Supporting information for:

Enantioselective Cobalt-Catalyzed Sequential Nazarov Cyclization/Electrophilic Fluorination: Access to Chiral *α*-Fluorocyclopentenones

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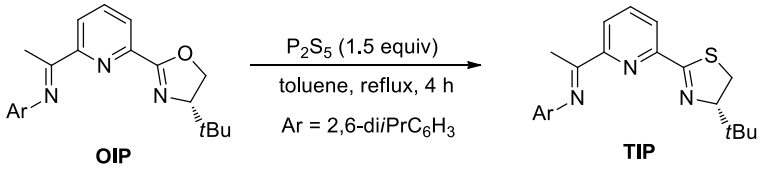
I. General Information

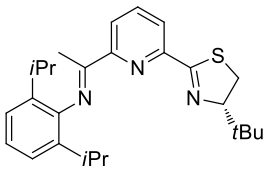
Toluene was distilled from sodium benzophenone ketyl prior to use. 1,2-Dichloroethane and dichloromethane were distilled from calcium hydride prior to use. Chlorobenzene (99%) was purchased from Aladdin and used as received. NFSI (97%) was purchased from Meryer Chemical and used as received. $Co(ClO_4)_2 \cdot 6H_2O$ and $Ni(ClO_4)_2 \cdot 6H_2O$ (reagent grade) were purchased from Energy Chemical and used as received. The other commercially available chemicals were used as received. NMR spectra were recorded on a Bruker-400 instrument or a Wuhan Zhongke-NiuJin-400 instrument. ^1H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). The following abbreviations (or combinations) were used to explain multiplicities: s =

singlet, d = doublet, t = triplet, m= multiplet, br = broad, q = quadruplet. Optical rotations were measured on a Perkin-Elmer 241 polarimeter equipped with a Na-lamp. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. Melting points were obtained using a WRR melting point apparatus (Laboratory Devices, Shanghai Precision & Scientific Instrument Co., Ltd.). HPLC analyses were performed on a Shimadzu SPD-20A. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electron ionization-time of flight) or ESI-TOF (electron spray ionization-time of flight). X-ray diffraction data was obtained on Gemini a ultra.

II. Synthesis and Structure Analysis of Thiazoline Iminopyridine Complexes



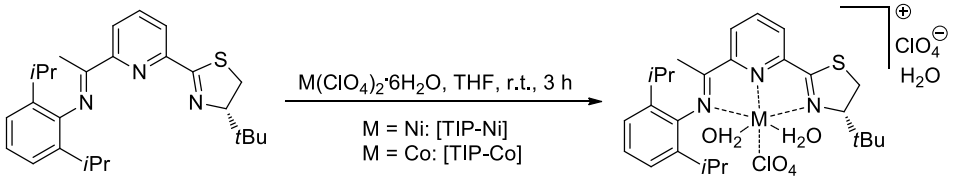
Procedure for the synthesis of thiazoline iminopyridine (TIP)[1]: To a solution of oxazoline iminopyridine (**OIP**)[2] (1.2169g, 3.0 mmol) in 30 ml of toluene were added P_2S_5 (1.0021 g, 4.5 mmol). The mixture was stirred vigorously under reflux for 4 h. After cooled down to room temperature, the reaction mixture was treated with a 20% aqueous solution of NaOH (30 mL). The aqueous phase was extracted with ether (3 x 30 ml). The combined organic layers were then washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography on silica gel (basified with PE/Et_3N = 100/1) by using PE/EA (20/1) as the eluent.



TIP

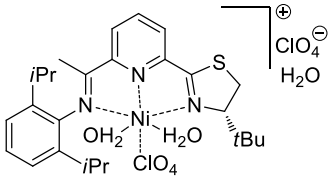
91% yield. Yellow solid. M.p. 126-128 ^{o}C; Optical Rotation: $[\alpha]_D^{20}$ = -56.2 (c = 0.96, $CHCl_3$); IR (neat): 2961, 2868, 1646, 1455, 1365, 1323, 1114 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.96-7.76 (m, 1H), 7.22-7.00 (m, 3H), 4.58-4.40 (m, 1H), 3.40-3.25 (m, 1H), 3.24-3.10 (m, 1H), 2.85-2.63 (m, 2H), 2.26 (s, 3H), 1.14 (d, *J* = 6.0 Hz, 12H), 1.08 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 168.4, 166.5, 155.6, 150.2, 146.3, 136.8, 135.7, 123.6, 123.0, 122.6, 122.5, 88.6, 35.5, 32.6, 28.2, 26.8, 23.2, 22.9, 22.8, 17.0; HRMS (ESI)

calculated for $[C_{26}H_{36}N_3S]^+$ $[M+H]^+$ requires m/z 422.2630, found m/z 422.2632.



TIP **TIP**·$M(ClO_4)_2$·$3H_2O$

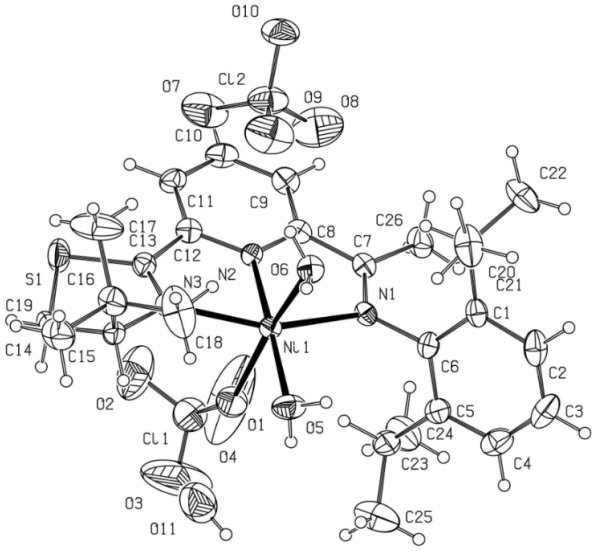
General procedure for the preparation of metal perchlorate complexes of TIP[3]: To a 50 mL flame-dried Schlenk flask cooled under a nitrogen atmosphere, **TIP** (1.0 equiv.), metal perchlorate (0.95 equiv.) and dry THF (0.1 M) were added. The mixture was left to stir for 3 h at room temperature and then the solvent was removed under reduced pressure. Dichloromethane or ether was added to the residue and the mixture was left to stir for another thirty minutes. Then the mixture was filtered, the filter residue was concentrated, washed with dichloromethane or ether three times and dried in vacuo to give the solid complexes.



TIP·$Ni(ClO_4)_2$·$3H_2O$ (**cat.2**)

TIP·$Ni(ClO_4)_2$·$3H_2O$ was prepared according to general procedure above by using **TIP** (0.4440 g, 1.05 mmol), $Ni(ClO_4)_2$·$6H_2O$ (0.3659 g, 1.00 mmol) to give **TIP**·$Ni(ClO_4)_2$·$3H_2O$ (0.6199 g, 85% yield) as a yellow green solid. The structure analysis was determined by X-ray diffraction analysis.

