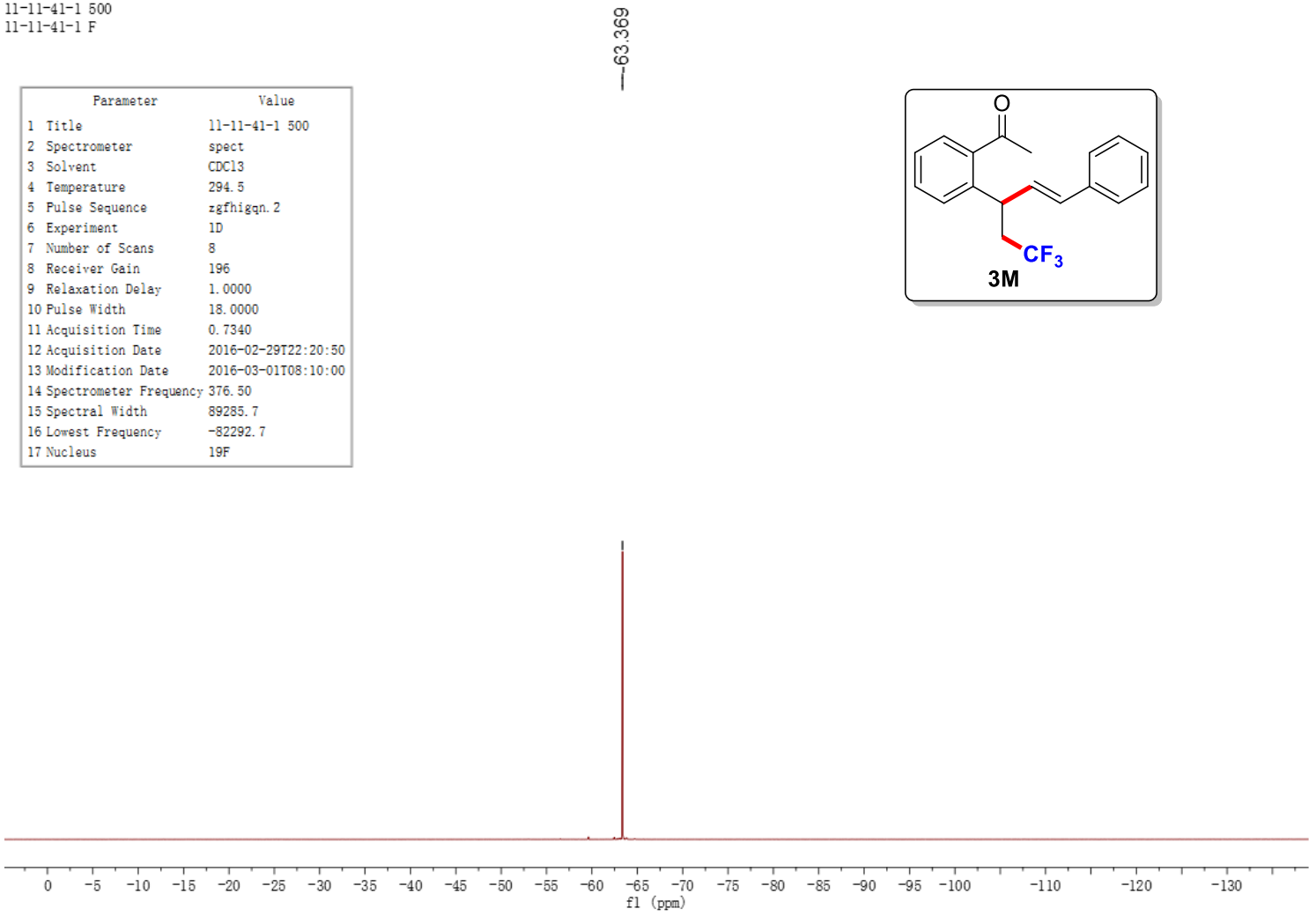


	Parameter	Value
1	Title	ll-11-41-1 500
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	256
8	Receiver Gain	193
9	Relaxation Delay	2.0000
10	Pulse Width	10.0000
11	Acquisition Time	1.1010
12	Acquisition Date	2016-02-29T23:34:34
13	Modification Date	2016-03-17T22:40:26
14	Spectrometer Frequency	125.77
15	Spectral Width	29761.9
16	Lowest Frequency	-2311.0
17	Nucleus	13C

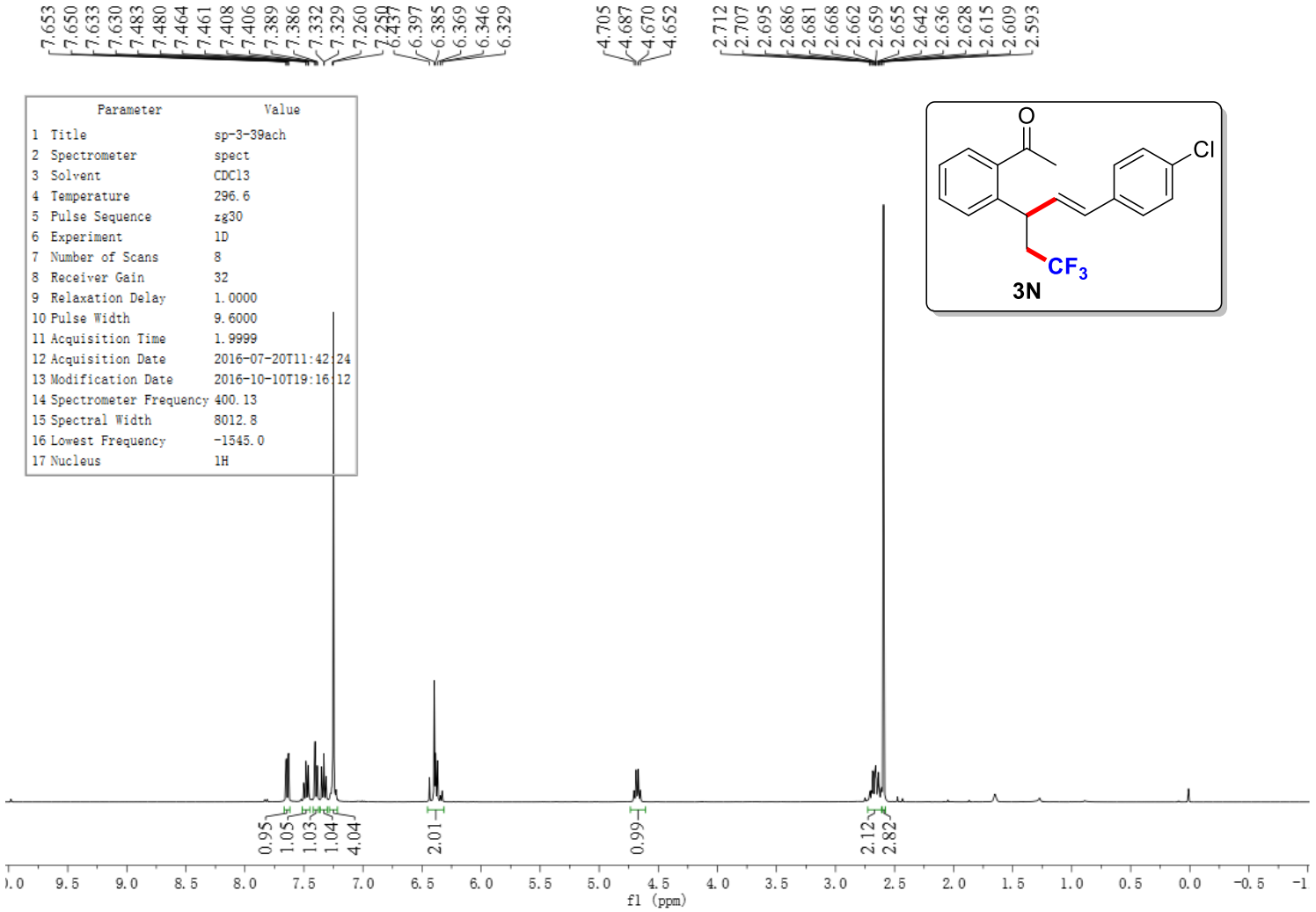
^{19}F NMR Spectrum of Compound **3M**

11-11-41-1 500
11-11-41-1 F

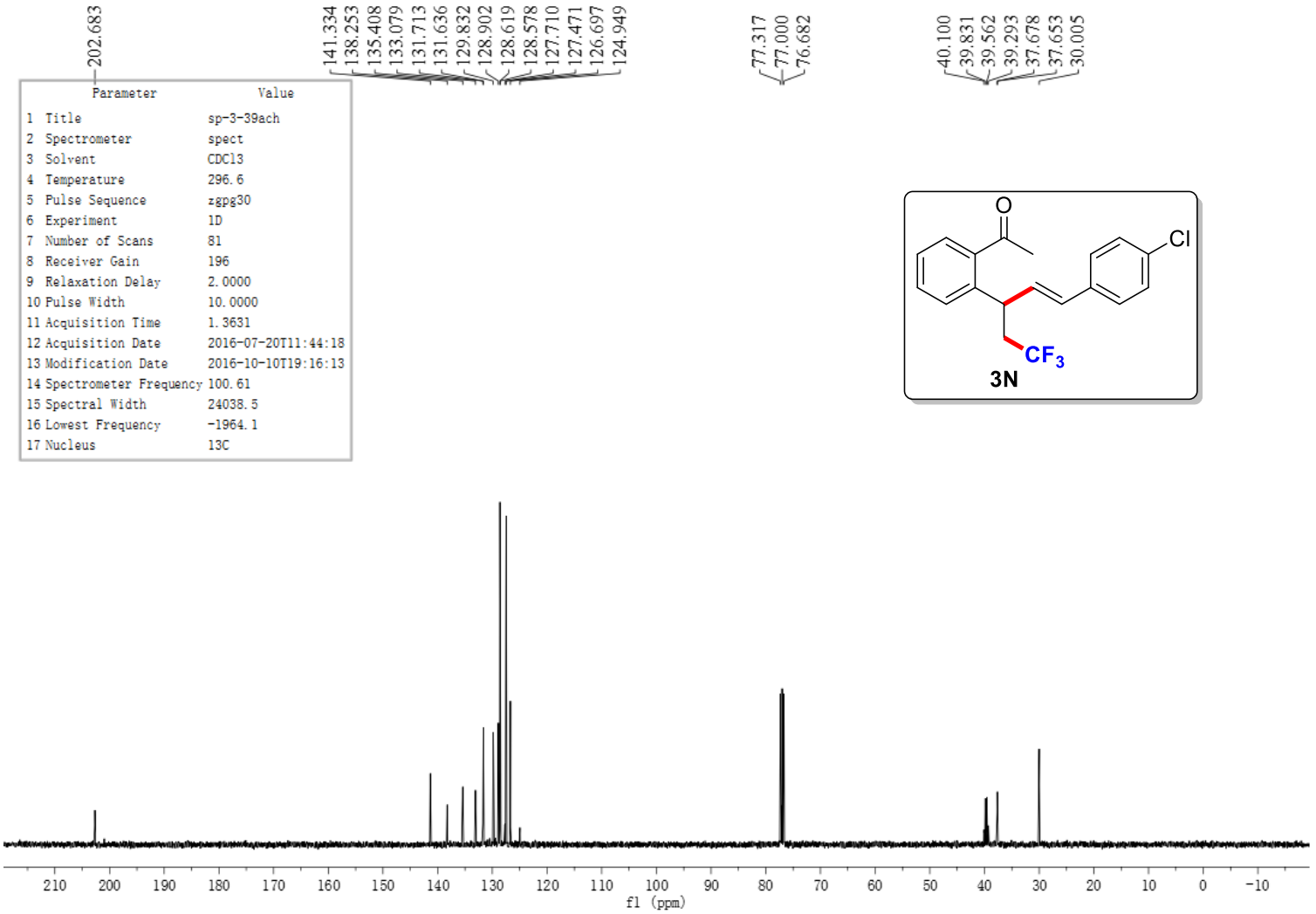
	Parameter	Value
1	Title	11-11-41-1 500
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.5
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-02-29T22:20:50
13	Modification Date	2016-03-01T08:10:00
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **3N**

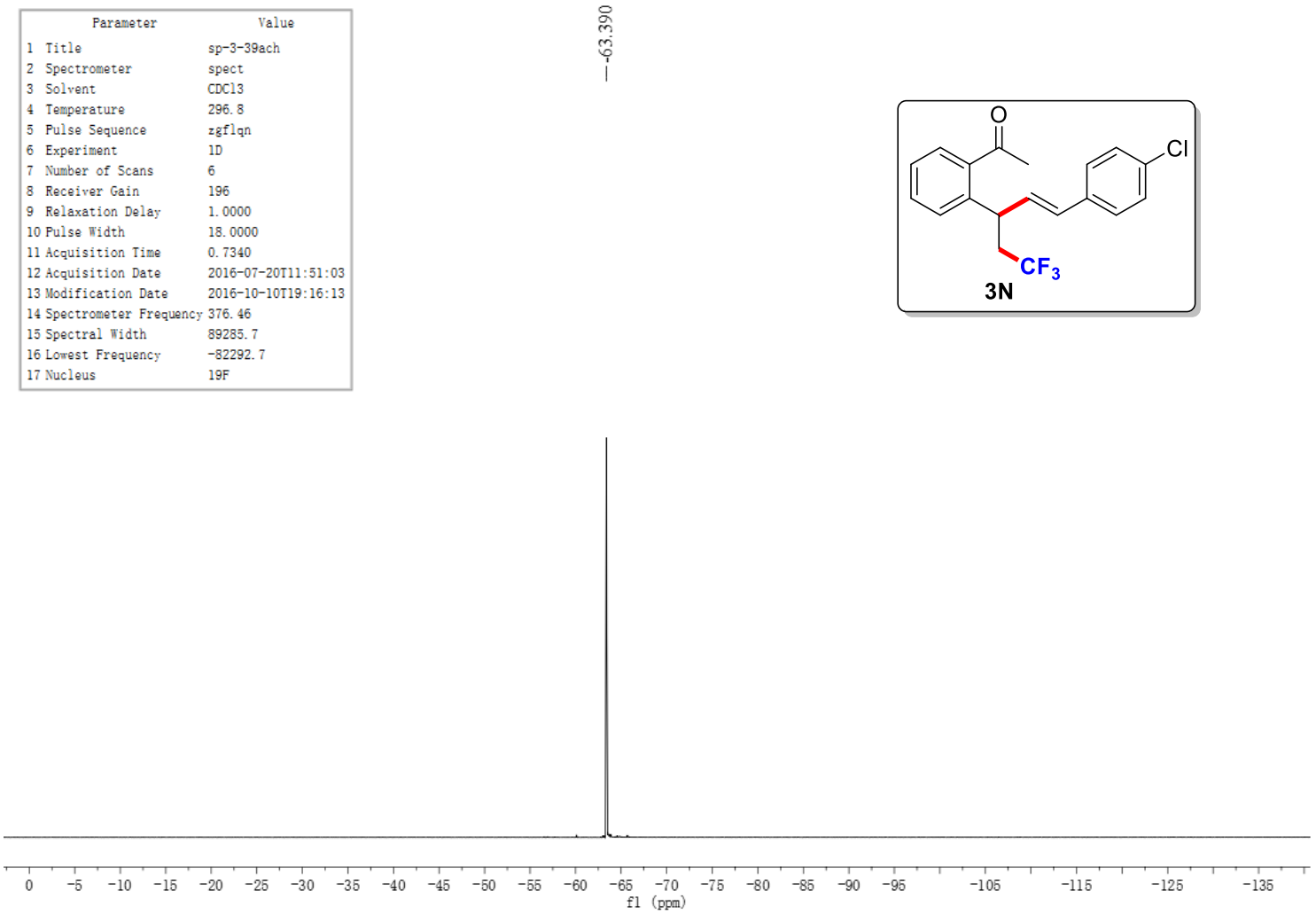


^{13}C NMR Spectrum of Compound **3N**

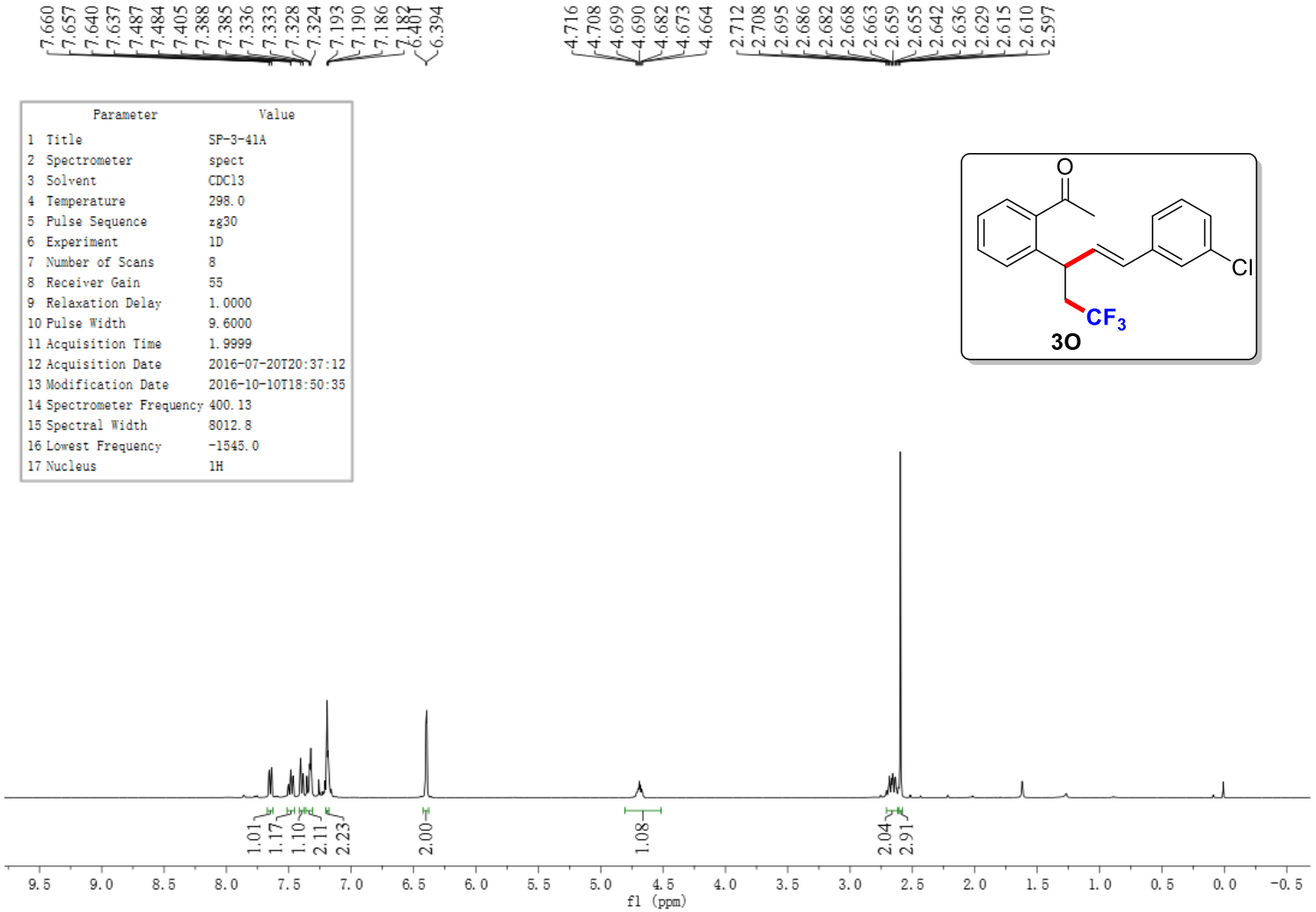


^{19}F NMR Spectrum of Compound **3N**

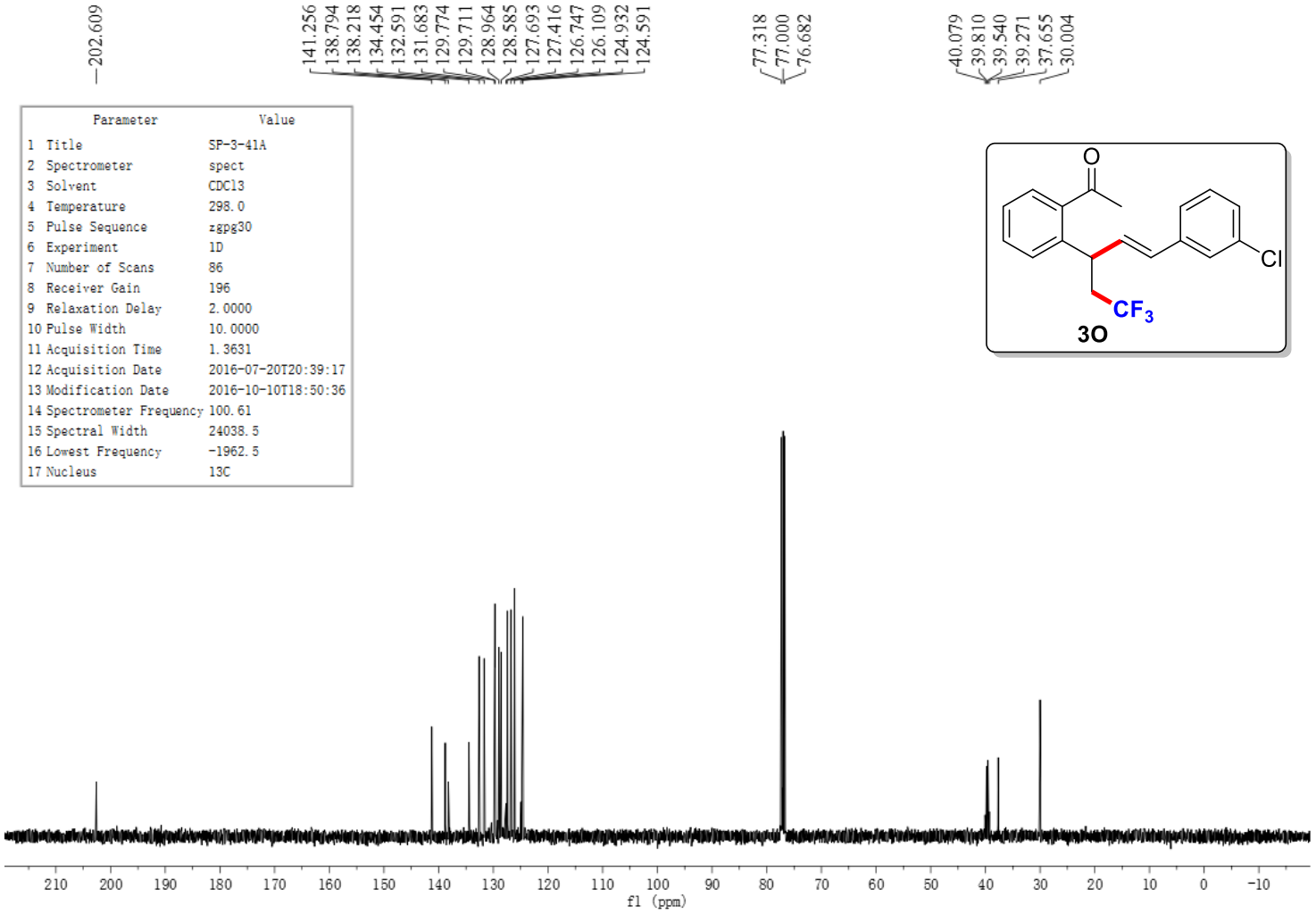
	Parameter	Value
1	Title	sp-3-39ach
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.8
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	6
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-07-20T11:51:03
13	Modification Date	2016-10-10T19:16:13
14	Spectrometer Frequency	376.46
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **3O**

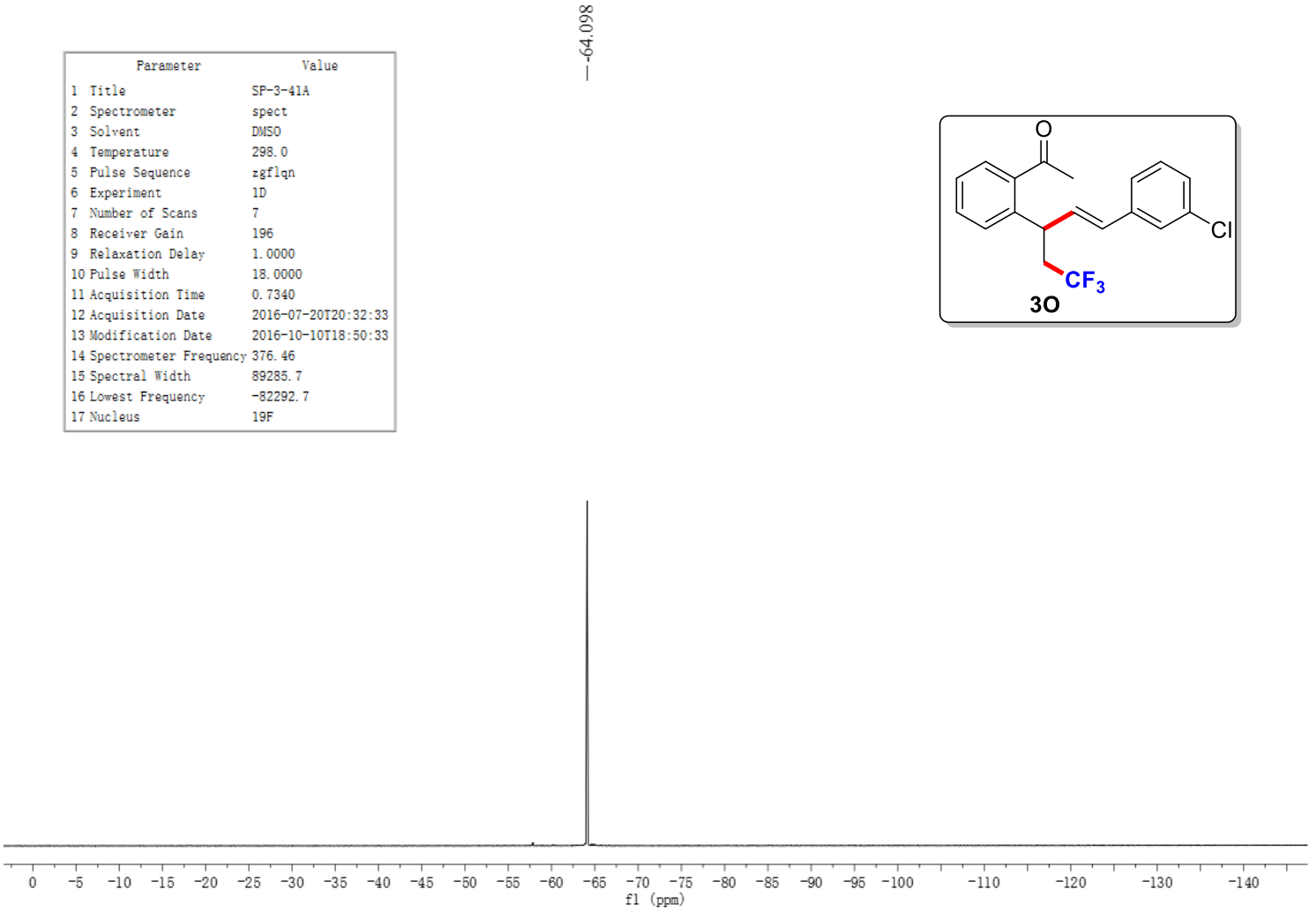


^{13}C NMR Spectrum of Compound **3O**

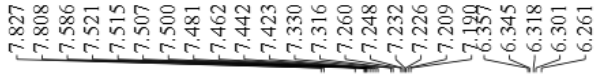


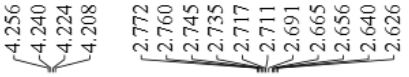
^{19}F NMR Spectrum of Compound **3O**

	Parameter	Value
1	Title	SP-3-41A
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	298.0
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	7
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-07-20T20:32:33
13	Modification Date	2016-10-10T18:50:33
14	Spectrometer Frequency	376.46
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

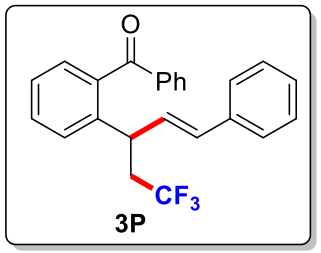


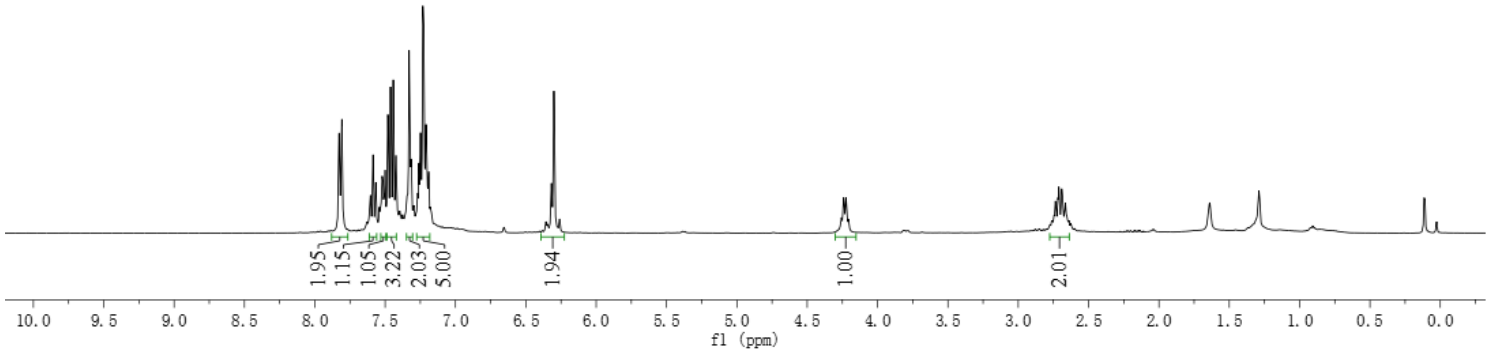
^{1}H NMR Spectrum of Compound **3P**



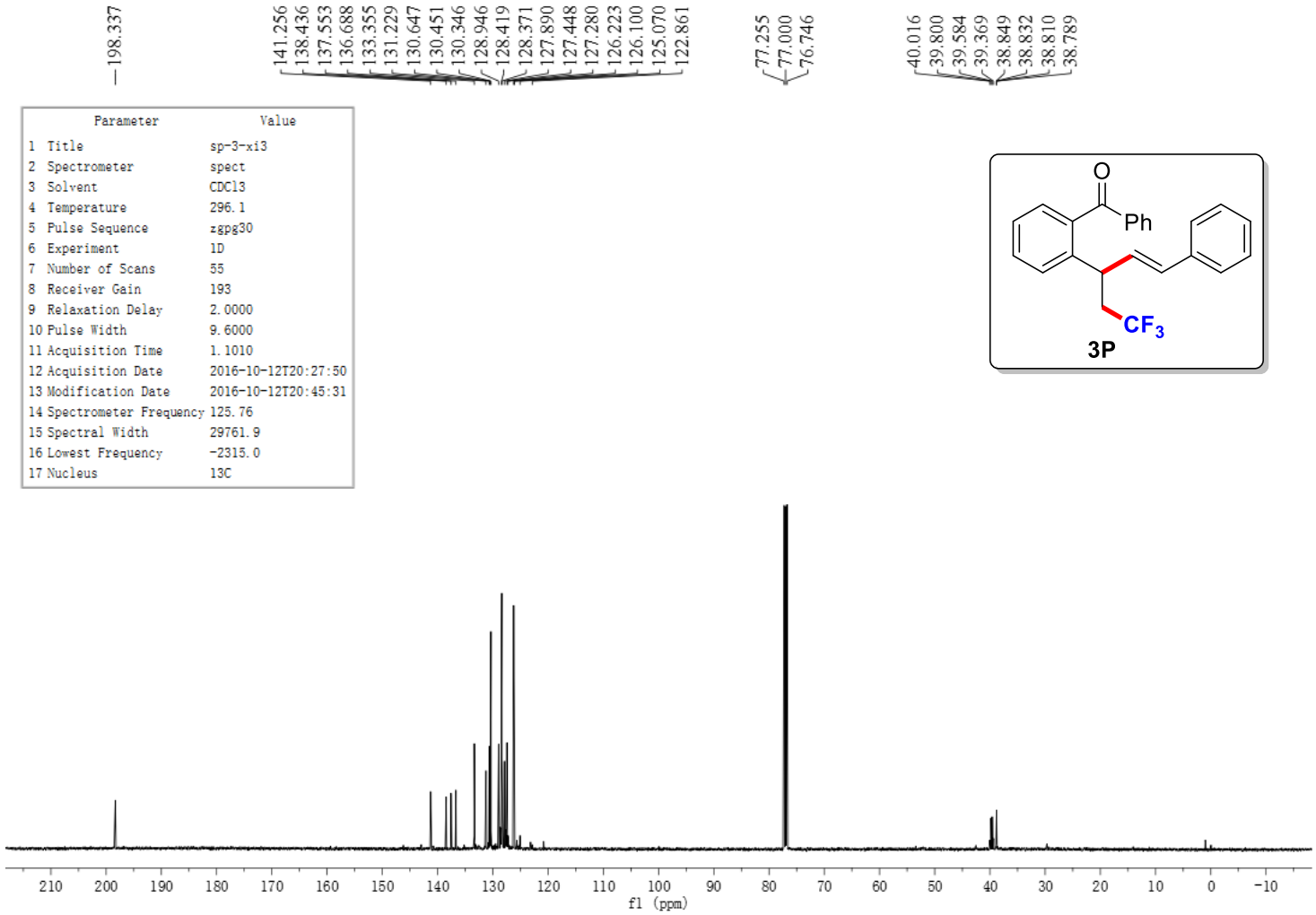


	Parameter	Value
1	Title	sp-3-20161016xi
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.7
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	32
9	Relaxation Delay	1.0000
10	Pulse Width	9.6000
11	Acquisition Time	1.9999
12	Acquisition Date	2016-10-16T22:46:21
13	Modification Date	2016-10-17T18:45:00
14	Spectrometer Frequency	400.13
15	Spectral Width	8012.8
16	Lowest Frequency	-1545.0
17	Nucleus	1H





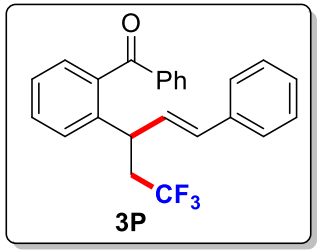
^{13}C NMR Spectrum of Compound **3P**



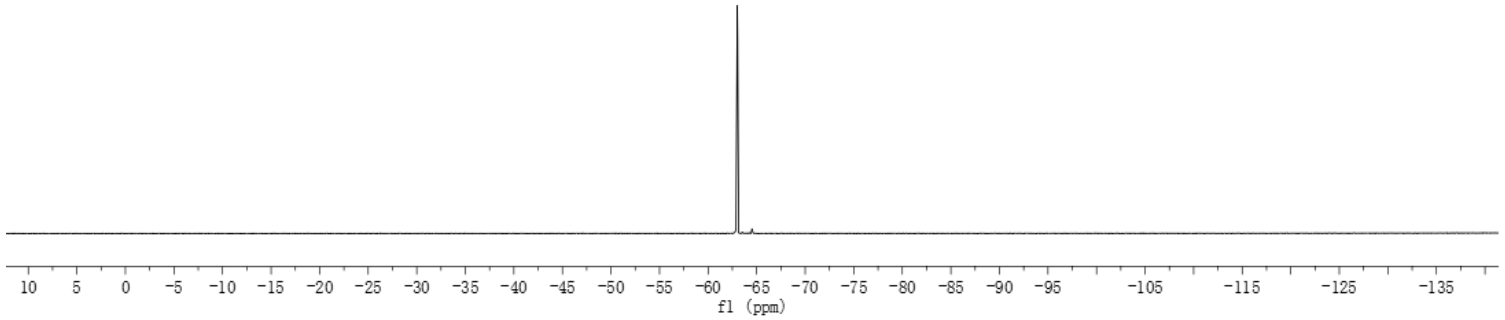
^{19}F NMR Spectrum of Compound **3P**

Parameter	Value
1 Title	sp-3xi4
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.1
5 Pulse Sequence	zgflqn
6 Experiment	1D
7 Number of Scans	9
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-10-10T16:48:23
13 Modification Date	2016-10-10T18:25:30
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F

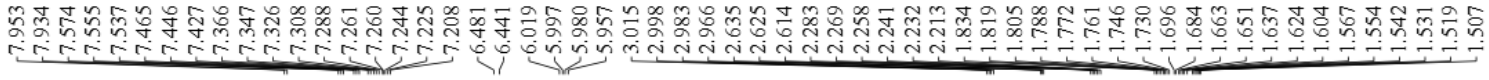
-63.007



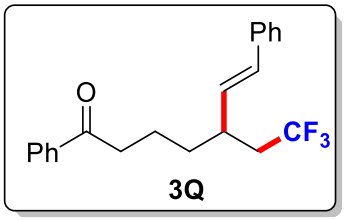
3P

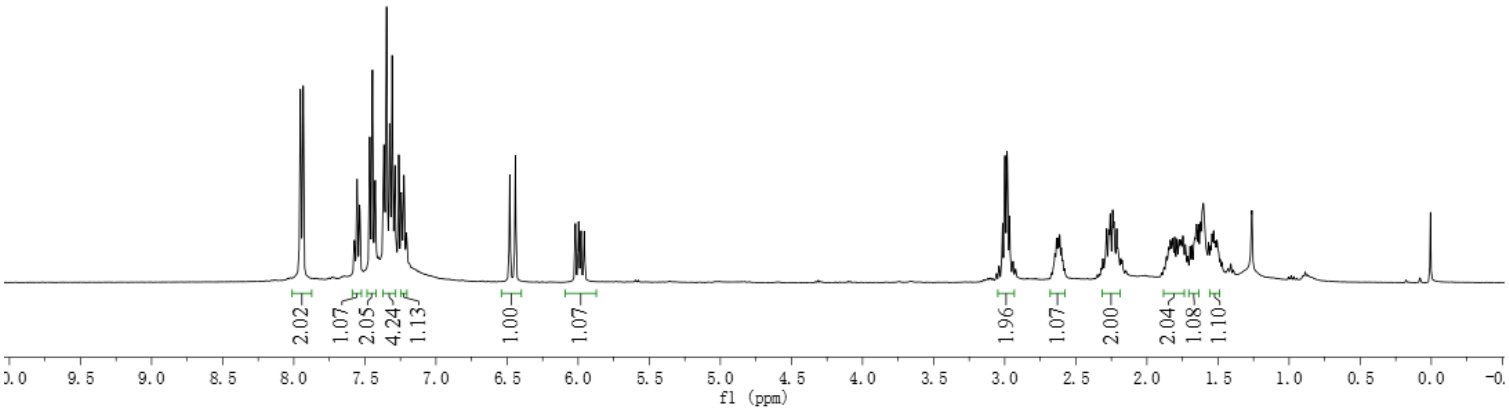


^{1}H NMR Spectrum of Compound **3Q**

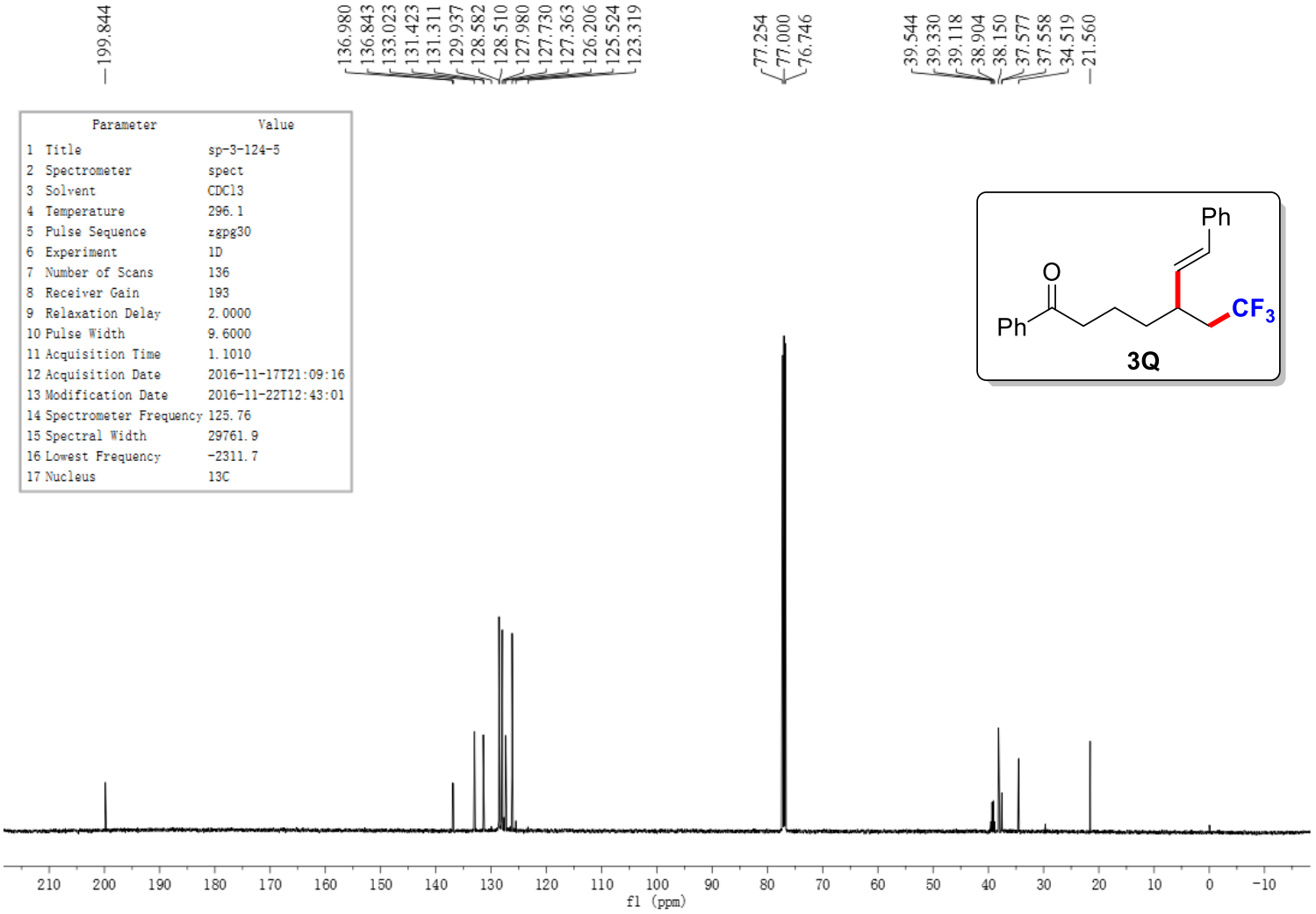


	Parameter	Value
1	Title	sp-3-124aCHF5
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	295.8
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	88
9	Relaxation Delay	1.0000
10	Pulse Width	9.6000
11	Acquisition Time	1.9999
12	Acquisition Date	2016-11-16T22:02:16
13	Modification Date	2016-11-16T23:37:37
14	Spectrometer Frequency	400.13
15	Spectral Width	8012.8
16	Lowest Frequency	-1544.2
17	Nucleus	1H



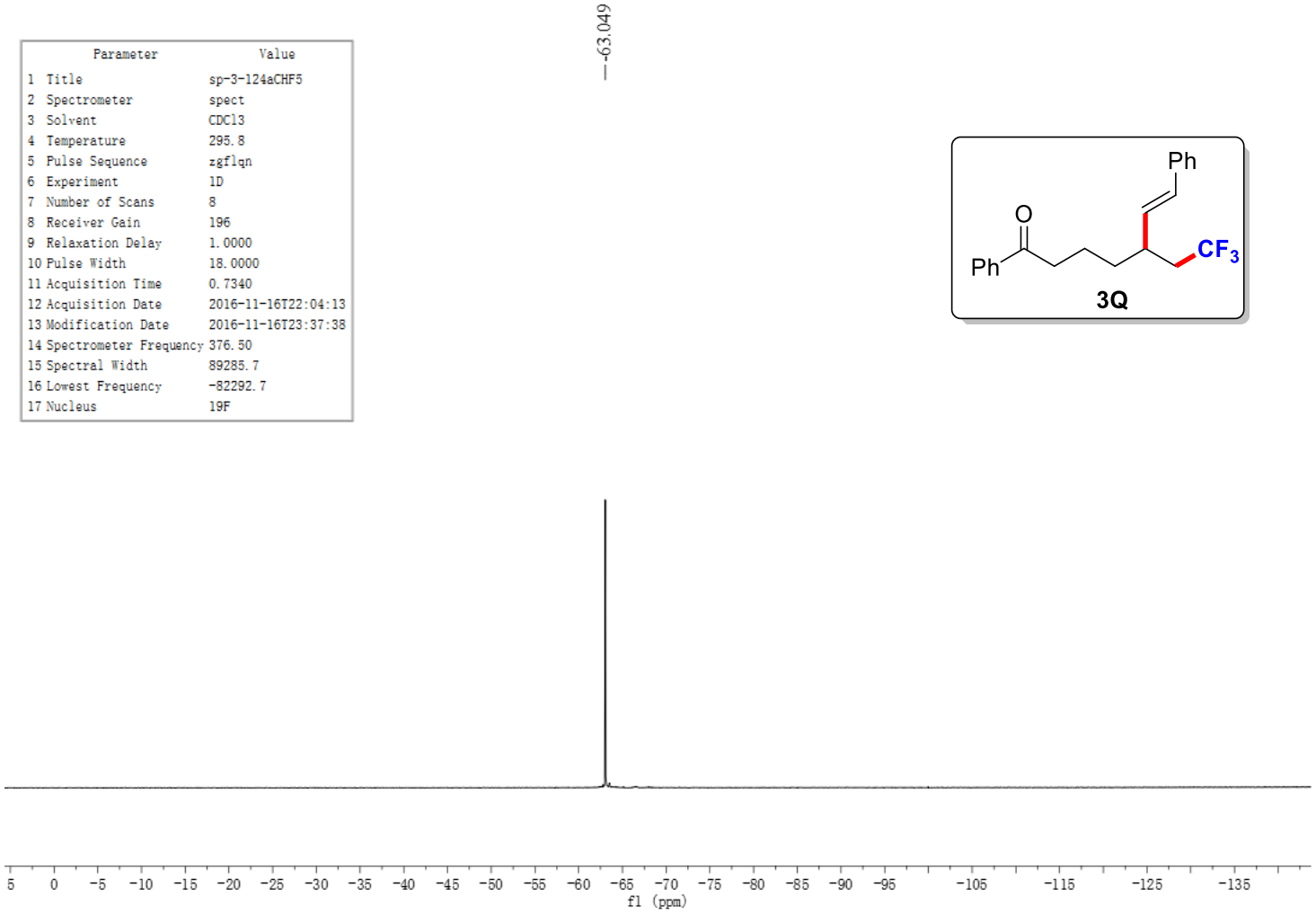


^{13}C NMR Spectrum of Compound **3Q**

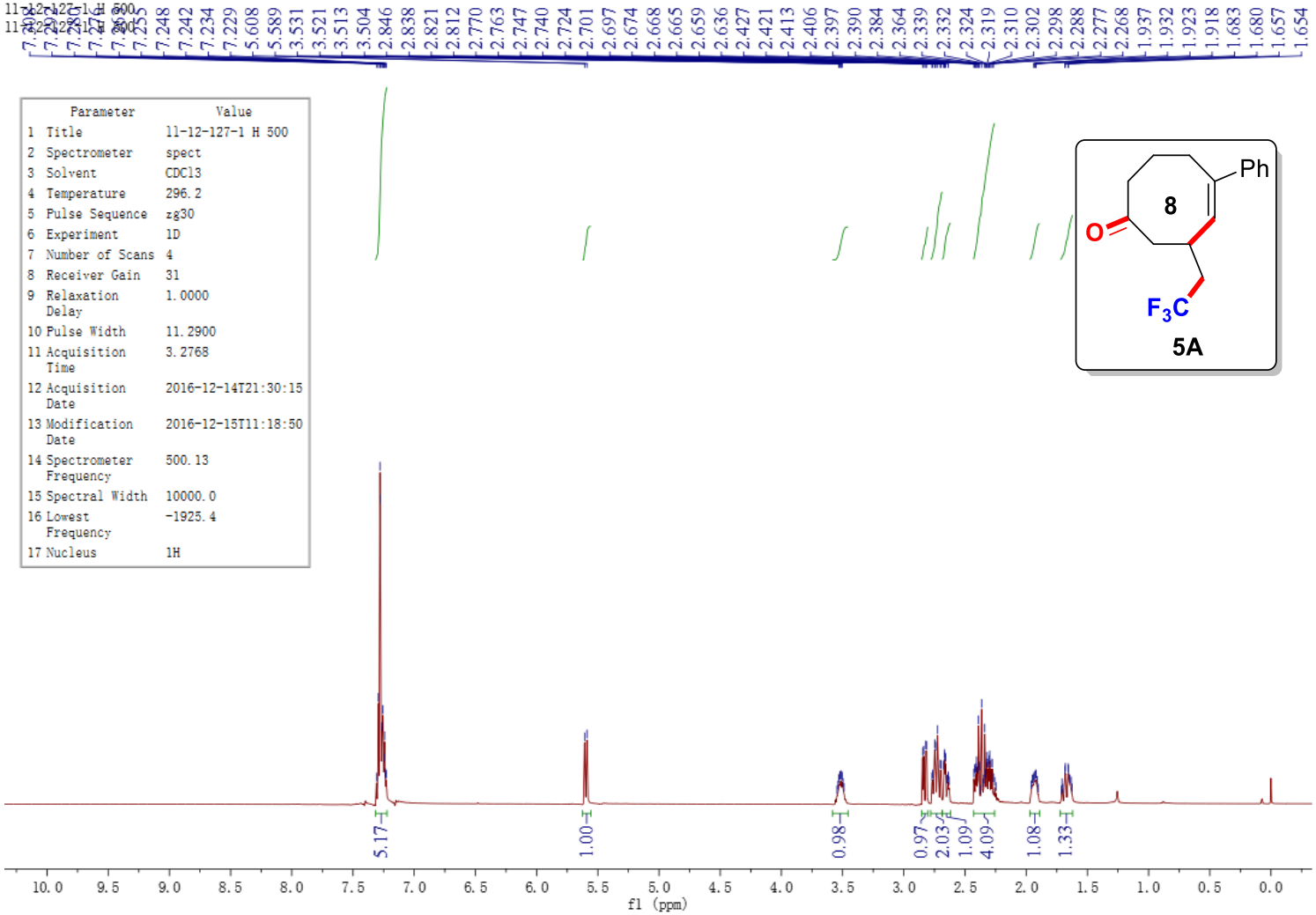


^{19}F NMR Spectrum of Compound **3Q**

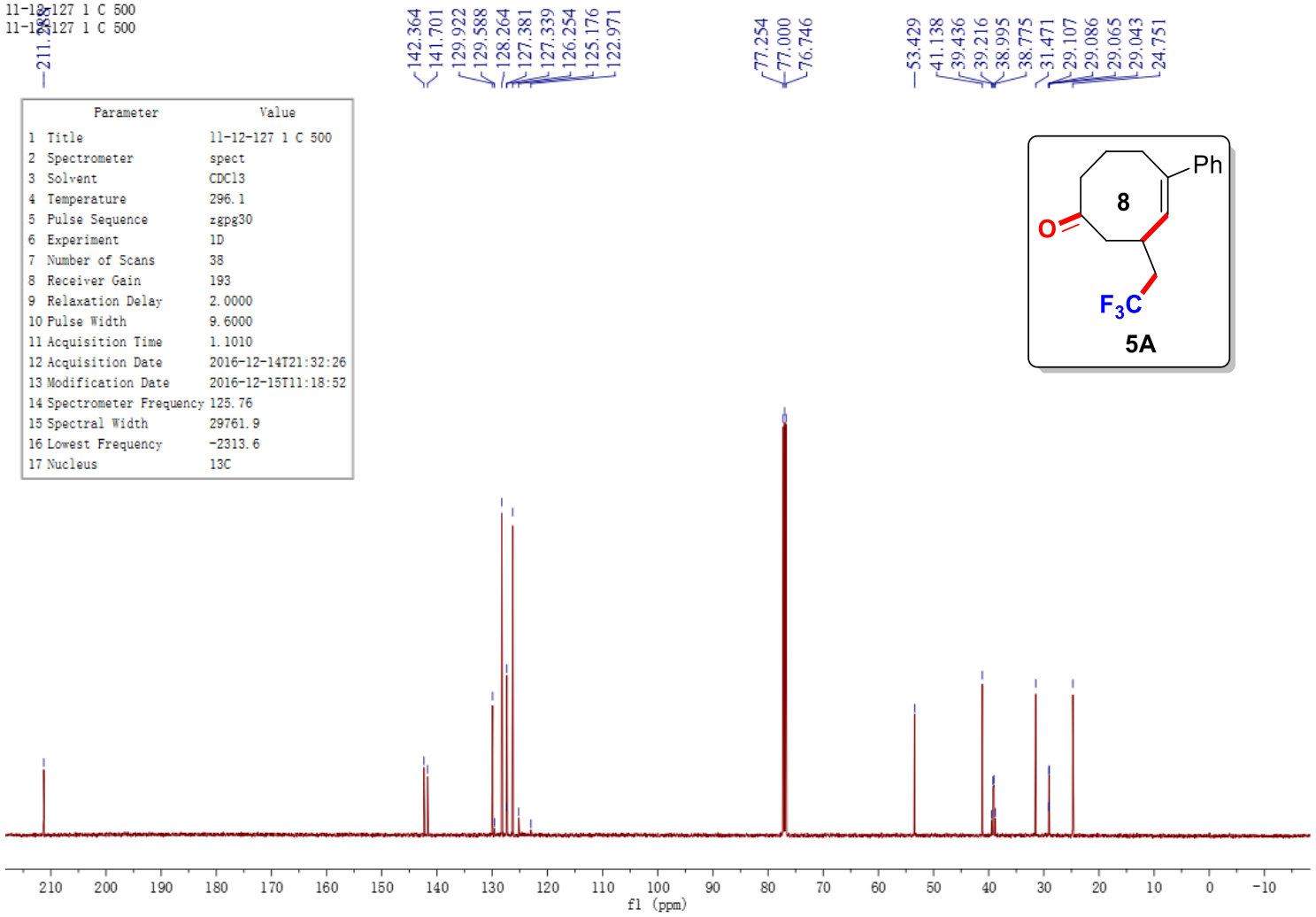
	Parameter	Value
1	Title	sp-3-124aCHF5
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	295.8
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-16T22:04:13
13	Modification Date	2016-11-16T23:37:38
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **5A**



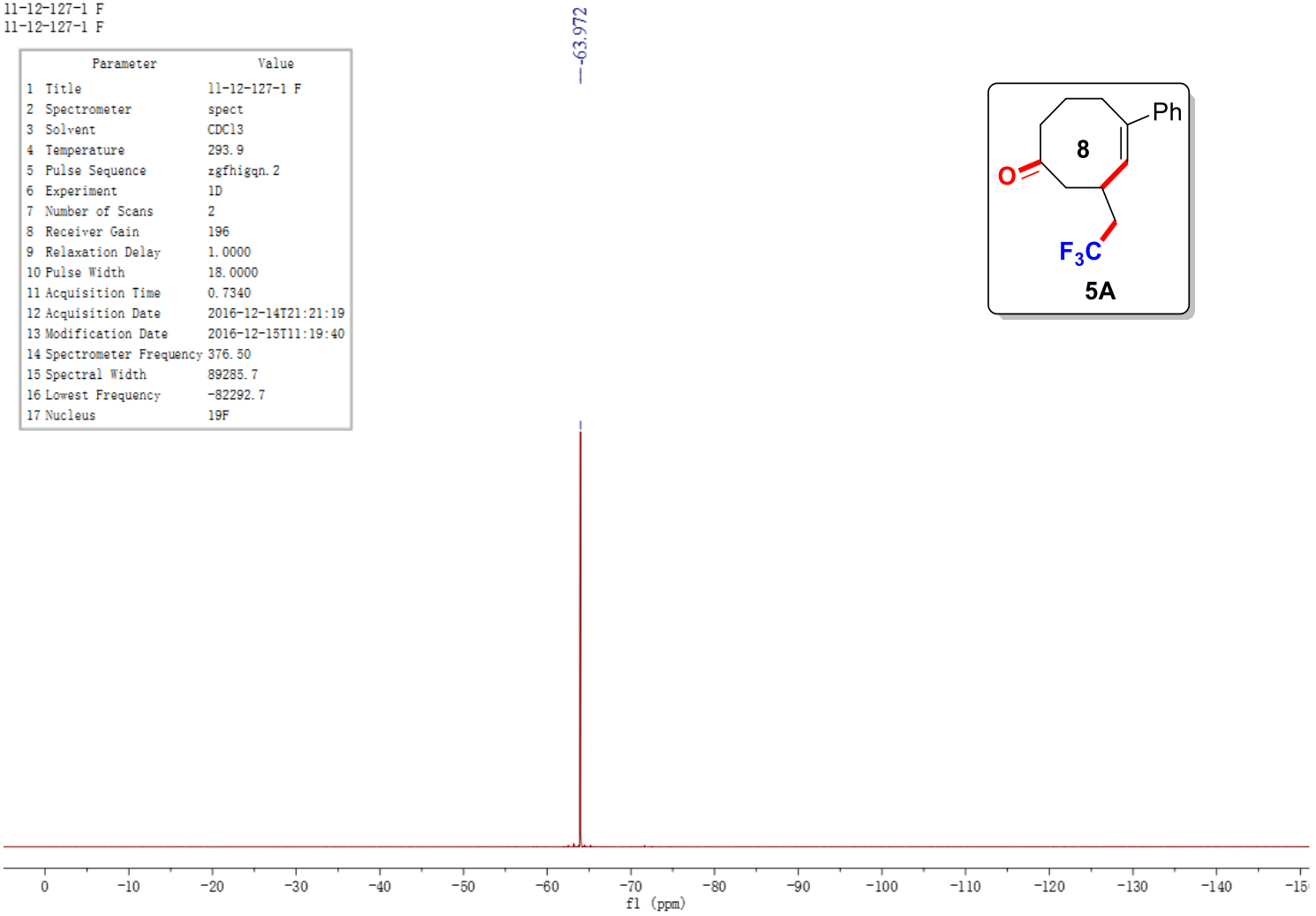
^{13}C NMR Spectrum of Compound **5A**



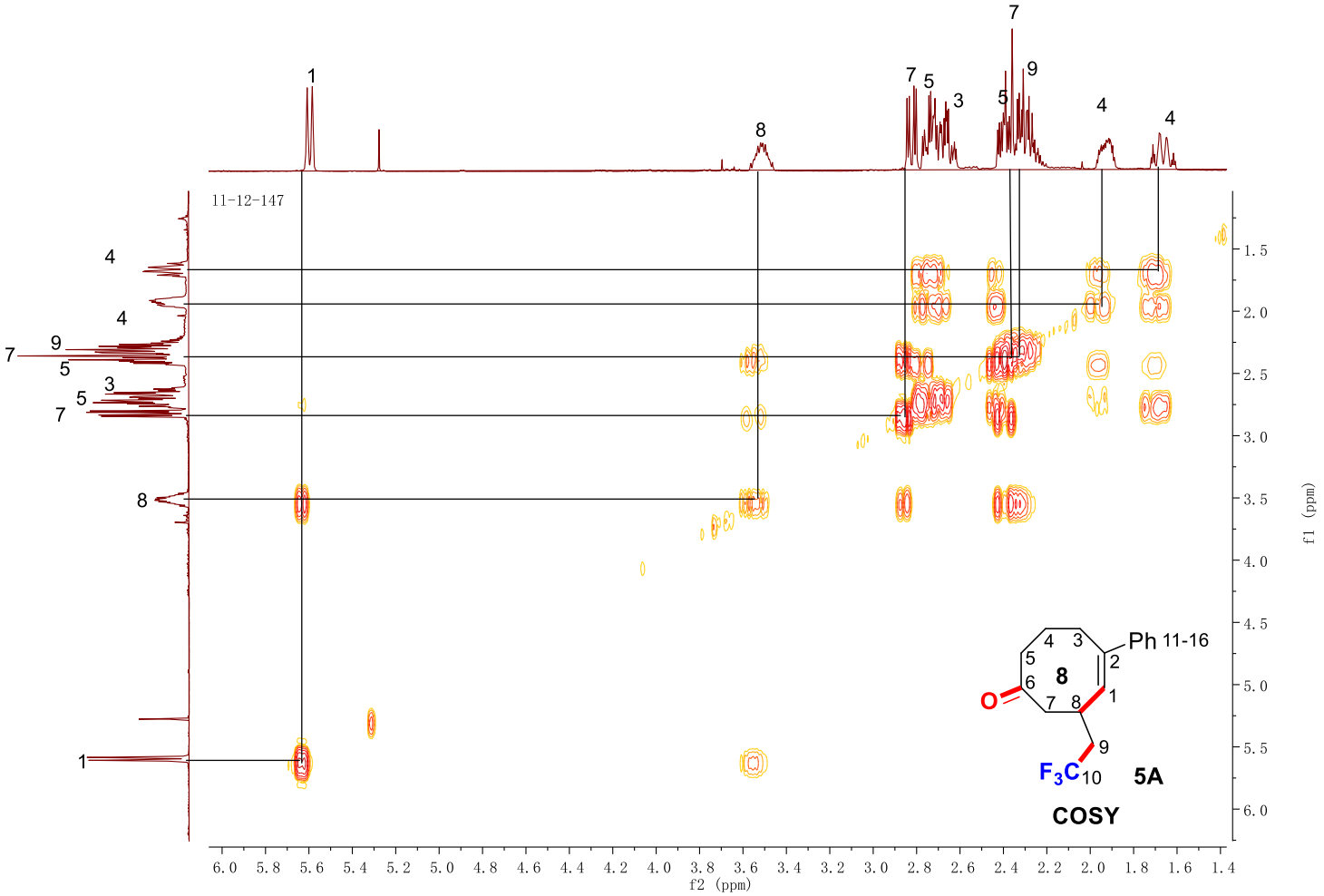
^{19}F NMR Spectrum of Compound **5A**

11-12-127-1 F
11-12-127-1 F

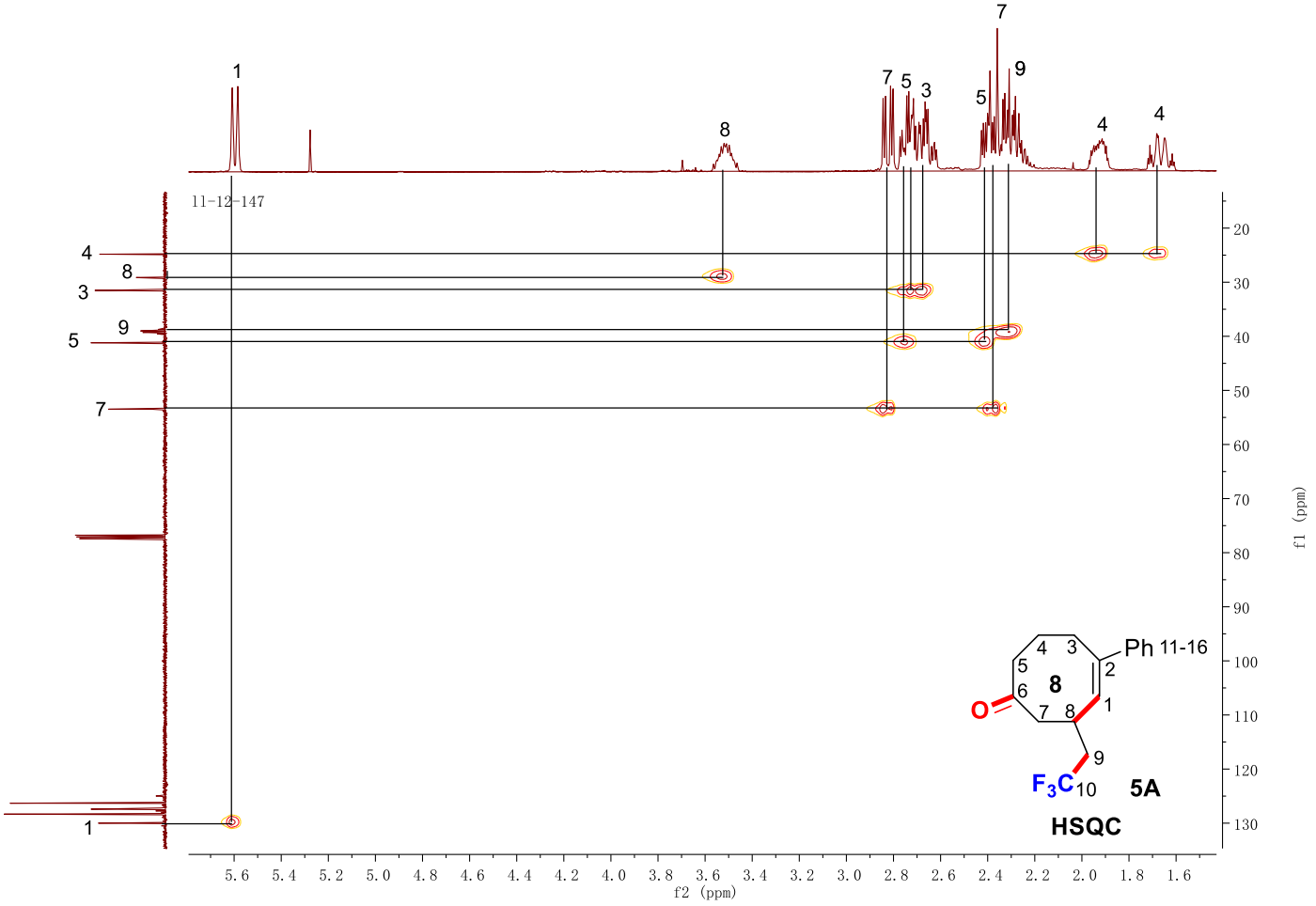
	Parameter	Value
1	Title	11-12-127-1 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.9
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	2
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-12-14T21:21:19
13	Modification Date	2016-12-15T11:19:40
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



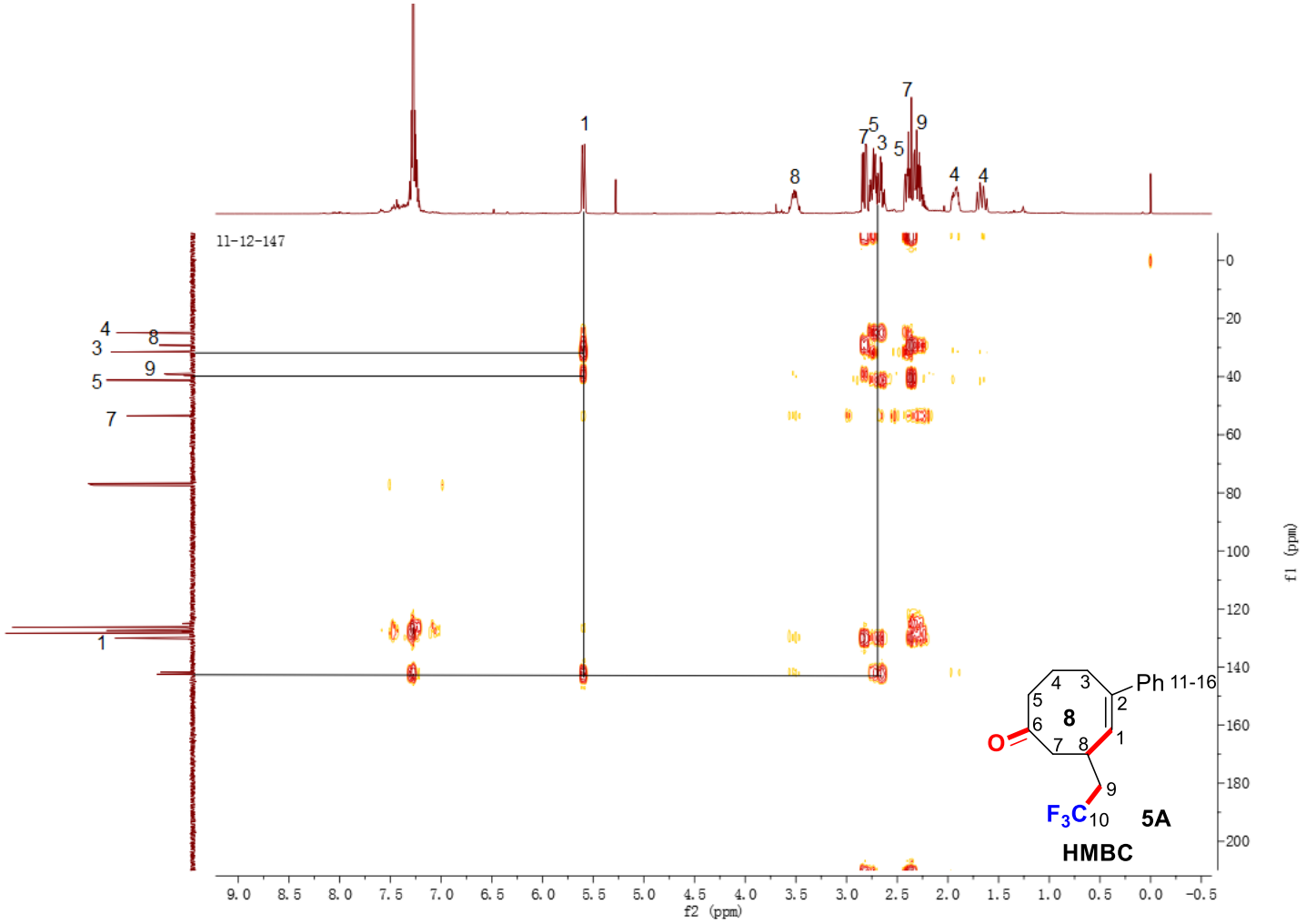
COSY of compound **5A**



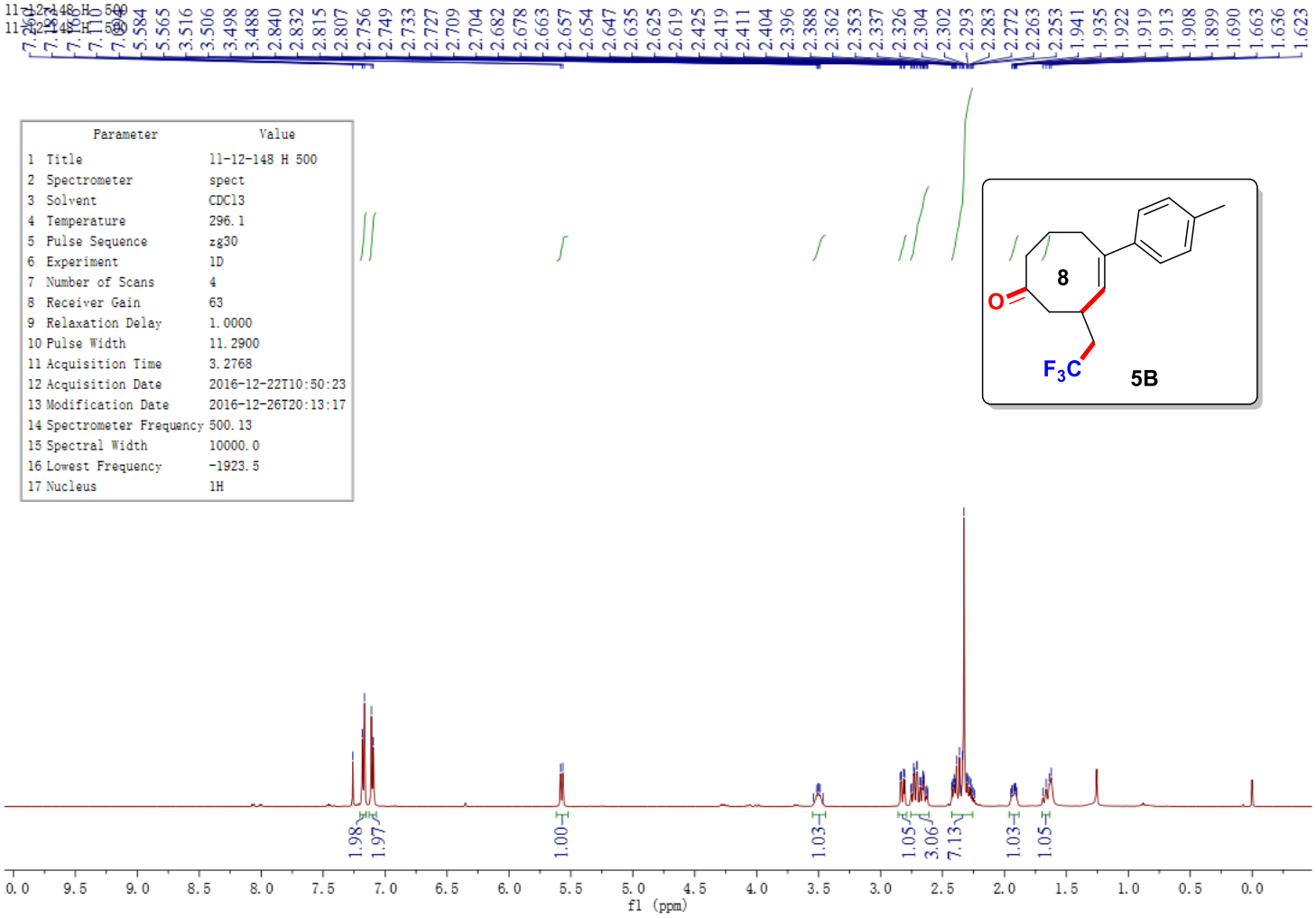
HSQC of compound **5A**



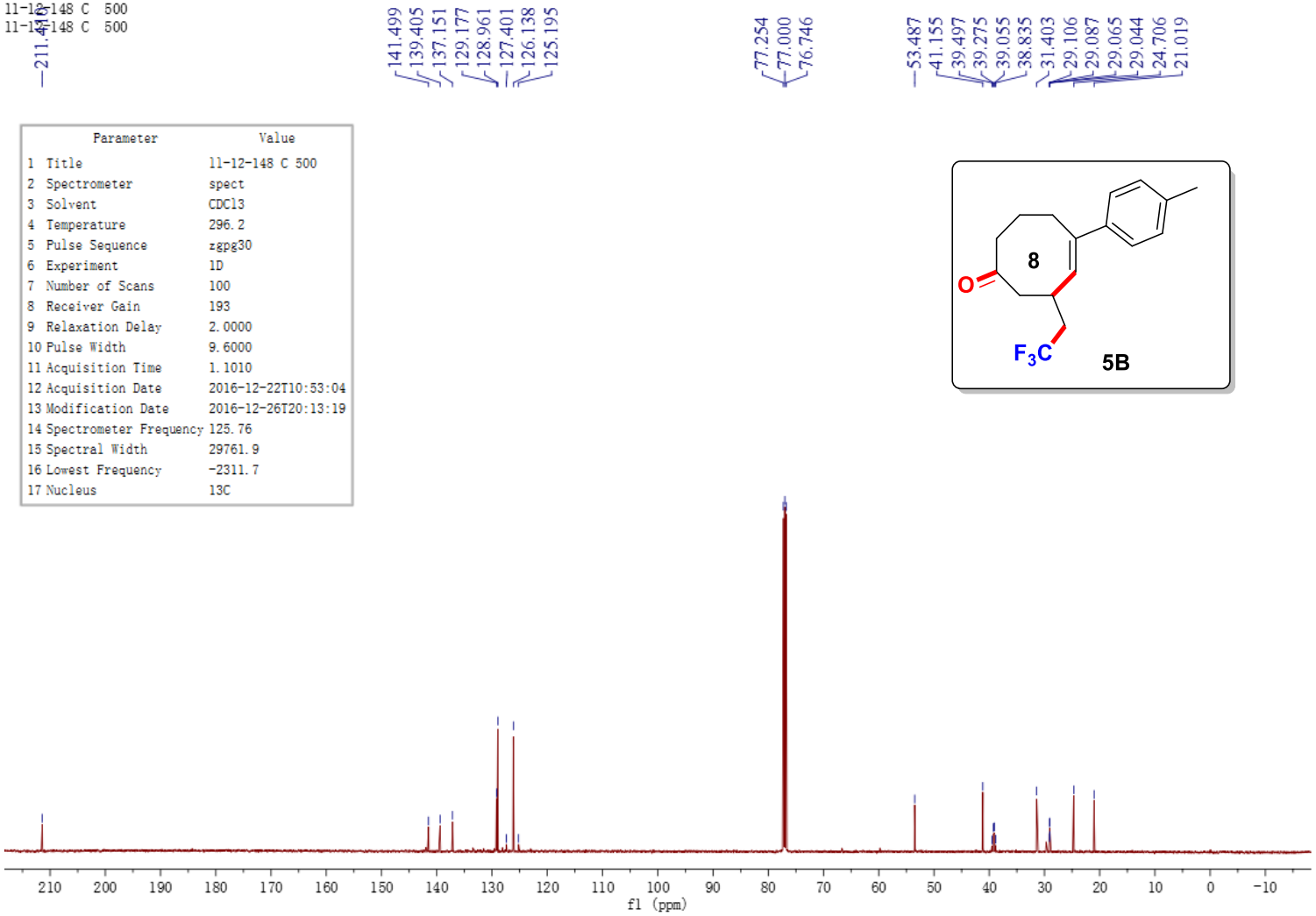
HMBC of compound **5A**



^{1}H NMR Spectrum of Compound **5B**



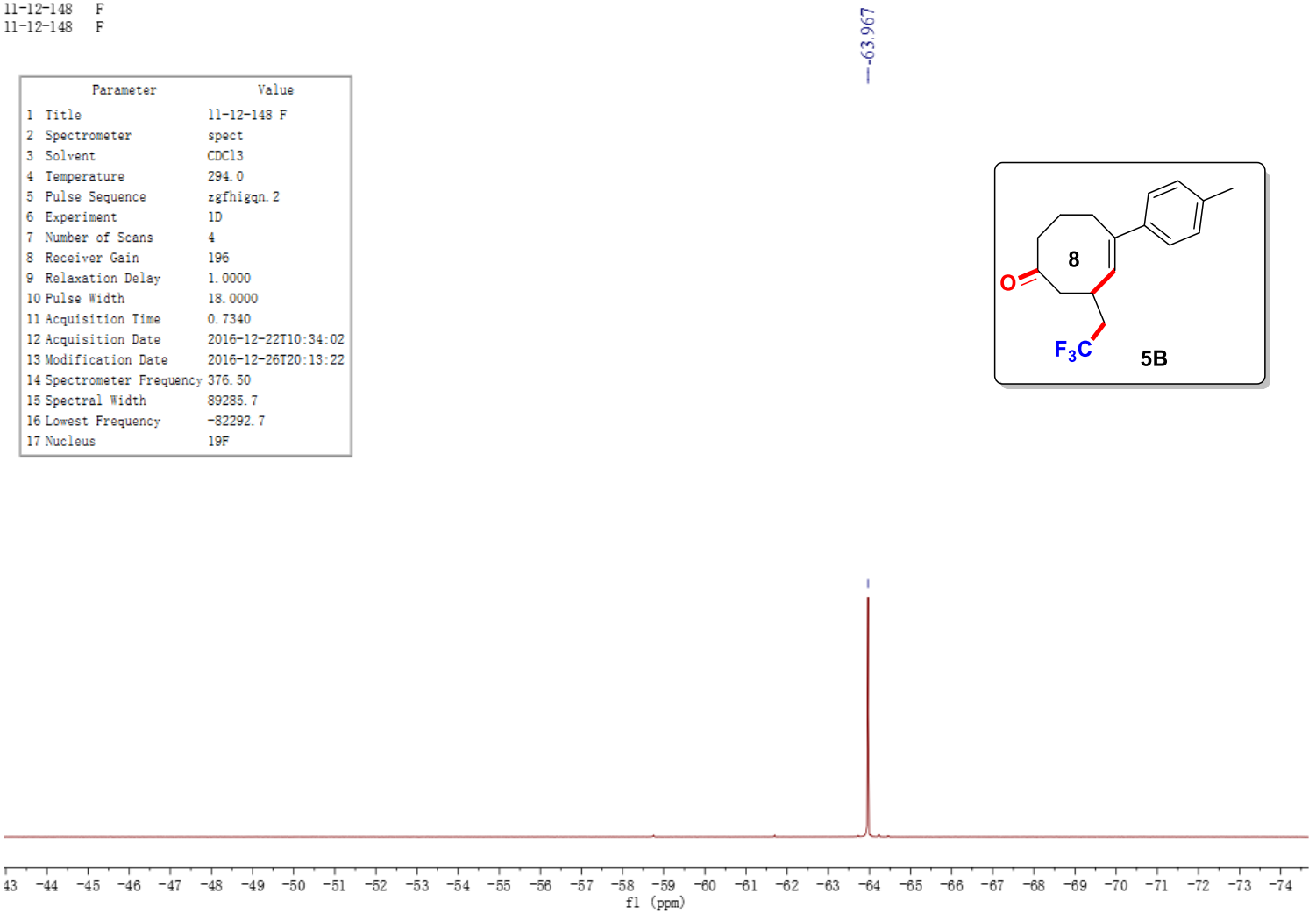
^{13}C NMR Spectrum of Compound **5B**



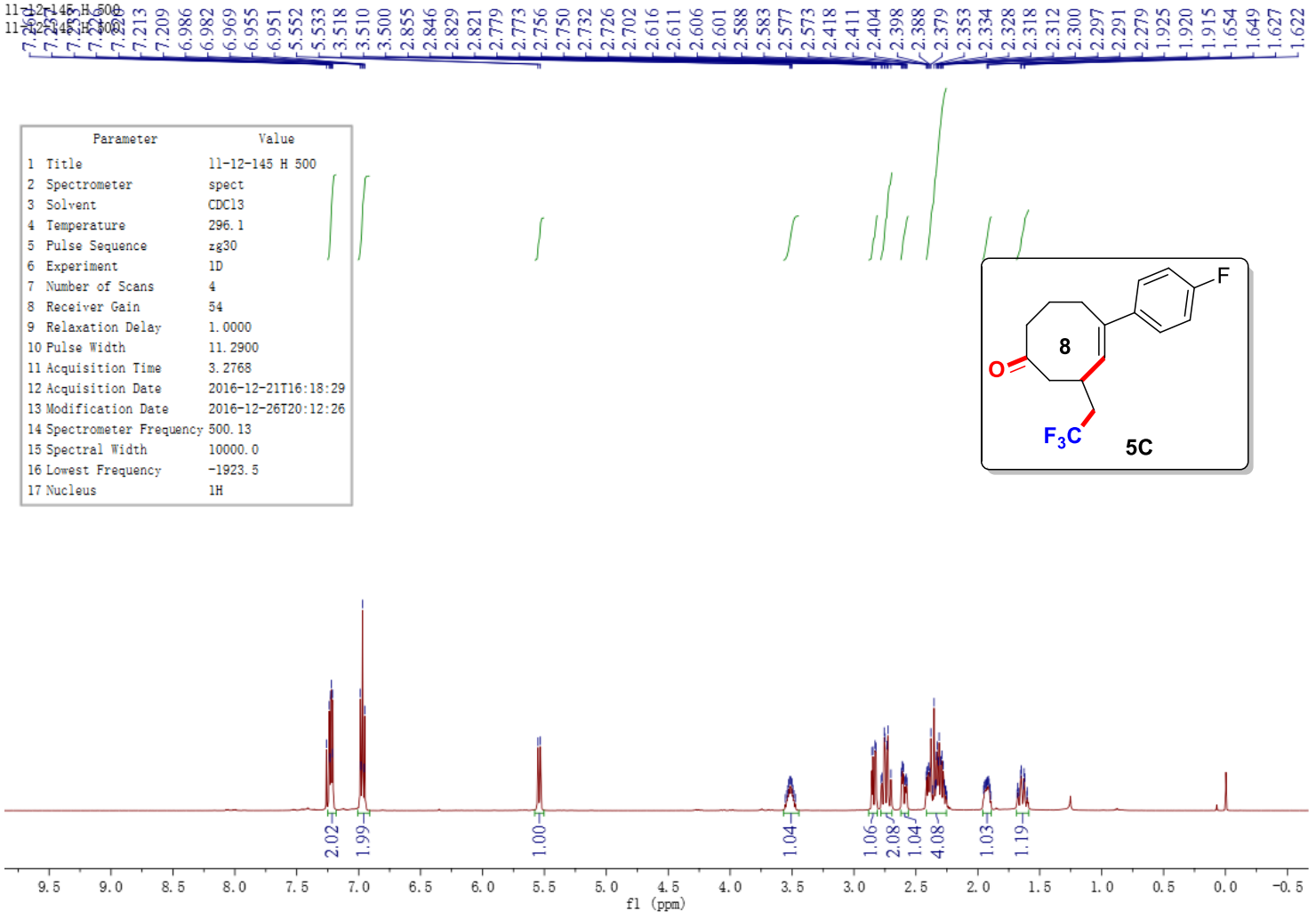
^{19}F NMR Spectrum of Compound **5B**

11-12-148 F
11-12-148 F

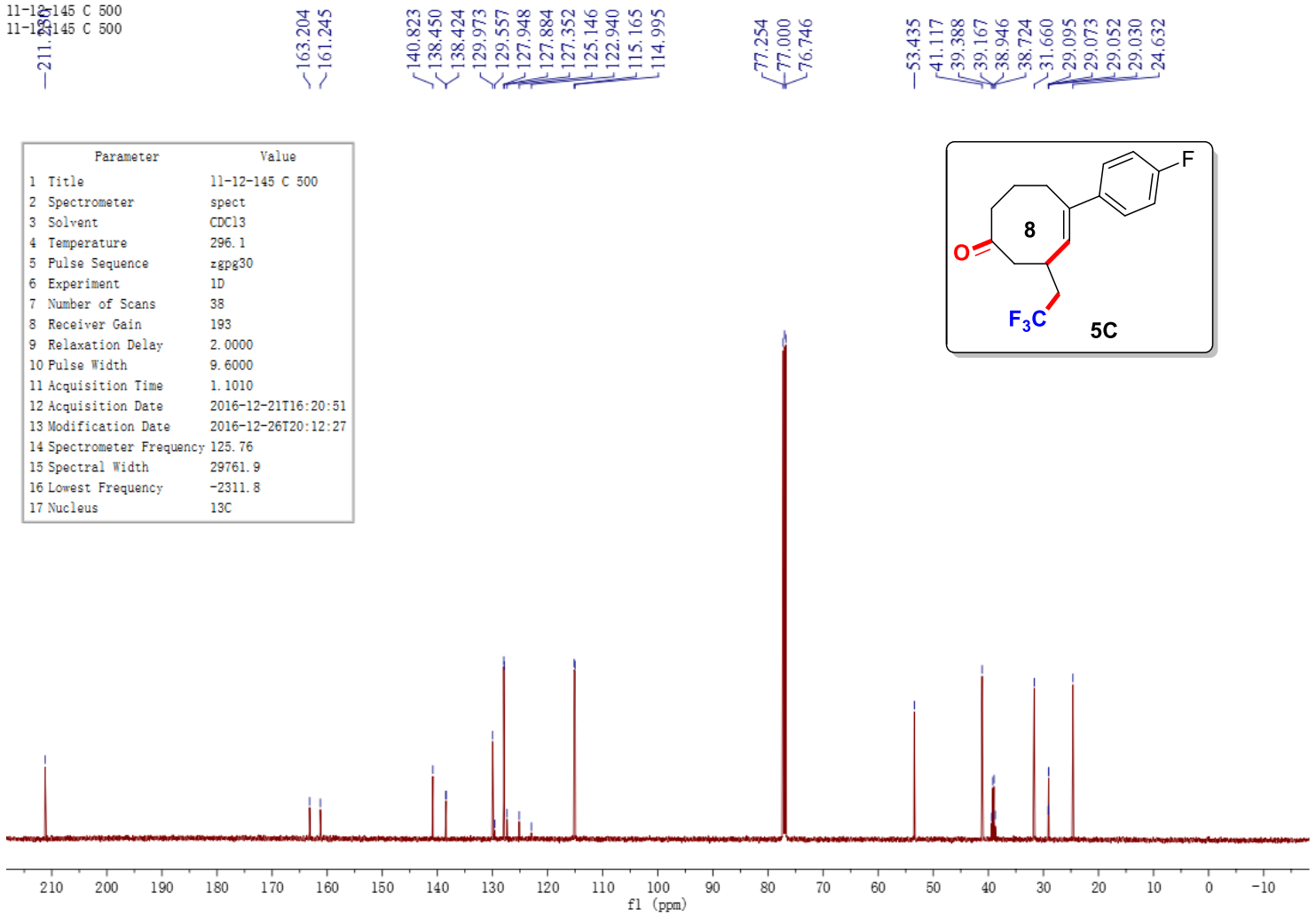
Parameter	Value
1 Title	11-12-148 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.0
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	4
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-12-22T10:34:02
13 Modification Date	2016-12-26T20:13:22
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