X-ray diffraction of TIP·$Ni(ClO_4)_2$·$3H_2O$:



(**CCDC number 1812597**)

Selected structure factors

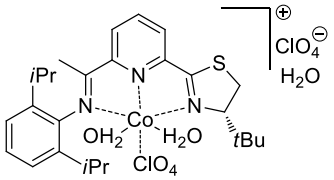
Empirical formula	$C_{26}H_{41}Cl_2N_3NiO_{11}S$
Formula weight	733.29
Temperature/K	293
Crystal system	orthorhombic
Space group	P 21 21 21
a/ Å	10.5089(6)
b/ Å	12.1755(6)
c/ Å	26.1145(17)
α/ ^{o}	90
β/ ^{o}	90
γ/^{o}	90
Volume/ $Å^3$	3341.4(3)
Z	4
Density(mg/mm^3)	1.458

Selected bond length for **TIP**·$Ni(ClO_4)_2·3H_2O$

Selected Bond Length	Distance (Å)
Ni1-N1	2.208(5)
Ni1-N2	1.982(5)
Ni1-N3	2.181(6)

Selected bond angles for **TIP**·$Ni(ClO_4)_2·3H_2O$

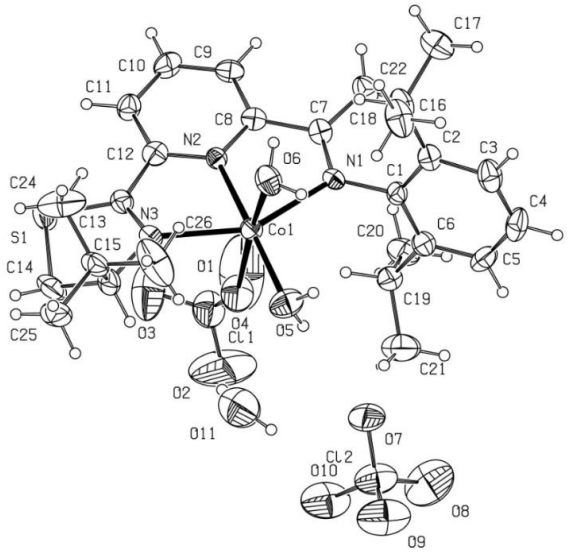
Selected Bond Angle	Degree (^{o})
N1-Ni1-N2	76.5(2)
N2-Ni1-N3	78.6(2)
N1-Ni1-N3	155.1(2)



TIP·$Co(ClO_4)_2·3H_2O$ (**cat.3**)

TIP·$Co(ClO_4)_2·3H_2O$ was prepared according to general procedure above by using **TIP** (0.4431 g, 1.05 mmol), $Co(ClO_4)_2·6H_2O$ (0.3670 g, 1.00 mmol) to give **TIP**·$Co(ClO_4)_2·3H_2O$ (0.6263 g, 85% yield) as a orange solid. The structure analysis was determined by X-ray diffraction analysis.

X-ray diffraction of TIP·$Co(ClO_4)_2·3H_2O$:



(**CCDC number 1817973**)

Selected structure factors

Empirical formula	$C_{26}H_{41}Cl_2N_3CoO_{11}S$
Formula weight	733.51
Temperature/K	293
Crystal system	orthorhombic
Space group	P 21 21 21
a/ Å	10.4327(8)
b/ Å	12.2783(7)
c/ Å	26.0967(19)
α/ ^{o}	90
β/ ^{o}	90
γ/^{o}	90
Volume/ $Å^3$	3342.9(4)
Z	4
Density(mg/mm^3)	1.457

Selected bond length for **TIP**·$Co(ClO_4)_2·3H_2O$

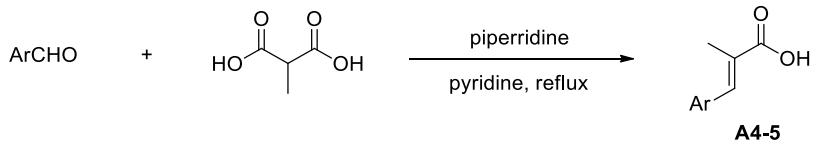
Selected Bond Length	Distance (Å)
Co1-N1	2.251(7)
Co1-N2	2.050(8)
Co1-N3	2.220(8)

Selected bond angles for **TIP**·$Co(ClO_4)_2·3H_2O$

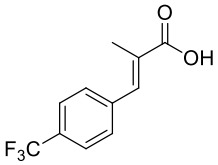
Selected Bond Angle	Degree (^{o})
N1-Co1-N2	74.6(3)
N2-Co1-N3	76.7(3)
N1-Co1-N3	151.0(3)

III. Preparation for Starting Materials

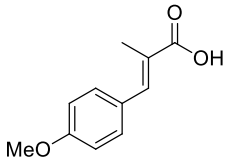
(*E*)-2-methyl-3-phenylacrylic (**A1**) acid and (*E*)-2,3-diphenylacrylic acid (**A2**) were purchased from Energy Chemical and used as received. (*E*)-2-methyl-3-(thiophen-2-yl)acrylic acid (**A3**) has been reported in our previous work[3].



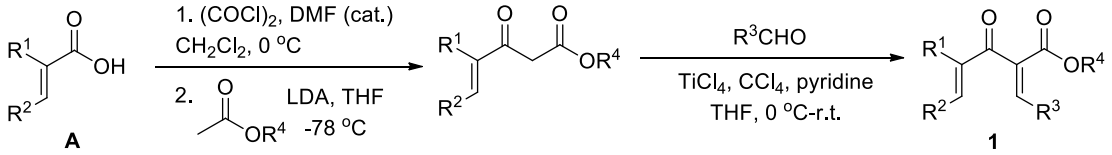
Compounds **A4** and **A5** were prepared according to a previously reported procedure[4]: A 100 mL of round-bottom flask was charged with aromatic aldehyde (1.0 equiv.), 2-methylmalonic acid (2.0 equiv.), piperridine (2.0 equiv.) and pyridine (30 mL). The mixture was heated to reflux for overnight. After cooled down to room temperature, the reaction mixture was poured into ice cold conc. HCl. The precipitate was collected through filtration and dried in vacuo which was used for next step without further purification.



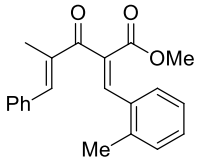
(*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)acrylic acid (**A4**)[4]. 83% yield. White solid. M.p. 151-153 ^{o}C; IR (neat): 2954, 2925, 1769, 1709, 1607, 1324, 1129 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 173.8, 139.4, 139.0 (q, *J* = 1.4 Hz), 130.4 (q, *J* = 32.1 Hz), 129.84, 129.82, 125.4 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 270.5 Hz), 13.7; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -62.8 (s); HRMS (EI) calculated for $[C_{11}H_9O_2F_3]^+$ requires m/z 230.0555, found m/z 230.0558.