^{1}H NMR Spectrum of Compound **5C**



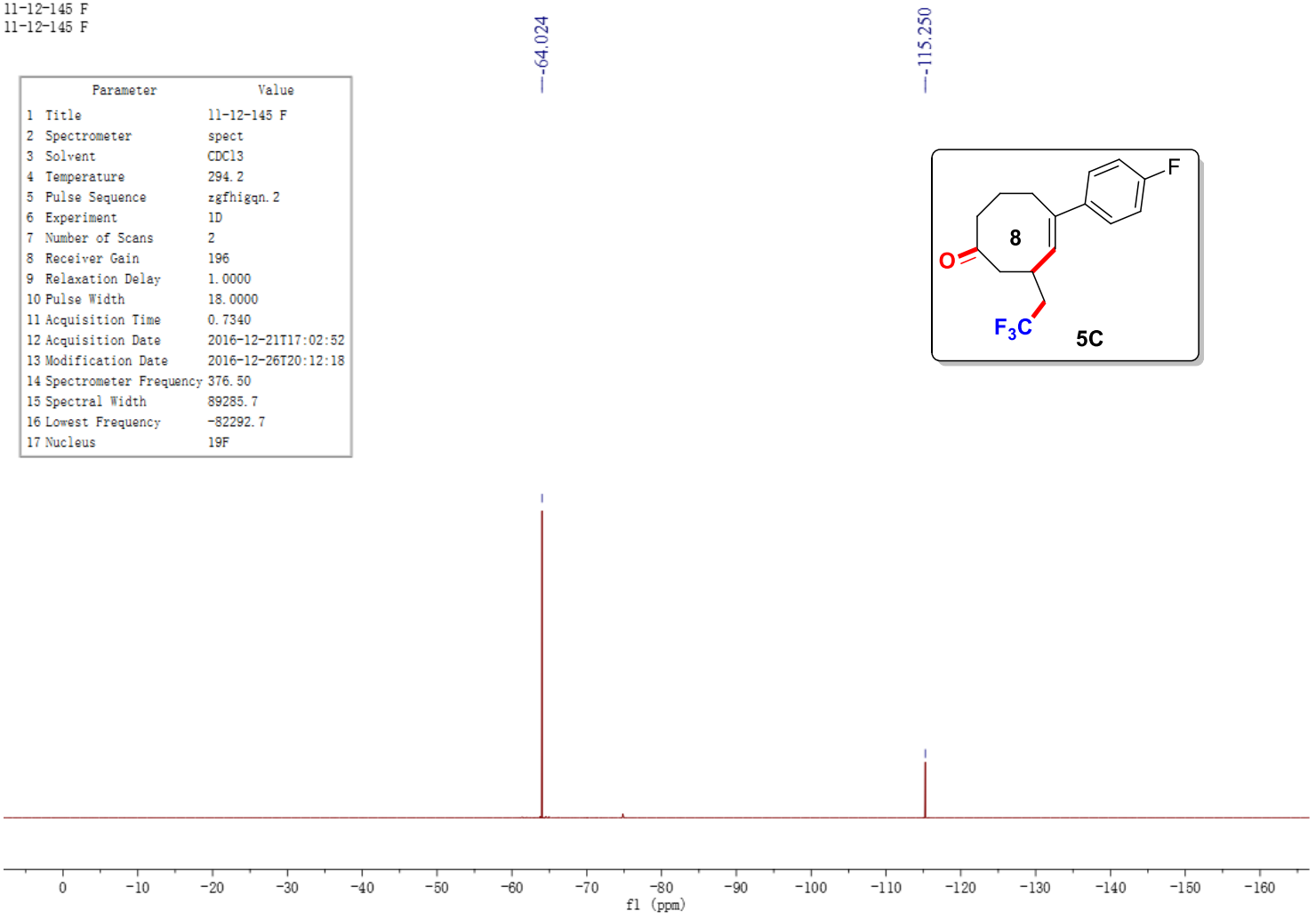
^{13}C NMR Spectrum of Compound **5C**



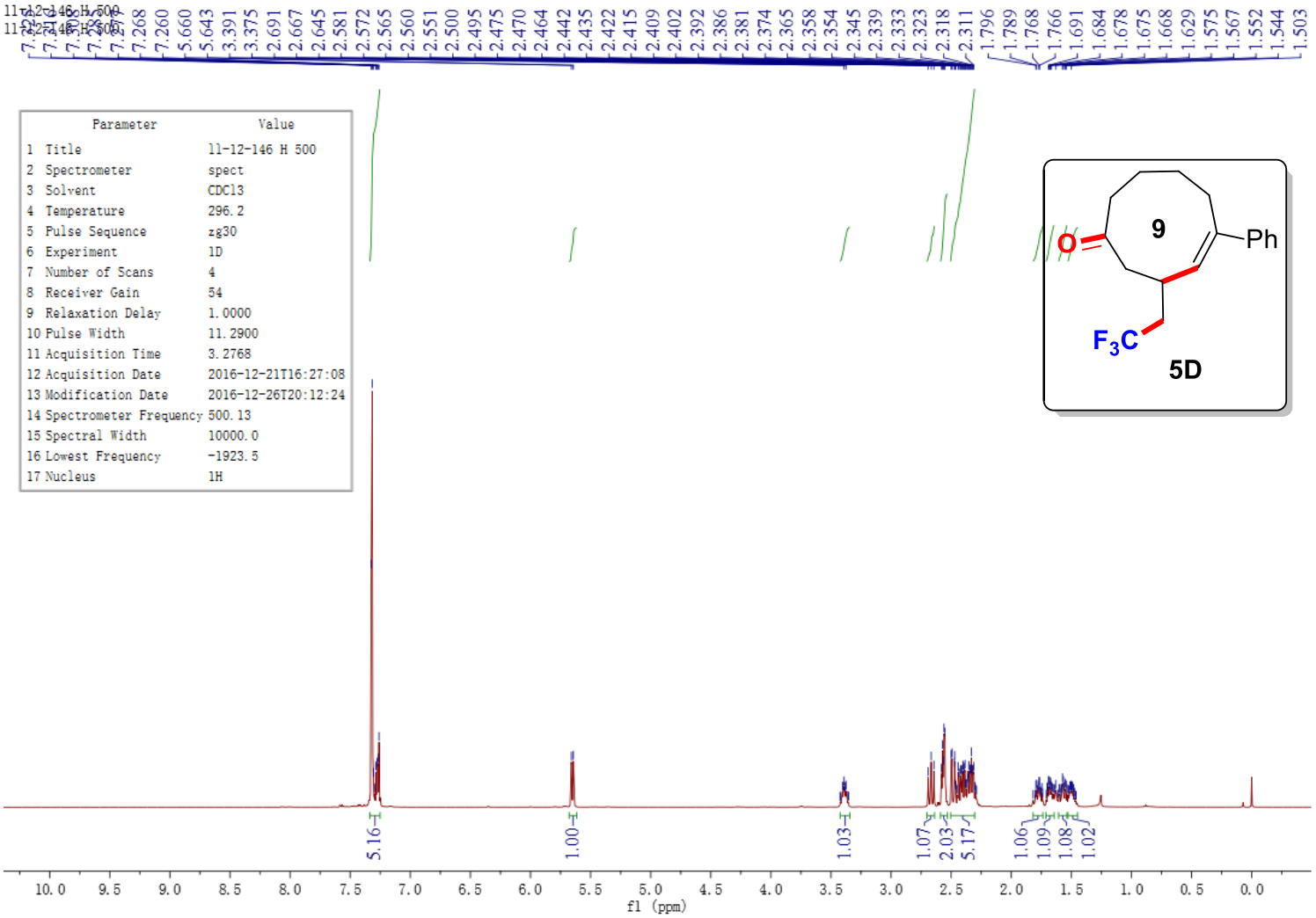
^{19}F NMR Spectrum of Compound **5C**

11-12-145 F
11-12-145 F

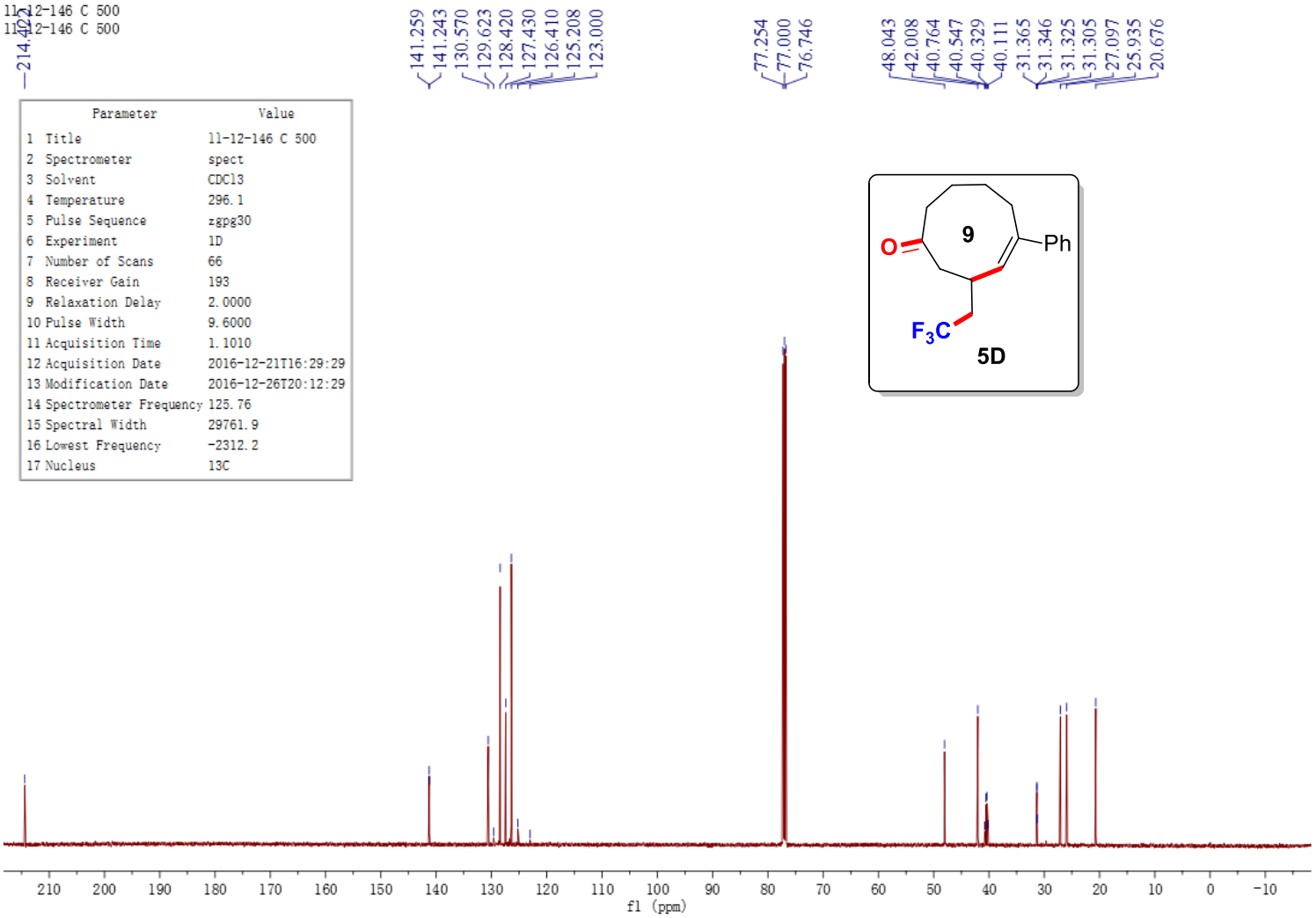
	Parameter	Value
1	Title	11-12-145 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.2
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	2
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-12-21T17:02:52
13	Modification Date	2016-12-26T20:12:18
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **5D**



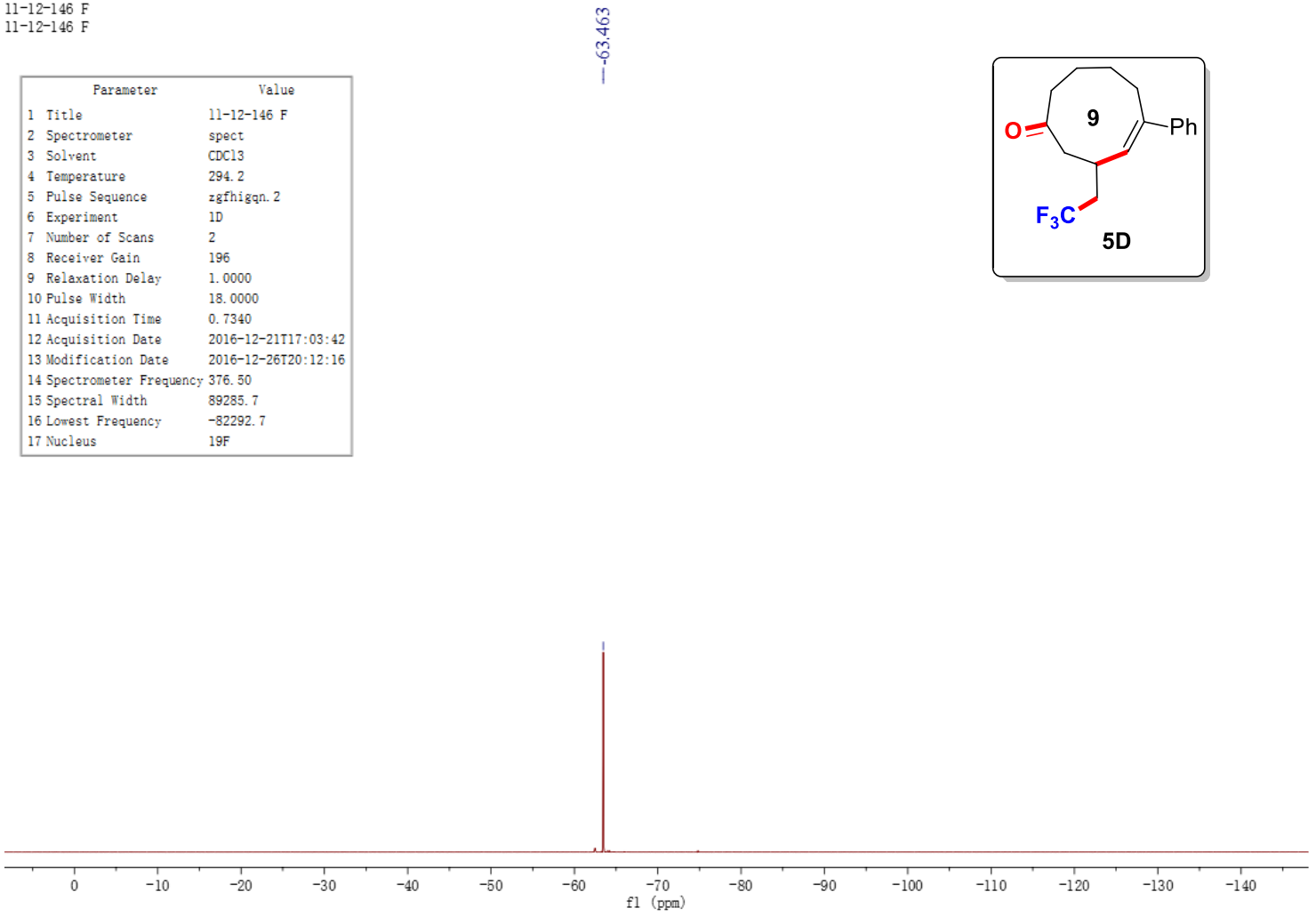
^{13}C NMR Spectrum of Compound **5D**



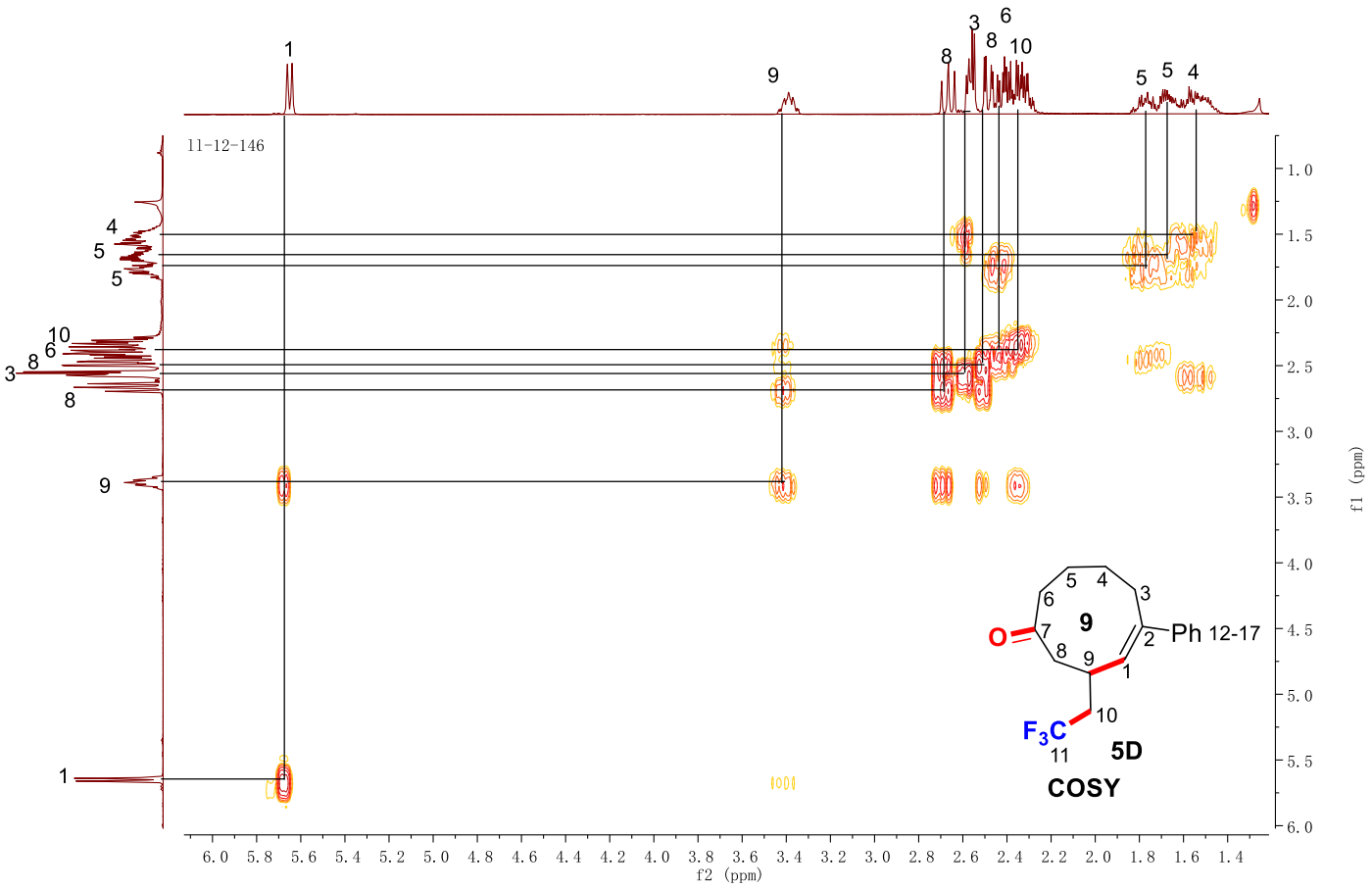
^{19}F NMR Spectrum of Compound **5D**

11-12-146 F
11-12-146 F

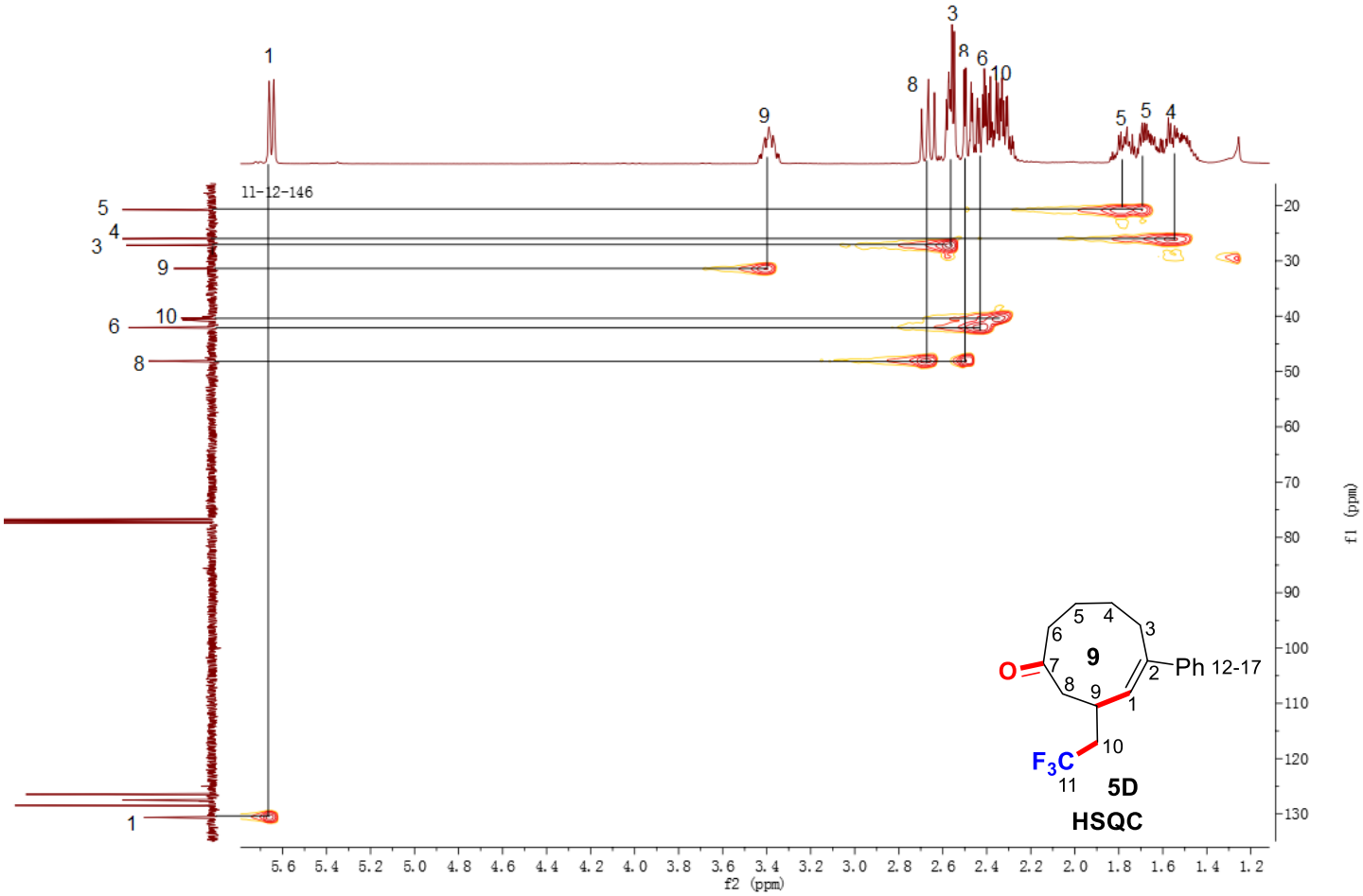
Parameter	Value
1 Title	11-12-146 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	294.2
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	2
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-12-21T17:03:42
13 Modification Date	2016-12-26T20:12:16
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



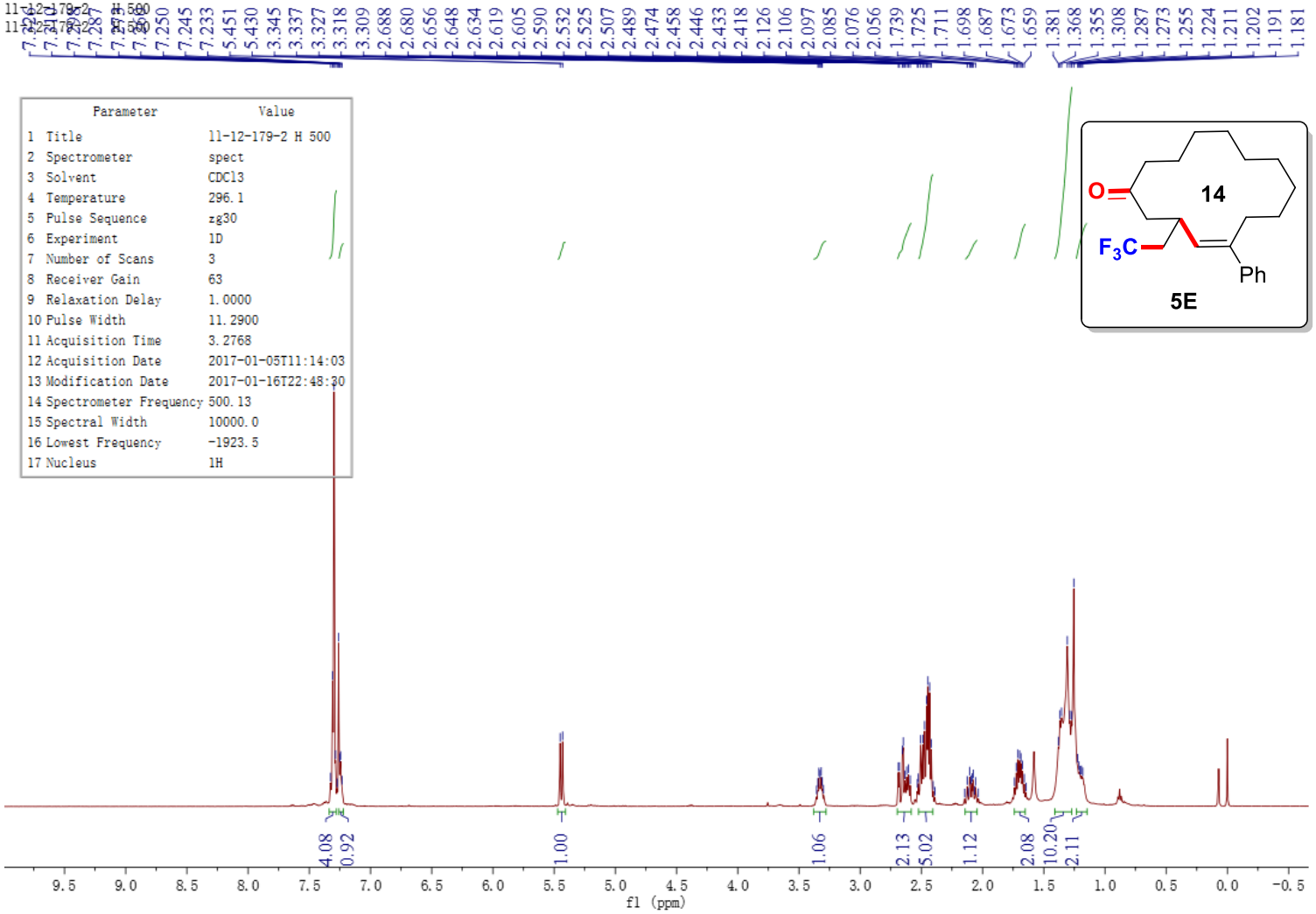
COSY of compound **5D**



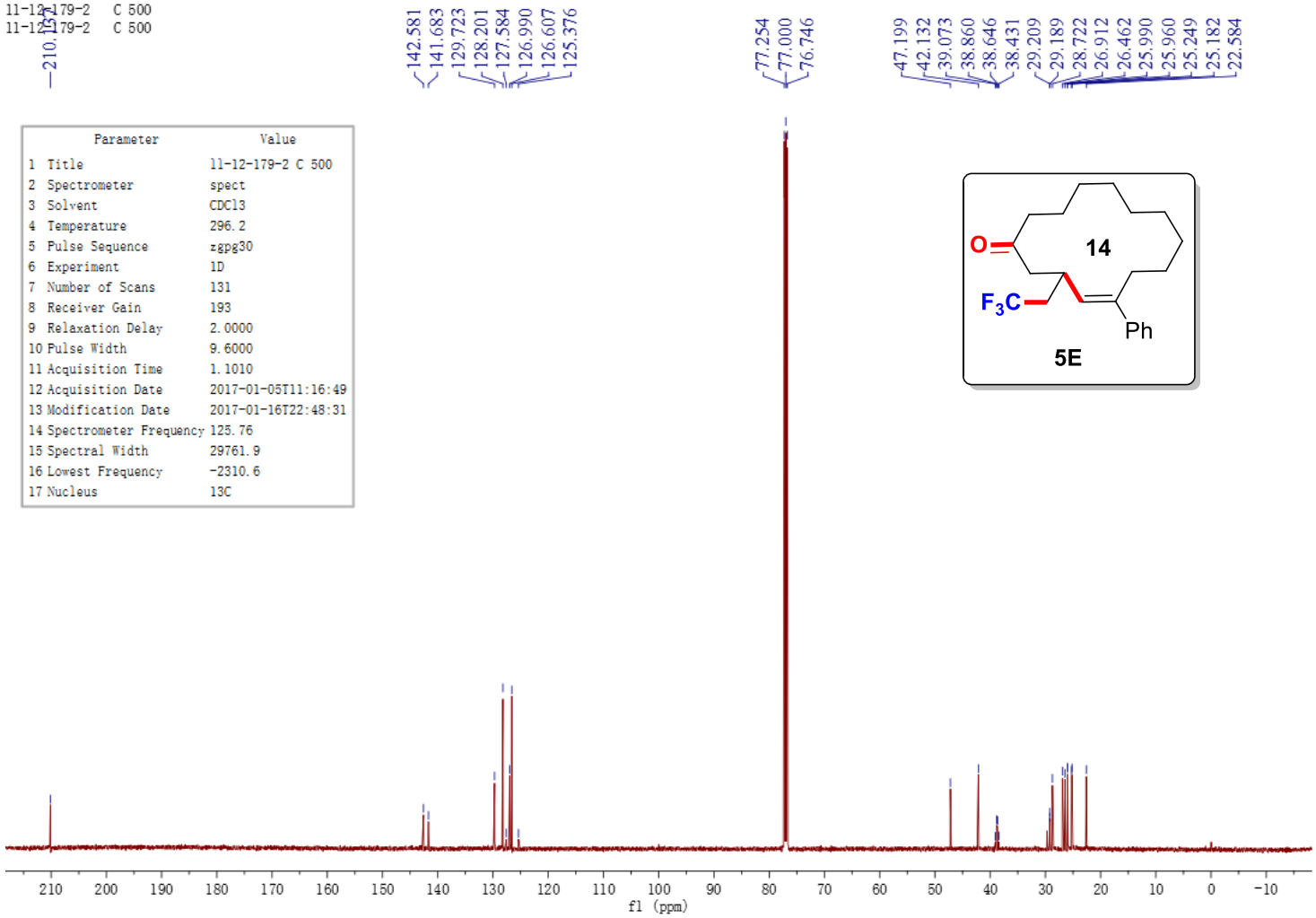
HSQC of compound **5D**



^{1}H NMR Spectrum of Compound **5E**



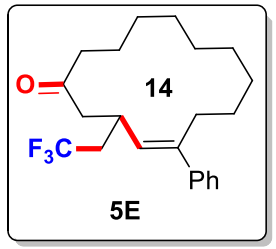
^{13}C NMR Spectrum of Compound **5E**



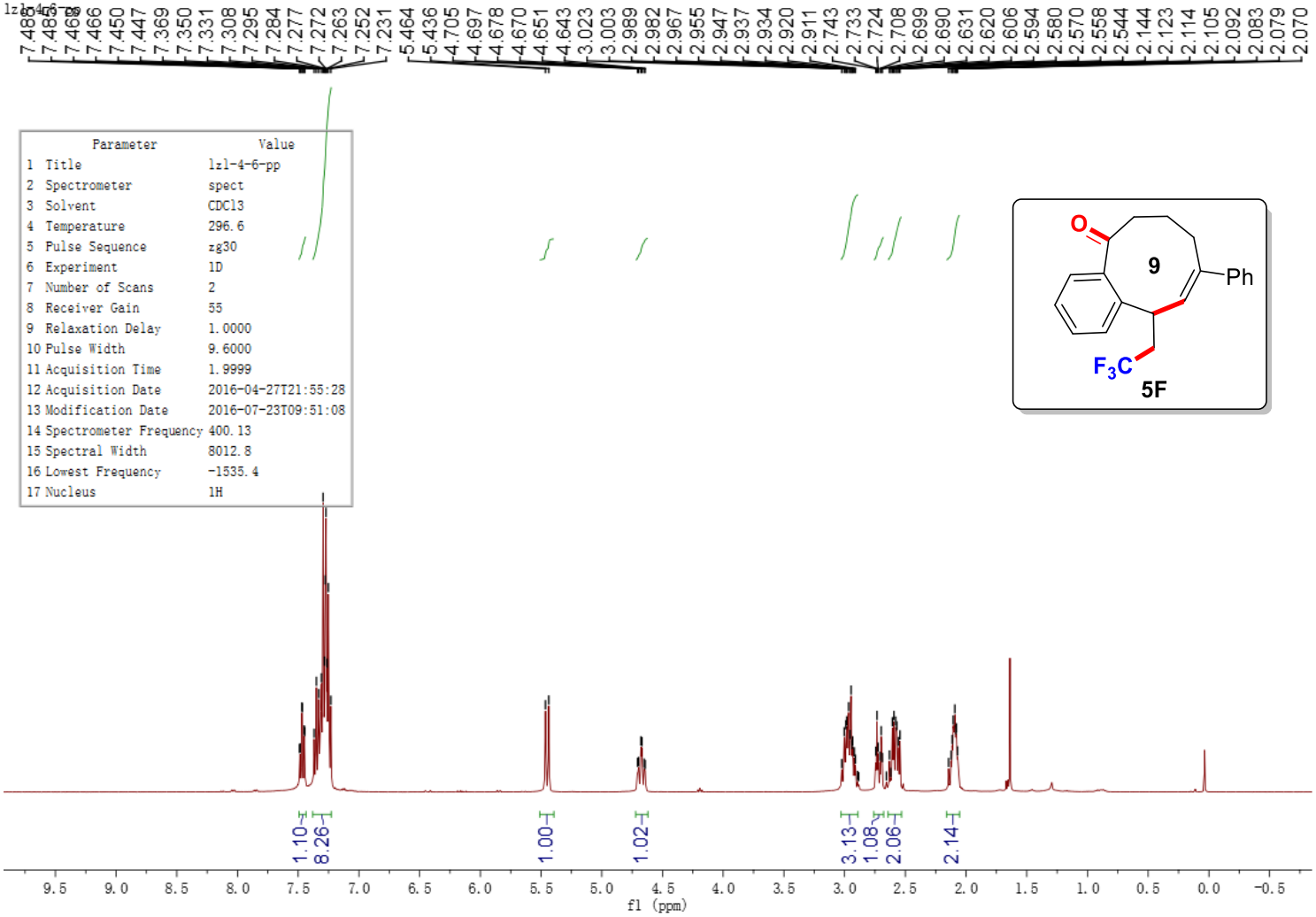
^{19}F NMR Spectrum of Compound **5E**

11-12-179-2 F
11-12-179-2 F

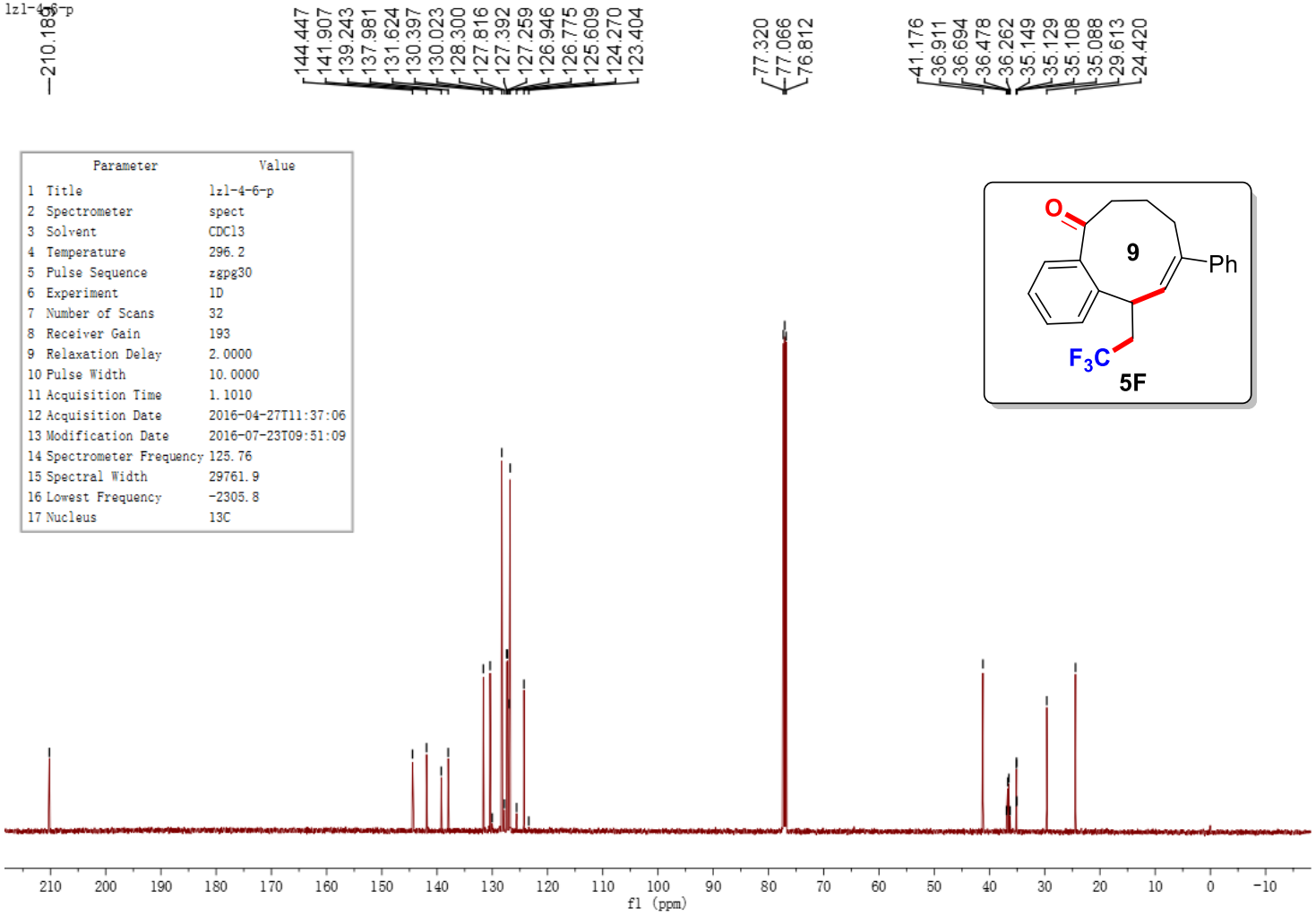
Parameter	Value
1 Title	11-12-179-2 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	293.9
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	2
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2017-01-05T10:59:10
13 Modification Date	2017-01-16T22:48:32
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



^{1}H NMR Spectrum of Compound **5F**



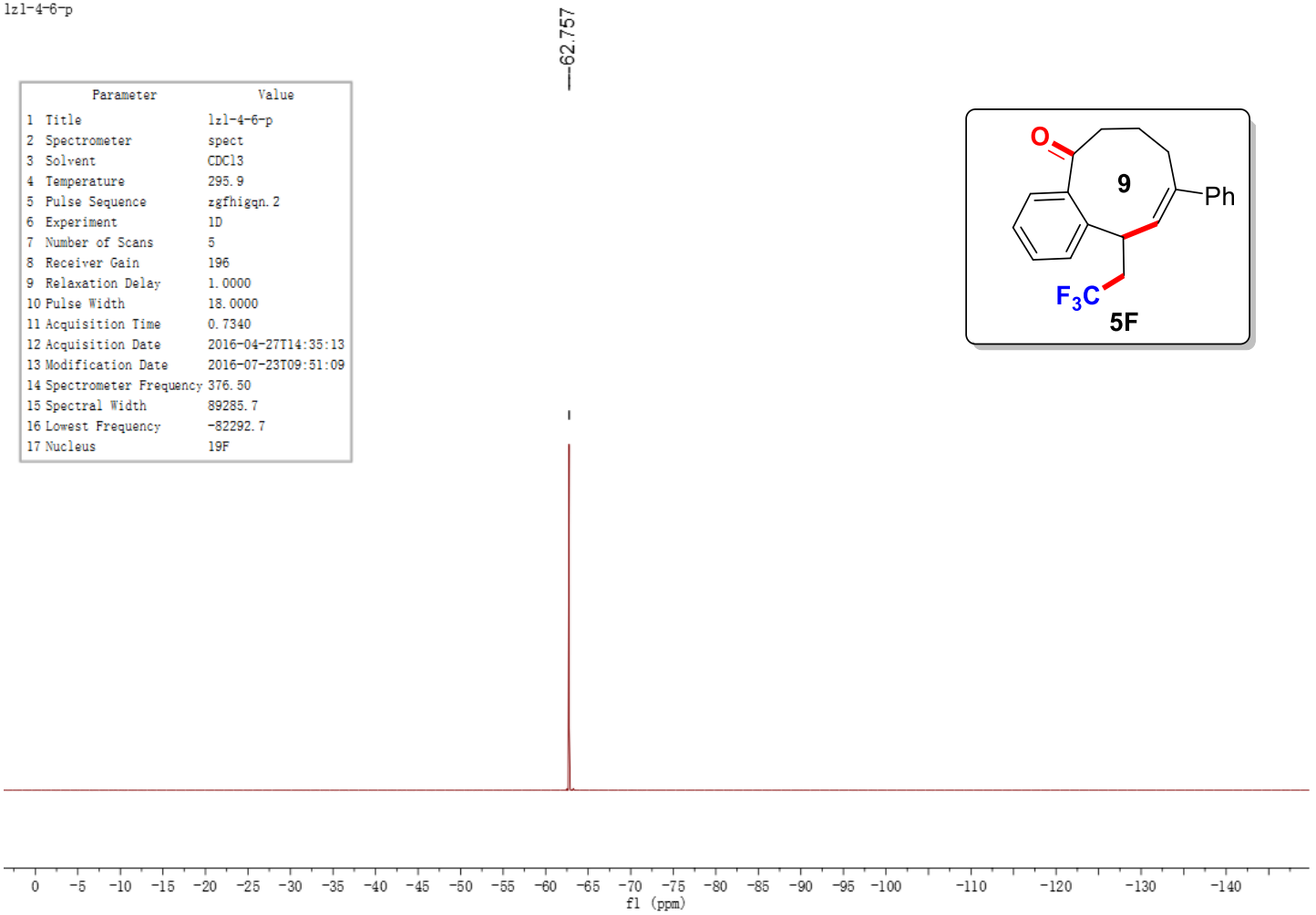
^{13}C NMR Spectrum of Compound **5F**



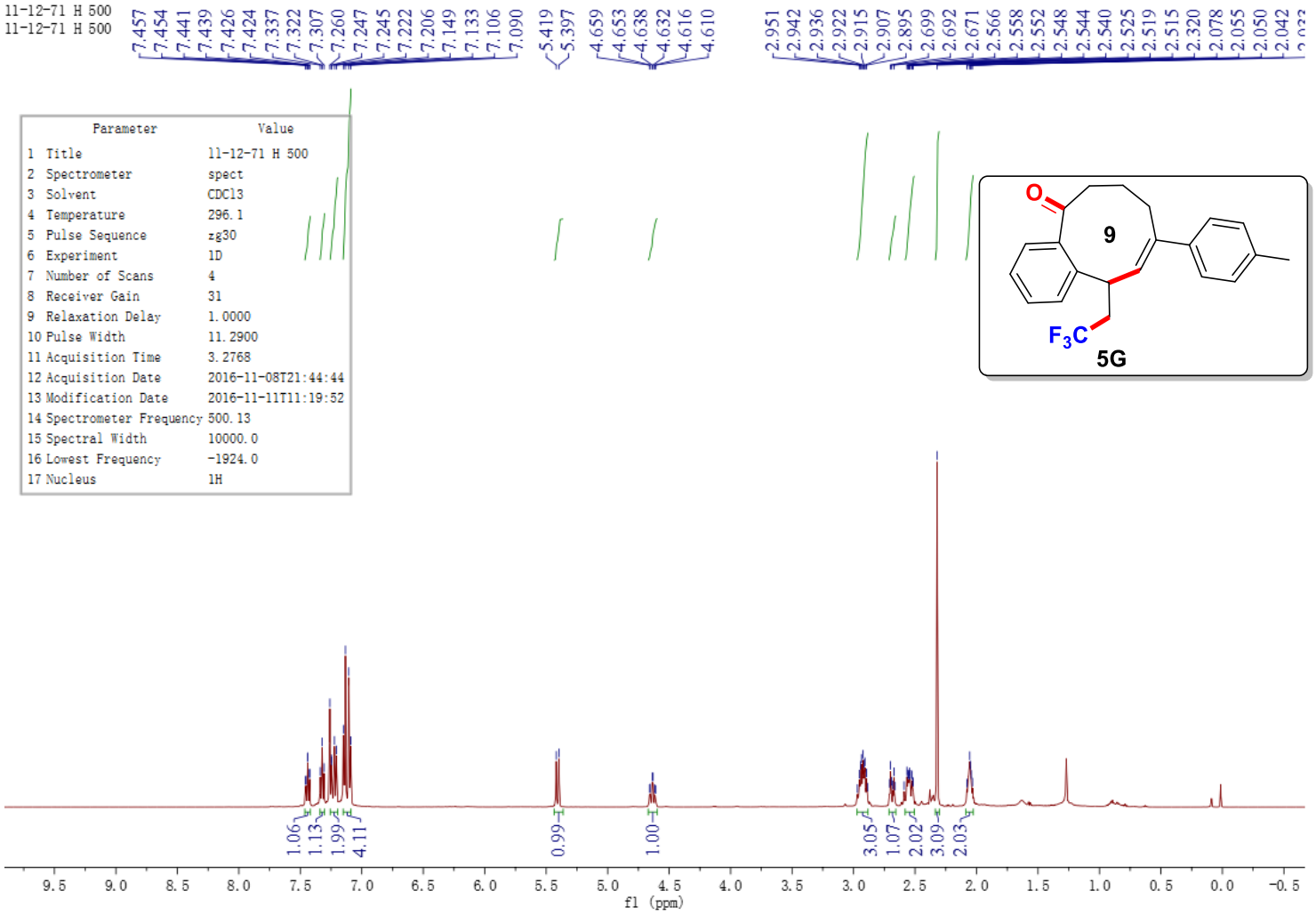
^{19}F NMR Spectrum of Compound **5F**

lzl-4-6-p

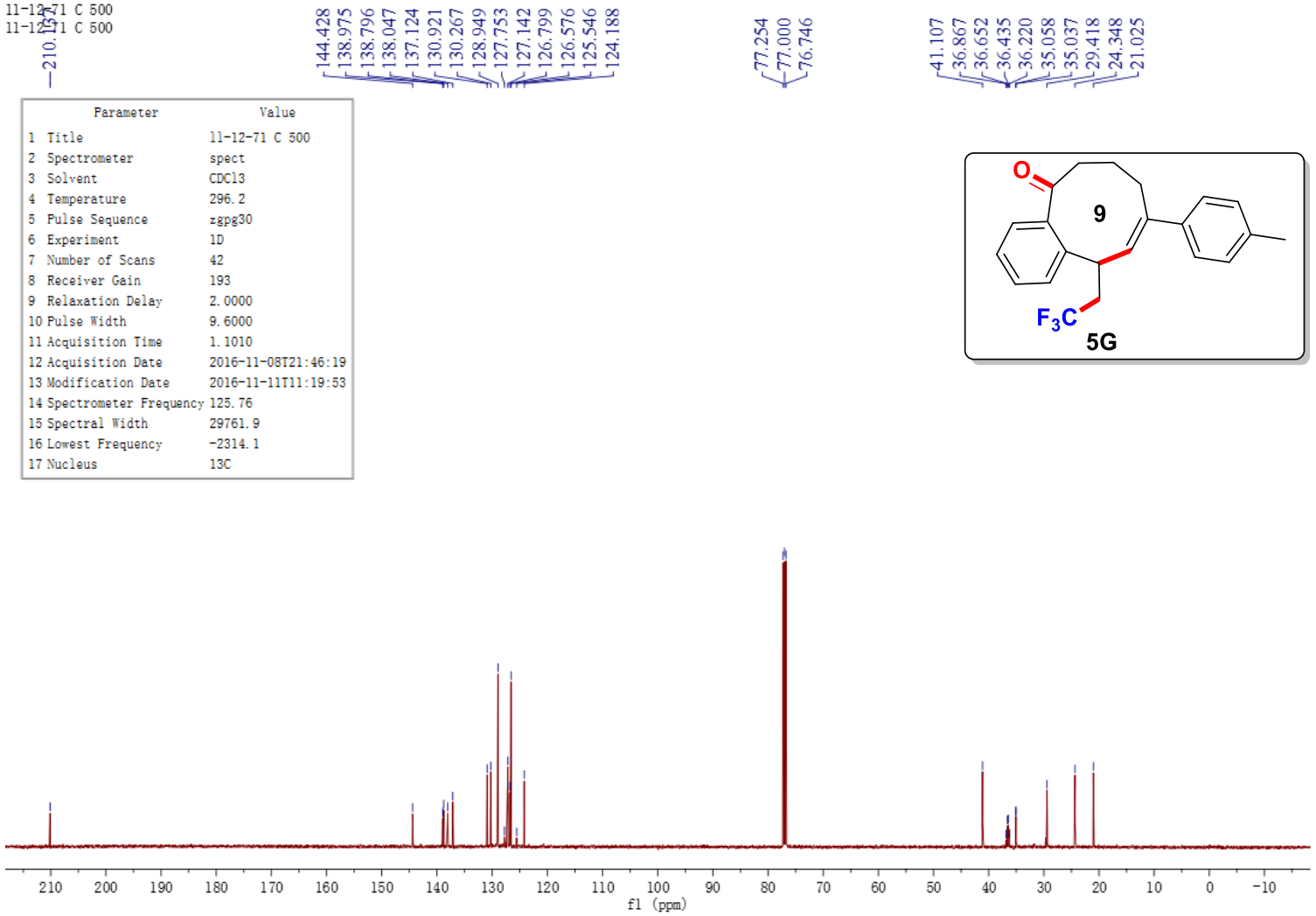
	Parameter	Value
1	Title	lzl-4-6-p
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	295.9
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	5
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-04-27T14:35:13
13	Modification Date	2016-07-23T09:51:09
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **5G**



^{13}C NMR Spectrum of Compound **5G**

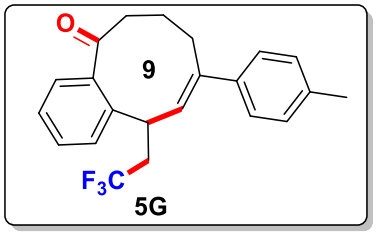


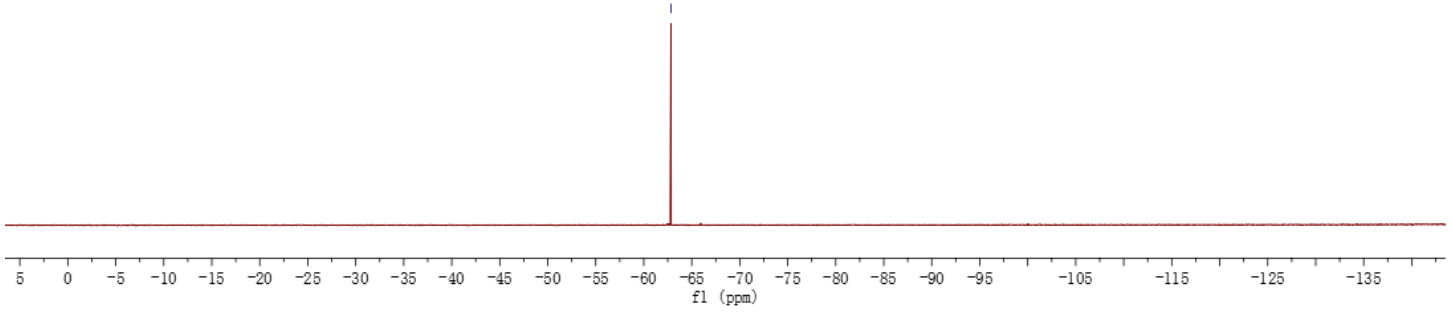
^{19}F NMR Spectrum of Compound **5G**

11-12-71 F
11-12-71 F

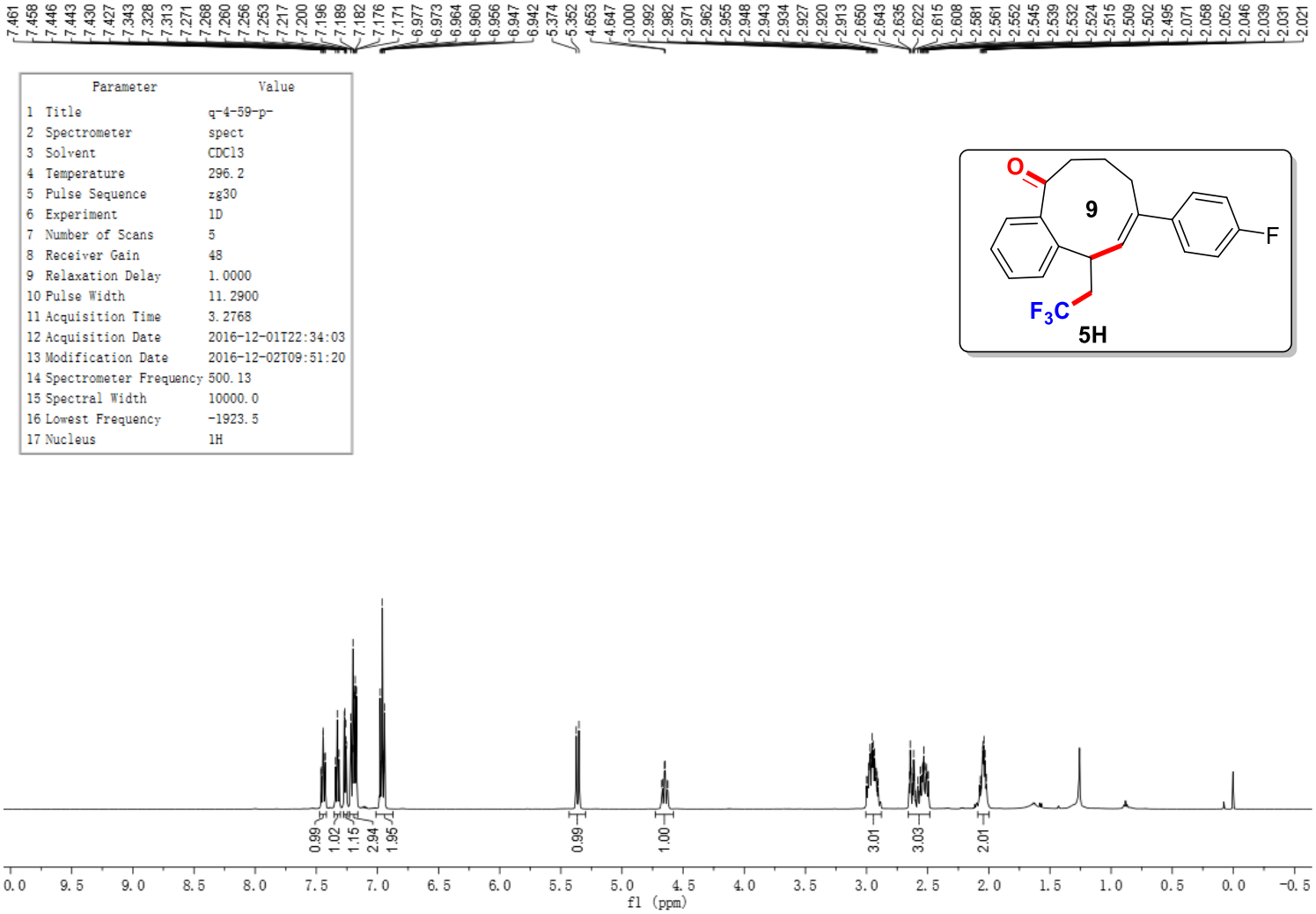
−62.826

	Parameter	Value
1	Title	11-12-71 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.9
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	2
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-10T10:50:07
13	Modification Date	2016-11-11T11:19:04
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

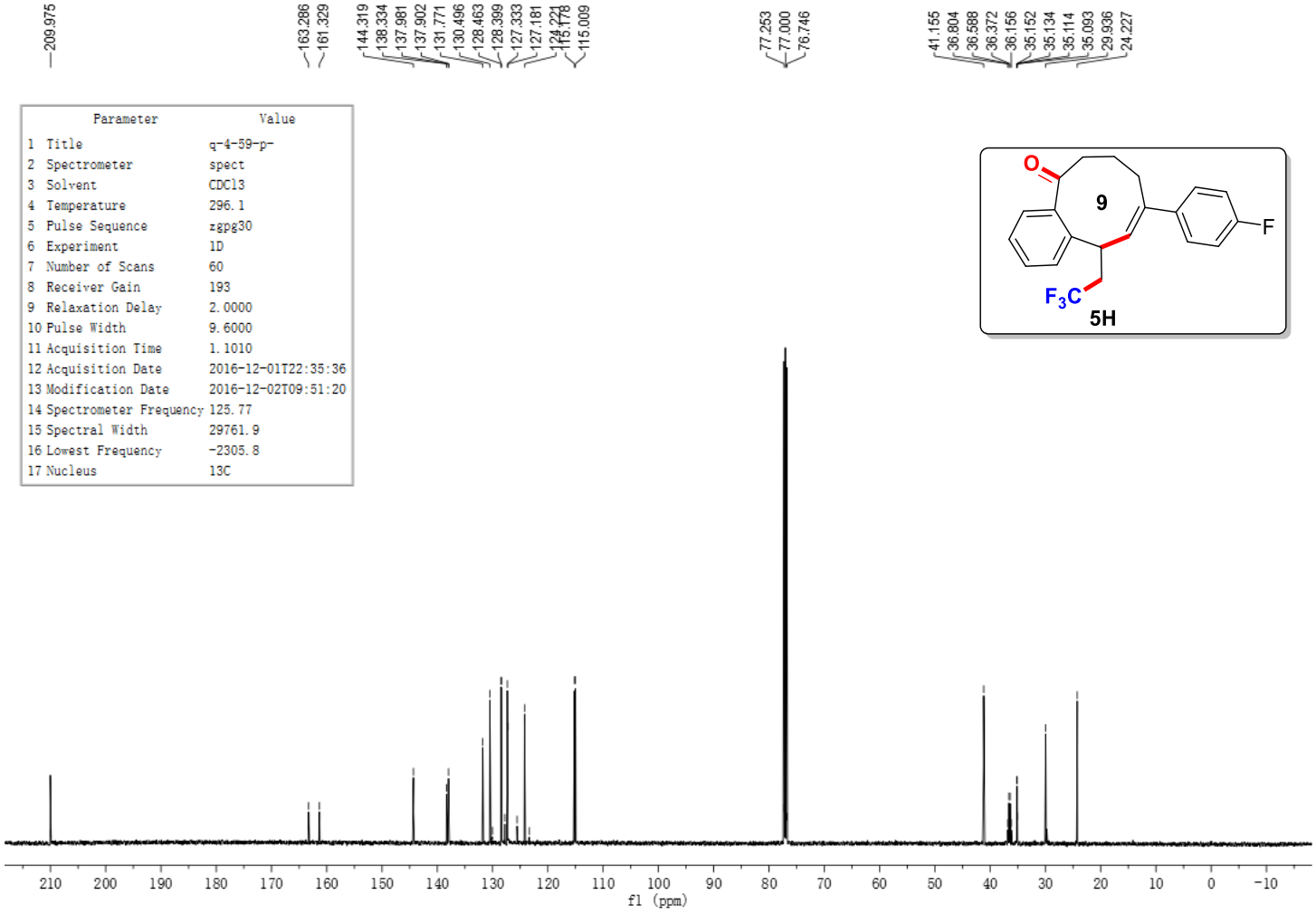




^{1}H NMR Spectrum of Compound **5H**

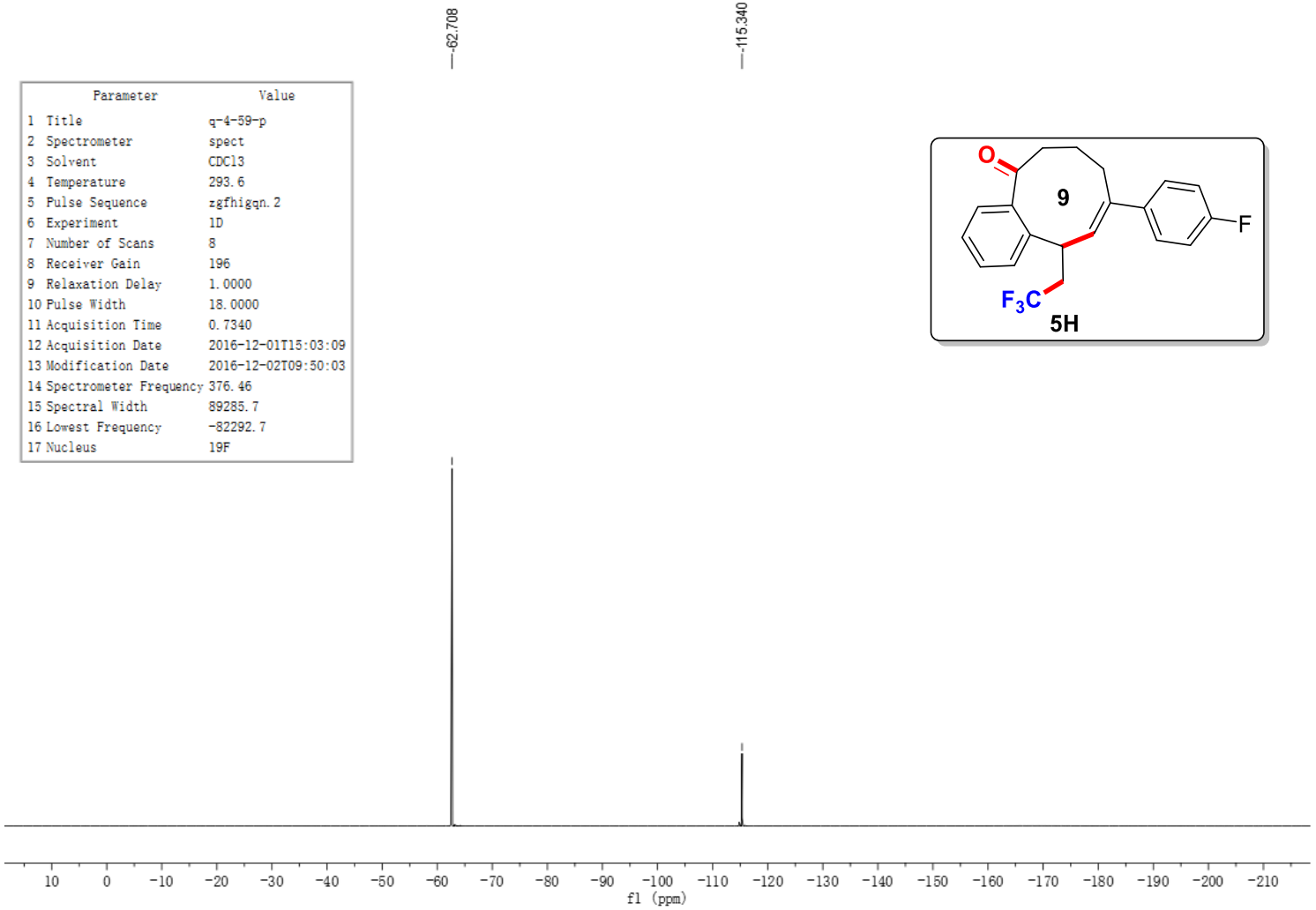


^{13}C NMR Spectrum of Compound **5H**

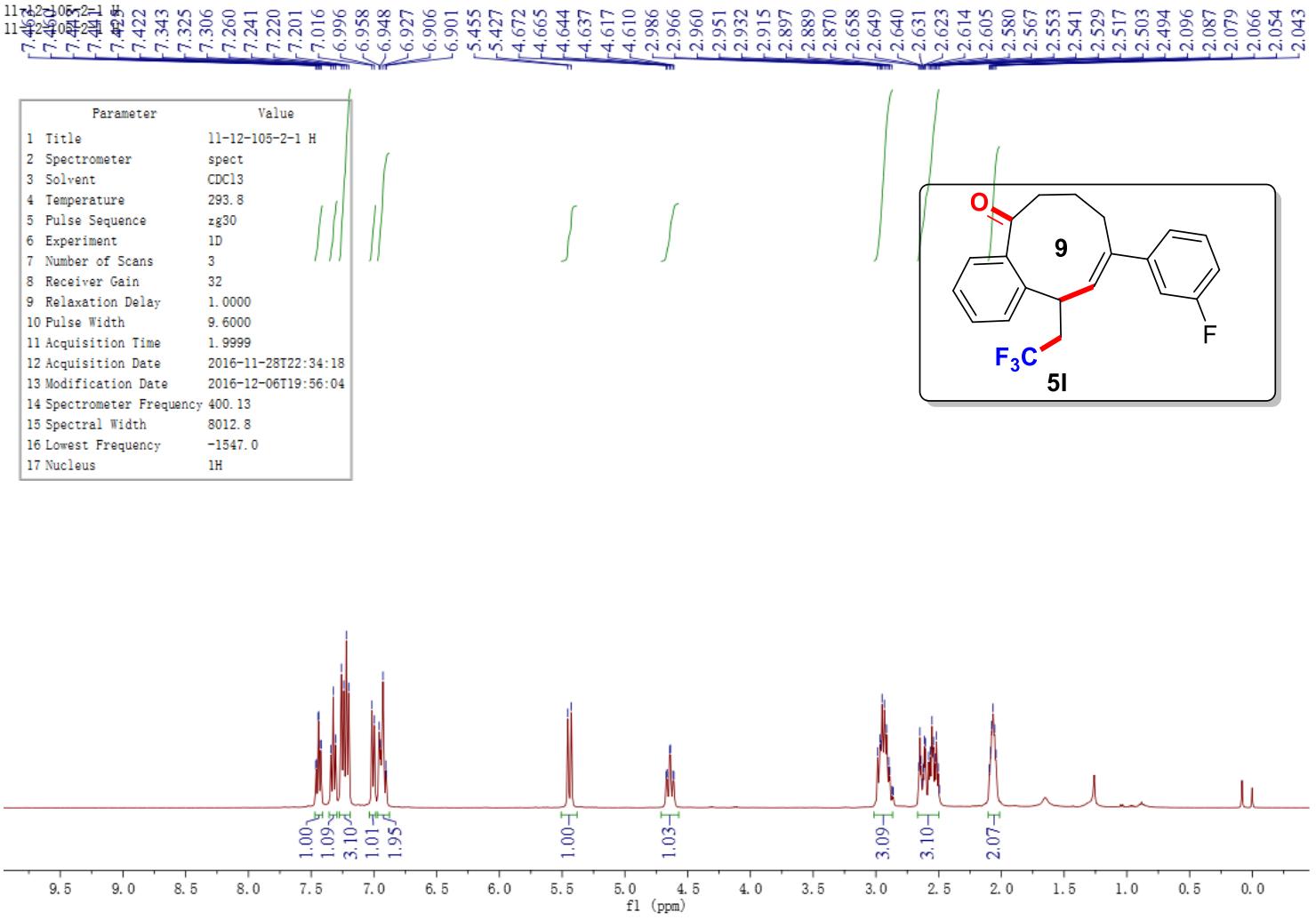


^{19}F NMR Spectrum of Compound **5H**

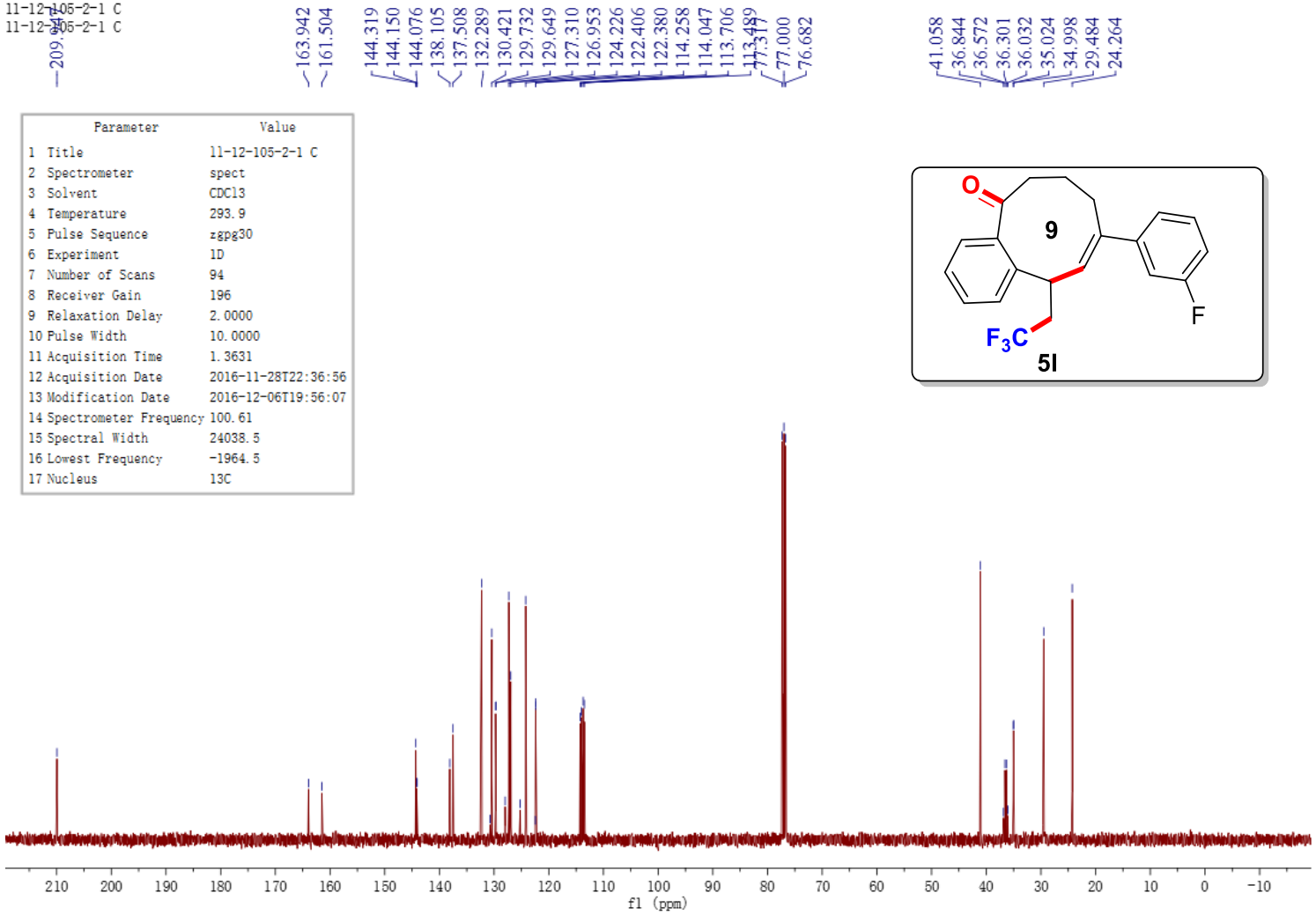
	Parameter	Value
1	Title	q-4-59-p
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.6
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-12-01T15:03:09
13	Modification Date	2016-12-02T09:50:03
14	Spectrometer Frequency	376.46
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **5I**



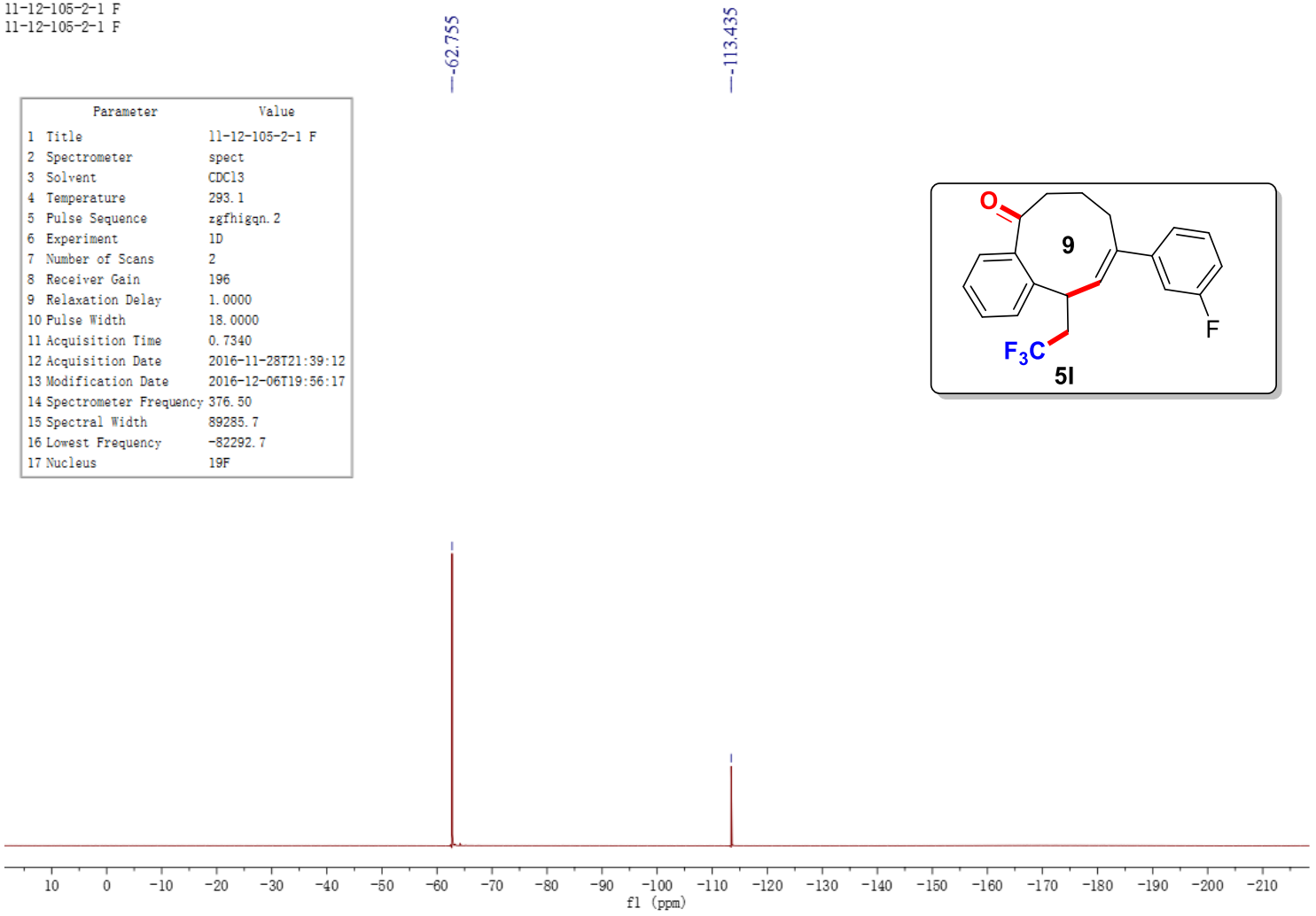
^{13}C NMR Spectrum of Compound **5I**



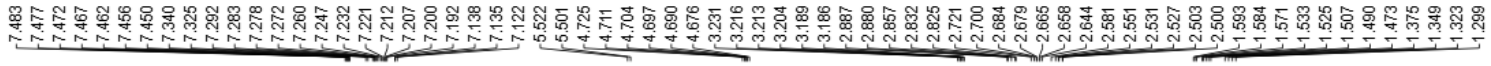
^{19}F NMR Spectrum of Compound **5I**

11-12-105-2-1 F
11-12-105-2-1 F

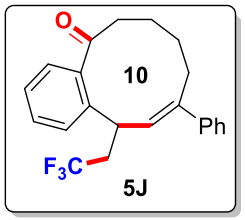
	Parameter	Value
1	Title	11-12-105-2-1 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.1
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	2
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-28T21:39:12
13	Modification Date	2016-12-06T19:56:17
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

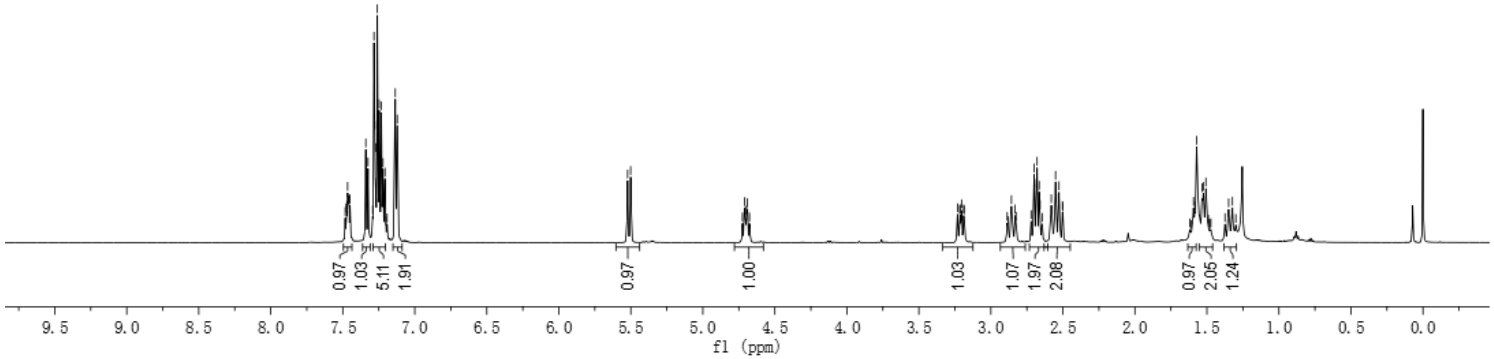


^{1}H NMR Spectrum of Compound **5J**

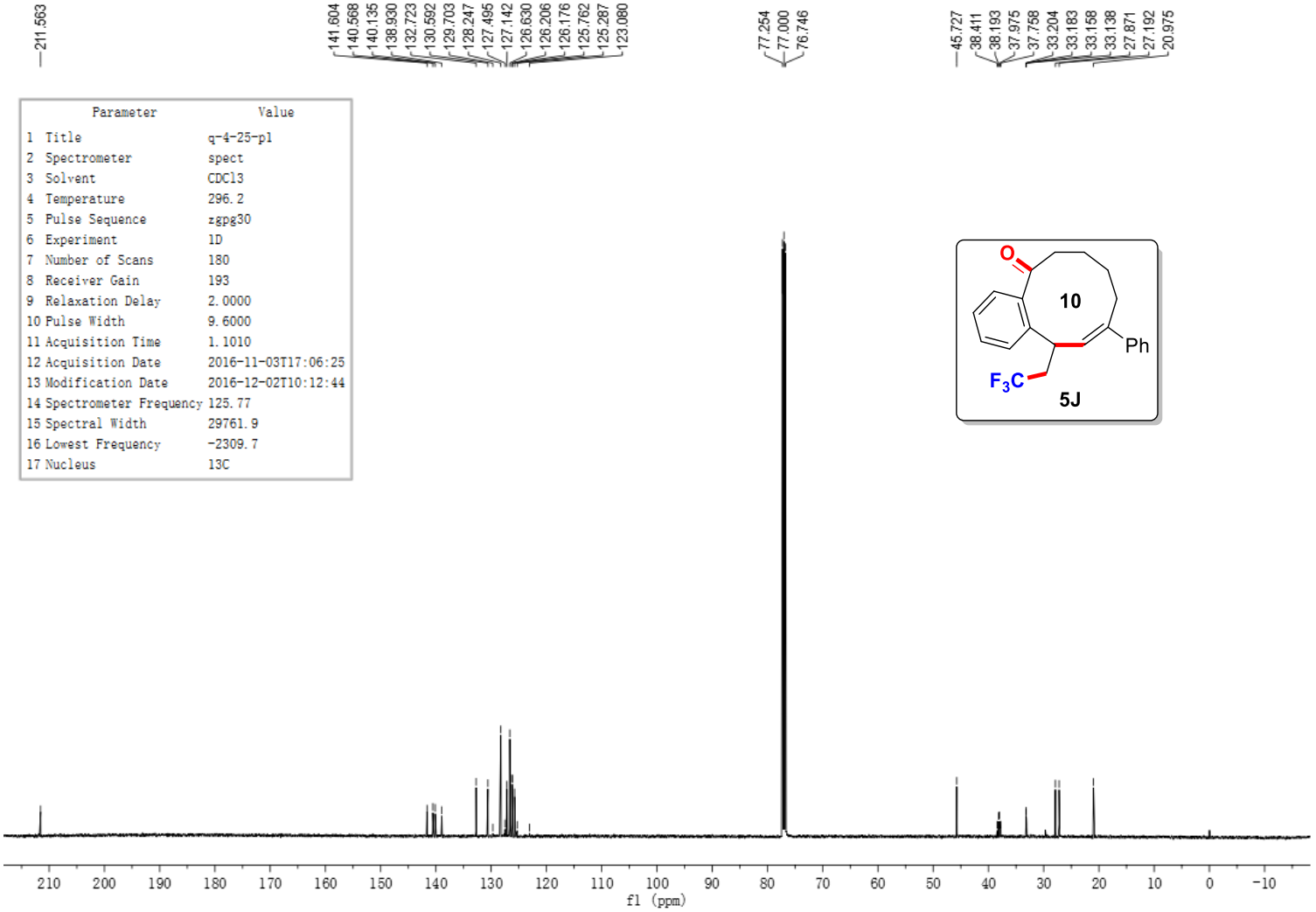


Parameter	Value
1 Title	q-4-25-p1
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	78
9 Relaxation Delay	1.0000
10 Pulse Width	11.2900
11 Acquisition Time	3.2768
12 Acquisition Date	2016-11-03T17:03:59
13 Modification Date	2016-12-02T10:12:44
14 Spectrometer Frequency	500.13
15 Spectral Width	10000.0
16 Lowest Frequency	-1924.0
17 Nucleus	1H



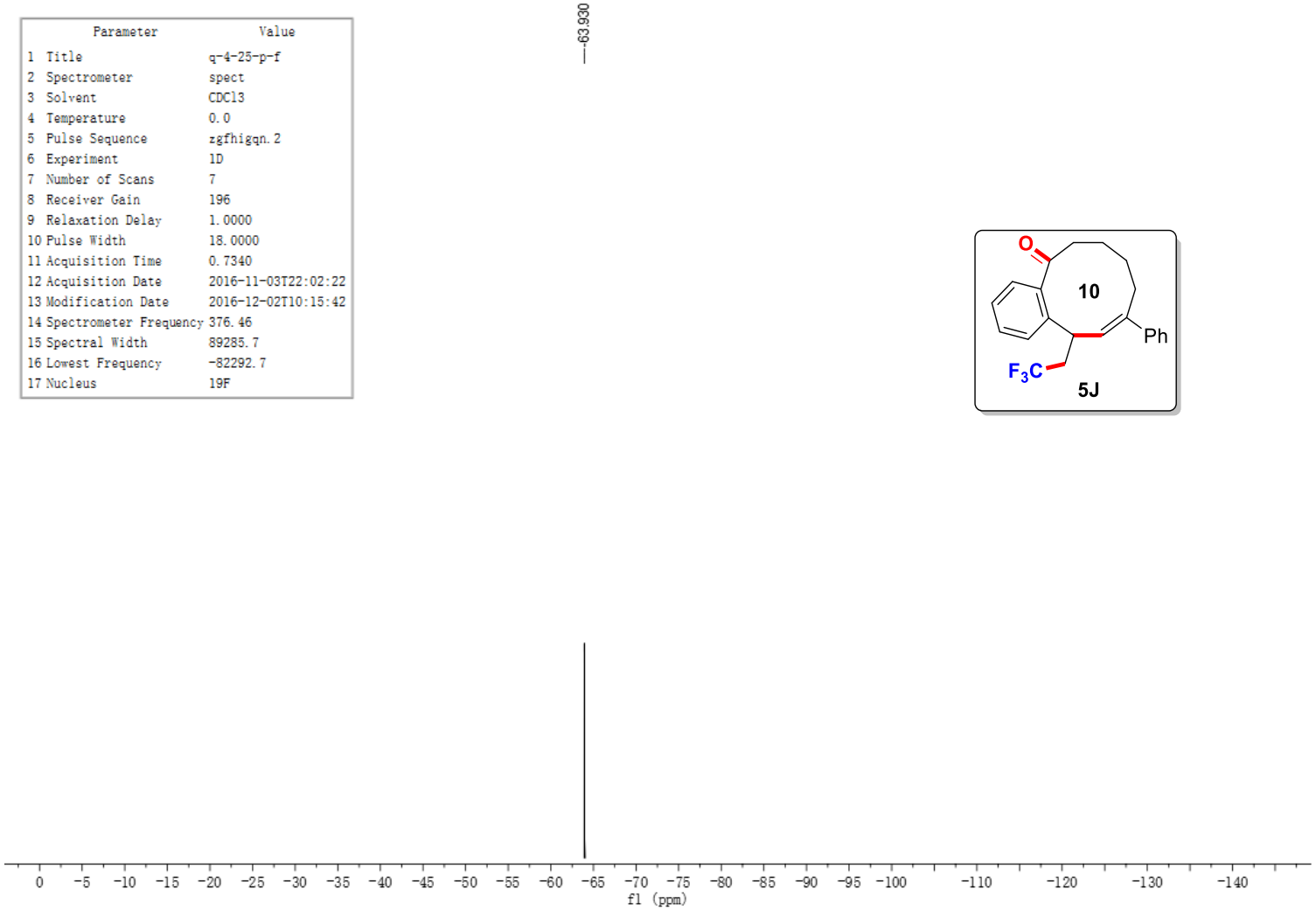


^{13}C NMR Spectrum of Compound **5J**

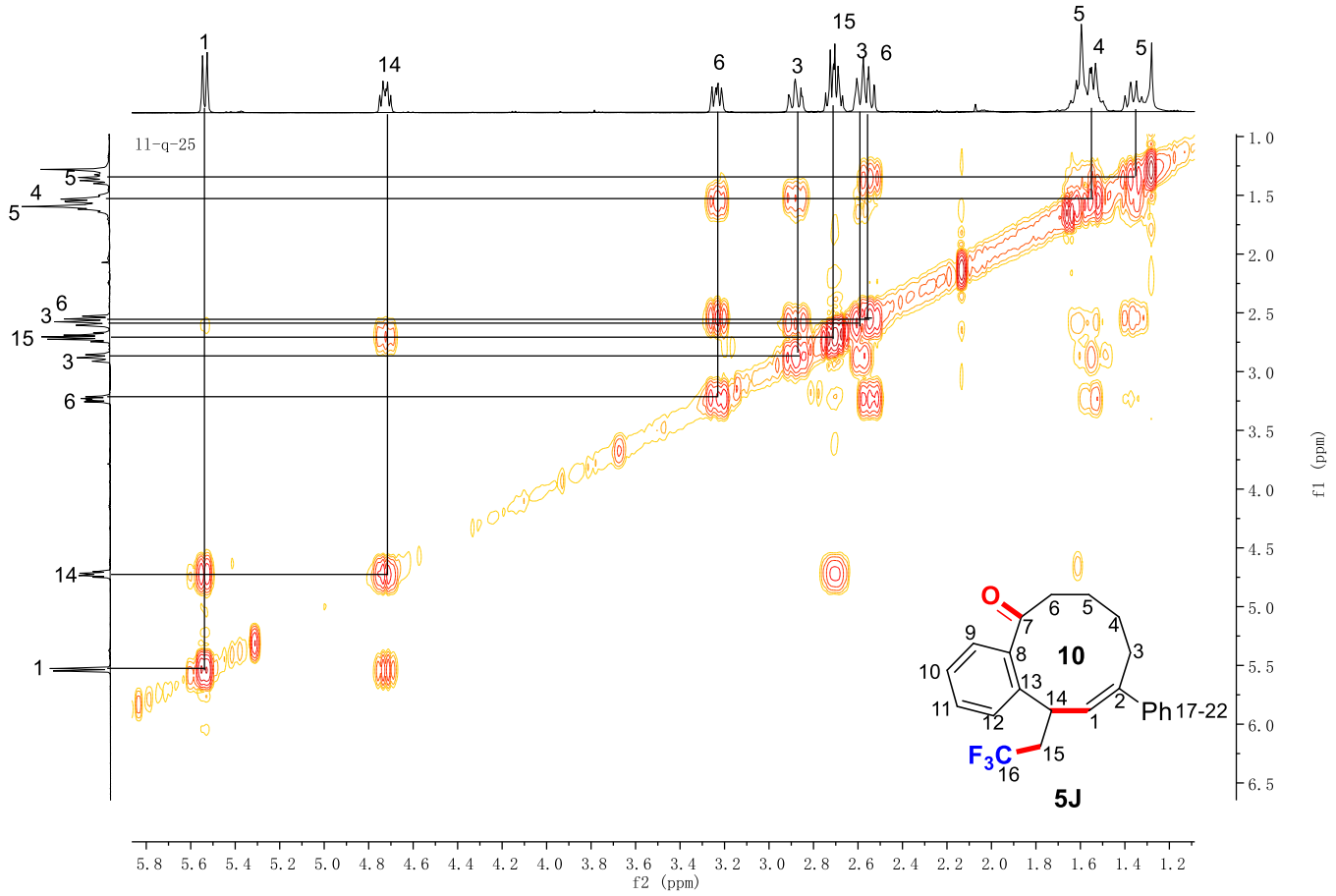


^{19}F NMR Spectrum of Compound **5J**

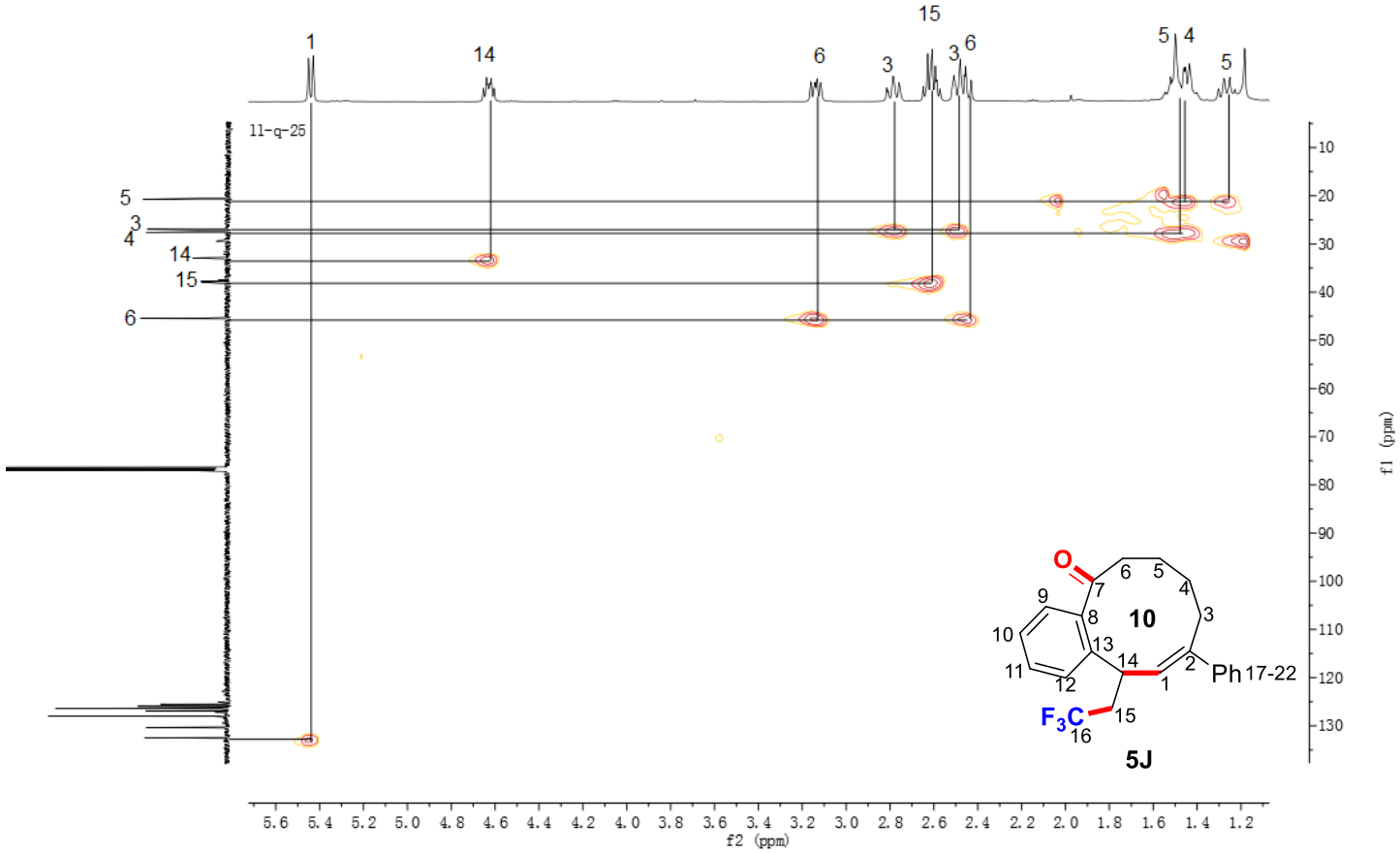
	Parameter	Value
1	Title	q-4-25-p-f
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	0.0
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	7
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-03T22:02:22
13	Modification Date	2016-12-02T10:15:42
14	Spectrometer Frequency	376.46
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