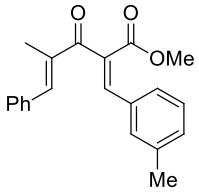
(*E*)-3-(4-methoxyphenyl)-2-methylacrylic acid (**A5**). 68% yield. Brown solid. M.p. 150-152 ^{o}C; IR (neat): 2955, 2924, 1665, 1601, 1512, 1280, 1254, 1182 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 2.16 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 174.5, 160.0, 140.8, 131.7, 128.2, 125.1, 113.9, 55.3, 13.7; HRMS (EI) calculated for $[C_{11}H_{12}O_3]^+$ requires m/z 192.0786, found m/z 192.0787.



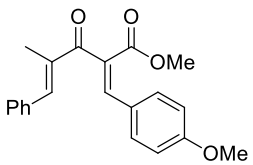
Compounds **1** were prepared according to our previously reported procedures[3]. **1a**, **1d** and **1t** have been reported in our previous work[3]. **1p** has been reported in a previous work[5]. The yields of products **1** were the last step yield.



(2*Z*,4*E*)-methyl 4-methyl-2-(2-methylbenzylidene)-3-oxo-5-phenylpent-4-enoate (**1b**). 58% yield. Yellow solid. M.p. 85-87 °C; IR (neat): 3026, 2952, 1719, 1652, 1621, 1254 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.42-7.27 (m, 4H), 7.26-7.13 (m, 5H), 7.12-7.03 (m, 1H), 3.83 (s, 3H), 2.42 (s, 3H), 2.05 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.5, 165.5, 142.8, 141.4, 137.3, 137.2, 135.4, 132.7, 132.2, 130.4, 129.9, 129.7, 128.9, 128.5, 128.4, 126.0, 52.6, 20.0, 12.5; HRMS (ESI) calculated for $[C_{21}H_{20}O_3Na]^+$ $[M+Na]^+$ requires m/z 343.1310, found m/z 343.1312.

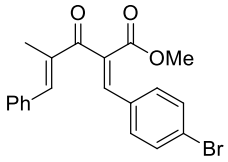


(2*Z*,4*E*)-methyl 4-methyl-2-(3-methylbenzylidene)-3-oxo-5-phenylpent-4-enoate (**1c**). 72% yield. Yellow solid. M.p. 64-66 °C; IR (neat): 3028, 2953, 1718, 1653, 1621, 1266, 1224 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.47 (s, 1H), 7.41-7.28 (m, 5H), 7.23-7.10 (m, 4H), 3.81 (s, 3H), 2.29 (s, 3H), 2.20 (d, 0.8H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.0, 165.7, 143.2, 142.6, 138.4, 136.9, 135.4, 133.0, 131.1, 130.81, 130.80, 129.9, 129.0, 128.6, 128.4, 127.0, 52.6, 21.3, 12.6; HRMS (ESI) calculated for $[C_{21}H_{20}O_3Na]^+$ $[M+Na]^+$ requires m/z 343.1310, found m/z 343.1315.

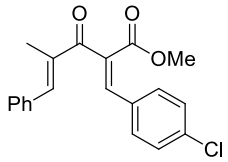


(2*Z*,4*E*)-methyl 2-(4-methoxybenzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1e**). 55% yield. Yellow solid. M.p. 75-77 °C; IR (neat): 2953, 2840, 1714, 1600, 1512, 1253, 1172 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.51 (s, 1H), 7.45-7.27

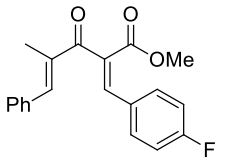
(m, 7H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 2.22 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.5, 166.0, 161.3, 143.0, 142.1, 136.9, 135.5, 132.1, 130.0, 129.0, 128.45, 128.41, 125.7, 114.3, 55.3, 52.4, 12.6; HRMS (EI) calculated for $[C_{21}H_{20}O_4]^+$ requires m/z 336.1362, found m/z 336.1360.



(2*Z*,4*E*)-methyl 2-(4-bromobenzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1f**). 84% yield. Yellow solid. M.p. 74-76 ^{o}C; IR (neat): 3027, 2952, 1719, 1651, 1621, 1252 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.52-7.41 (m, 3H), 7.40-7.28 (m, 5H), 7.22 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.20 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.6, 165.4, 143.5, 140.8, 136.8, 135.2, 132.1, 132.0, 131.9, 131.2, 130.0, 129.2, 128.5, 124.8, 52.7, 12.5; HRMS (EI) calculated for $[C_{20}H_{17}O_3Br]^+$ requires m/z 384.0361, found m/z 384.0364.

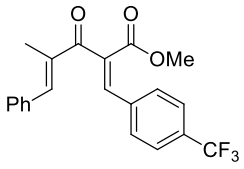


(2*Z*,4*E*)-methyl 2-(4-chlorobenzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1g**). 73% yield. Yellow solid. M.p. 66-68 ^{o}C; IR (neat): 3058, 2952, 1717, 1651, 1621, 1253 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.46 (s, 1H), 7.42-7.24 (m, 9H), 3.82 (s, 3H), 2.21 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.6, 165.4, 143.5, 140.8, 136.7, 136.3, 135.1, 131.7, 131.5, 131.1, 130.0, 129.2, 129.1, 128.4, 52.7, 12.5; HRMS (ESI) calculated for $[C_{20}H_{17}O_3ClNa]^+$ $[M+Na]^+$ requires m/z 363.0764, found m/z 363.0768.

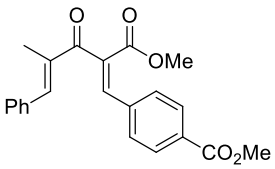


(2*Z*,4*E*)-methyl 2-(4-fluorobenzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1h**). 73% yield. Yellow solid. M.p. 69-71 ^{o}C; IR (neat): 3030, 2954, 1717, 1651, 1509, 1257 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.47 (s, 1H), 7.43-7.28 (m, 7H), 7.08-6.95 (m, 2H), 3.81 (s, 3H), 2.21 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.8, 165.6, 163.6 (d, *J* = 251.3 Hz) , 143.4, 141.0, 136.8, 135.3, 132.0 (d, *J* = 7.9 Hz), 131.0,

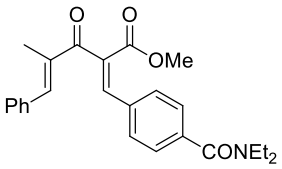
129.9, 129.4 (d, J = 2.4 Hz), 129.2, 128.5, 116.0 (d, J = 21.4 Hz), 52.6, 12.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -108.6--108.9 (m) (for decoupling spectrum, see: ^{19}F NMR: (376 MHz, $CDCl_3$) δ -108.7); HRMS (ESI) calculated for $[C_{20}H_{17}O_3FNa]^+$ $[M+Na]^+$ requires m/z 347.1059, found m/z 347.1062.



(2*Z*,4*E*)-methyl 4-methyl-3-oxo-5-phenyl-2-(4-(trifluoromethyl)benzylidene)pent-4-enoate (**1i**). 76% yield. Yellow solid. M.p. 35-37 ^{o}C; IR (neat): 3029, 2955, 1721, 1653, 1621, 1324, 1255 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.52-7.42 (m, 3H), 7.41-7.28 (m, 5H), 3.84 (s, 3H), 2.20 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.2, 165.2, 143.9, 140.3, 136.8, 136.5, 135.0, 133.6, 131.6 (q, J = 32.1 Hz), 130.0, 129.9, 129.3, 128.5, 125.7 (q, J = 3.6 Hz), 123.6 (q, J = 270.5 Hz), 52.8, 12.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -63.0 (s); HRMS (ESI) calculated for $[C_{21}H_{18}F_3O_3]^+$ $[M+H]^+$ requires m/z 375.1208, found m/z 375.1206.

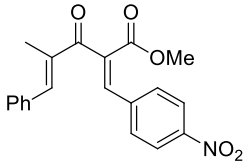


Methyl 4-((1*Z*,4*E*)-2-(methoxycarbonyl)-4-methyl-3-oxo-5-phenyl-penta-1,4-dien-1-yl)benzoate (**1j**). 86% yield. Yellow solid. M.p. 105-107 ^{o}C; IR (neat): 2952, 2846, 1720, 1651, 1435, 1253, 1200 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.94 (s, 1H), 7.50-7.40 (m, 3H), 7.39-7.26 (m, 5H), 3.89 (s, 3H), 3.83 (s, 3H), 2.19 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.2, 166.2, 165.2, 143.7, 140.7, 137.4, 136.8, 135.1, 133.4, 131.2, 129.90, 129.86, 129.6, 129.2, 128.4, 52.7, 52.2, 12.5; HRMS (EI) calculated for $[C_{22}H_{20}O_5]^+$ requires m/z 364.1311, found m/z 364.1313.

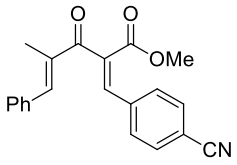


(2*Z*,4*E*)-methyl 2-(4-(diethylcarbamoyl)benzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1k**). 88% yield. Yellow solid. M.p. 60-62 ^{o}C; IR (neat): 2928, 1719, 1626, 1432, 1254, 1205 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.46 (s, 1H), 7.43-7.28 (m, 9H), 3.83 (s, 3H), 3.63-3.40 (m, 2H), 3.30-3.05

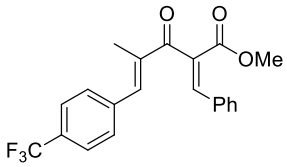
(m, 2H), 2.20 (d, *J* = 0.8 Hz, 3H), 1.35-0.94 (m, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.6, 170.1, 165.4, 143.6, 141.2, 138.8, 136.7, 135.1, 133.8, 132.1, 129.9, 129.2, 128.4, 126.7, 52.7, 43.1, 39.2, 14.1, 12.8, 12.5; HRMS (EI) calculated for $[C_{25}H_{27}NO_4]^+$ requires m/z 405.1940, found m/z 405.1944.



(2*Z*,4*E*)-methyl 4-methyl-2-(4-nitrobenzylidene)-3-oxo-5-phenylpent-4-enoate (**1l**). 77% yield. Yellow solid. M.p. 90-92 ^{o}C; IR (neat): 3076, 2954, 1720, 1651, 1521, 1346, 1253 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.48-7.27 (m, 6H), 3.85 (s, 3H), 2.21 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.7, 164.9, 148.1, 144.1, 139.3, 139.1, 136.7, 135.1, 134.8, 130.3, 130.0, 129.5, 128.5, 123.9, 53.0, 12.5; HRMS (ESI) calculated for $[C_{20}H_{18}NO_5]^+$ $[M+H]^+$ requires m/z 352.1185, found m/z 352.1185.

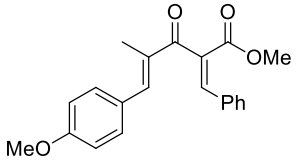


(2*Z*,4*E*)-methyl 2-(4-cyanobenzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1m**). 84% yield. Yellow solid. M.p. 74-76 ^{o}C; IR (neat): 3057, 2953, 2229, 1721, 1651, 1621, 1255, 1205 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.52-7.28 (m, 8H), 3.84 (s, 3H), 2.19 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.7, 164.9, 144.0, 139.6, 137.5, 136.8, 134.9, 134.7, 132.4, 130.0, 129.9, 129.4, 128.5, 118.0, 113.3, 52.9, 12.5; HRMS (ESI) calculated for $[C_{21}H_{18}NO_3]^+$ $[M+H]^+$ requires m/z 332.1287, found m/z 332.1286.

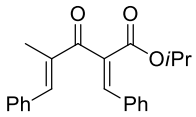


(2*Z*,4*E*)-methyl 2-benzylidene-4-methyl-3-oxo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (**1n**). 54% yield. Yellow solid. M.p. 63-65 ^{o}C; IR (neat): 2954, 1720, 1657, 1620, 1323, 1255, 1123 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 7.42-7.28 (m, 7H), 3.83 (s, 3H), 2.16 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.5, 165.5, 142.8, 141.0, 138.9, 138.7, 133.1, 130.89, 130.87, 130.4,

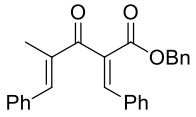
129.85, 129.80, 128.8, 125.3 (q, J = 3.6 Hz), 123.8 (q, J = 270.5 Hz), 52.6, 12.6; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -62.8 (s); HRMS (EI) calculated for $[C_{21}H_{17}F_3O_3]^+$ requires m/z 374.1130, found m/z 374.1130.



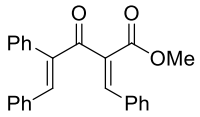
(2*Z*,4*E*)-methyl 2-benzylidene-5-(4-methoxyphenyl)-4-methyl-3-oxopent-4-enoate (**1o**). 62% yield. Yellow solid. M.p. 101-103 ^{o}C; IR (neat): 2953, 2840, 1717, 1599, 1510, 1253, 1175 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.43 (s, 1H), 7.40-7.20 (m, 7H), 6.88 (d, J = 8.4 Hz, 2H), 3.88-3.73 (m, 6H), 2.22 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.6, 165.8, 160.3, 143.3, 142.0, 134.7, 133.2, 132.0, 131.4, 130.2, 129.9, 128.7, 128.0, 113.9, 55.3, 52.5, 12.5; HRMS (EI) calculated for $[C_{21}H_{20}O_4]^+$ requires m/z 336.1362, found m/z 336.1360.



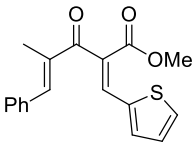
(2*Z*,4*E*)-*iso*propyl 2-benzylidene-4-methyl-3-oxo-5-phenylpent-4-enoate (**1q**). 76% yield. Yellow solid. M.p. 38-40 ^{o}C; IR (neat): 2980, 2927, 1714, 1654, 1622, 1253, 1198 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.46 (s, 1H), 7.43-7.27 (m, 10H), 5.23-5.08 (m, 1H), 2.20 (s, 3H), 1.26 (d, J = 6.4 Hz, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.0, 164.7, 142.6, 141.8, 137.2, 135.5, 133.2, 132.1, 130.1, 129.9, 129.8, 128.9, 128.7, 128.4, 69.1, 21.7, 12.6; HRMS (EI) calculated for $[C_{22}H_{22}O_3]^+$ requires m/z 334.1569, found m/z 334.1572.