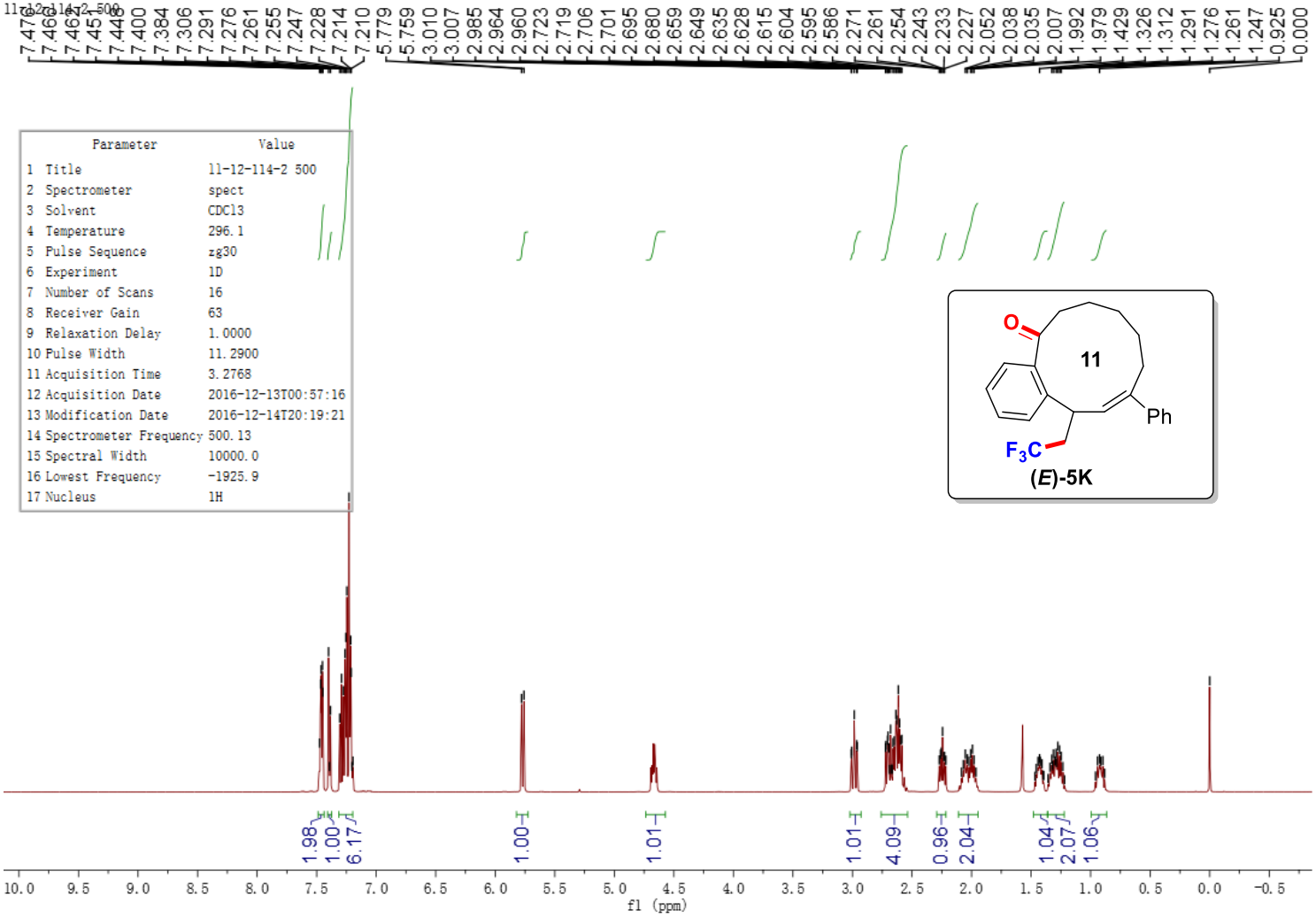
COSY of compound **5J**



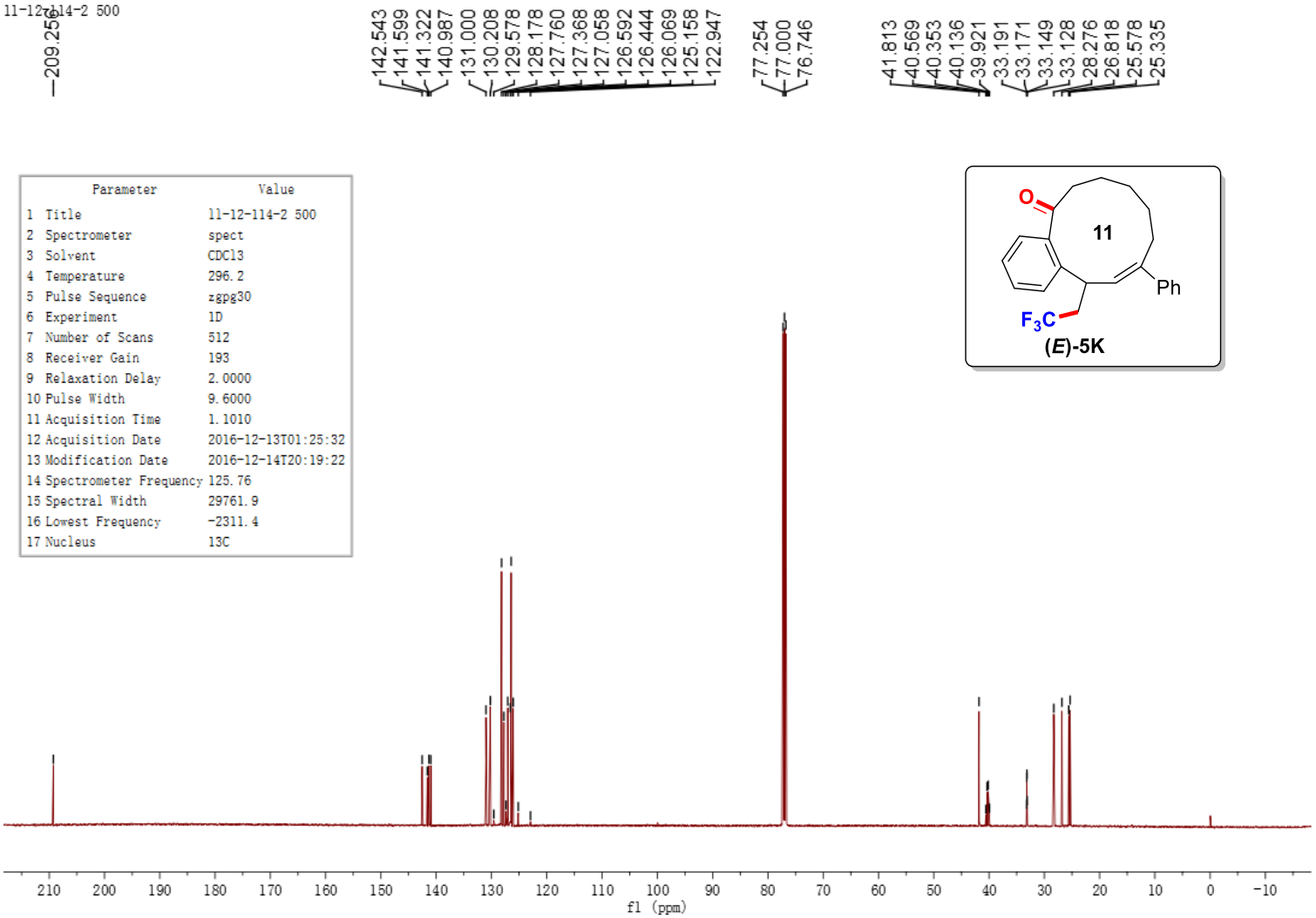
HSQC of compound **5J**



^{1}H NMR Spectrum of Compound (*E*)-**5K**

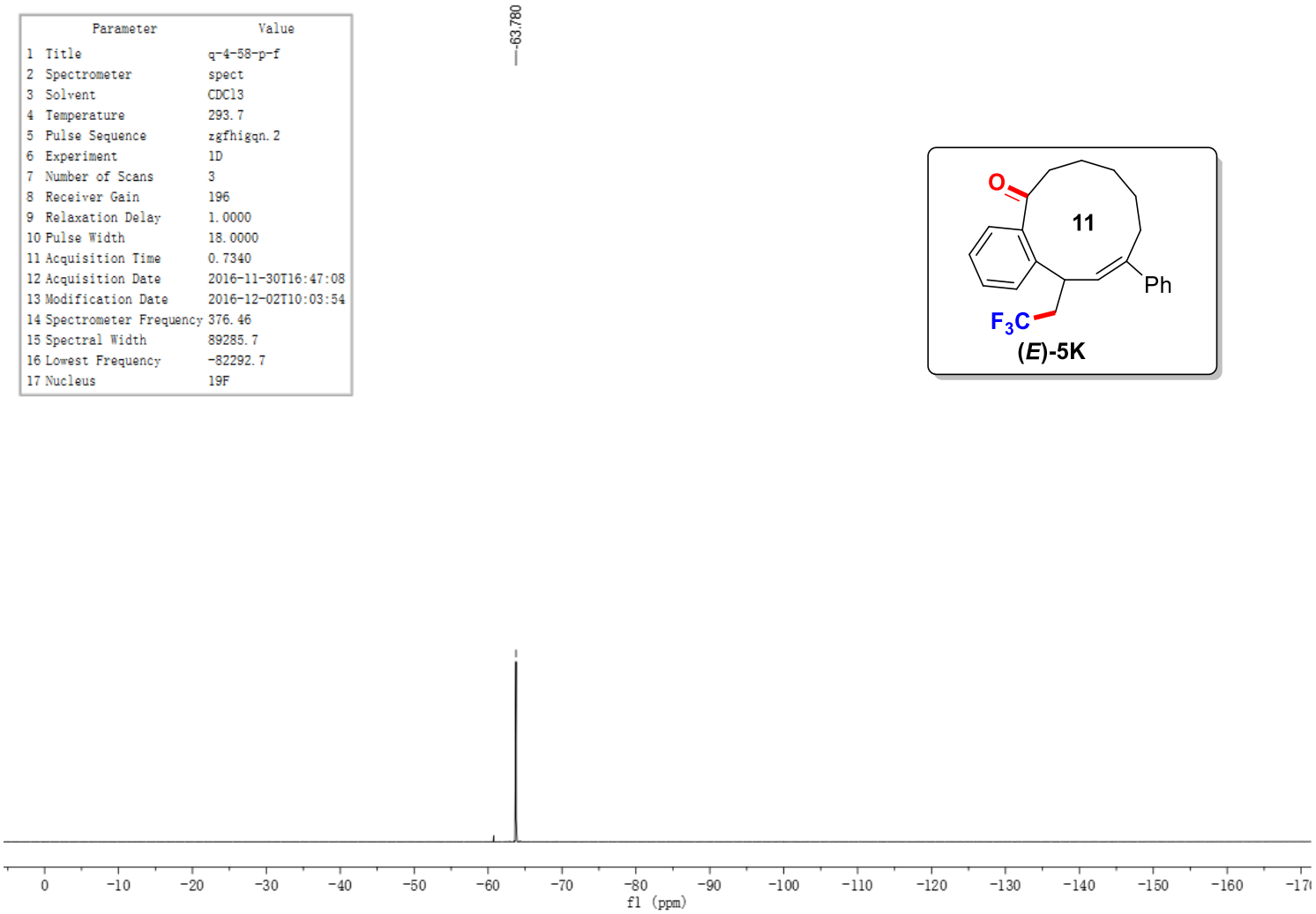


^{13}C NMR Spectrum of Compound (*E*)-**5K**

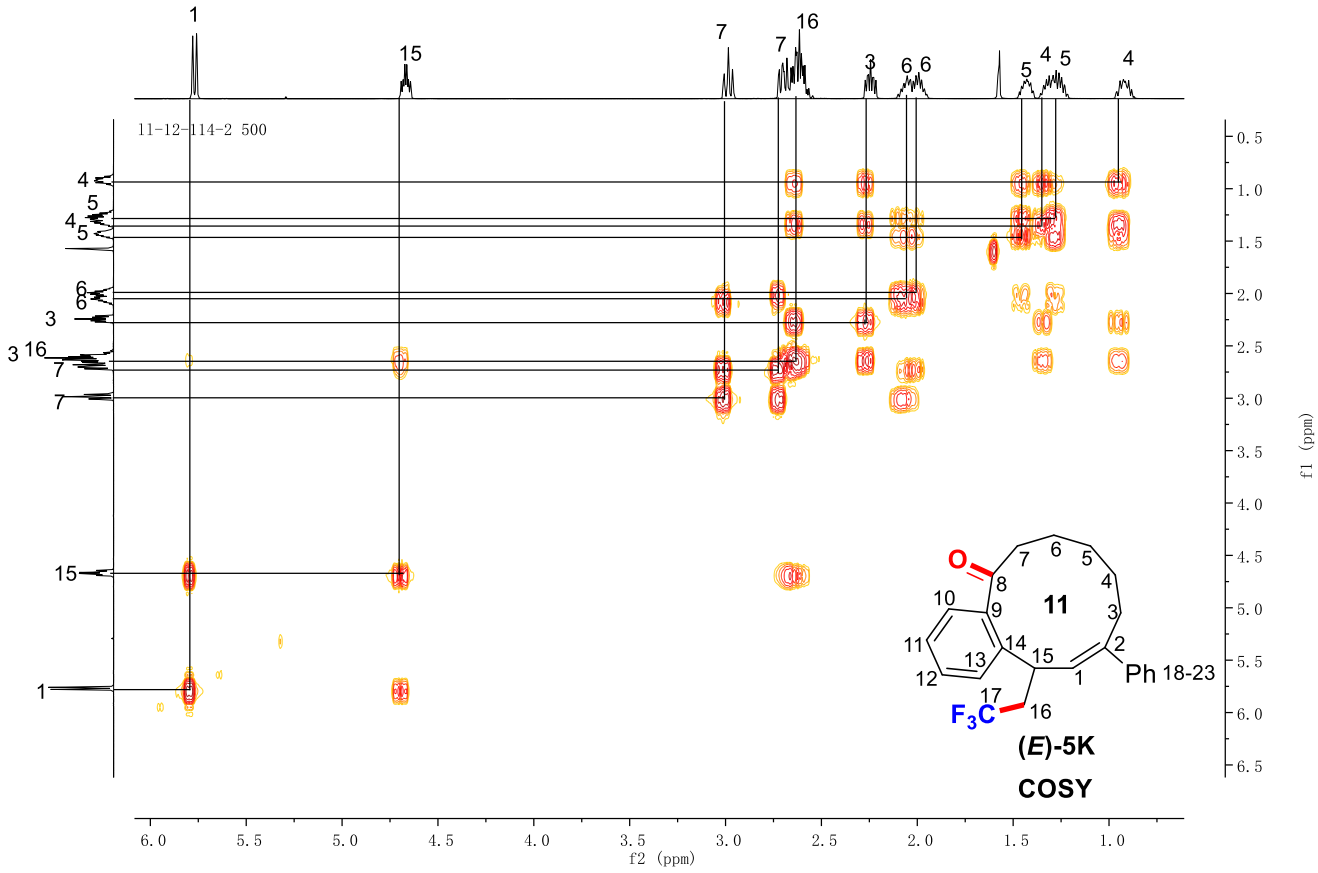


^{19}F NMR Spectrum of Compound (*E*)-**5K**

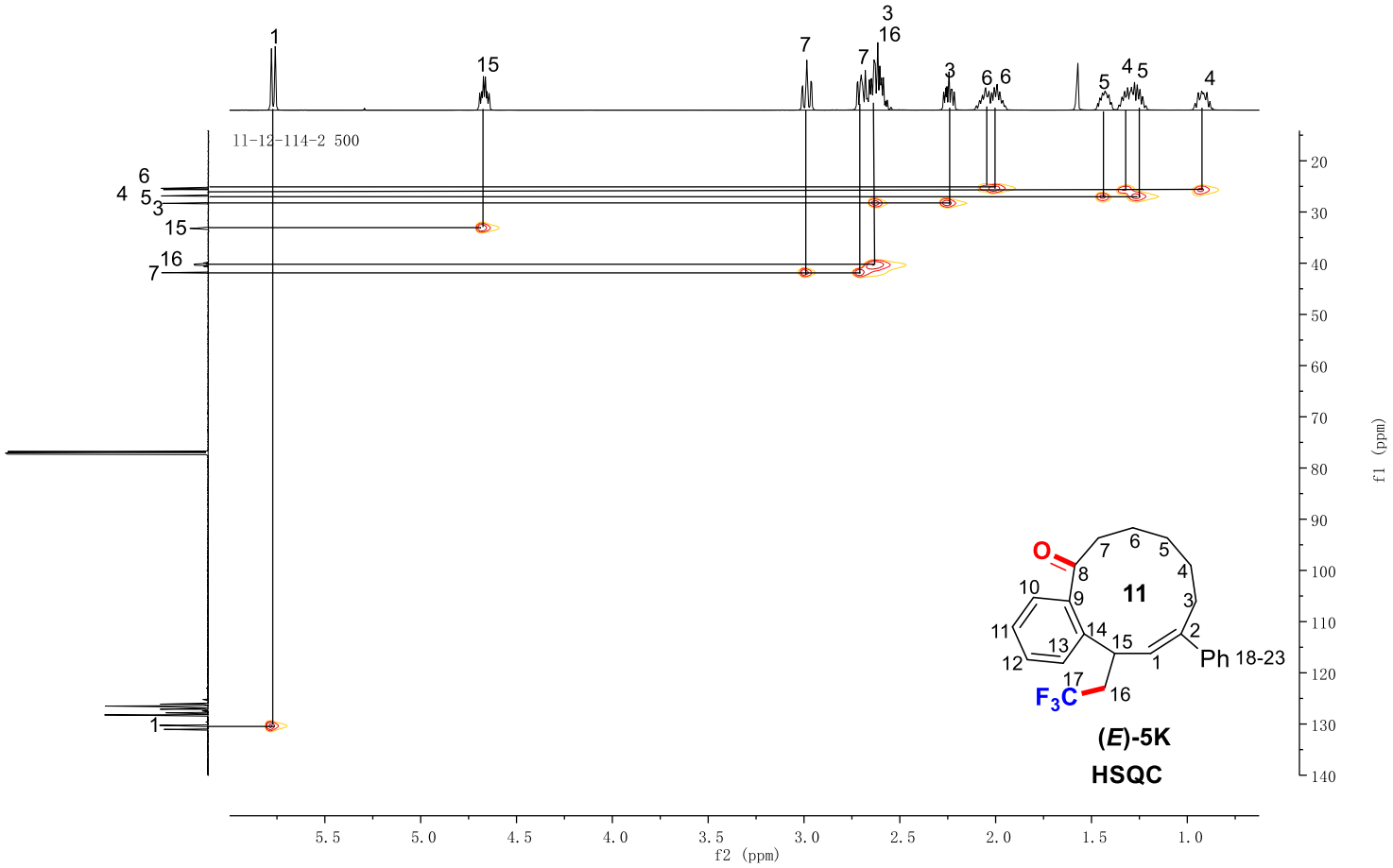
	Parameter	Value
1	Title	q-4-58-p-f
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	3
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-11-30T16:47:08
13	Modification Date	2016-12-02T10:03:54
14	Spectrometer Frequency	376.46
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



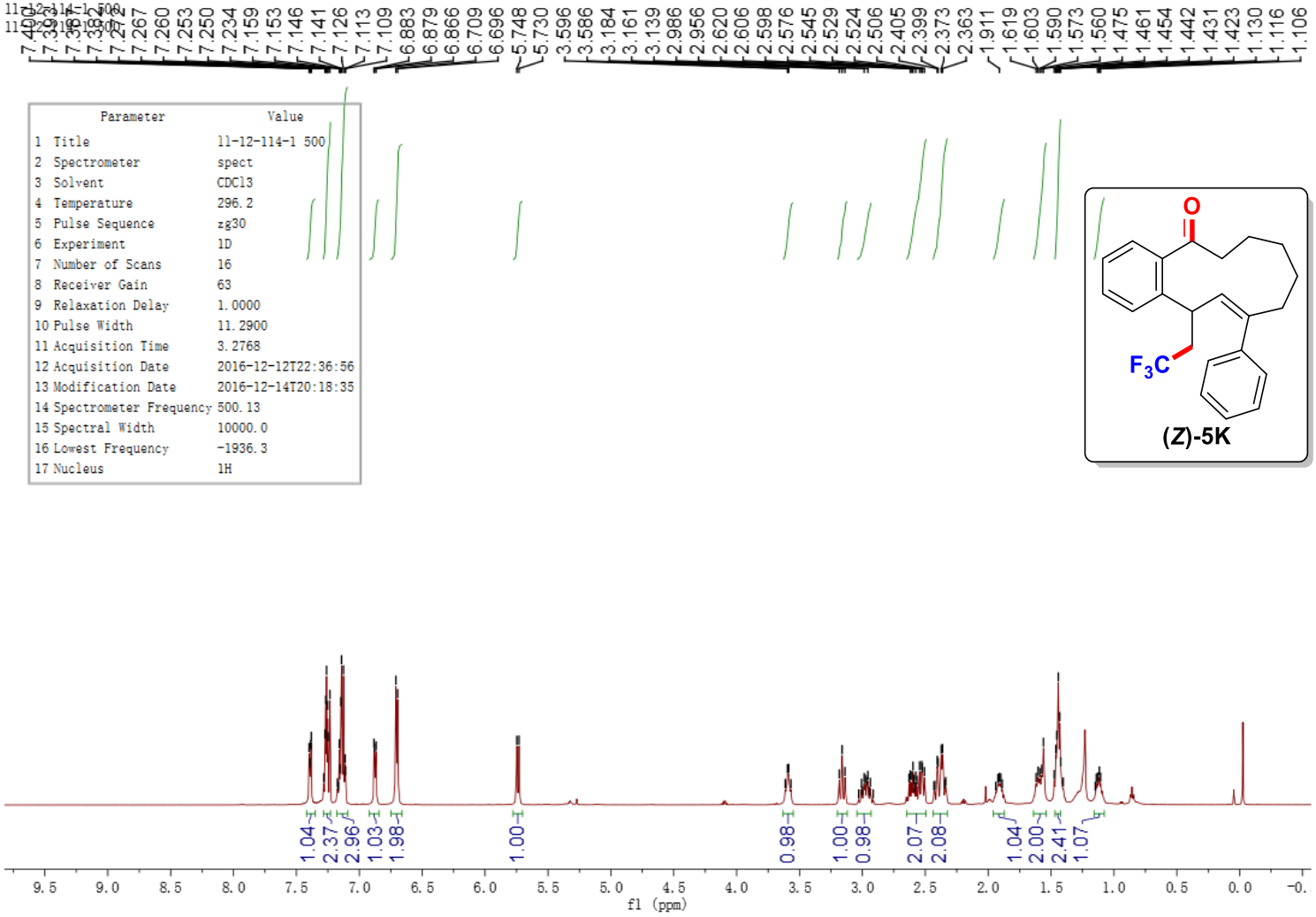
COSY of compound (*E*)-**5K**



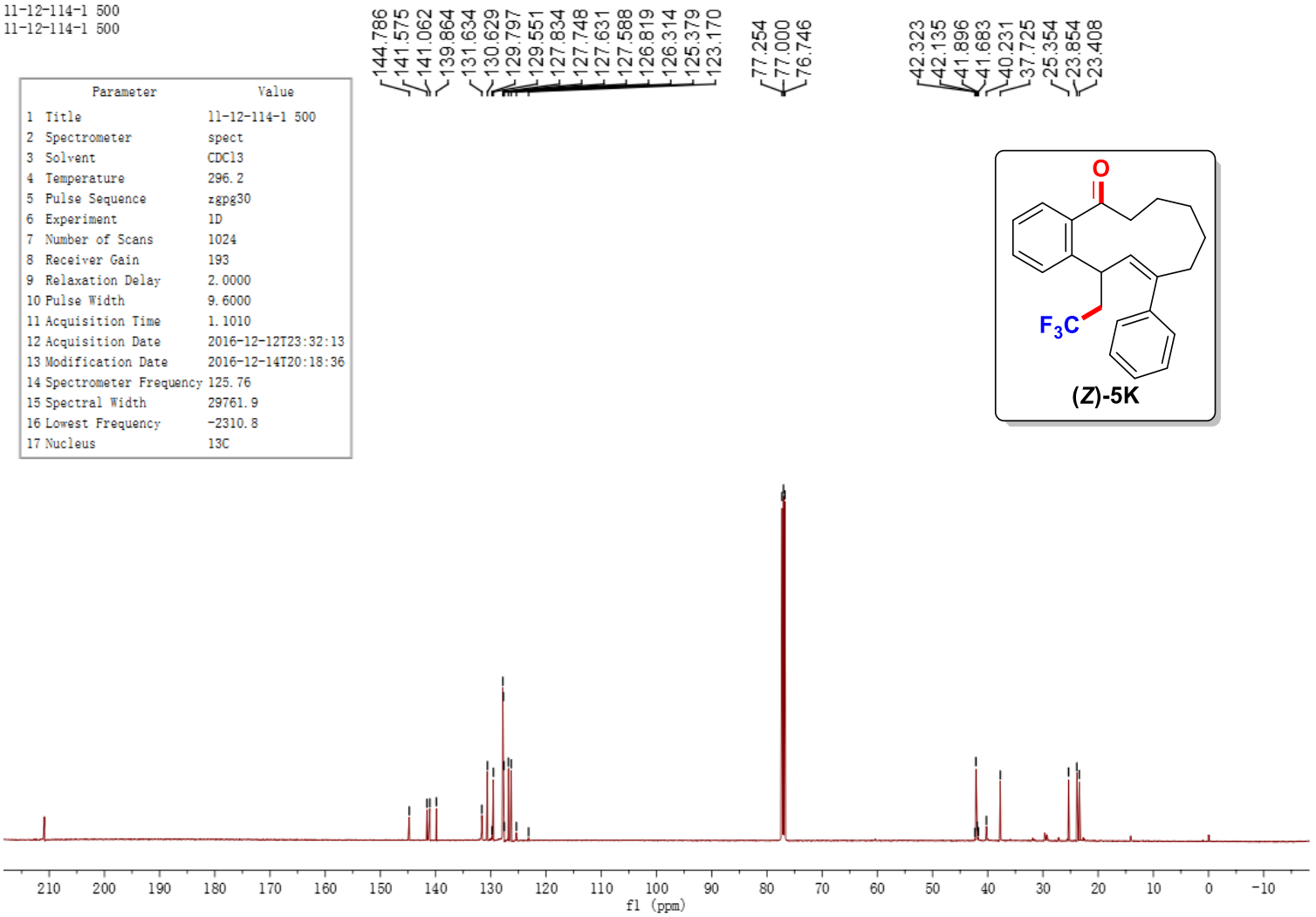
HSQC of compound (*E*)-**5K**



^{1}H NMR Spectrum of Compound (*Z*)-**5K**



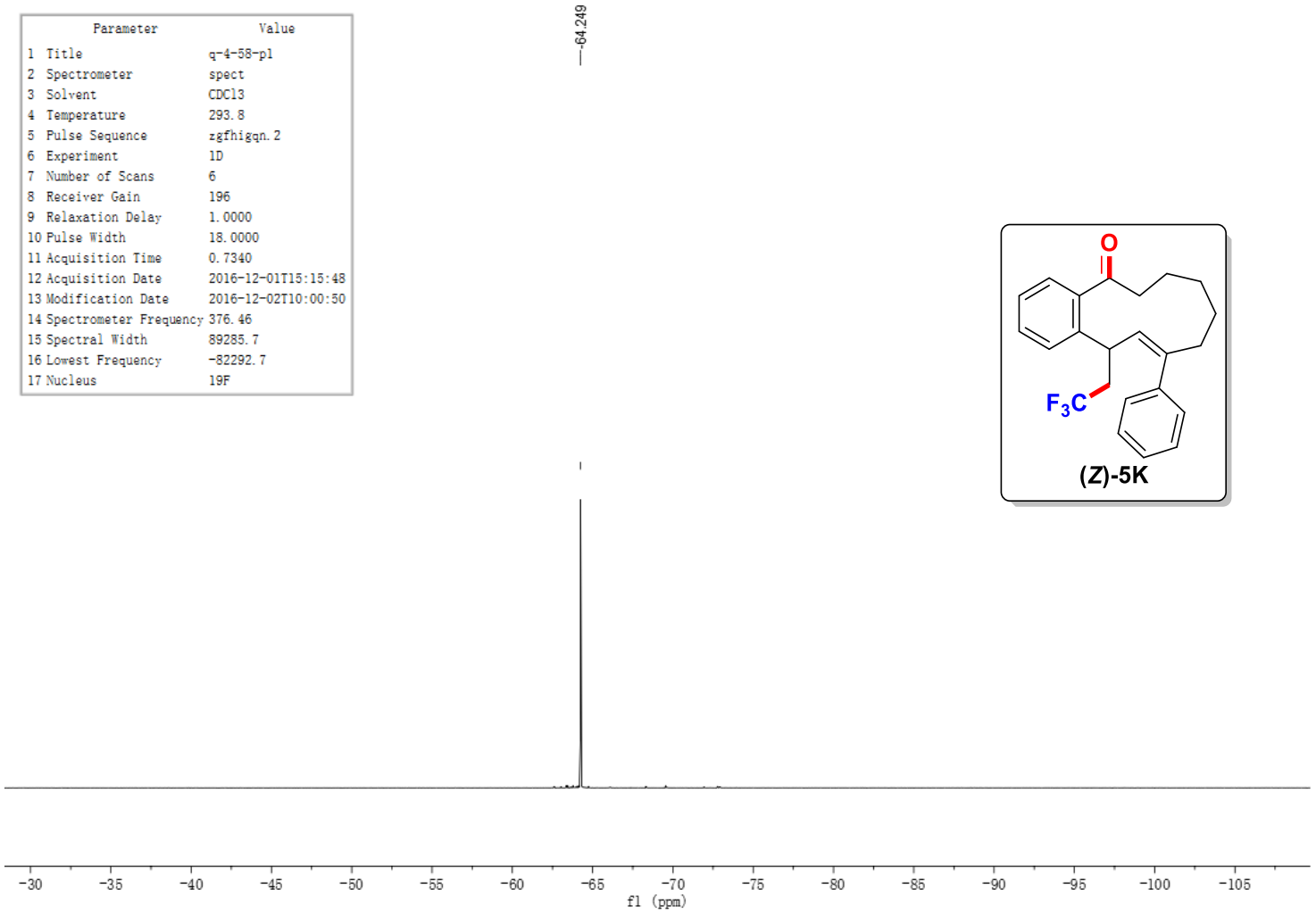
^{13}C NMR Spectrum of Compound (*Z*)-**5K**



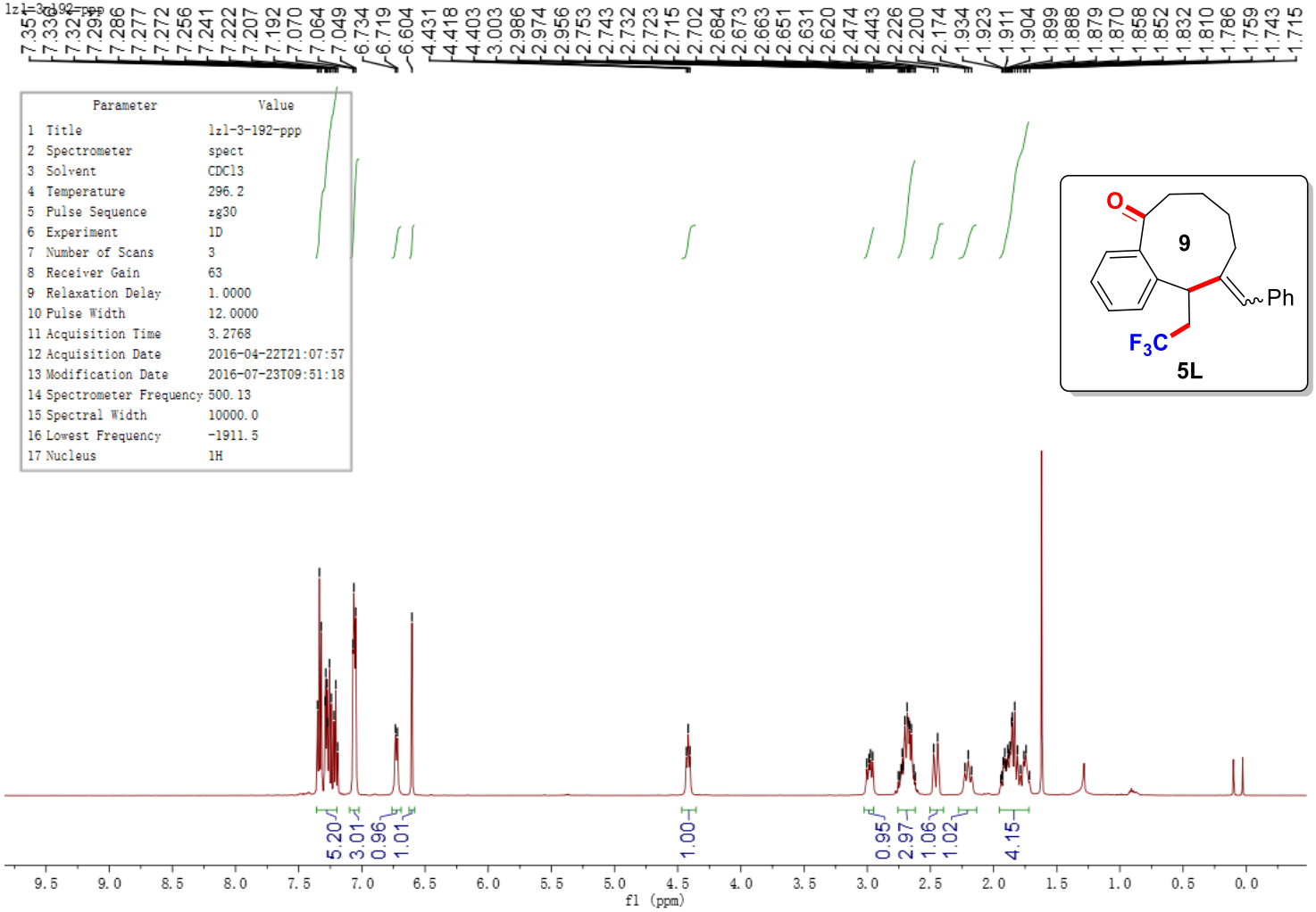
	Parameter	Value
1	Title	11-12-114-1 500
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	193
9	Relaxation Delay	2.0000
10	Pulse Width	9.6000
11	Acquisition Time	1.1010
12	Acquisition Date	2016-12-12T23:32:13
13	Modification Date	2016-12-14T20:18:36
14	Spectrometer Frequency	125.76
15	Spectral Width	29761.9
16	Lowest Frequency	-2310.8
17	Nucleus	13C

^{19}F NMR Spectrum of Compound (*Z*)-**5K**

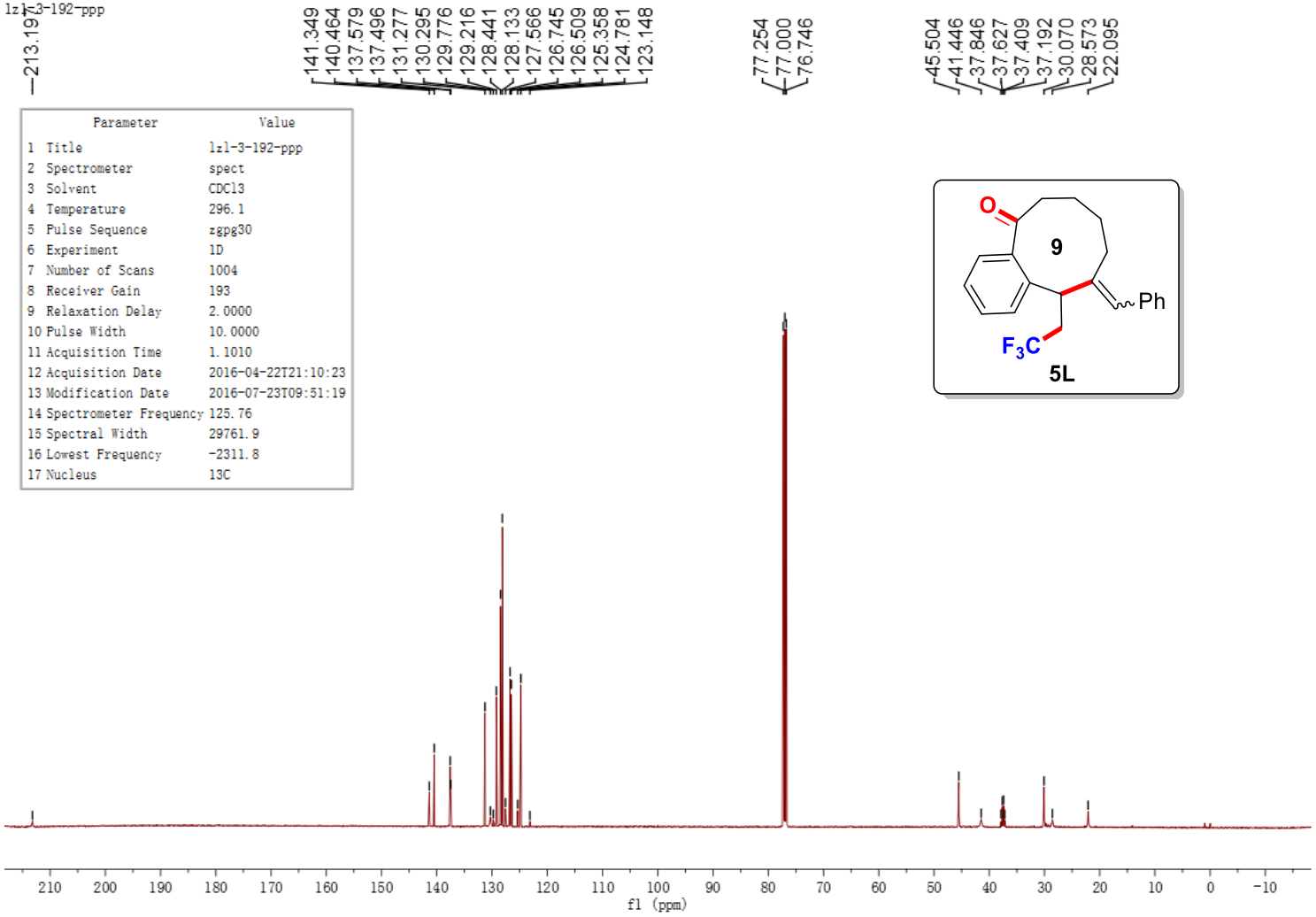
Parameter	Value
1 Title	q-4-58-p1
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	293.8
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	6
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2016-12-01T15:15:48
13 Modification Date	2016-12-02T10:00:50
14 Spectrometer Frequency	376.46
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F



^{1}H NMR Spectrum of Compound **5L**



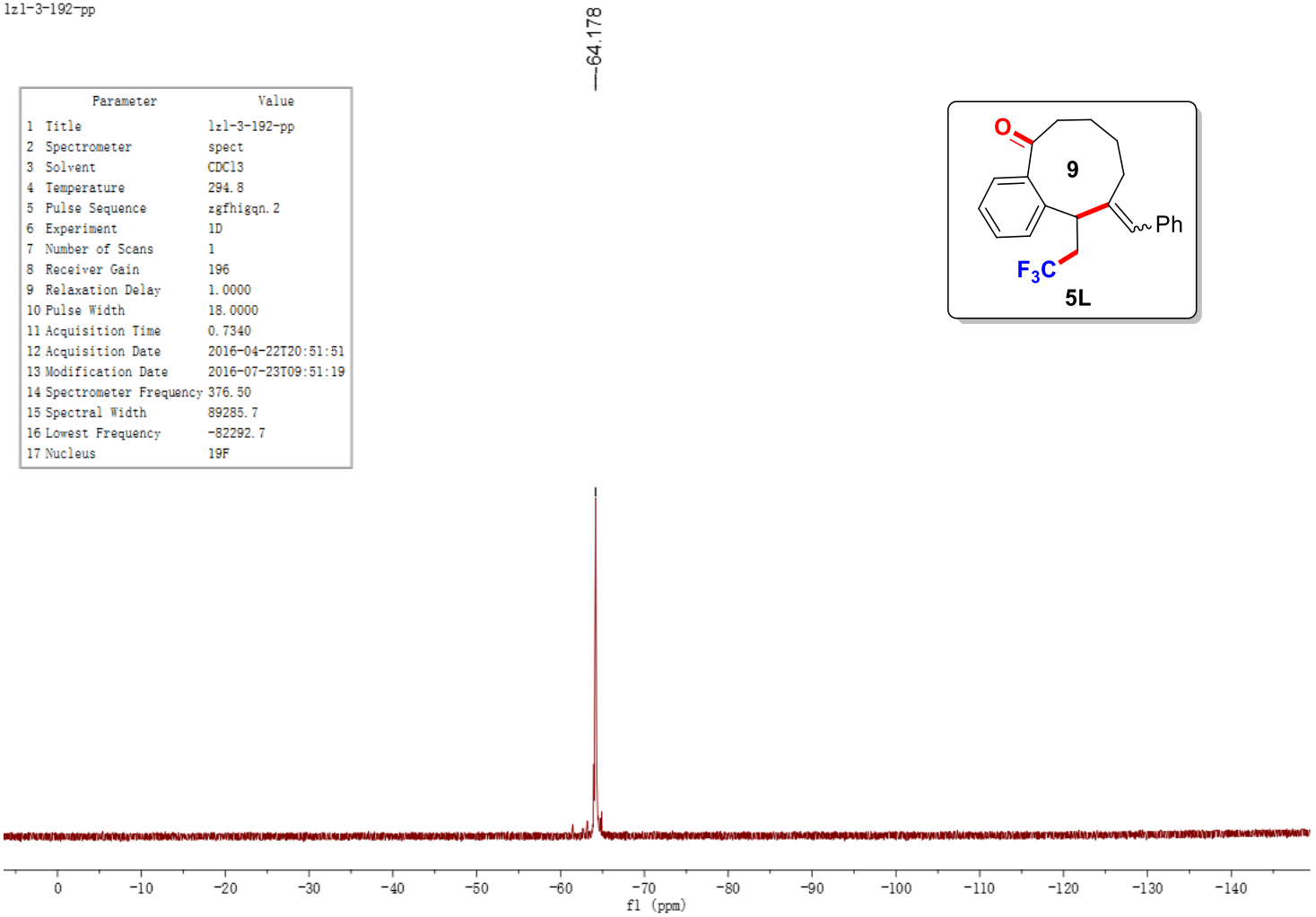
^{13}C NMR Spectrum of Compound **5L**



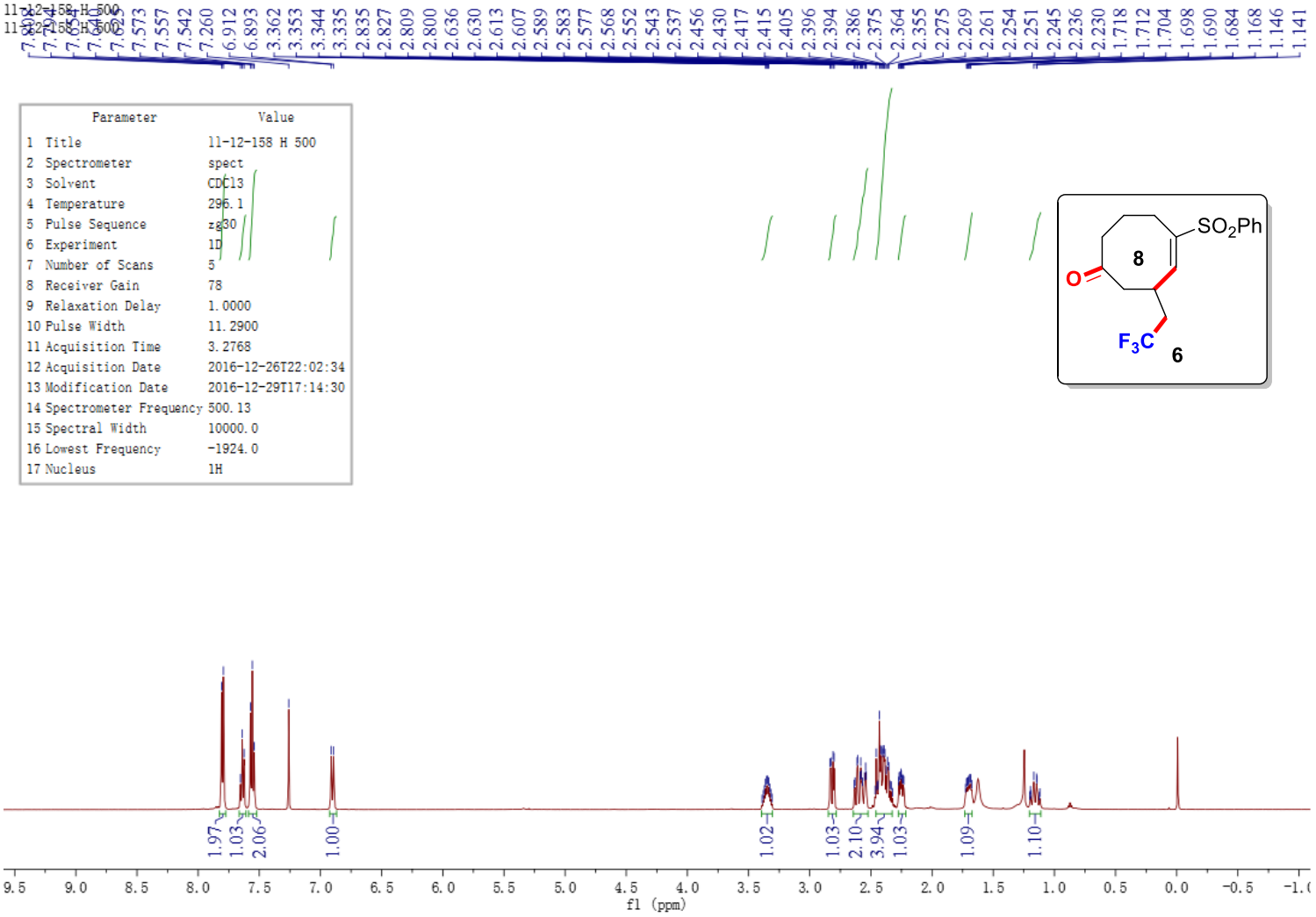
^{19}F NMR Spectrum of Compound **5L**

lzl-3-192-pp

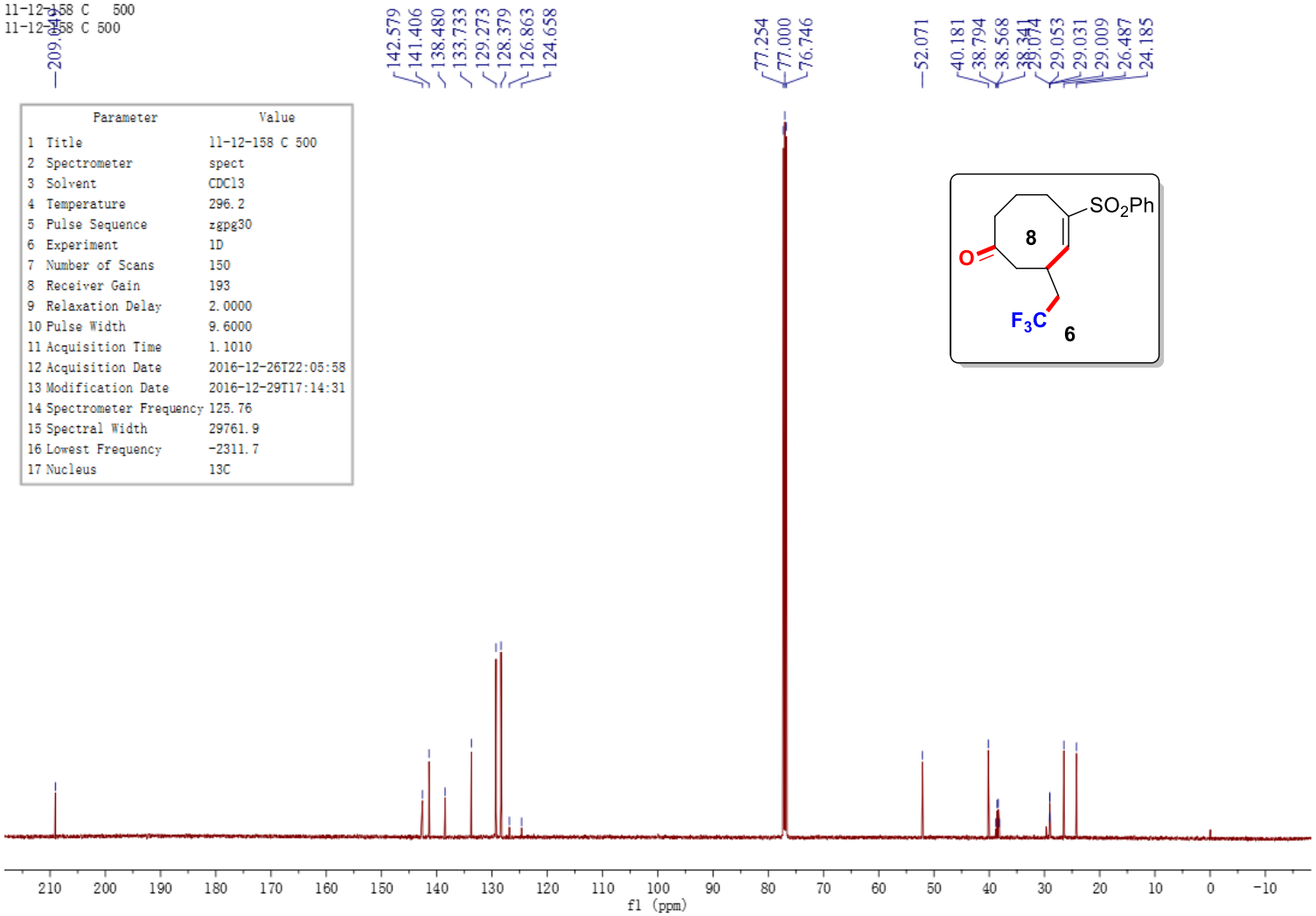
	Parameter	Value
1	Title	lzl-3-192-pp
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.8
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	1
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-04-22T20:51:51
13	Modification Date	2016-07-23T09:51:19
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **6**