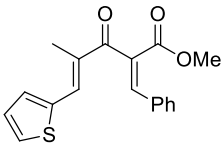
(2*Z*,4*E*)-benzyl 2-benzylidene-4-methyl-3-oxo-5-phenylpent-4-enoate (**1r**). 55% yield. Yellow solid. M.p. 56-58 ^{o}C; IR (neat): 3061, 3031, 1715, 1652, 1621, 1245, 1188, 1016 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.46 (s, 1H), 7.42-7.20 (m, 15H), 5.23 (s, 2H), 2.18 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.8, 165.0, 143.2, 142.7, 137.1, 135.6, 135.3, 133.0, 131.2, 130.4, 130.0, 129.9, 129.0, 128.8, 128.5, 128.4, 128.1, 127.7, 66.9, 12.6; HRMS (EI) calculated for $[C_{26}H_{23}O_3]^+$ requires m/z 382.1569, found m/z 382.1565.



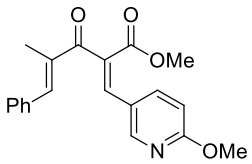
(2*Z*,4*E*)-methyl 2-benzylidene-3-oxo-4,5-diphenylpent-4-enoate (**1s**). 70% yield. Orange oil. IR (neat): 3056, 2951, 1720, 1657, 1620, 1254, 1199 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.65 (s, 1H), 7.50-7.42 (m, 2H), 7.40-7.30 (m, 6H), 7.20-7.14 (m, 1H), 7.13-7.04 (m, 4H), 7.00-6.92 (m, 2H), 3.81 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.2, 165.4, 143.1, 142.0, 140.2, 135.1, 134.1, 133.1, 131.6, 130.9, 130.3, 130.0, 129.7, 129.4, 128.71, 128.65, 128.1, 128.0, 52.4; HRMS (EI) calculated for $[C_{25}H_{20}O_3]^+$ requires m/z 368.1412, found m/z 368.1412.



(2*Z*,4*E*)-methyl 4-methyl-3-oxo-5-phenyl-2-(thiophen-2-ylmethylene)pent-4-enoate (**1u**). 67% yield. Yellow solid. M.p. 100-102 ^{o}C; IR (neat): 3013, 2924, 1709, 1649, 1607, 1248, 1200 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.56 (s, 1H), 7.48-7.30 (m, 6H), 7.27 (d, *J* = 3.6 Hz, 1H), 7.02 (dd, *J* = 3.6, 5.2 Hz, 1H), 3.80 (s, 3H), 2.27 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.4, 165.6, 143.3, 137.1, 136.4, 135.4, 134.4, 133.9, 131.4, 130.1, 129.1, 128.4, 128.1, 127.7, 52.5, 12.7; HRMS (EI) calculated for $[C_{18}H_{16}O_3S]^+$ requires m/z 312.0820, found m/z 312.0823.

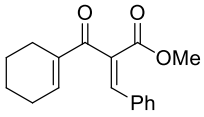


(2*Z*,4*E*)-methyl 2-benzylidene-4-methyl-3-oxo-5-(thiophen-2-yl)pent-4-enoate (**1v**). 47% yield. Yellow solid. M.p. 104-106 ^{o}C; IR (neat): 2952, 2924, 1716, 1645, 1603, 1252, 1183 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.65 (s, 1H), 7.58-7.50 (m, 1H), 7.40-7.25 (m, 5H), 7.25-7.20 (m, 1H), 7.12-7.05 (m, 1H), 3.79 (s, 3H), 2.28 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.7, 165.7, 142.3, 139.1, 135.8, 133.3, 133.1, 133.0, 131.0, 130.9, 130.3, 130.0, 128.8, 127.6, 52.6, 12.5; HRMS (EI) calculated for $[C_{18}H_{16}O_3S]^+$ requires m/z 312.0820, found m/z 312.0822.

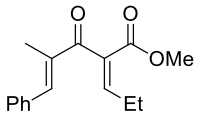


(2*Z*,4*E*)-methyl 2-((6-methoxypyridin-3-yl)methylene)-4-methyl-3-oxo-5-phenylpent-4-enoate (**1w**). 68% yield. Yellow solid. M.p. 92-94 ^{o}C; IR (neat): 3024, 2951, 1717, 1650, 1596, 1494, 1261, 1205 cm^{-1}; ^{1}H NMR: (400 MHz,

$CDCl_3$) δ 8.24 (d, *J* = 2.4 Hz, 1H), 7.83 (s, 1H), 7.56-7.46 (m, 2H), 7.42-7.30 (m, 5H), 6.67 (d, *J* = 8.8 Hz, 1H), 3.93 (s, 3H), 3.81 (s, 3H), 2.24 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.9, 165.5, 165.0, 150.3, 143.5, 138.7, 138.5, 136.8, 135.2, 130.1, 130.0, 129.2, 128.5, 122.5, 111.3, 53.8, 52.6, 12.6; HRMS (ESI) calculated for $[C_{20}H_{20}NO_4]^+$ $[M+H]^+$ requires m/z 338.1392, found m/z 338.1395.

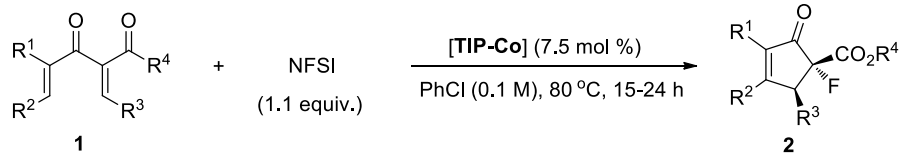


(*Z*)-methyl 2-(cyclohex-1-enecarbonyl)-3-phenylacrylate (**1x**). 71% yield. Yellow oil. IR (neat): 2933, 2861, 1717, 1655, 1633, 1253, 1199 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.36-7.28 (m, 5H), 6.86-6.80 (m, 1H), 3.80 (s, 3H), 2.40-2.30 (m, 2H), 2.16-2.06 (m, 2H), 1.70-1.50 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.6, 165.7, 145.3, 141.8, 139.1, 133.2, 131.2, 130.1, 129.9, 128.6, 52.4, 26.1, 22.6, 21.6, 21.3; HRMS (EI) calculated for $[C_{17}H_{18}O_3]^+$ requires m/z 270.1256, found m/z 270.1258.



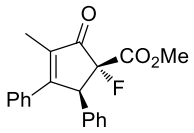
(*Z*)-methyl 2-((*E*)-2-methyl-3-phenylacryloyl)pent-2-enoate (**1y**). 23% yield. Yellow oil. IR (neat): 2968, 2876, 1723, 1656, 1437, 1241, 1211 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49-7.33 (m, 6H), 7.10 (t, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 2.25-2.07 (m, 5H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.9, 165.1, 148.6, 143.4, 137.6, 135.4, 132.7, 129.9, 129.1, 128.5, 52.2, 23.1, 12.7, 12.4; HRMS (EI) calculated for $[C_{16}H_{18}O_3]^+$ requires m/z 258.1256, found m/z 258.1256.