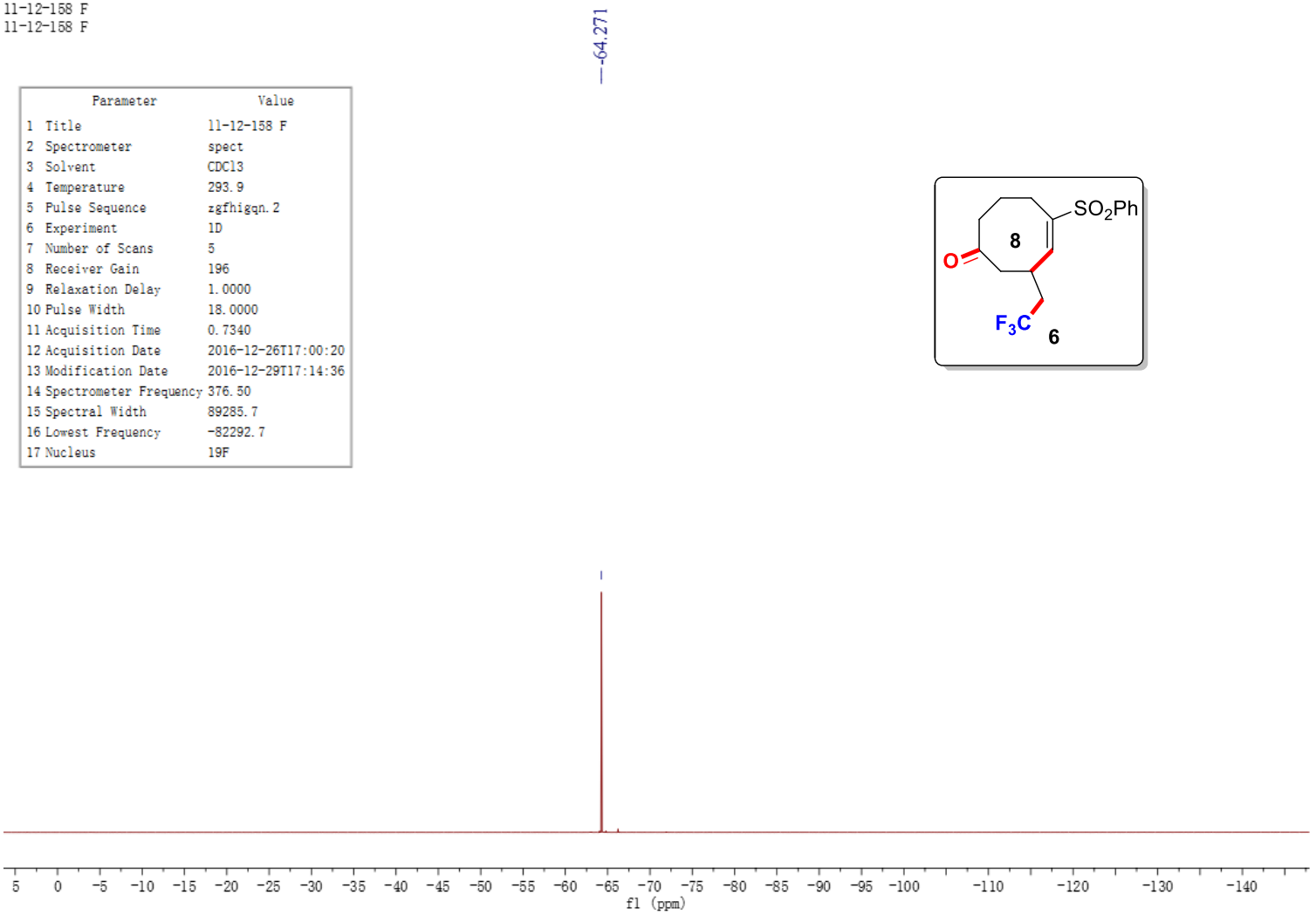
^{13}C NMR Spectrum of Compound **6**



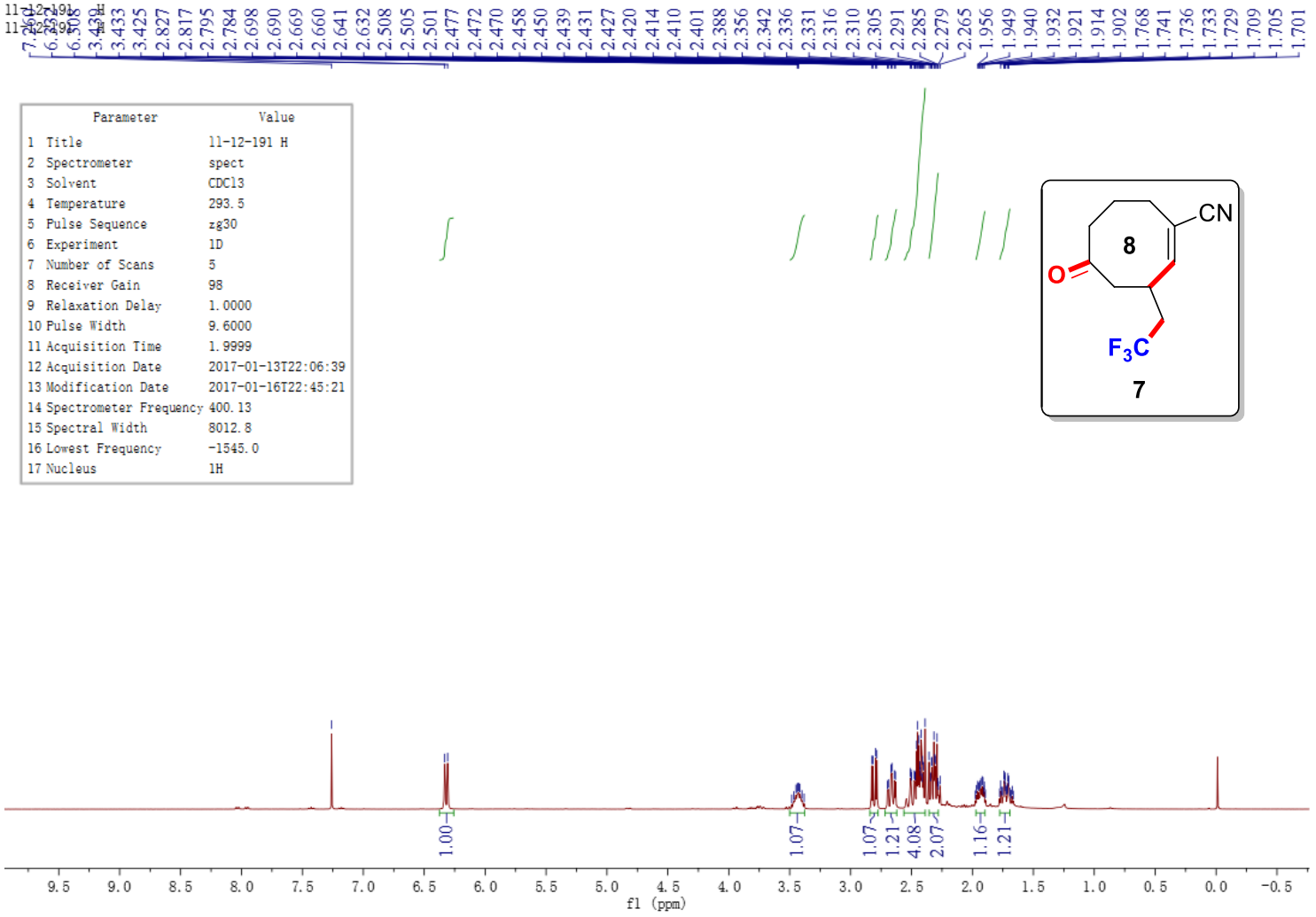
^{19}F NMR Spectrum of Compound **6**

11-12-158 F
11-12-158 F

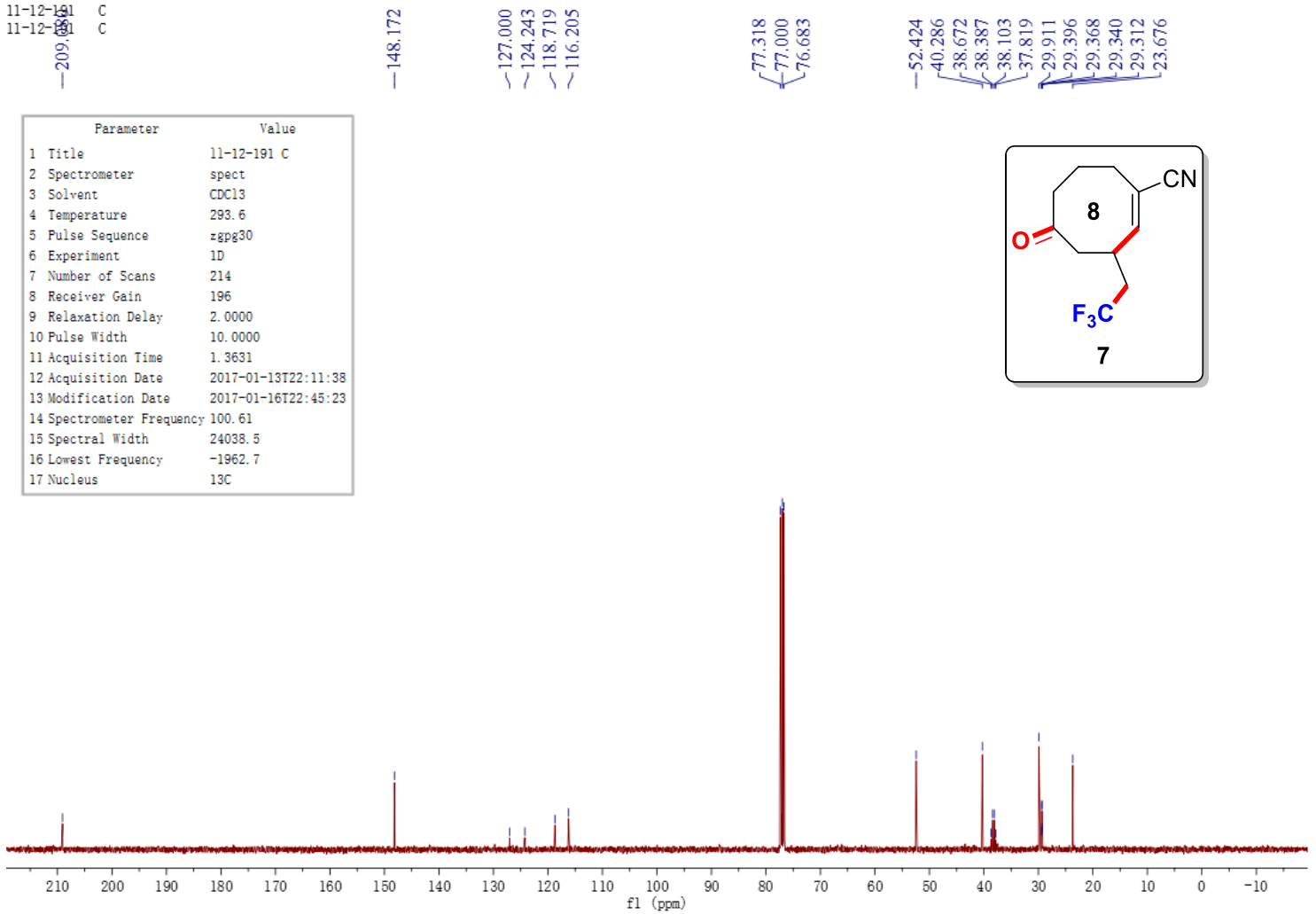
	Parameter	Value
1	Title	11-12-158 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.9
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	5
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2016-12-26T17:00:20
13	Modification Date	2016-12-29T17:14:36
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **7**



^{13}C NMR Spectrum of Compound **7**

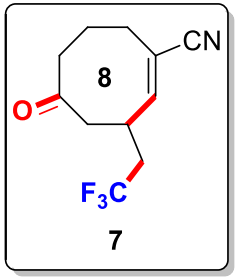


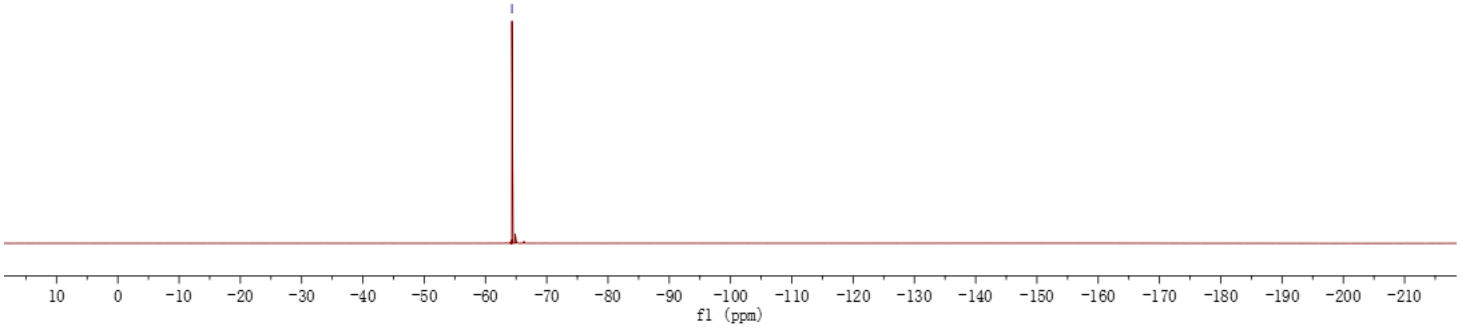
^{19}F NMR Spectrum of Compound **7**

11-12-191 F
11-12-191 F

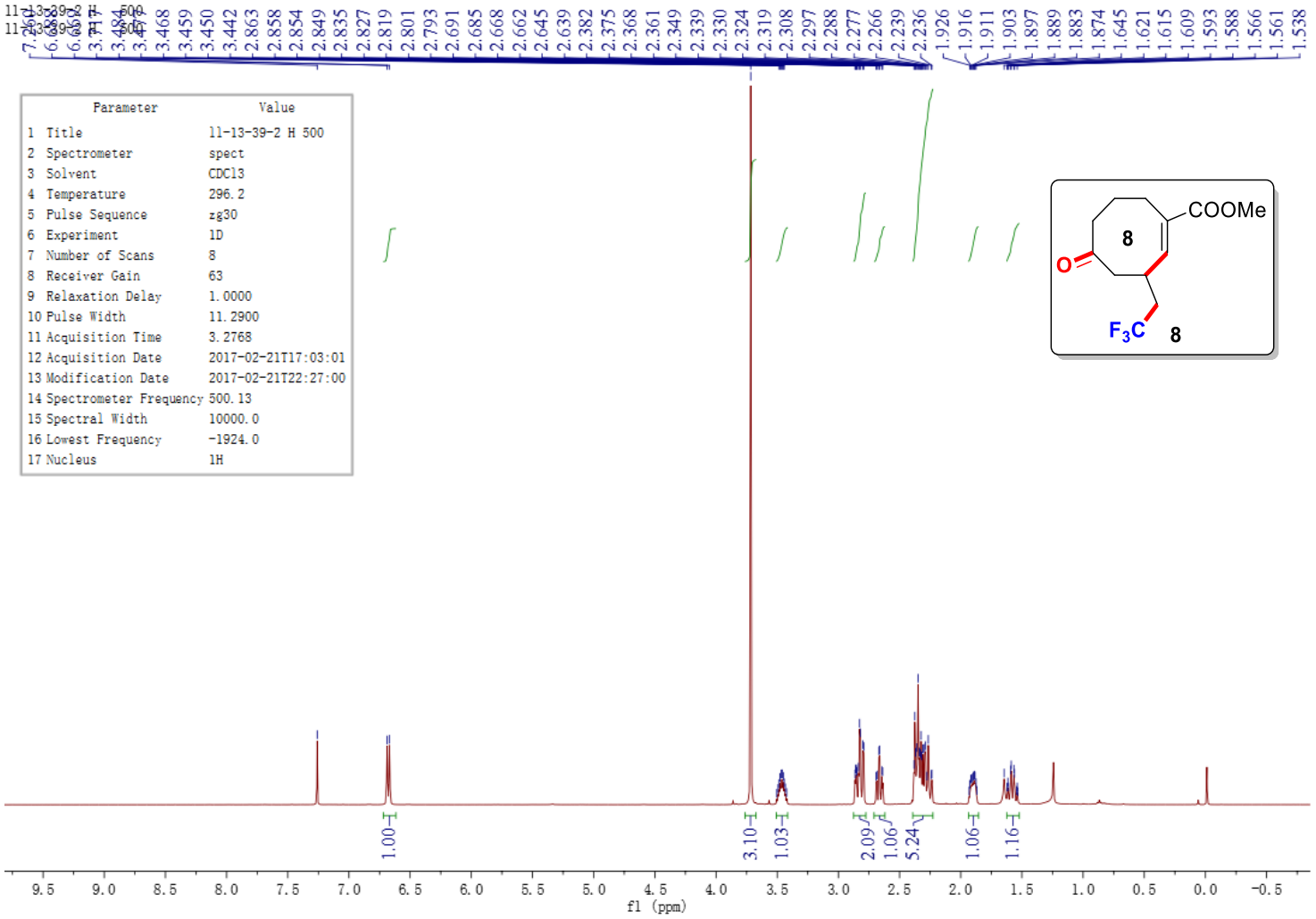
-64.319

	Parameter	Value
1	Title	11-12-191 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	293.5
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	4
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2017-01-13T22:08:33
13	Modification Date	2017-01-16T22:45:22
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

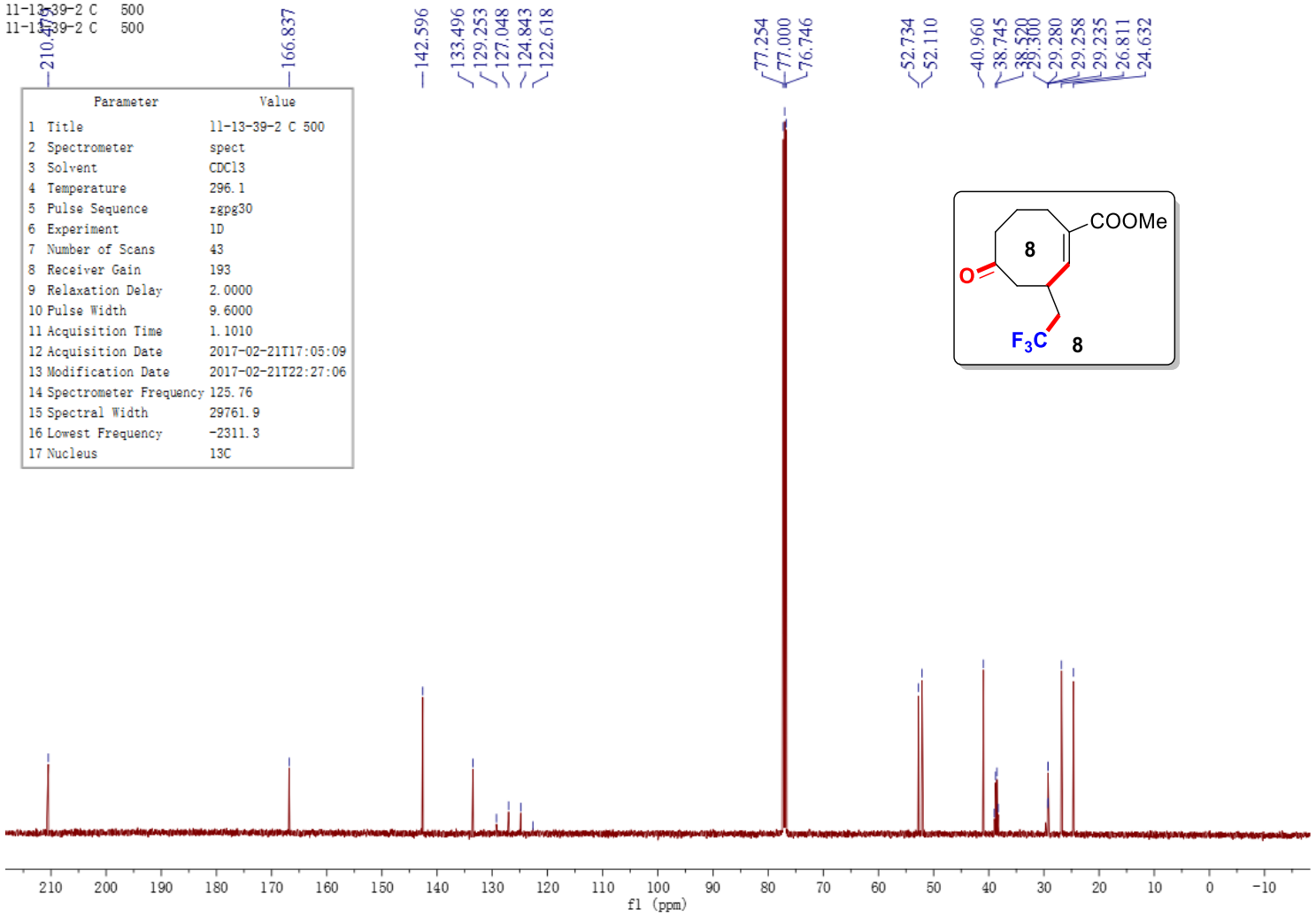




^{1}H NMR Spectrum of Compound **8**



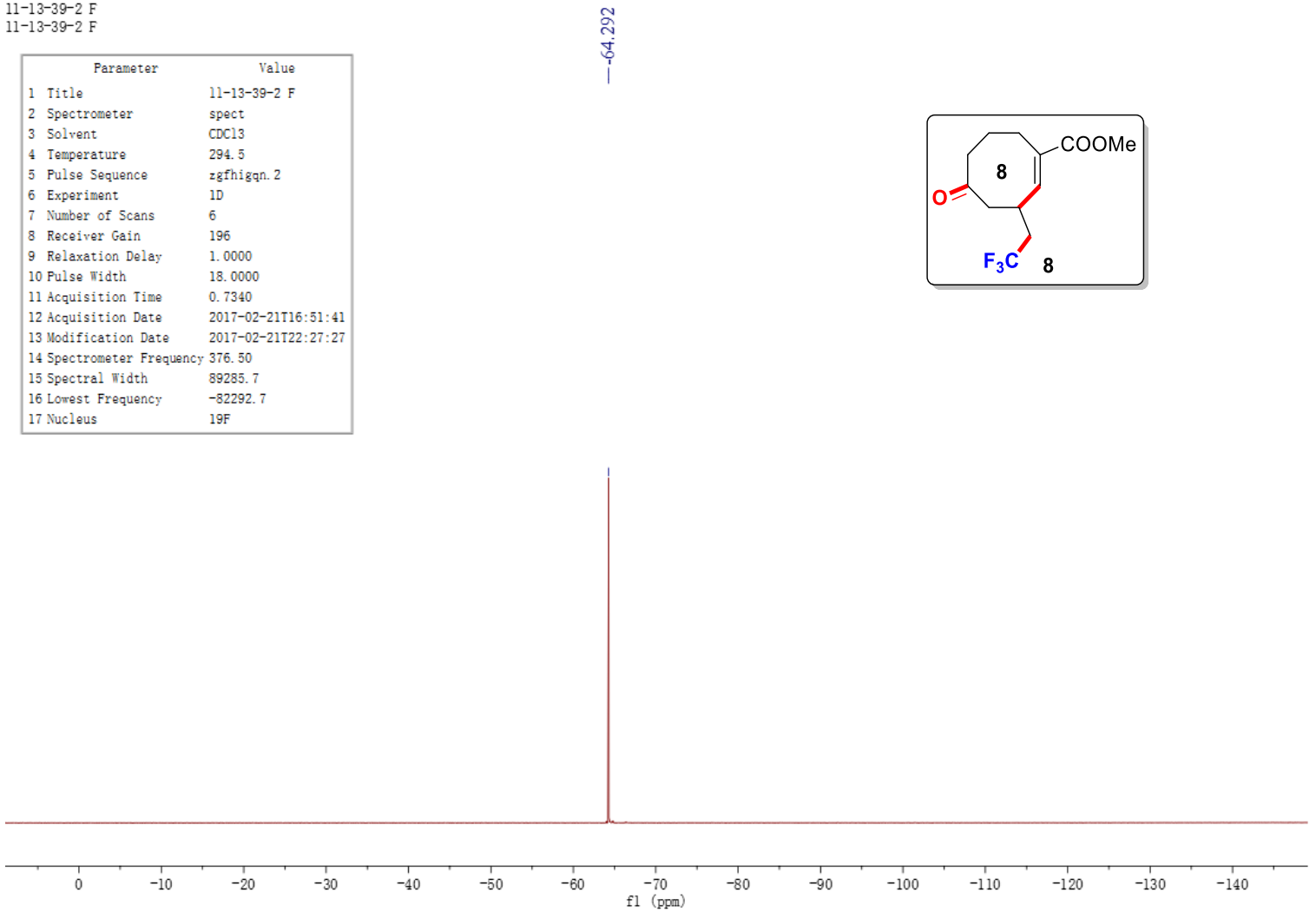
^{13}C NMR Spectrum of Compound **8**



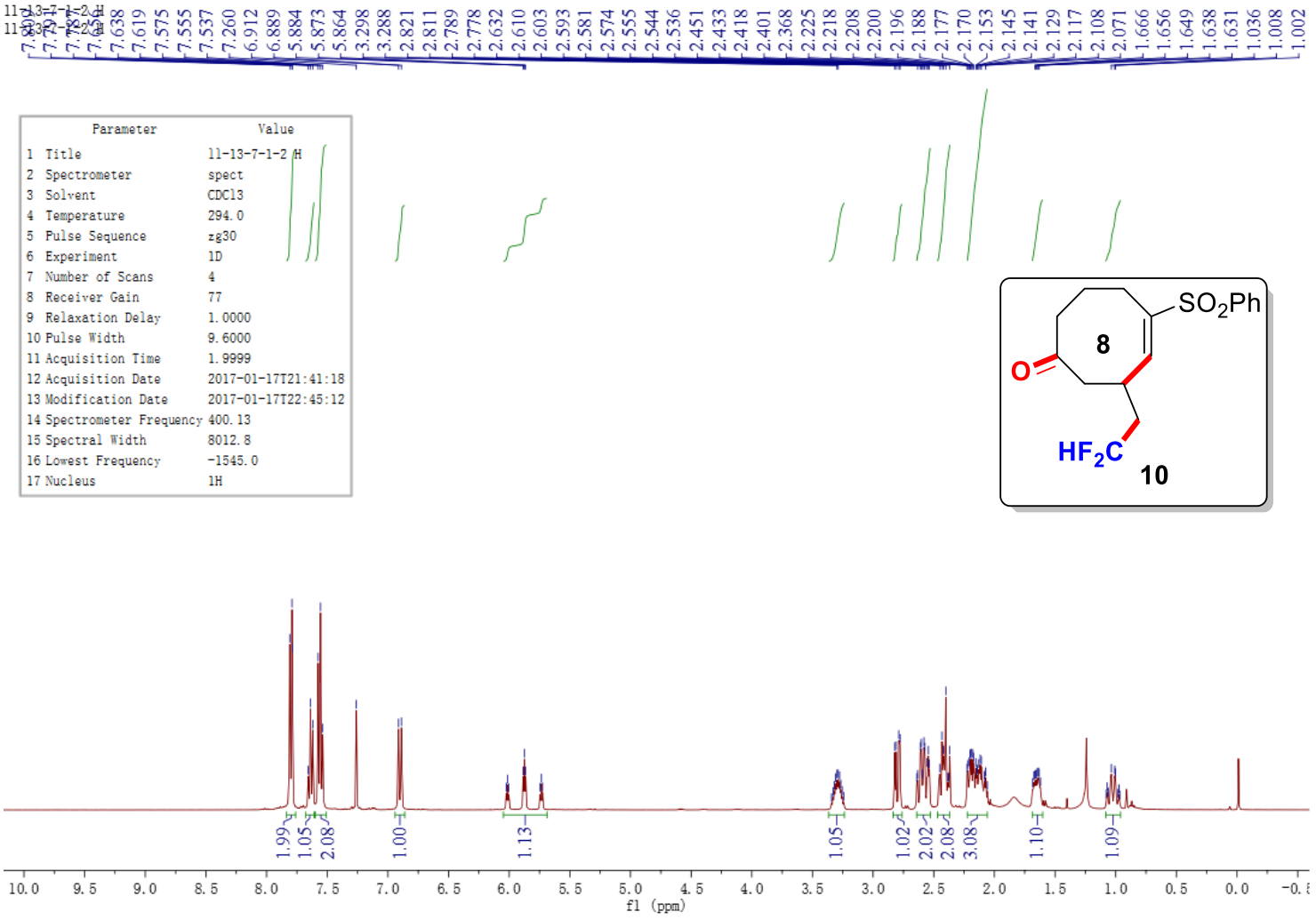
^{19}F NMR Spectrum of Compound **8**

11-13-39-2 F
11-13-39-2 F

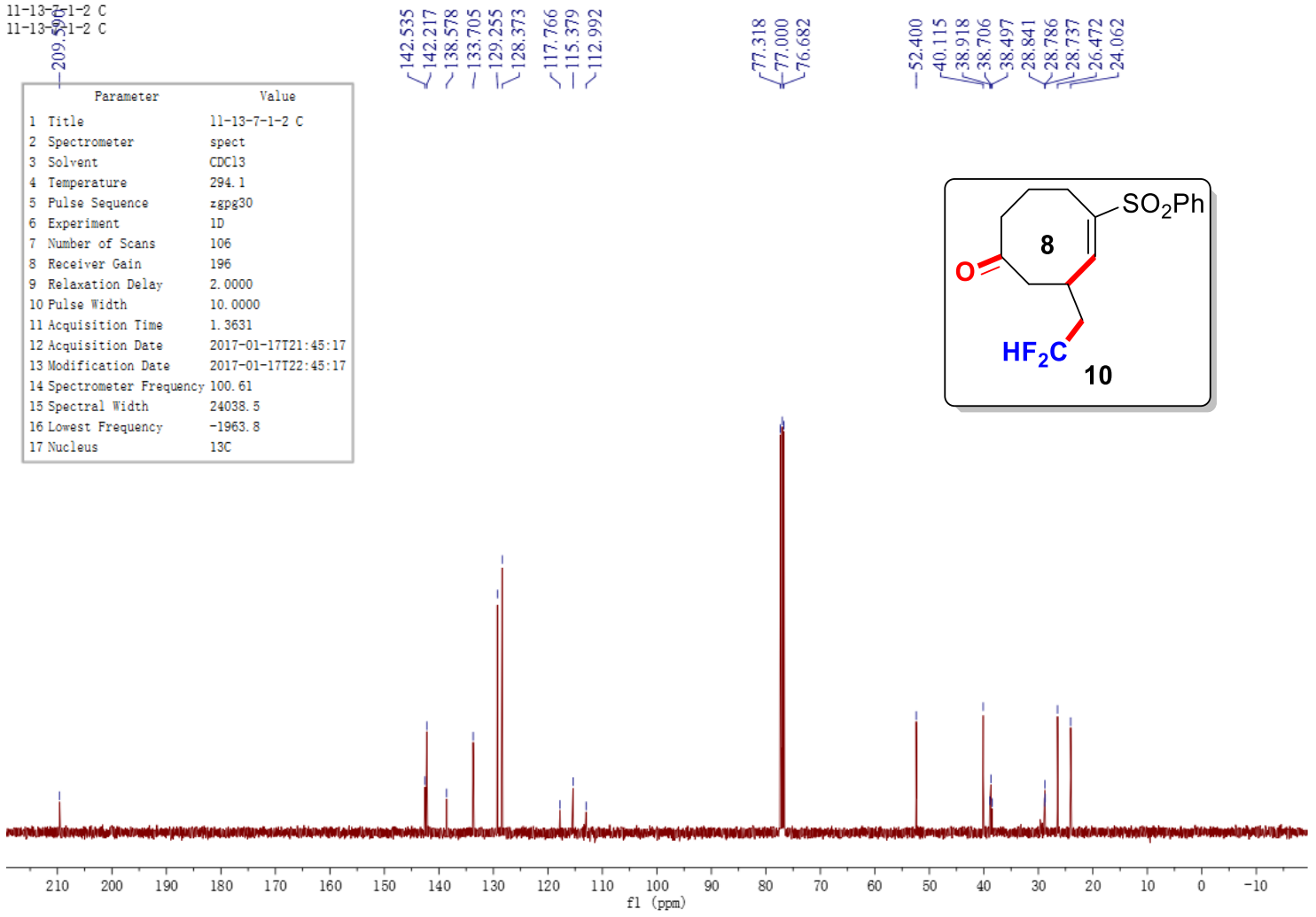
	Parameter	Value
1	Title	11-13-39-2 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.5
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	6
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2017-02-21T16:51:41
13	Modification Date	2017-02-21T22:27:27
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



^{1}H NMR Spectrum of Compound **10**



^{13}C NMR Spectrum of Compound **10**

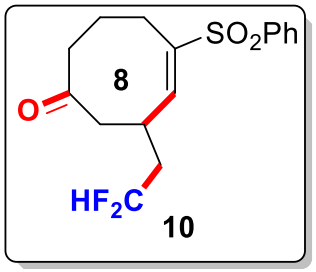


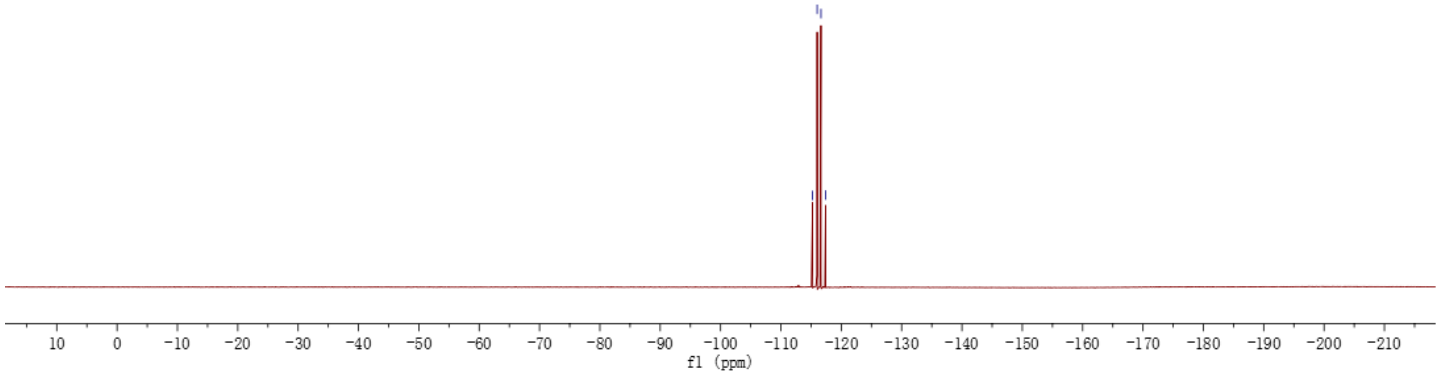
^{19}F NMR Spectrum of Compound **10**

11-13-7-1-2 F
11-13-7-1-2 F

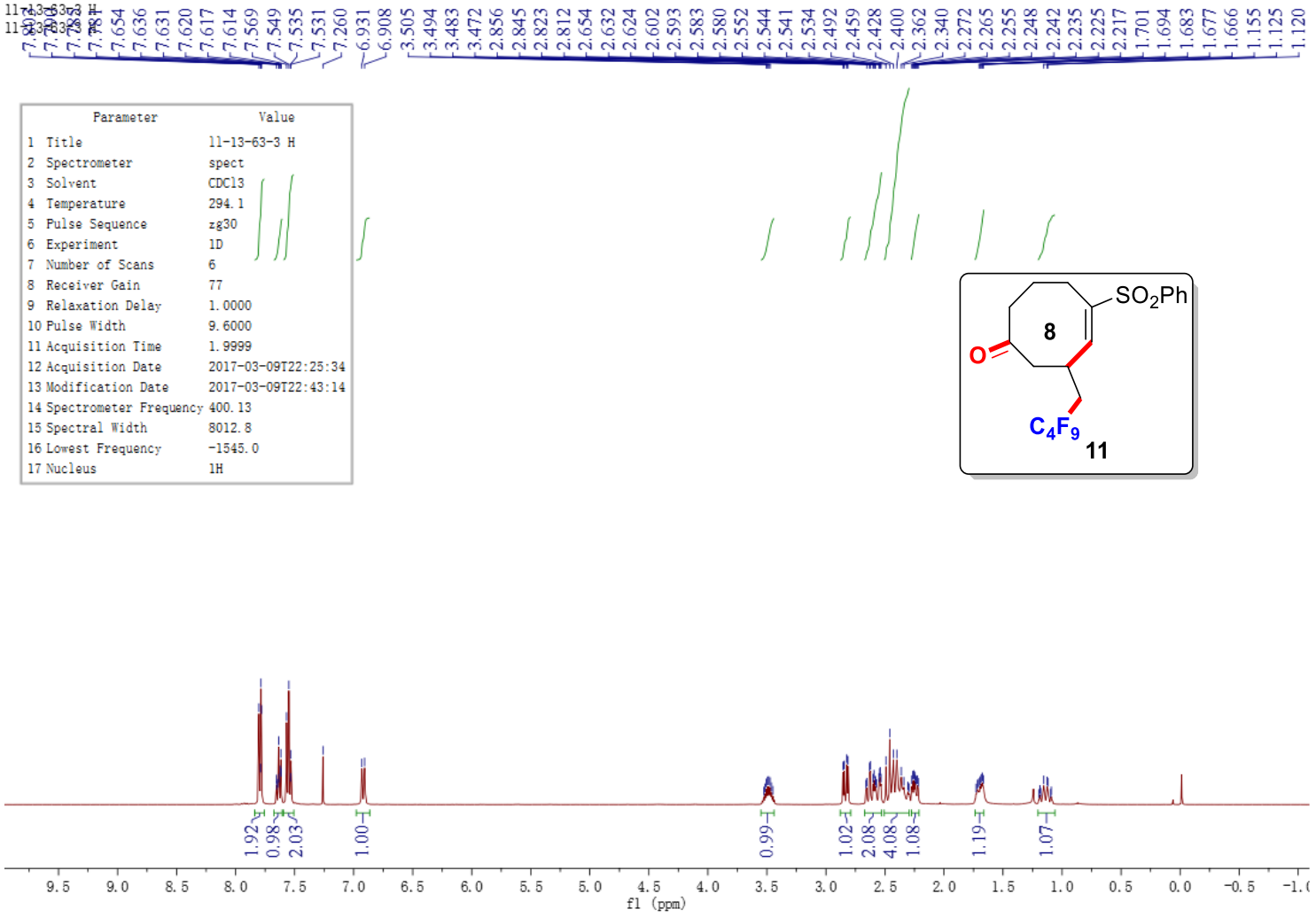
	Parameter	Value
1	Title	11-13-7-1-2 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.0
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	6
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2017-01-17T21:43:20
13	Modification Date	2017-01-17T22:45:15
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

-115.247
-116.006
-116.639
-117.398

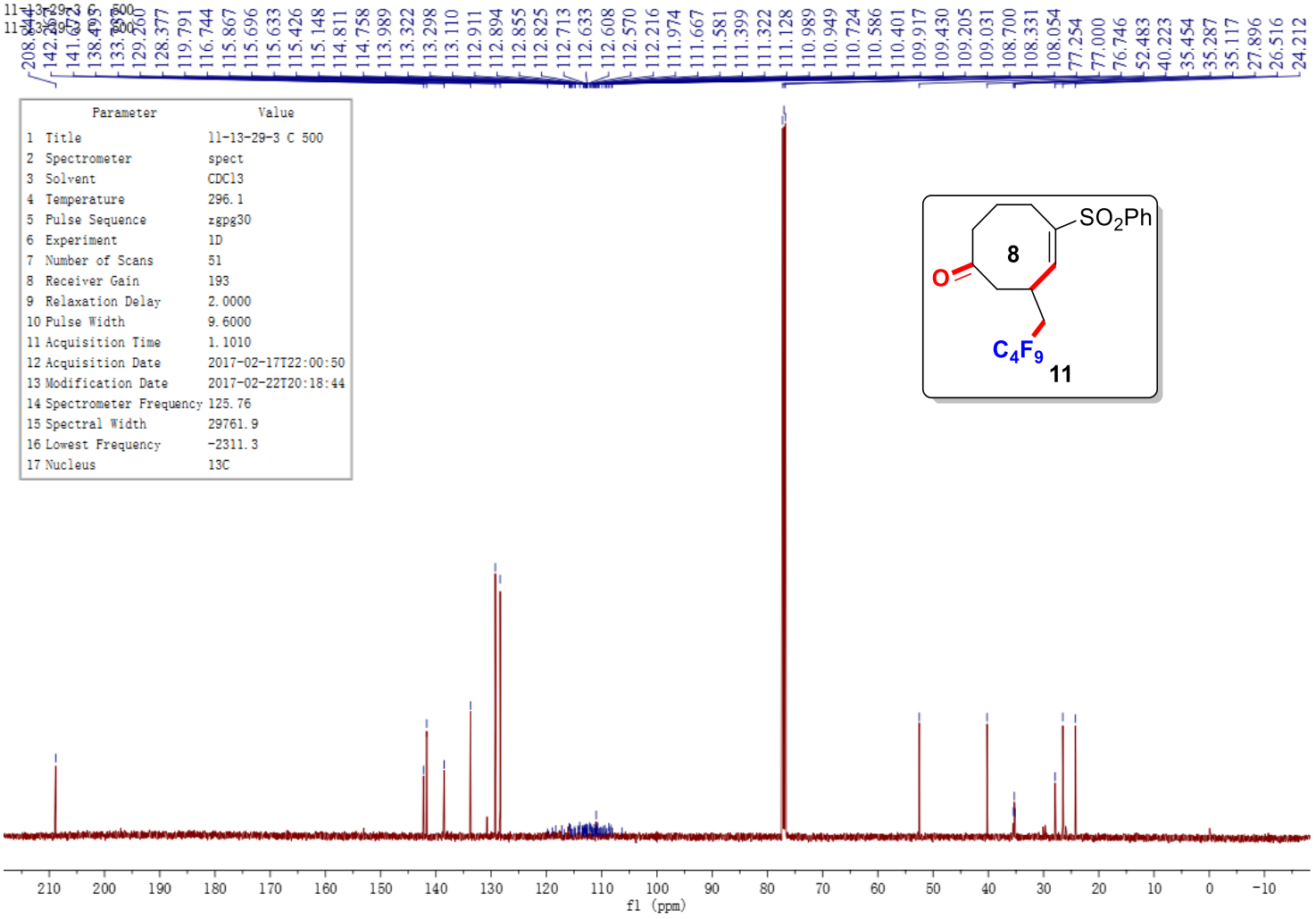




^{1}H NMR Spectrum of Compound **11**



^{13}C NMR Spectrum of Compound **11**



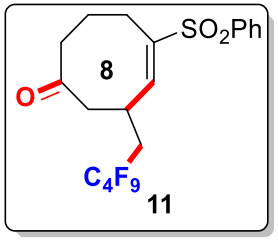
^{19}F NMR Spectrum of Compound **11**

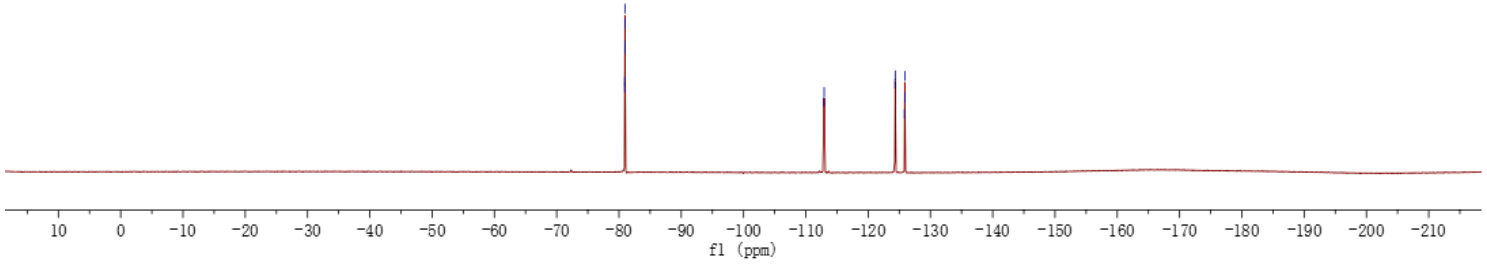
11-13-29-3 F
11-13-29-3 F

	Parameter	Value
1	Title	11-13-29-3 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.1
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	12
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2017-02-17T22:07:43
13	Modification Date	2017-02-22T20:18:52
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

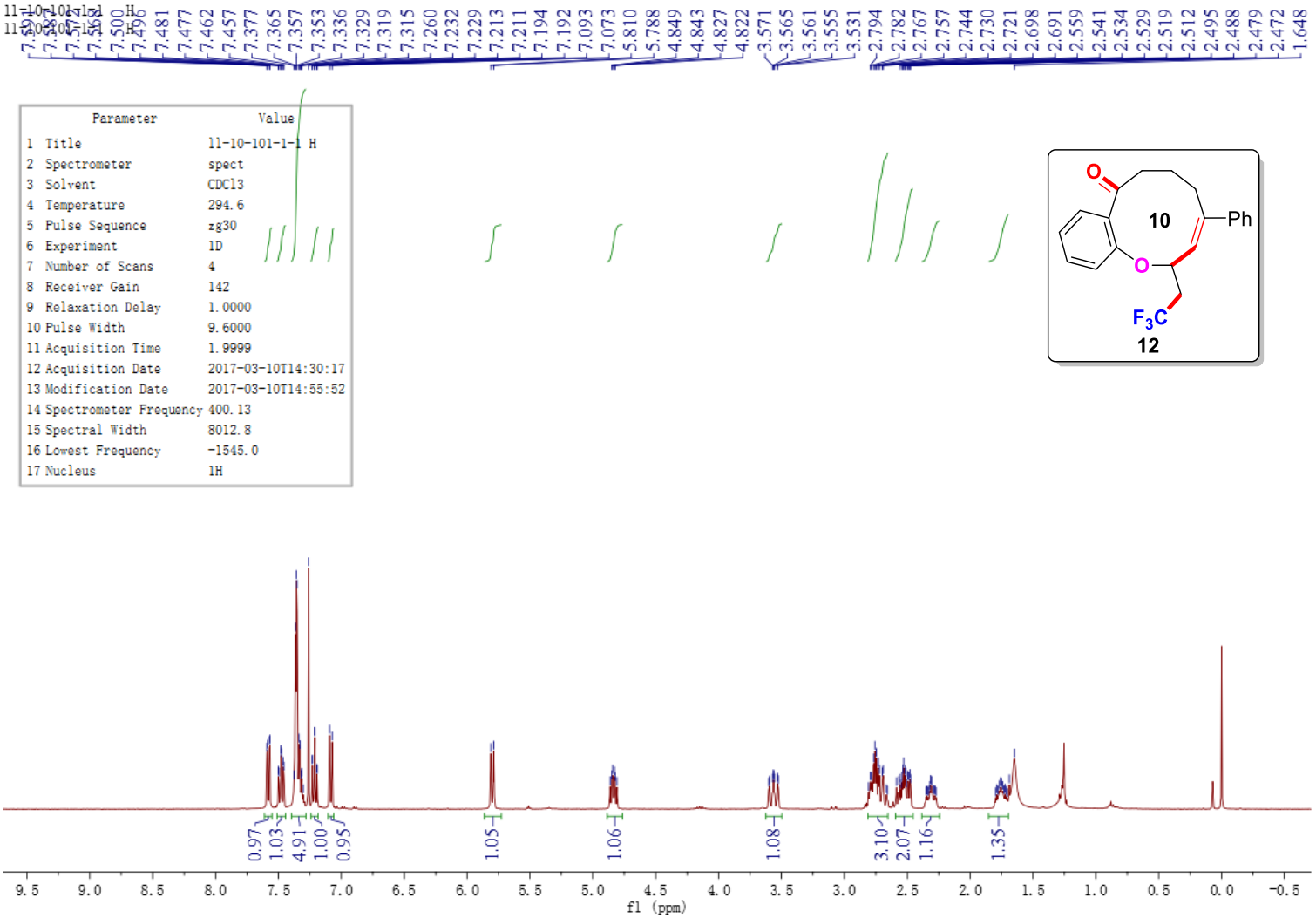
-80.933
-80.941
-80.959
-80.966
-80.973
-80.983

-112.915
-112.942
-124.331
-124.351
-125.852
-125.888
-125.917

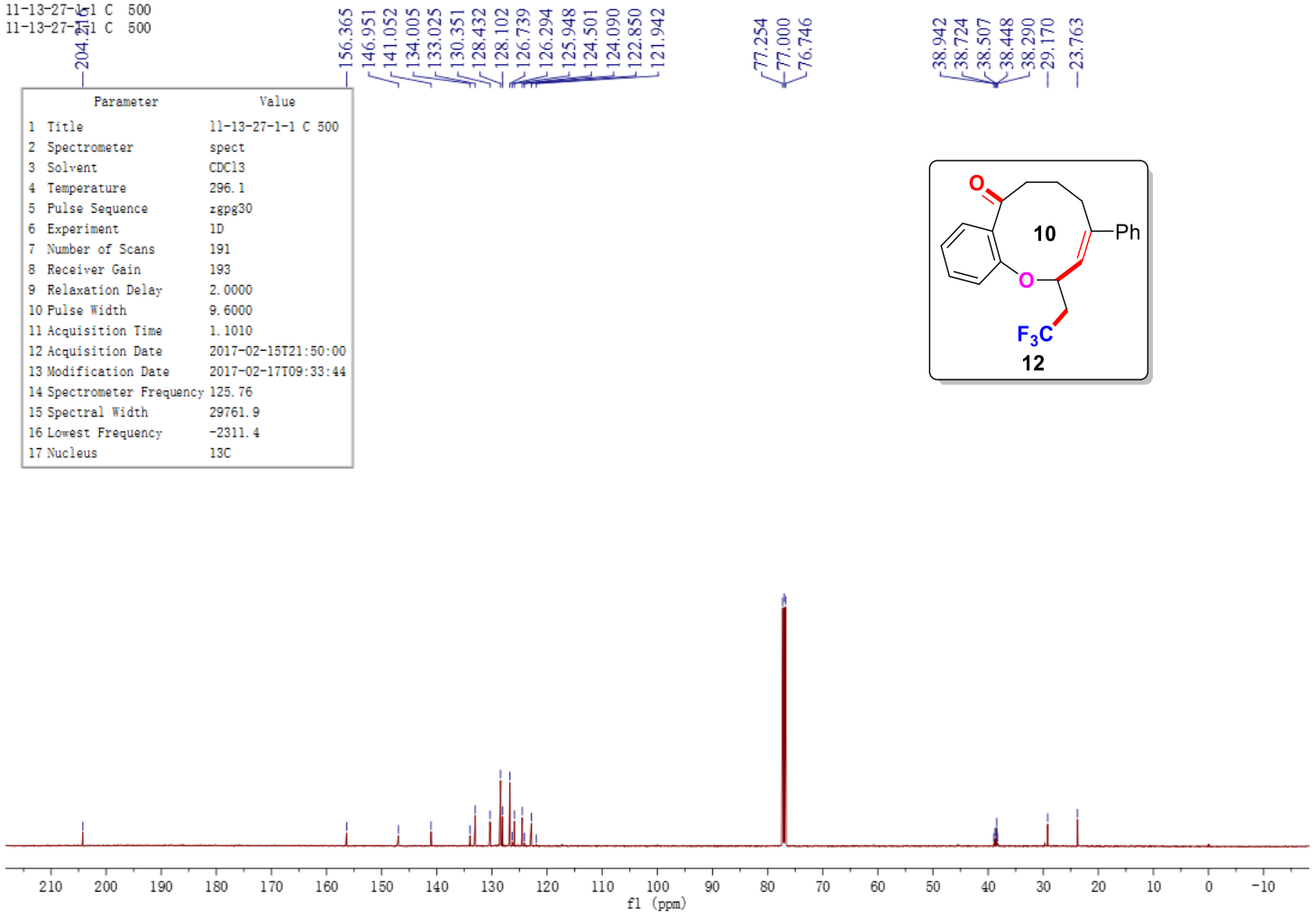




^{1}H NMR Spectrum of Compound **12**



^{13}C NMR Spectrum of Compound **12**

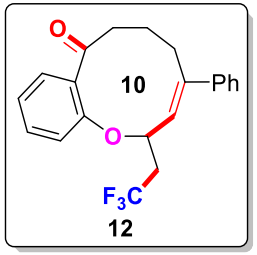


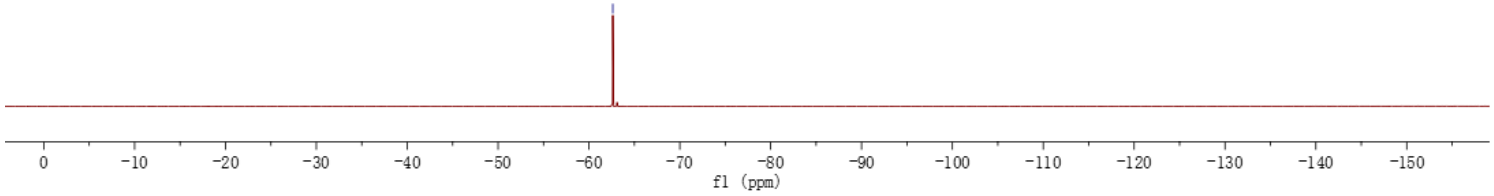
^{19}F NMR Spectrum of Compound **12**

11-10-101-1-1 H
11-10-101-1-1 H

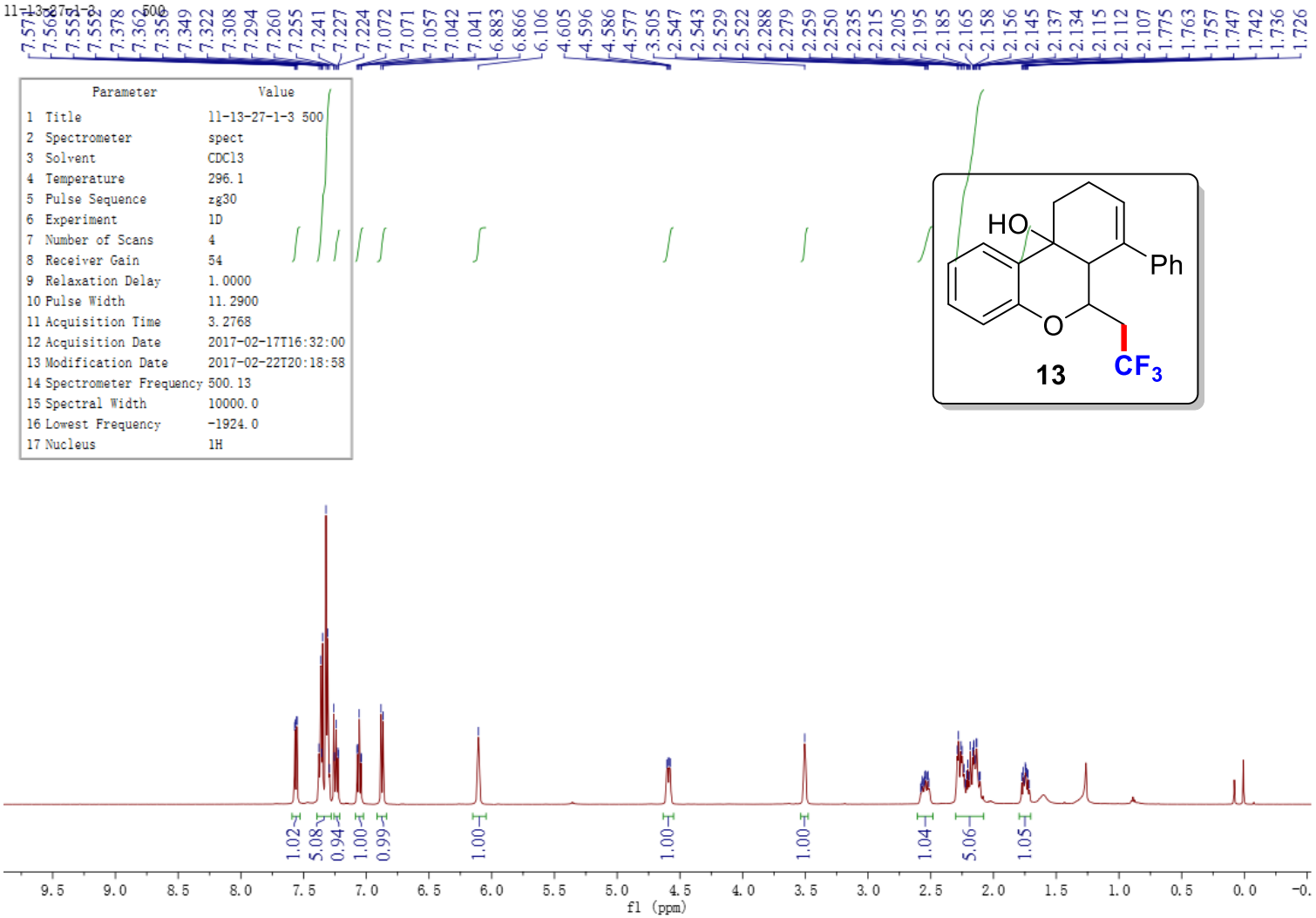
-62.624

	Parameter	Value
1	Title	11-10-101-1-1 H
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.6
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	4
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2017-03-10T14:31:56
13	Modification Date	2017-03-10T14:55:53
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F

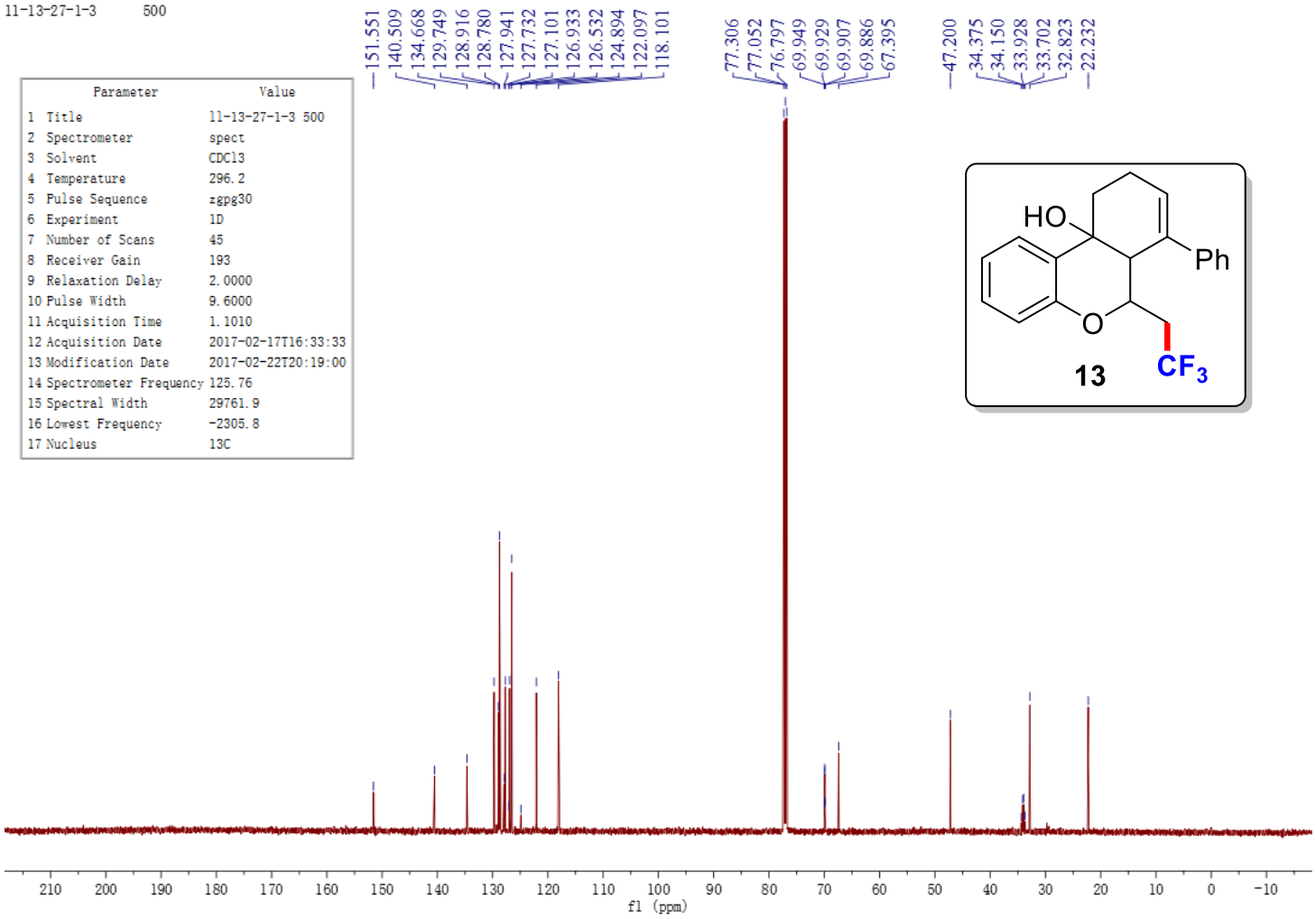




^{1}H NMR Spectrum of Compound **13**



^{13}C NMR Spectrum of Compound **13**

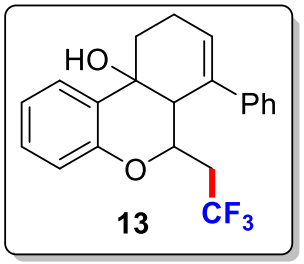


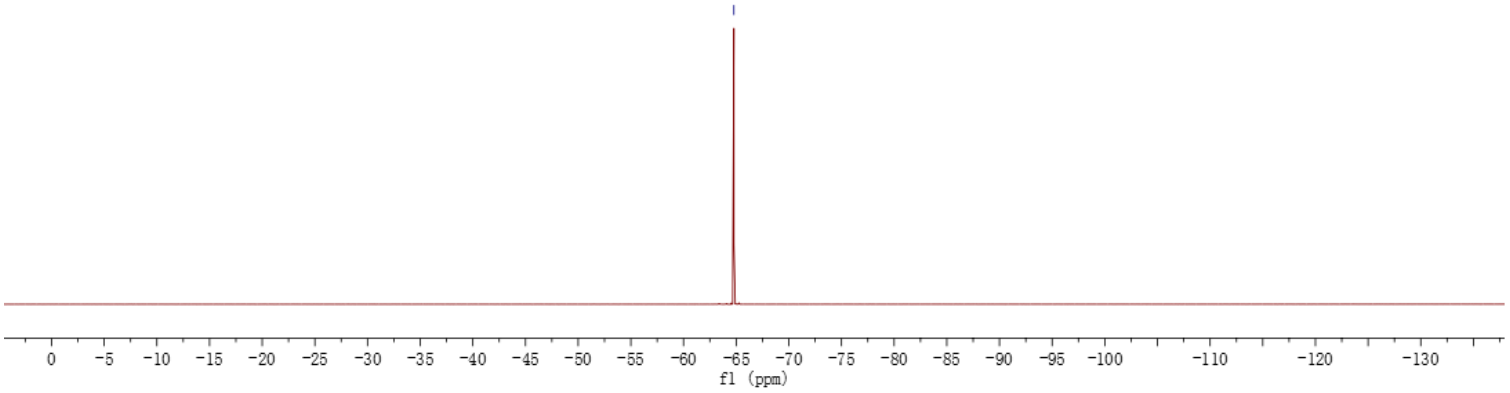
^{19}F NMR Spectrum of Compound **13**

11-13-27-1-3 F
11-13-27-1-3 F

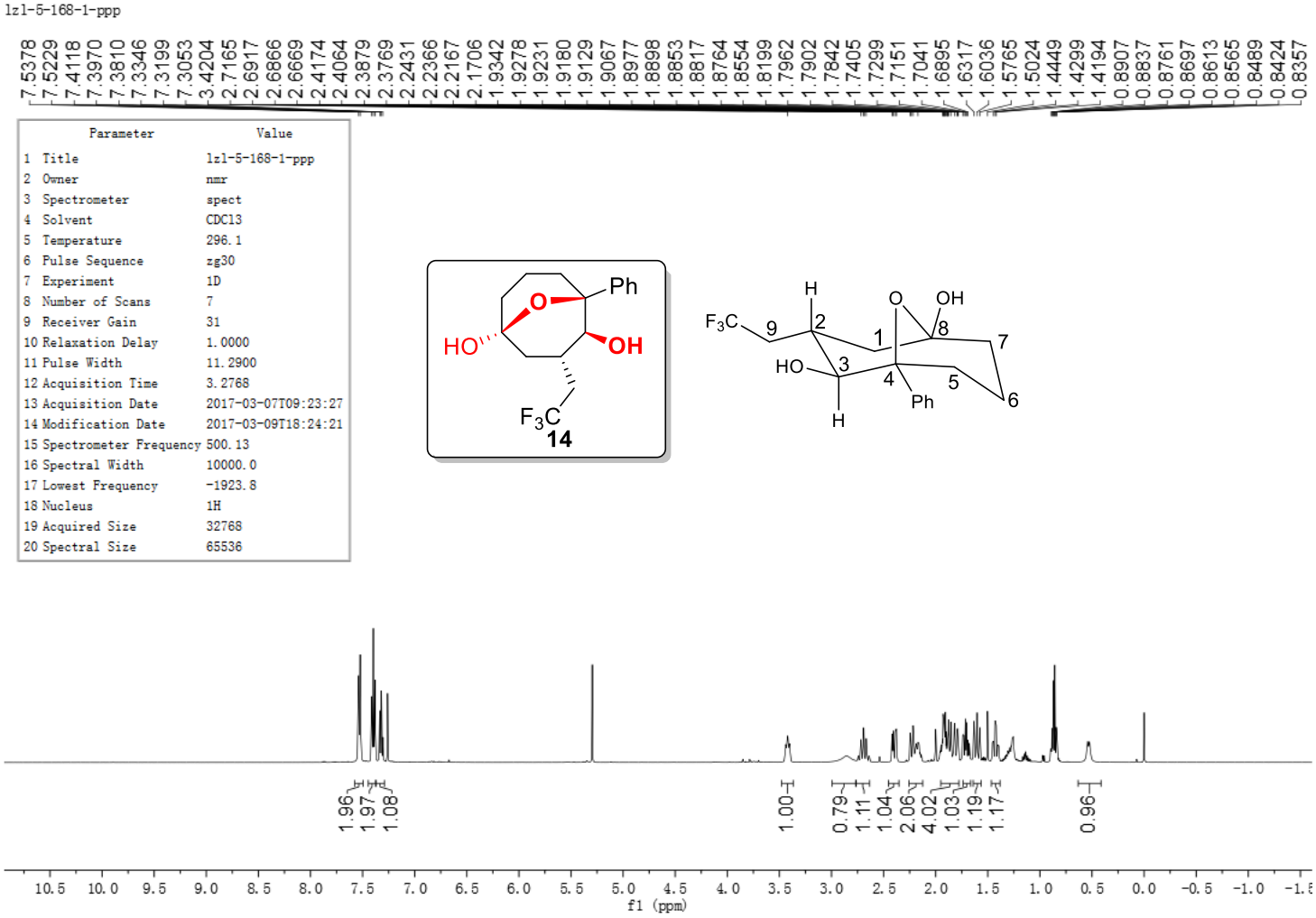
Parameter	Value
1 Title	11-13-27-1-3 F
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	293.9
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	196
9 Relaxation Delay	1.0000
10 Pulse Width	18.0000
11 Acquisition Time	0.7340
12 Acquisition Date	2017-02-17T11:01:18
13 Modification Date	2017-02-22T20:19:24
14 Spectrometer Frequency	376.50
15 Spectral Width	89285.7
16 Lowest Frequency	-82292.7
17 Nucleus	19F

-64.785





^{1}H NMR Spectrum of Compound **14**

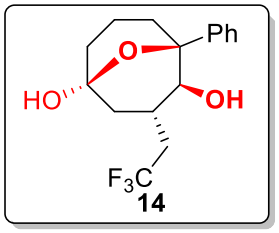


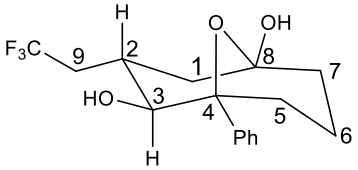
^{13}C NMR Spectrum of Compound **14**

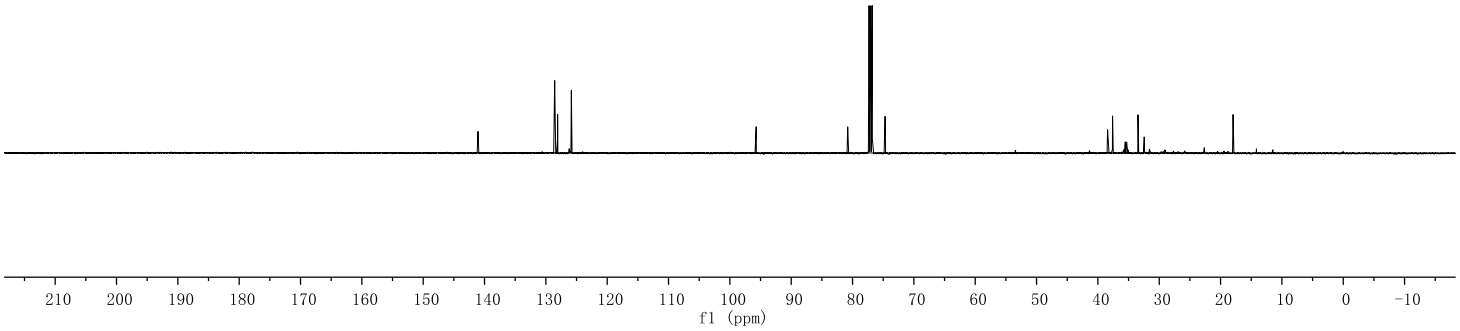
lzl-5-168-1-ppp

Parameter	Value
1 Title	lzl-5-168-1-ppp
2 Owner	nmr
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.1
6 Pulse Sequence	zgpg30
7 Experiment	1D
8 Number of Scans	68
9 Receiver Gain	193
10 Relaxation Delay	2.0000
11 Pulse Width	9.6000
12 Acquisition Time	1.1010
13 Acquisition Date	2017-03-07T09:25:41
14 Modification Date	2017-03-09T18:24:21
15 Spectrometer Frequency	125.76
16 Spectral Width	29761.9
17 Lowest Frequency	-2305.8
18 Nucleus	13C
19 Acquired Size	32768
20 Spectral Size	65536

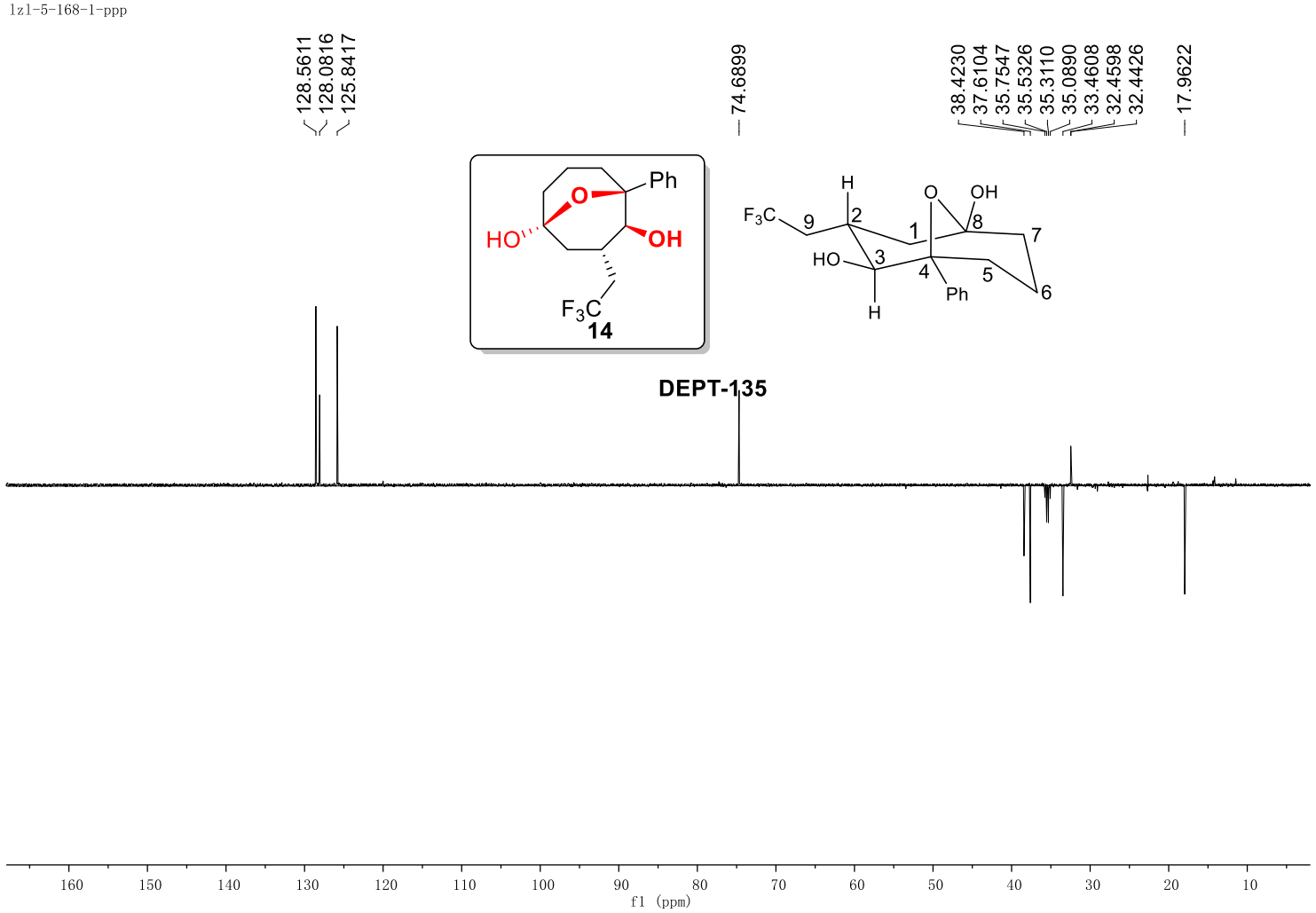
141.0685, 130.6101, 128.5615, 128.4074, 128.0823, 126.2040, 125.8421, 124.0005, 95.7130, 80.7904, 38.4229, 37.6104, 35.7545, 35.5326, 35.3108, 35.0887, 33.4604, 32.4592, 32.4424, 17.9617



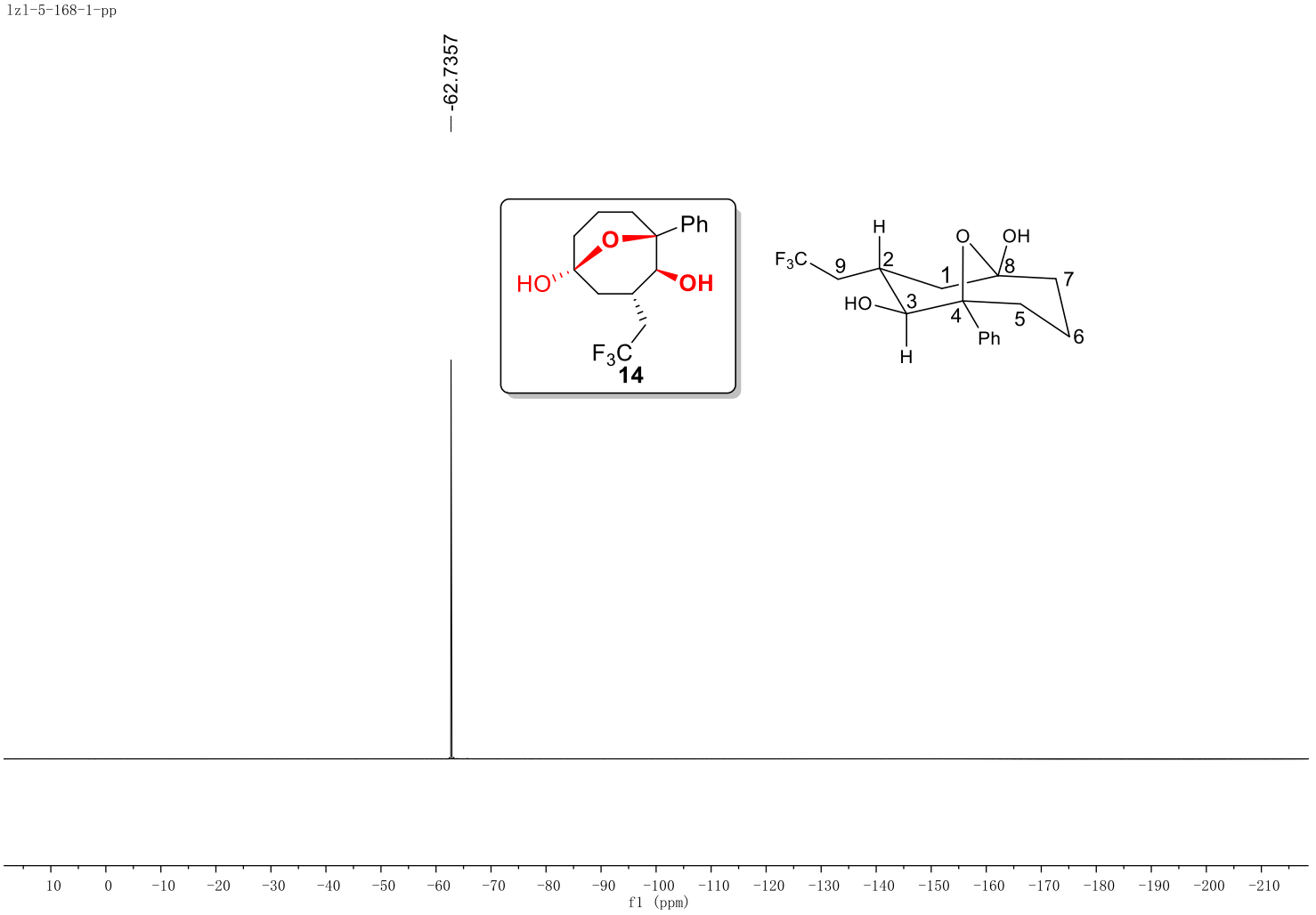




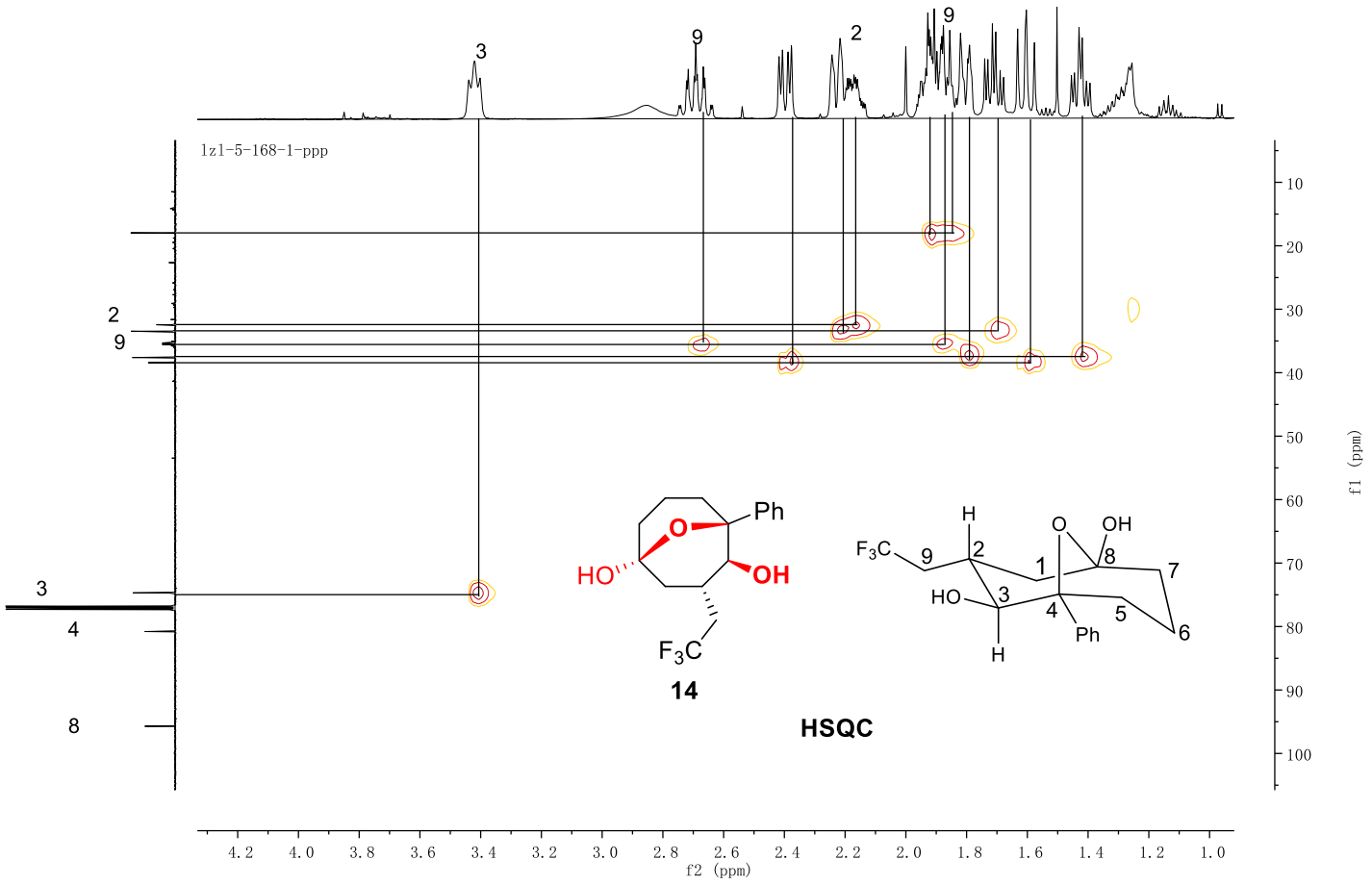
DEPT Spectrum of Compound **14**



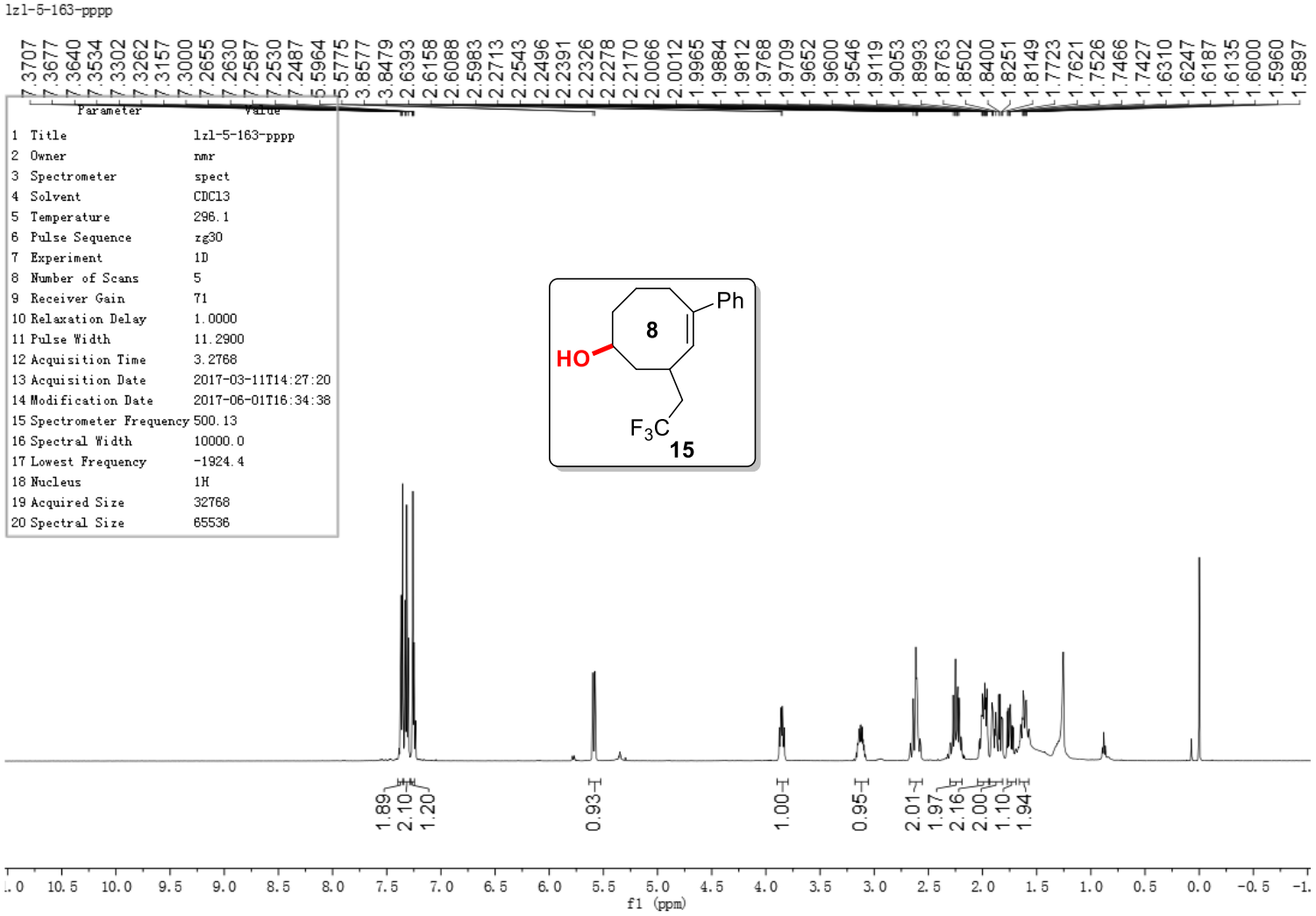
^{19}F NMR Spectrum of Compound **14**



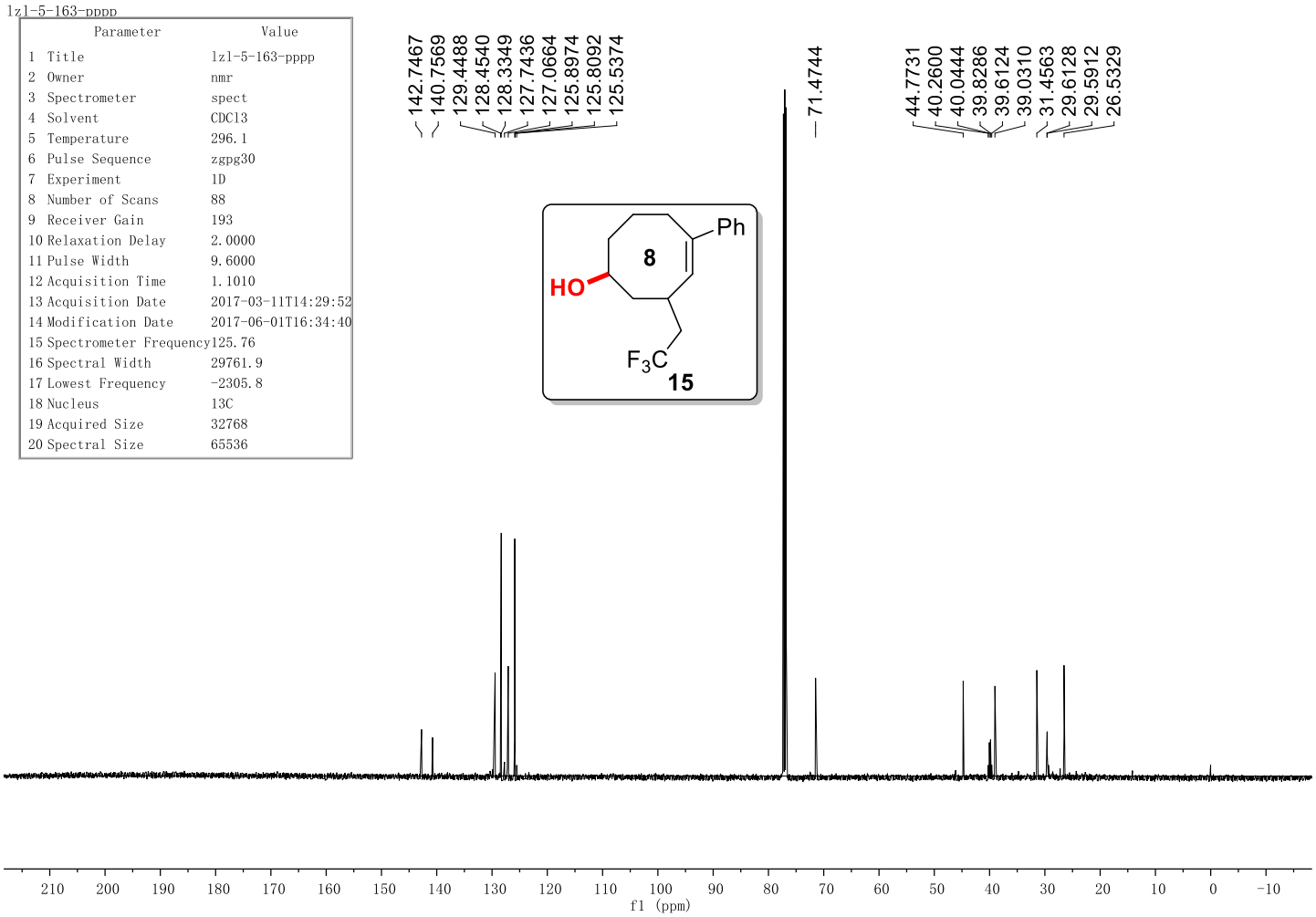
HSQC of compound **4**



^{1}H NMR Spectrum of Compound **15**



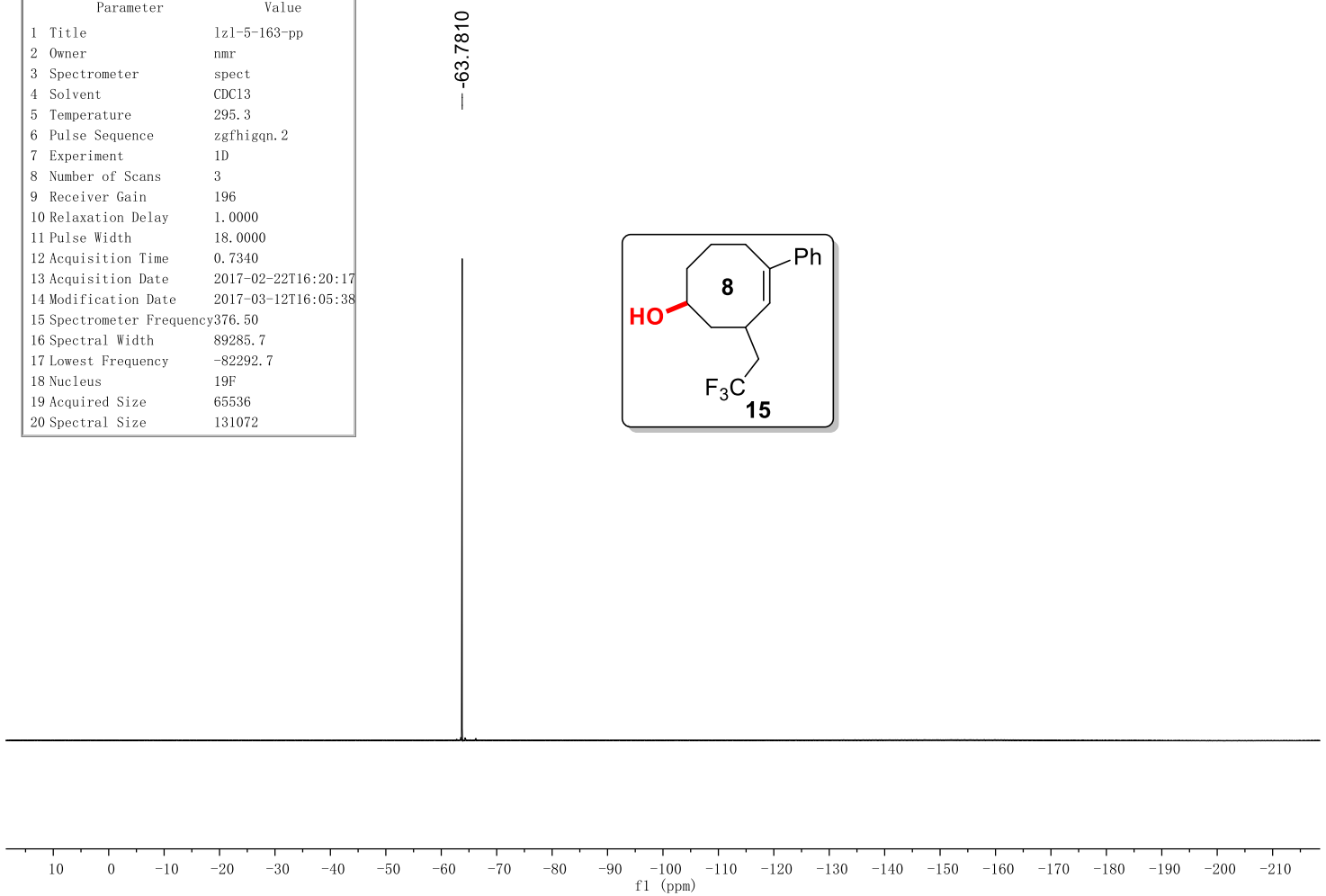
^{13}C NMR Spectrum of Compound **15**



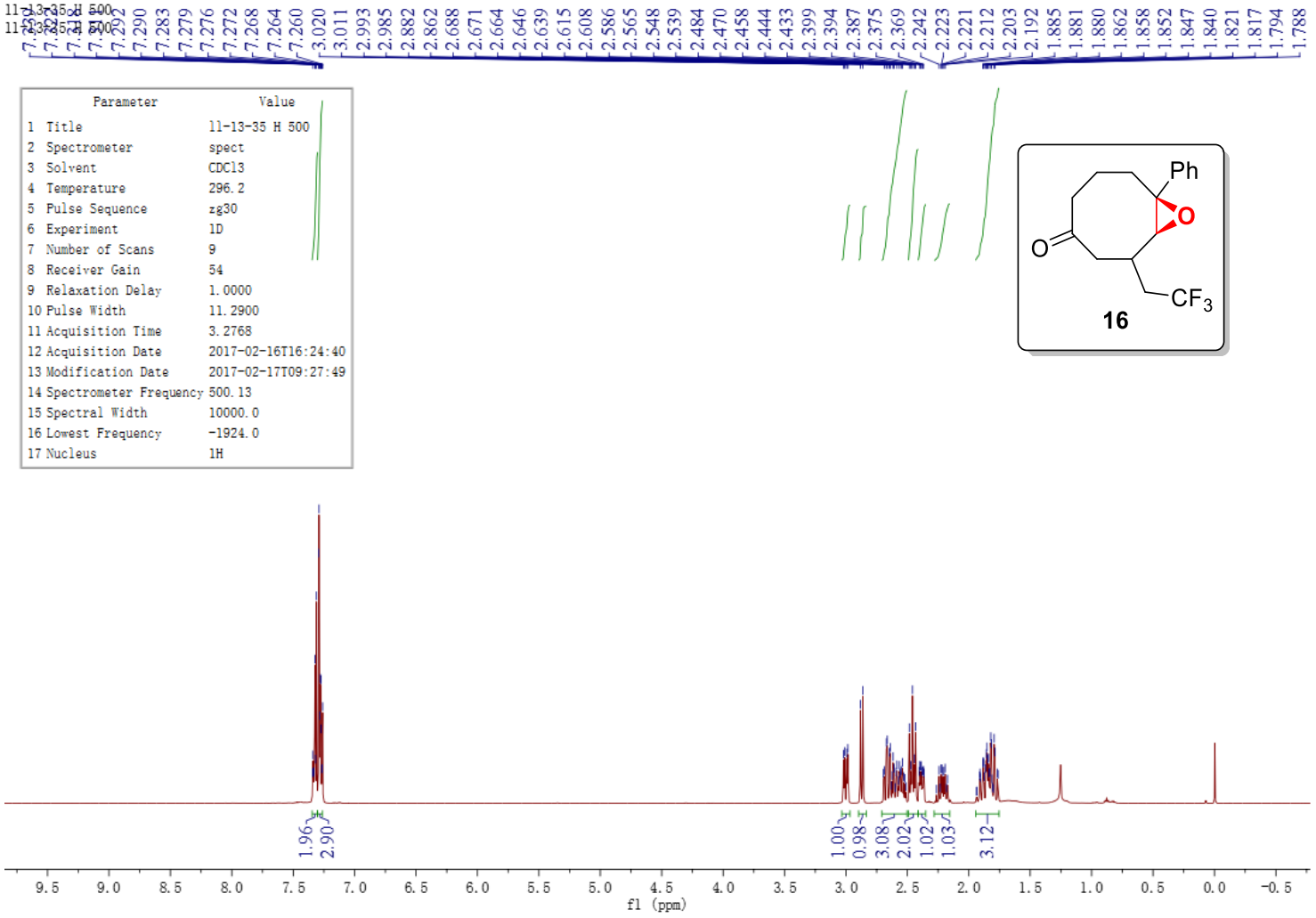
^{19}F NMR Spectrum of Compound **15**

lzl-5-163-pp

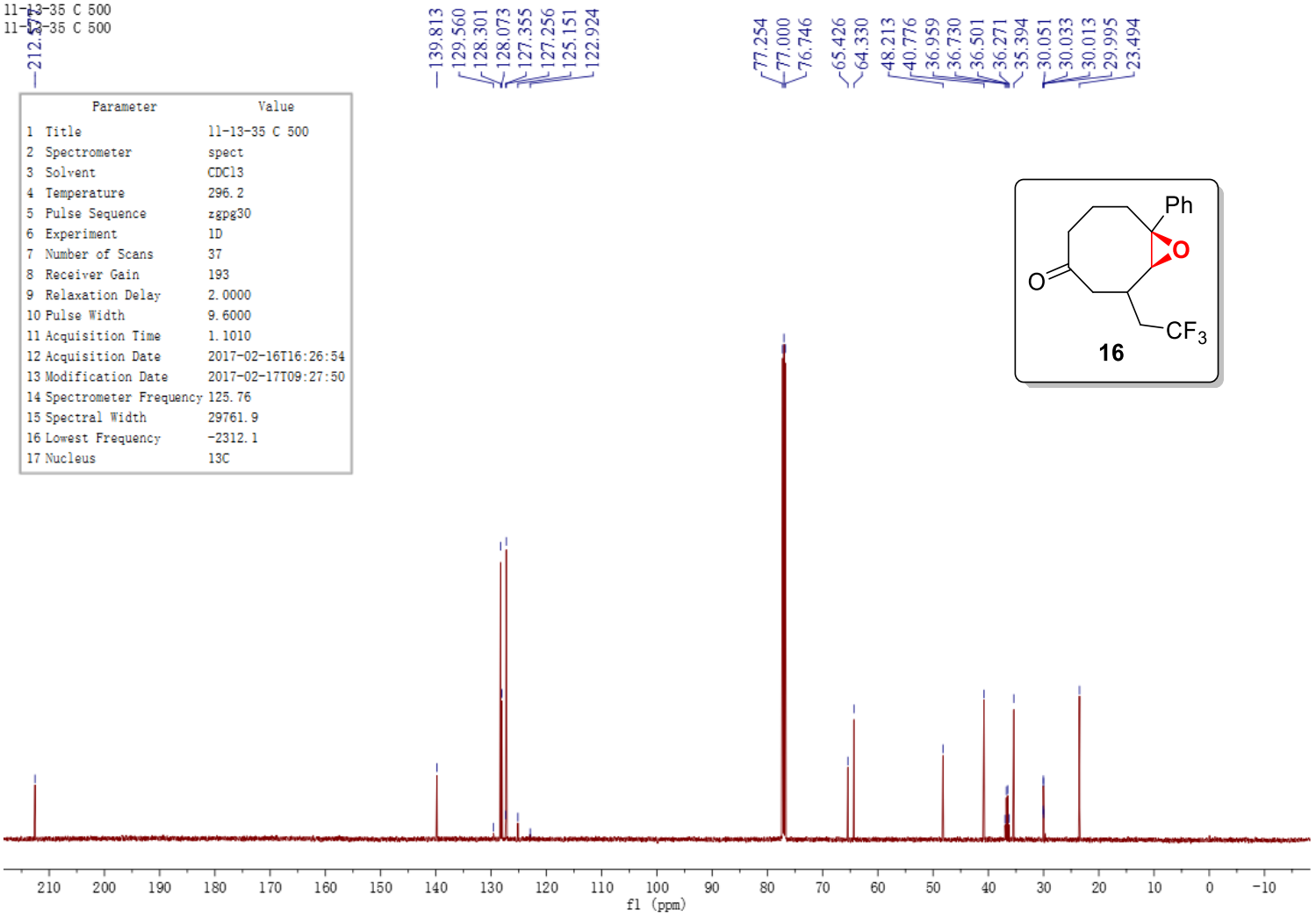
	Parameter	Value
1	Title	lzl-5-163-pp
2	Owner	nmr
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	295.3
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Number of Scans	3
9	Receiver Gain	196
10	Relaxation Delay	1.0000
11	Pulse Width	18.0000
12	Acquisition Time	0.7340
13	Acquisition Date	2017-02-22T16:20:17
14	Modification Date	2017-03-12T16:05:38
15	Spectrometer Frequency	376.50
16	Spectral Width	89285.7
17	Lowest Frequency	-82292.7
18	Nucleus	19F
19	Acquired Size	65536
20	Spectral Size	131072