IV. Enantioselective Cobalt-Catalyzed Sequential Nazarov Cyclization/Electrophilic Fluorination

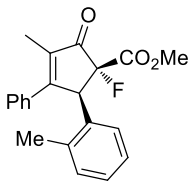


General procedure for enantioselective cobalt-catalyzed sequential Nazarov cyclization/electrophilic fluorination: To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, TIP·$Co(ClO_4)_2 \cdot 3H_2O$ (7.5 mol %), **1** (0.5 mmol), NFSI (0.55 mmol) and chlorobenzene (5 mL) were added. Then the flask was sealed with a screw cap and heated to 80 °C

for 15-24 h. After cooled down to room temperature, the mixture was filtered through a pad of silica gel and washed with ether. The filtrate was concentrated under reduced pressure and purified by flash column chromatography using PE/EA as the eluent to give the corresponding products **2** with excellent diastereoselectivity (>20/1) (determined by NMR analysis). The racemic products **2** were synthesized by using racemic catalyst according to the same procedure above.

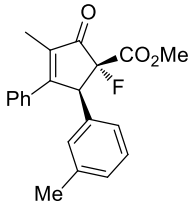


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-4,5-diphenylcyclopent-3-enecarboxylate (**2a**). The product **2a** was prepared according to the general procedure above by using **1a** (0.1536 g, 0.5 mmol), NFSI (0.1735 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2a** (0.1503 g, 93% yield) as a white solid. M.p. 113-115 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +495.3 (c = 1.02, $CHCl_3$), 96% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 9.3 (minor), 14.4 (major); IR (neat): 2954, 2924, 1767, 1713, 1618, 1441, 1347, 1220 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.30 (m, 5H), 7.22-7.10 (m, 3H), 7.09-7.00 (m, 2H), 4.98-4.80 (m, 1H), 3.24 (s, 3H), 2.17 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.8 (d, *J* = 17.5 Hz), 165.9 (d, *J* = 29.1 Hz), 165.7 (d, *J* = 3.6 Hz), 136.9, 134.5 (d, *J* = 2.2 Hz), 133.6, 130.1, 129.5, 128.64, 128.60, 128.2, 127.7, 97.0 (d, *J* = 199.8 Hz), 57.1 (d, *J* = 23.3 Hz), 52.0 (d, *J* = 1.4 Hz), 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.0 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{20}H_{17}O_3F]^+$ requires m/z 324.1162, found m/z 324.1160.

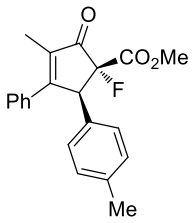


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-4-phenyl-5-(*o*-tolyl)cyclopent-3-enecarboxylate (**2b**). The product **2b** was prepared according to the general procedure above by using **1b** (0.1605 g, 0.5 mmol), NFSI (0.1738 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2b** (0.1628 g, 96% yield) as a white solid. M.p. 175-177 ^oC;

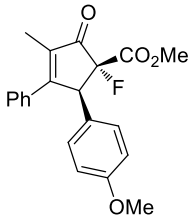
Optical Rotation: $[\alpha]_D^{20}$ = +490.1 (c = 1.02, $CHCl_3$), 95% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 6.9 (minor), 9.9 (major); IR (neat): 2954, 2924, 1766, 1713, 1618, 1442, 1347 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.07-6.98 (m, 1H), 6.92-6.80 (m, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.20-5.05 (m, 1H), 3.19 (s, 3H), 2.54 (s, 3H), 2.18 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.2 (d, *J* = 17.5 Hz), 166.7 (d, *J* = 4.4 Hz), 166.1 (d, *J* = 29.1 Hz), 137.6, 136.8, 133.8, 133.1 (d, *J* = 2.2 Hz), 130.4, 130.1, 129.6, 128.6, 128.5, 127.5, 125.2, 97.0 (d, *J* = 199.0 Hz), 53.1 (d, *J* = 24.0 Hz), 51.9, 20.0 (d, *J* = 1.4 Hz), 10.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -155.6 (d, *J* = 23.3 Hz); HRMS (EI) calculated for $[C_{21}H_{19}O_3F]^+$ requires m/z 338.1318, found m/z 338.1321.



(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-4-phenyl-5-(*m*-tolyl)cyclopent-3-enecarboxylate (**2c**). The product **2c** was prepared according to the general procedure above by using **1c** (0.1605 g, 0.5 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2 \cdot 3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2c** (0.1611 g, 95% yield) as a white solid. M.p. 53-55 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +505.1 (c = 1.03, $CHCl_3$), 87% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 7.9 (minor), 10.8 (major); IR (neat): 3025, 2953, 1766, 1713, 1618, 1439, 1347, 1226, 1090 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.28 (m, 5H), 7.07-7.00 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.90-4.77 (m, 1H), 3.25 (s, 3H), 2.22 (s, 3H), 2.16 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.8 (d, *J* = 18.2 Hz), 166.0 (d, *J* = 29.2 Hz), 165.9 (d, *J* = 4.4 Hz), 137.8, 136.7, 134.4 (d, *J* = 1.5 Hz), 133.6, 130.2, 130.0, 128.6, 128.5, 128.4, 127.9, 126.5, 97.0 (d, *J* = 199.8 Hz), 57.0 (d, *J* = 23.3 Hz), 51.9, 21.1, 10.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -157.9 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{21}H_{19}O_3F]^+$ requires m/z 338.1318, found m/z 338.1316.

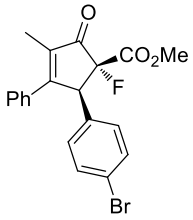


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-4-phenyl-5-(*p*-tolyl)cyclopent-3-enecarboxylate (**2d**). The product **2d** was prepared according to the general procedure above by using **1d** (0.1608 g, 0.5 mmol), NFSI (0.1738 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2d** (0.1624 g, 96% yield) as a white solid. M.p. 140-142 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +419.0 (c = 1.00, $CHCl_3$), 97% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 9.7 (minor), 13.8 (major); IR (neat): 2953, 2924, 1766, 1713, 1617, 1439, 1347, 1219 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.28 (m, 5H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.93-4.78 (m, 1H), 3.26 (s, 3H), 2.22 (s, 3H), 2.15 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.9 (d, *J* = 18.2 Hz), 166.0 (d, *J* = 29.2 Hz), 165.9 (d, *J* = 4.4 Hz), 137.4, 136.8, 133.7, 131.4 (d, *J* = 2.1 Hz), 130.1, 129.4, 128.9, 128.7, 128.6, 97.0 (d, *J* = 199.1 Hz), 56.8 (d, *J* = 23.4 Hz), 52.0 (d, *J* = 1.5 Hz), 21.0, 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.2 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{21}H_{19}O_3F]^+$ requires m/z 338.1318, found m/z 338.1320.