^{1}H NMR Spectrum of Compound **16**



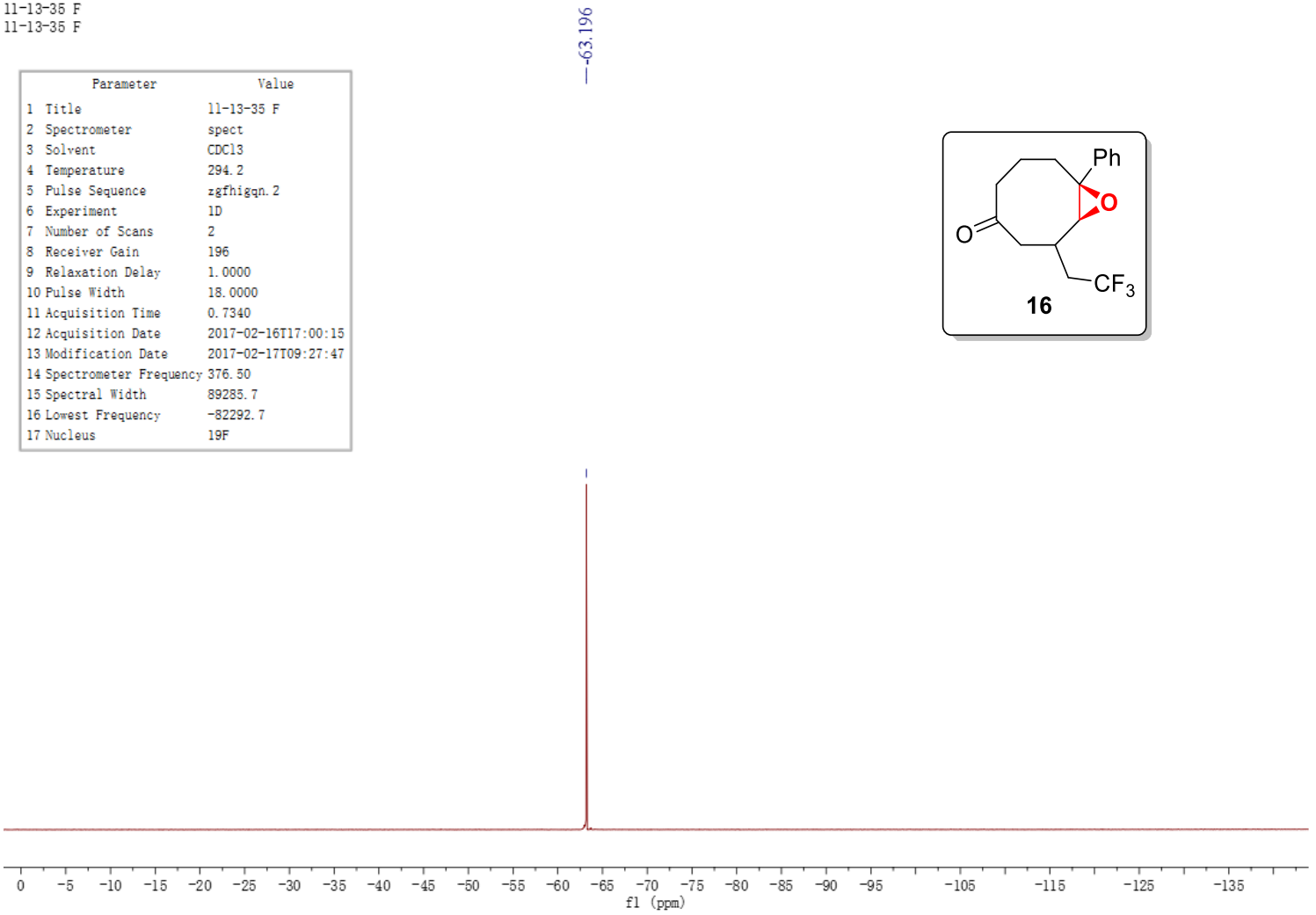
^{13}C NMR Spectrum of Compound **16**



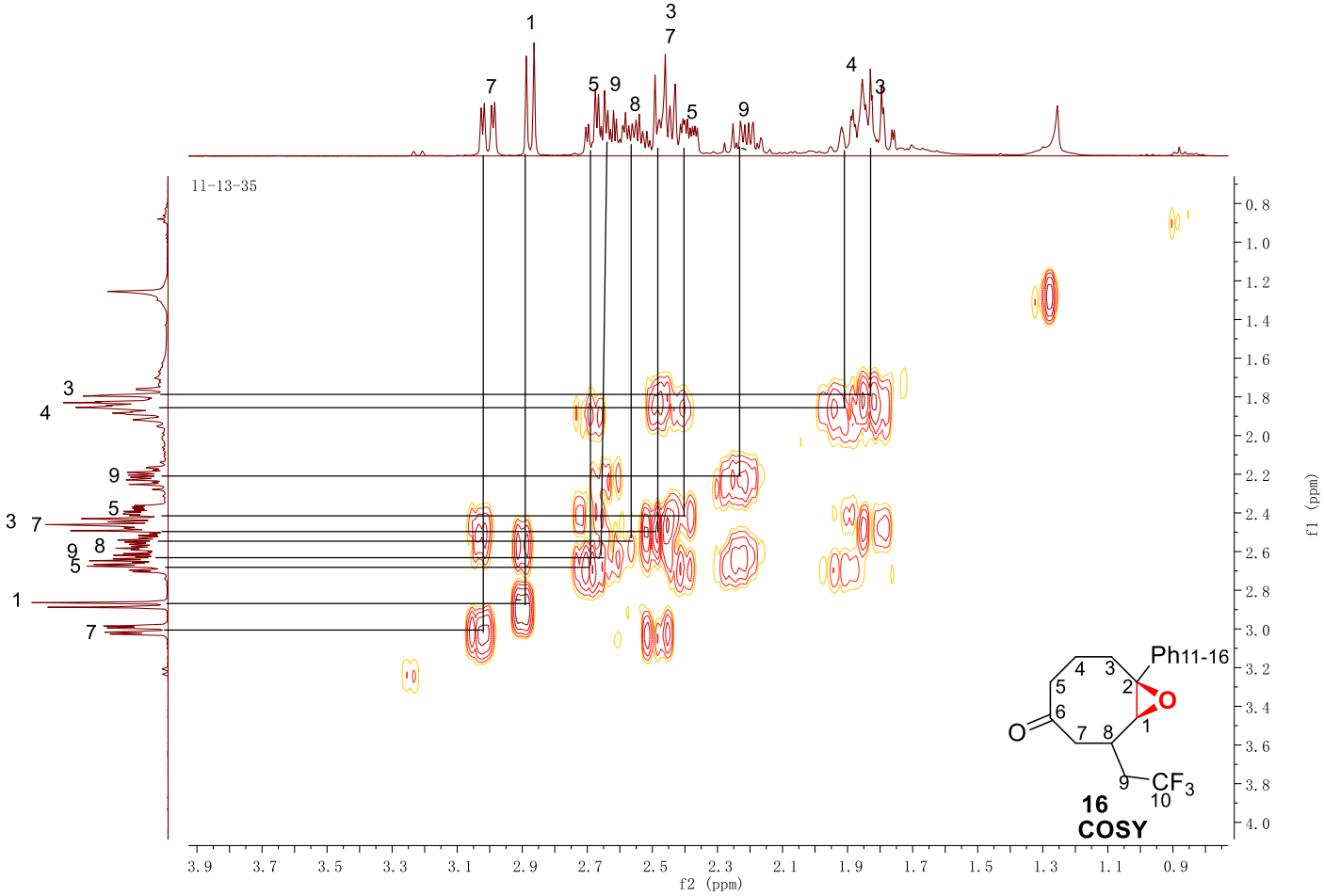
^{19}F NMR Spectrum of Compound **16**

11-13-35 F
11-13-35 F

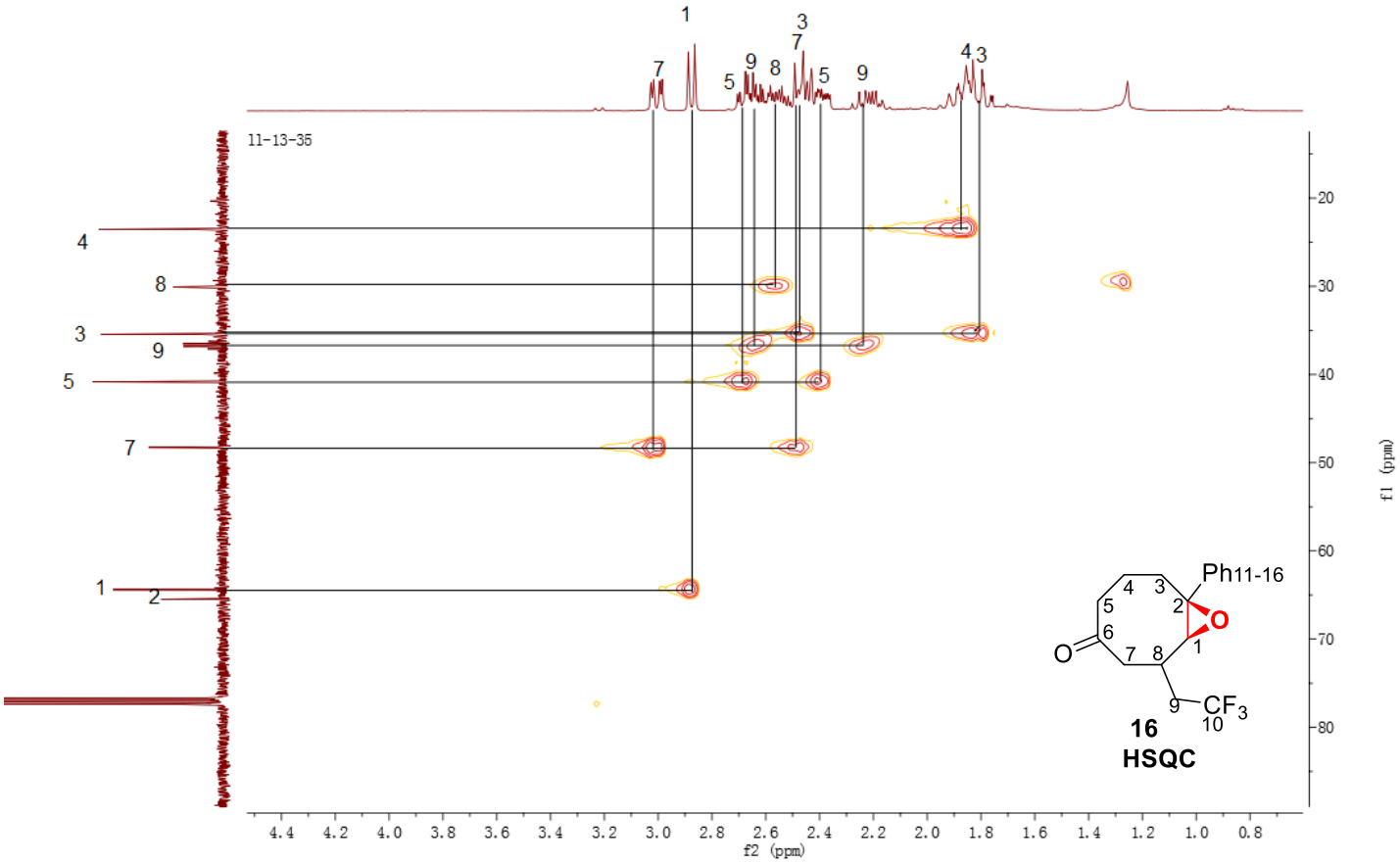
	Parameter	Value
1	Title	11-13-35 F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	294.2
5	Pulse Sequence	zgfhigqn.2
6	Experiment	1D
7	Number of Scans	2
8	Receiver Gain	196
9	Relaxation Delay	1.0000
10	Pulse Width	18.0000
11	Acquisition Time	0.7340
12	Acquisition Date	2017-02-16T17:00:15
13	Modification Date	2017-02-17T09:27:47
14	Spectrometer Frequency	376.50
15	Spectral Width	89285.7
16	Lowest Frequency	-82292.7
17	Nucleus	19F



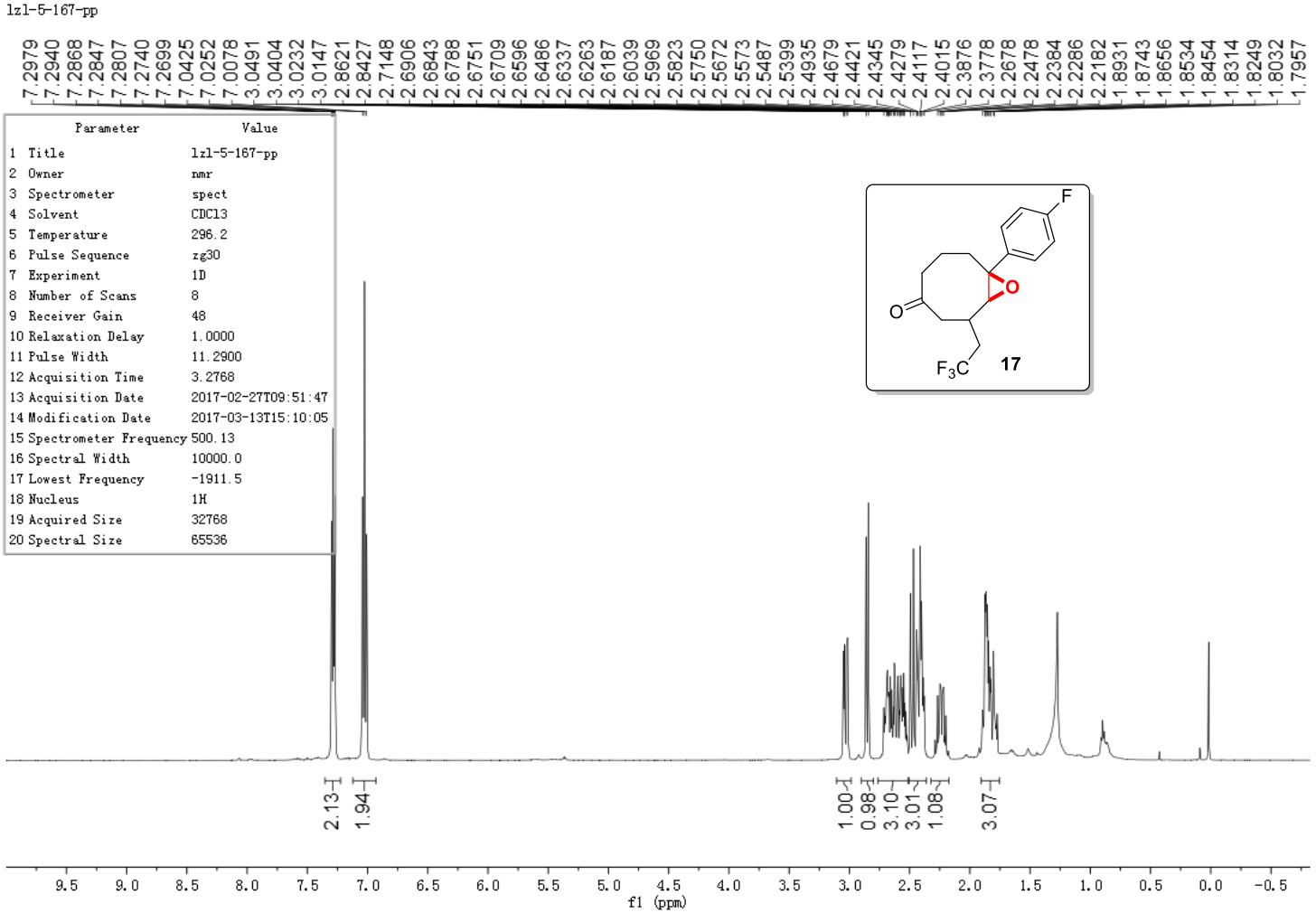
COSY of compound **16**



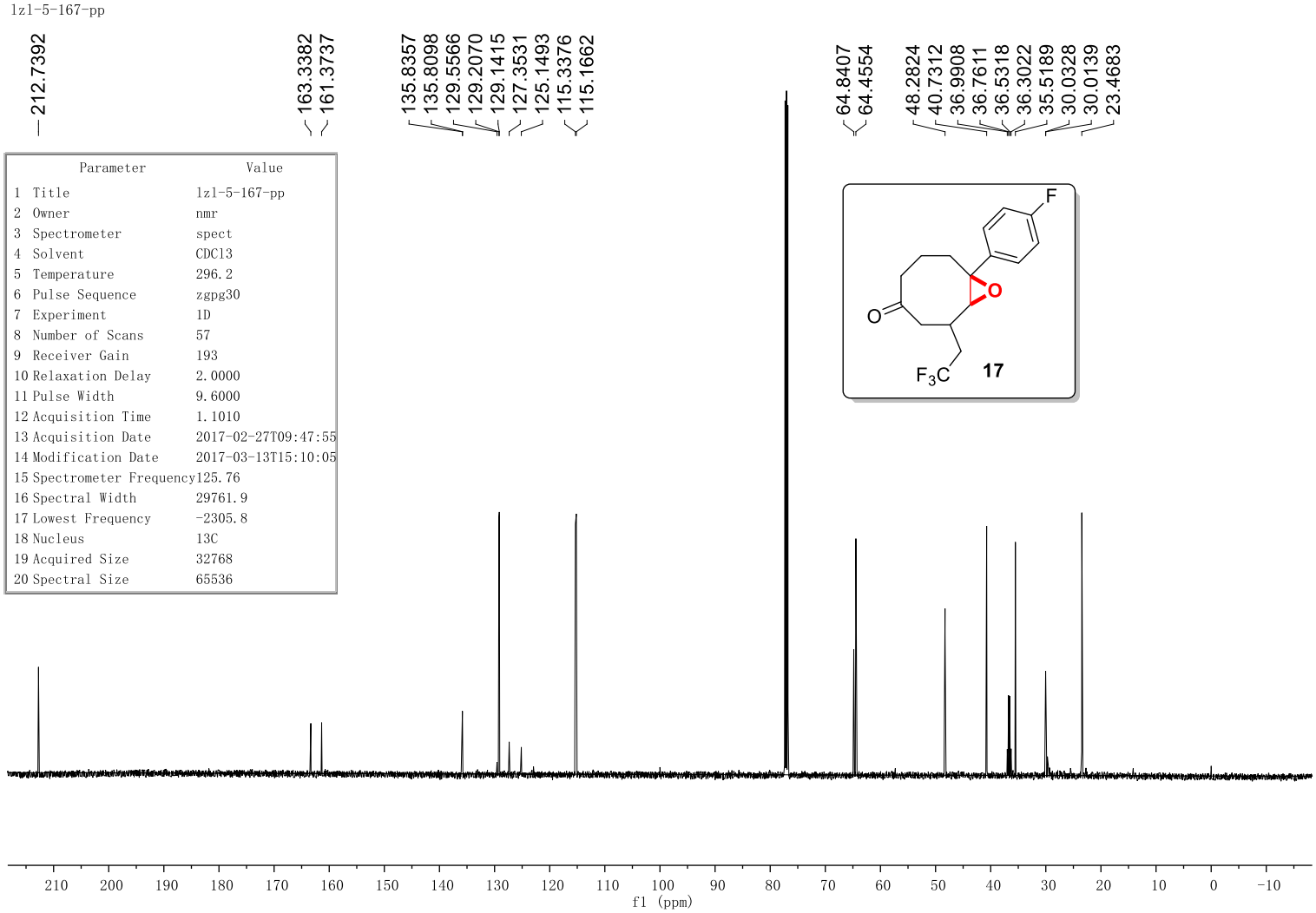
HSQC of compound **16**



^{1}H NMR Spectrum of Compound **17**



^{13}C NMR Spectrum of Compound **17**

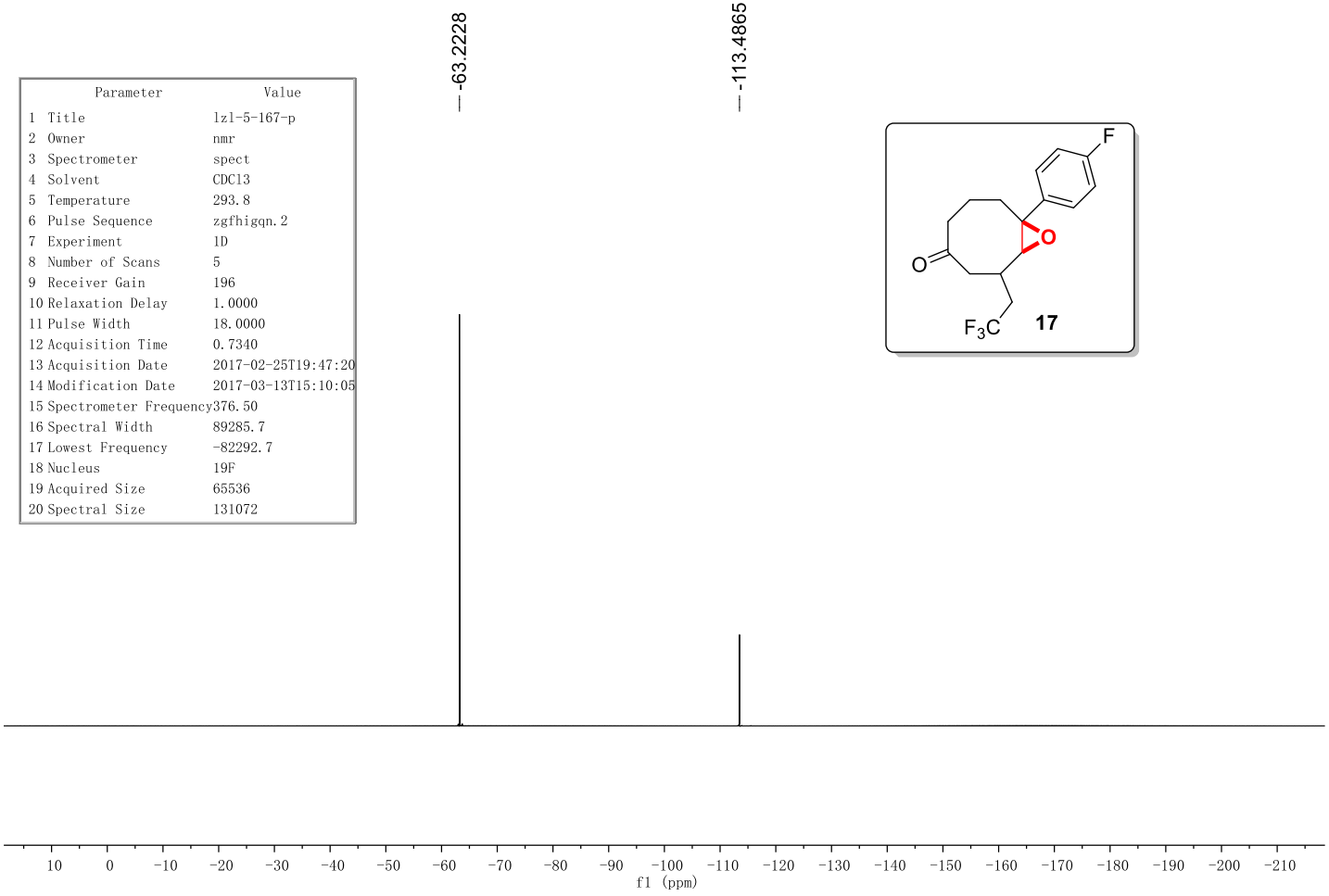


	Parameter	Value
1	Title	lzl-5-167-pp
2	Owner	nmr
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Number of Scans	57
9	Receiver Gain	193
10	Relaxation Delay	2.0000
11	Pulse Width	9.6000
12	Acquisition Time	1.1010
13	Acquisition Date	2017-02-27T09:47:55
14	Modification Date	2017-03-13T15:10:05
15	Spectrometer Frequency	125.76
16	Spectral Width	29761.9
17	Lowest Frequency	-2305.8
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536

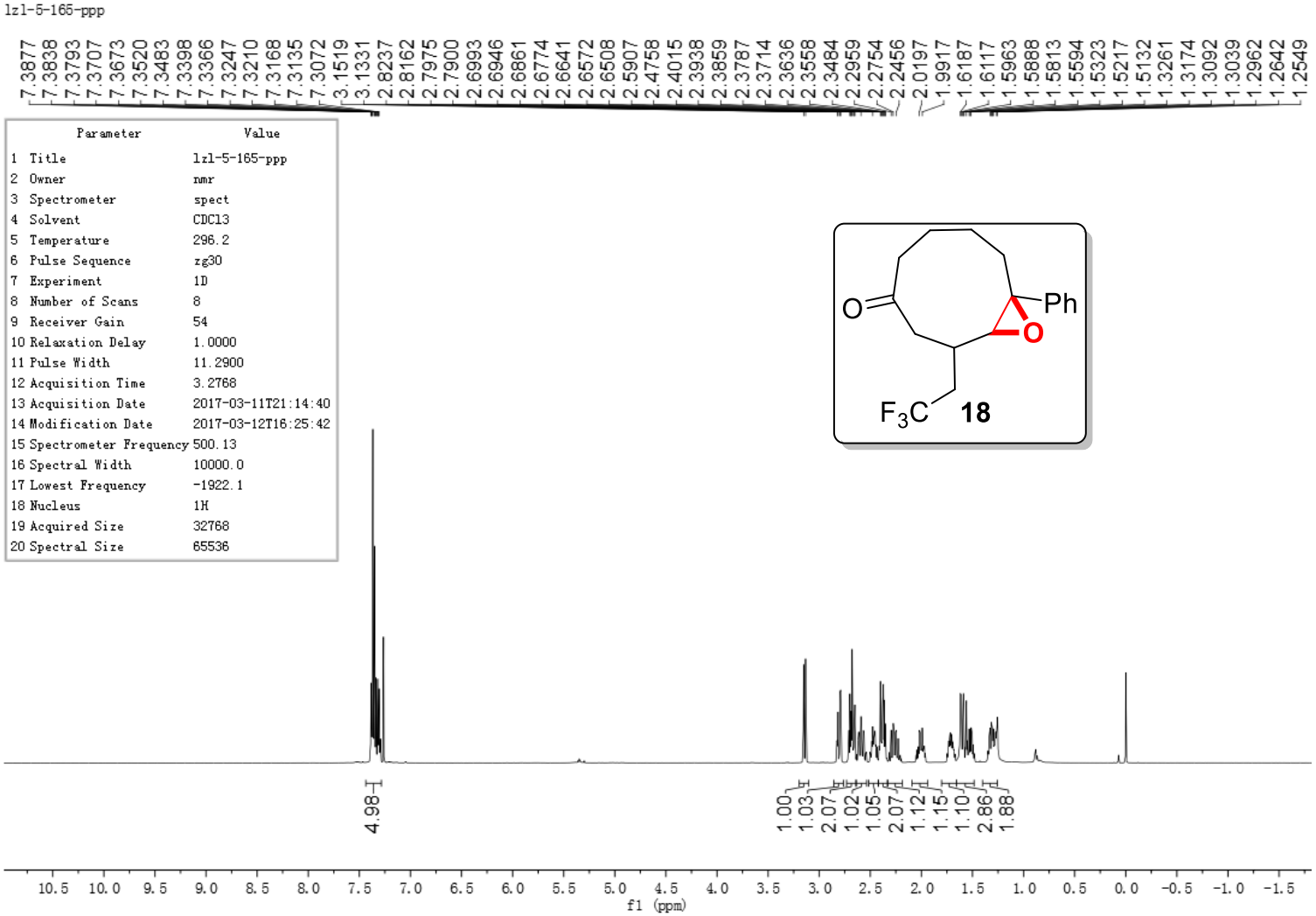
^{19}F NMR Spectrum of Compound **17**

lzl-5-167-p

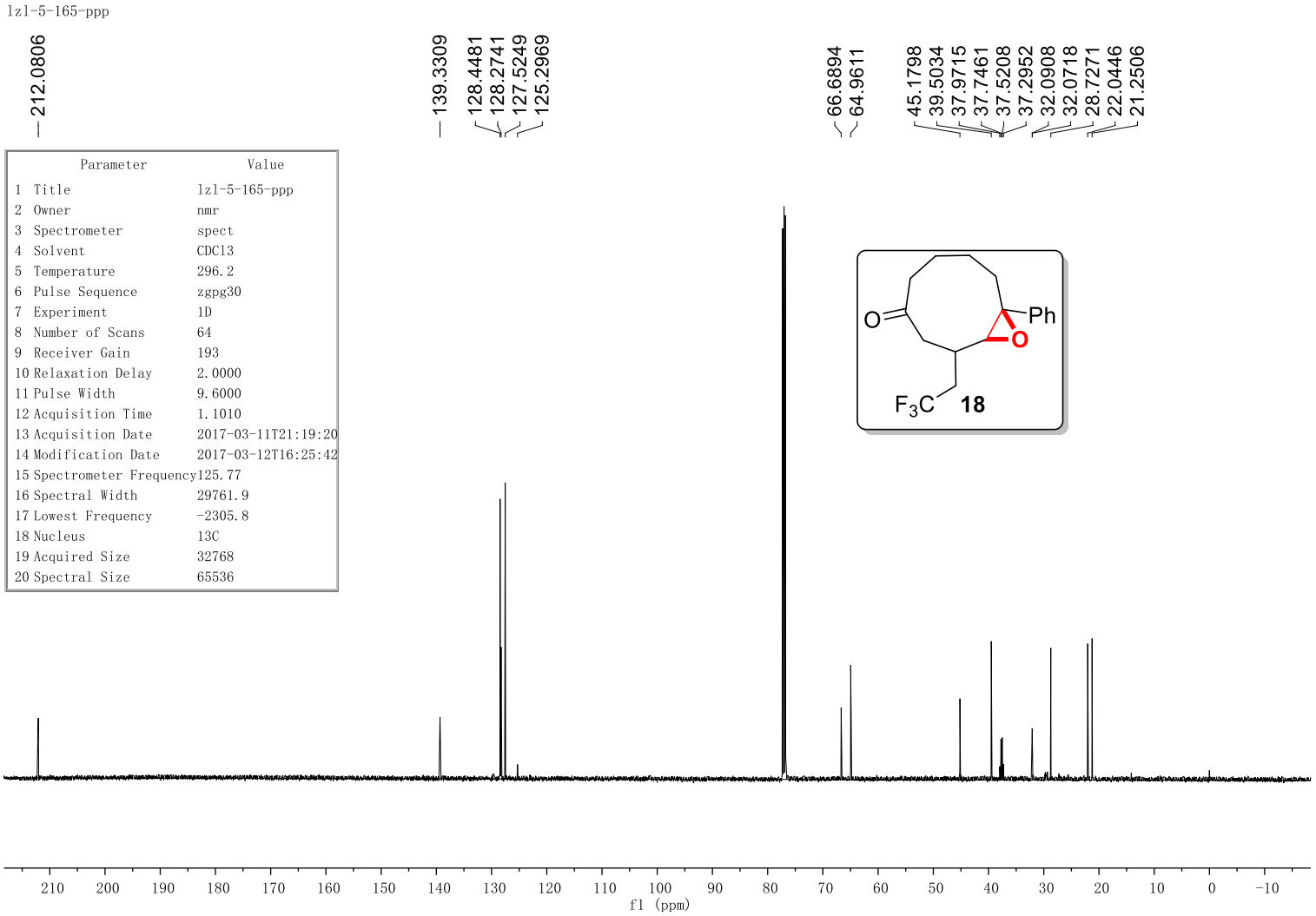
	Parameter	Value
1	Title	lzl-5-167-p
2	Owner	nmr
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	293.8
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Number of Scans	5
9	Receiver Gain	196
10	Relaxation Delay	1.0000
11	Pulse Width	18.0000
12	Acquisition Time	0.7340
13	Acquisition Date	2017-02-25T19:47:20
14	Modification Date	2017-03-13T15:10:05
15	Spectrometer Frequency	376.50
16	Spectral Width	89285.7
17	Lowest Frequency	-82292.7
18	Nucleus	19F
19	Acquired Size	65536
20	Spectral Size	131072



^{1}H NMR Spectrum of Compound **18**



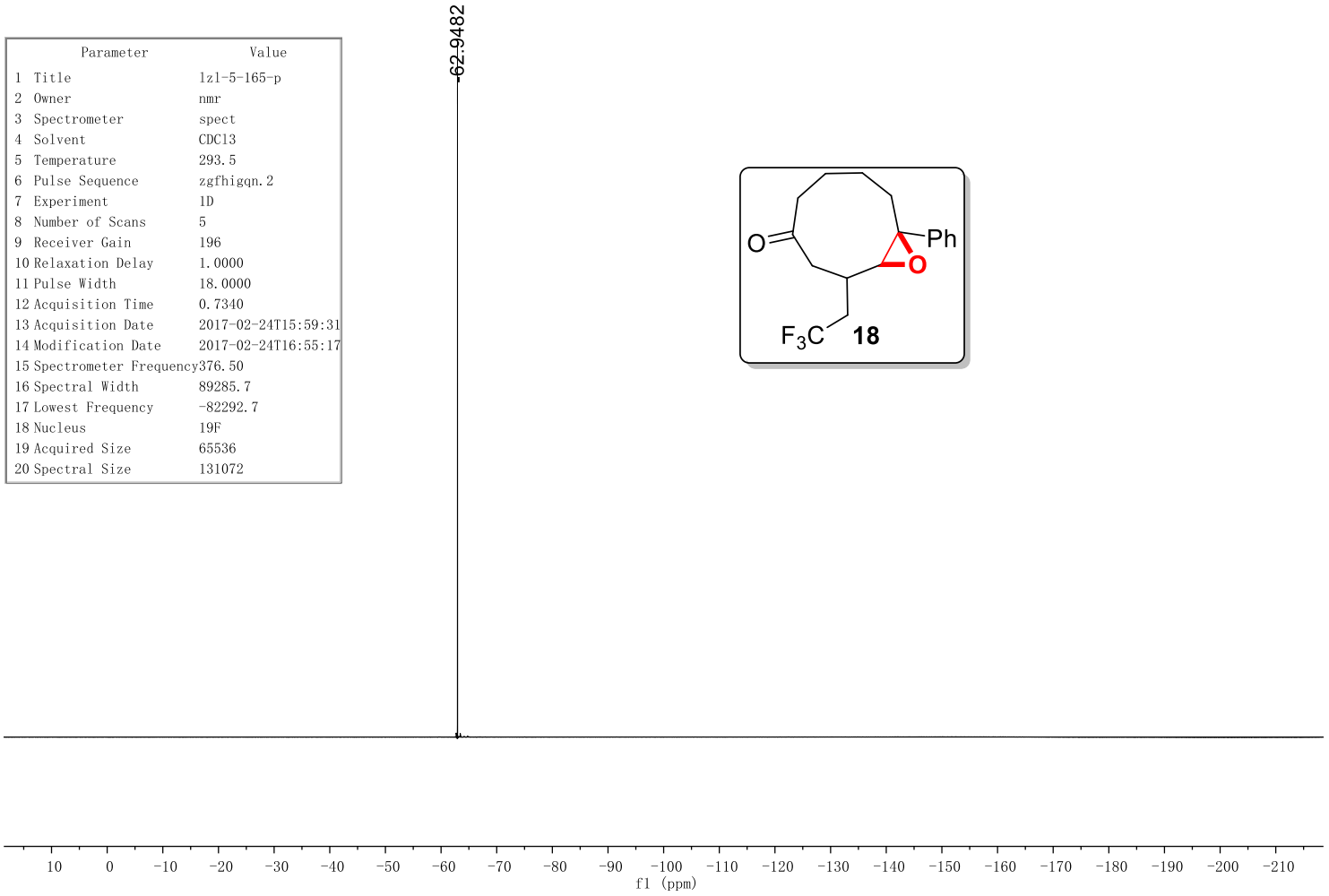
^{13}C NMR Spectrum of Compound **18**



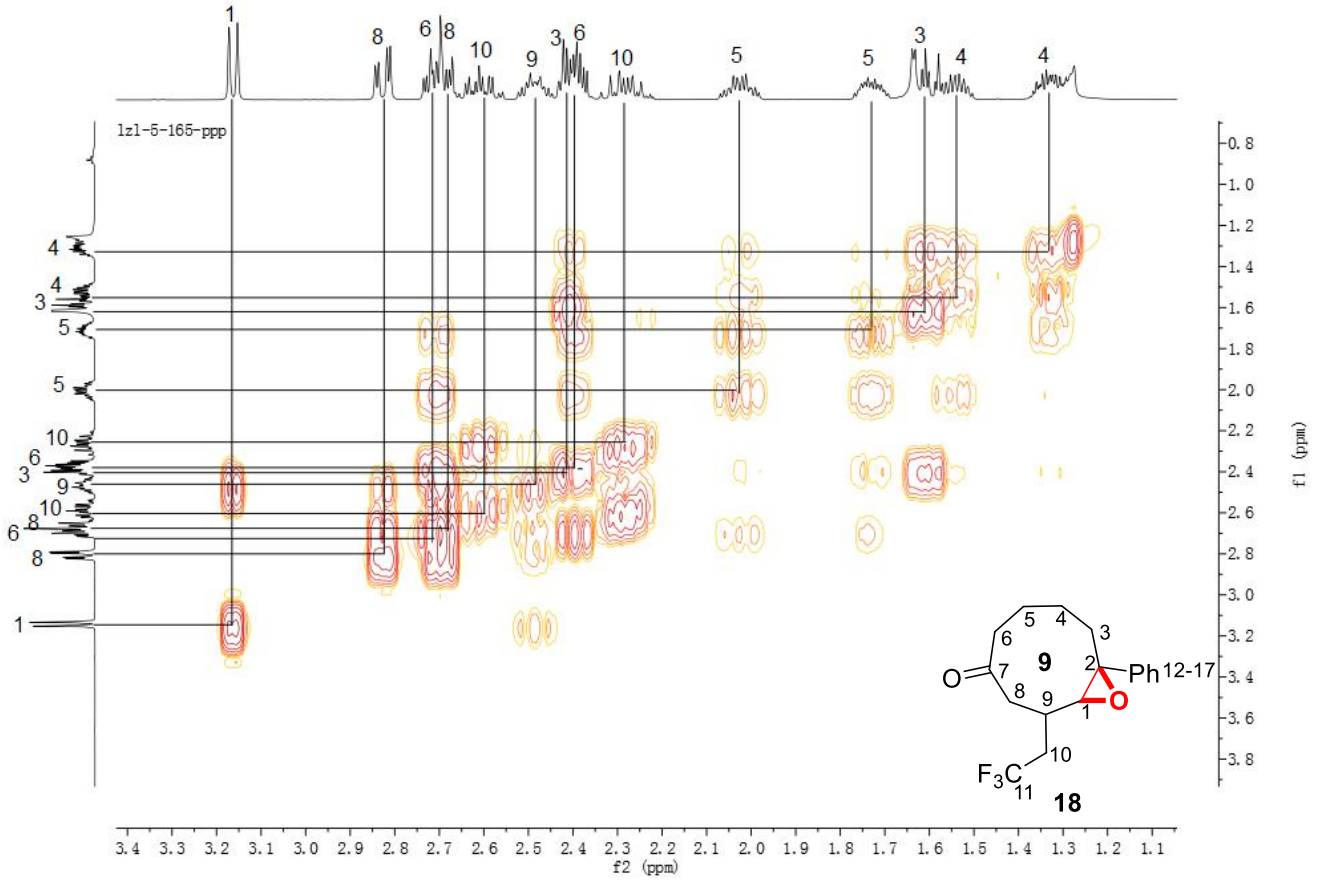
^{19}F NMR Spectrum of Compound **18**

lzl-5-165-p

	Parameter	Value
1	Title	lzl-5-165-p
2	Owner	nmr
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	293.5
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Number of Scans	5
9	Receiver Gain	196
10	Relaxation Delay	1.0000
11	Pulse Width	18.0000
12	Acquisition Time	0.7340
13	Acquisition Date	2017-02-24T15:59:31
14	Modification Date	2017-02-24T16:55:17
15	Spectrometer Frequency	376.50
16	Spectral Width	89285.7
17	Lowest Frequency	-82292.7
18	Nucleus	19F
19	Acquired Size	65536
20	Spectral Size	131072



COSY of compound **18**



HSQC of compound **18**