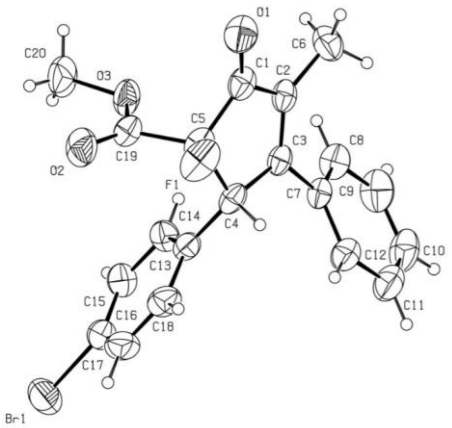
(1*R*,2*S*)-(+)-methyl 1-fluoro-2-(4-methoxyphenyl)-4-methyl-5-oxo-3-phenylcyclopent-3-enecar boxylate (**2e**). The product **2e** was prepared according to the general procedure above by using **1e** (0.1855 g, 0.55 mmol), NFSI (0.1580 g, 0.50 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-6/1) as the eluent to give (+)-**2e** (0.1610 g, 91% yield) as a white solid. M.p. 124-126 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +391.1 (c = 0.98, $CHCl_3$), 81% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 9.5 (minor), 13.7 (major); IR (neat): 2954, 2926, 1765, 1712, 1612, 1513, 1441, 1251 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.46-7.30 (m, 5H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.92-4.75 (m, 1H), 3.70 (s, 3H), 3.29 (s, 3H), 2.15 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ

197.9 (d, *J* = 17.5 Hz), 166.1 (d, *J* = 28.4 Hz), 165.9 (d, *J* = 3.6 Hz), 158.9, 136.8, 133.7, 130.6, 130.1, 128.7, 128.6, 126.4 (d, *J* = 2.2 Hz), 113.6, 97.0 (d, *J* = 199.7 Hz), 56.4 (d, *J* = 24.1 Hz), 55.1, 52.1, 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.4 (d, *J* = 22.9 Hz); HRMS (EI) calculated for $[C_{21}H_{19}O_4F]^+$ requires m/z 354.1267, found m/z 354.1269.



(1*R*,2*S*)-(+)-methyl 2-(4-bromophenyl)-1-fluoro-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2f**). The product **2f** was prepared according to the general procedure above by using **1f** (0.1929 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2f** (0.1898 g, 94% yield) as a white solid. M.p. 134-136 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +406.3 (c = 1.01, $CHCl_3$), 92% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 11.4 (minor), 15.8 (major); IR (neat): 3060, 2954, 1765, 1714, 1618, 1489, 1347, 1239 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.44-7.34 (m, 5H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.92-4.78 (m, 1H), 3.31 (s, 3H), 2.15 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.3 (d, *J* = 18.2 Hz), 165.8 (d, *J* = 29.1 Hz), 165.0 (d, *J* = 4.4 Hz), 137.2, 133.6 (d, *J* = 1.4 Hz), 133.3, 131.4, 131.2, 130.3, 128.8, 128.6, 121.9, 96.7 (d, *J* = 201.2 Hz), 56.4 (d, *J* = 24.1 Hz), 52.2 (d, *J* = 1.4 Hz), 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.3 (d, *J* = 24.8 Hz); HRMS (EI) calculated for $[C_{20}H_{16}O_3FBr]^+$ requires m/z 402.0267, found m/z 402.0263.

X-ray diffraction of (+)-2f:



(**CCDC number: 1832033**)

Bond precision: C-C = 0.0073 A Wavelength=0.71073

Cell: a=9.6137(6) b=11.7958(7) c=16.1824(9)
alpha=90 beta=90 gamma=90
Temperature: 293 K

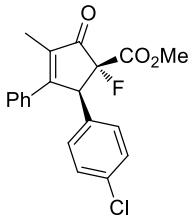
	Calculated	Reported
Volume	1835.11(19)	1835.11(19)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H16 Br F O3	C20 H16 Br F O3
Sum formula	C20 H16 Br F O3	C20 H16 Br F O3
Mr	403.23	403.24
Dx,g cm-3	1.459	1.460
Z	4	4
Mu (mm-1)	2.264	2.264
F000	816.0	816.0
F000'	815.26	
h,k,lmax	11,14,19	11,14,19
Nref	3365[1934]	3363
Tmin,Tmax	0.370,0.636	0.704,1.000
Tmin'	0.339	

Correction method= # Reported T Limits: Tmin=0.704 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.74/1.00 Theta(max)= 25.347

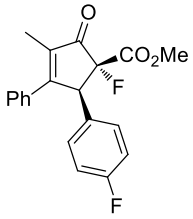
R(reflections)= 0.0354(2353) wR2(reflections)= 0.0852(3363)

S = 1.018 Npar= 228

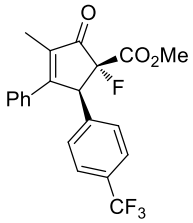


(1*R*,2*S*)-(+)-methyl 2-(4-chlorophenyl)-1-fluoro-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2g**). The product **2g** was prepared according to the general procedure above by using **1g** (0.1708 g, 0.50 mmol), NFSI (0.1737 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2g** (0.1671 g, 93% yield) as a white solid. M.p. 151-153 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +448.5 (c = 0.98, $CHCl_3$), 94% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 10.2 (minor), 14.8 (major); IR (neat): 3059, 2955, 1766, 1713, 1618, 1493, 1347, 1220 cm^{-1}; ^1H NMR: (400

MHz, $CDCl_3$) δ 7.44-7.33 (m, 5H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.94-4.80 (m, 1H), 3.31 (s, 3H), 2.15 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.4 (d, *J* = 18.2 Hz), 165.8 (d, *J* = 29.1 Hz), 165.1 (d, *J* = 4.3 Hz), 137.2, 133.8, 133.3, 133.1 (d, *J* = 2.2 Hz), 130.9, 130.3, 128.8, 128.6, 128.5, 96.8 (d, *J* = 201.3 Hz), 56.4 (d, *J* = 24.0 Hz), 52.2, 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.4 (d, *J* = 23.3 Hz); HRMS (EI) calculated for $[C_{20}H_{16}O_3FCl]^+$ requires m/z 358.0772, found m/z 358.0769.

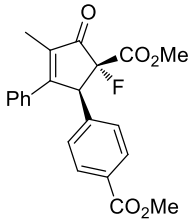


(1*R*,2*S*)-(+)-methyl 1-fluoro-2-(4-fluorophenyl)-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2h**). The product **2h** was prepared according to the general procedure above by using **1h** (0.1625 g, 0.50 mmol), NFSI (0.1735 g, 0.55 mmol), $TIP{\cdot}Co(ClO_4)_2{\cdot}3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2h** (0.1580 g, 92% yield) as a white solid. M.p. 168-170 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +467.5 (c = 1.02, $CHCl_3$), 94% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 8.9 (minor), 14.0 (major); IR (neat): 2955, 2925, 1766, 1714, 1618, 1510, 1348, 1223, 1092 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 5H), 7.08-6.97 (m, 2H), 6.92-6.82 (m, 2H), 4.95-4.80 (m, 1H), 3.30 (s, 3H), 2.16 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.5 (d, *J* = 18.2 Hz), 165.9 (d, *J* = 29.1 Hz), 165.3 (d, *J* = 4.4 Hz), 162.0 (d, *J* = 246.4 Hz), 137.1, 133.4, 131.3, 131.2, 130.4 (dd, *J* = 2.2, 3.6 Hz), 130.2, 128.7, 128.6, 115.3, 115.1, 96.9 (d, *J* = 200.6 Hz), 56.3 (d, *J* = 24.1 Hz), 52.1 (d, *J* = 1.5 Hz), 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -113.6--113.8 (m, 1F), -158.5 (d, *J* = 24.4 Hz, 1F); HRMS (EI) calculated for $[C_{20}H_{16}O_3F_2]^+$ requires m/z 342.1068, found m/z 342.1065.



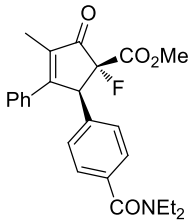
(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-4-phenyl-5-(4-(trifluoromethyl)phenyl)cyclopent-3-enecarboxylate (**2i**). The product **2i** was prepared according to the general procedure above by using **1i** (0.1874 g, 0.50 mmol), NFSI (0.1735 g, 0.55

mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0277 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2i** (0.1782 g, 91% yield) as a white solid. M.p. 148-150 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +401.2 (c = 0.99, $CHCl_3$), 91% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 7.0 (minor), 8.4 (major); IR (neat): 2960, 2924, 1763, 1713, 1614, 1438, 1247, 1165, 1066 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.43-7.34 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.04-4.88 (m, 1H), 3.26 (s, 3H), 2.18 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.1 (d, *J* = 18.3 Hz), 165.7 (d, *J* = 29.1 Hz), 164.7 (d, *J* = 4.4 Hz), 138.8, 137.5, 133.2, 130.5, 130.0 (q, *J* = 32.1 Hz), 129.99, 128.9, 128.6, 125.1 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.5 Hz), 96.8 (d, *J* = 199.9 Hz), 56.7 (d, *J* = 24.1 Hz), 52.2 (d, *J* = 1.5 Hz), 10.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -62.7 (s, 3F), -158.1 (d, *J* = 24.4 Hz, 1F); HRMS (EI) calculated for $[C_{21}H_{16}O_3F_4]^+$ requires m/z 392.1036, found m/z 392.1035.

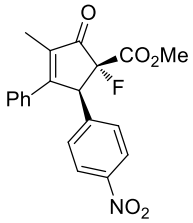


(+)-Methyl 4-((1*S*,5*R*)-5-fluoro-5-(methoxycarbonyl)-3-methyl-4-oxo-2-phenylcyclopent-2-en-1-yl)benzoate (**2j**). The product **2j** was prepared according to the general procedure above by using **1j** (0.1826 g, 0.50 mmol), NFSI (0.1735 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-5/1) as the eluent to give (+)-**2j** (0.1796 g, 91% yield) as a white solid. M.p. 194-196 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +403.6 (c = 1.02, $CHCl_3$), 90% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 12.3 (minor), 15.6 (major); IR (neat): 2954, 2924, 1767, 1715, 1612, 1437, 1281 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.45-7.30 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.02-4.88 (m, 1H), 3.85 (s, 3H), 3.26 (s, 3H), 2.17 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.2 (d, *J* = 18.2 Hz), 166.4, 165.7 (d, *J* = 28.4 Hz), 164.9 (d, *J* = 4.3 Hz), 139.8 (d, *J* = 1.4 Hz), 137.2, 133.3, 130.4, 129.7, 129.6, 129.4, 128.8, 128.6, 96.8 (d, *J* = 201.3 Hz), 56.9 (d, *J* = 24.0 Hz), 52.2, 52.1, 10.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.1 (d, *J* = 24.4 Hz); HRMS (EI)

calculated for $[C_{22}H_{19}O_5F]^+$ requires m/z 382.1217, found m/z 382.1220.

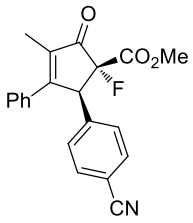


(1*R*,2*S*)-(+)-methyl 2-(4-(diethylcarbamoyl)phenyl)-1-fluoro-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2k**). The product **2k** was prepared according to the general procedure above by using **1k** (0.2030 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 24 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (2/1-1/1) as the eluent to give (+)-**2k** (0.1486 g, 70% yield) as a white solid. M.p. 109-111 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +298.4 (c = 0.99, $CHCl_3$), 75% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, *n* = 220 nm, t_r 11.1 (major), 12.0 (minor); IR (neat): 2954, 2925, 1767, 1714, 1624, 1435, 1288 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.46-7.32 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.00-4.85 (m, 1H), 3.60-3.38 (m, 2H), 3.28 (s, 3H), 3.20-3.00 (m, 2H), 2.16 (d, *J* = 2.0 Hz, 3H), 1.28-0.92 (m, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.3 (d, *J* = 17.5 Hz), 170.4, 165.7 (d, *J* = 29.2 Hz), 165.3 (d, *J* = 4.4 Hz), 137.0, 136.5, 135.6 (d, *J* = 2.2 Hz), 133.2, 130.2, 129.5, 128.7, 128.5, 126.2, 96.8 (d, *J* = 200.5 Hz), 56.7 (d, *J* = 24.0 Hz), 51.9, 43.1, 39.3, 14.0, 12.7, 10.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.3 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{25}H_{26}NO_4F]^+$ requires m/z 423.1846, found m/z 423.1847.

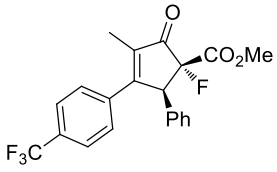


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-5-(4-nitrophenyl)-2-oxo-4-phenylcyclopent-3-enecarboxylate (**2l**). The product **2l** was prepared according to the general procedure above by using **1l** (0.1761 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-5/1) as the eluent to give (+)-**2l** (0.1663 g, 70% yield) as a white solid. M.p. 201-203 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +377.4 (c = 0.95, $CHCl_3$), 83% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 15.8 (minor),

19.5 (major); IR (neat): 2955, 2925, 1766, 1715, 1607, 1521, 1347 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.48-7.33 (m, 5H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.10-4.95 (m, 1H), 3.31 (s, 3H), 2.18 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.6 (d, *J* = 18.2 Hz), 165.4 (d, *J* = 29.2 Hz), 164.1 (d, *J* = 4.4 Hz), 147.3, 142.1 (d, *J* = 2.2 Hz), 137.6, 132.9, 130.59, 130.57, 128.9, 128.5, 123.3, 96.6 (d, *J* = 203.5 Hz), 56.5 (d, *J* = 24.8 Hz), 52.3 (d, *J* = 1.5 Hz), 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.3 (d, *J* = 23.3 Hz); HRMS (EI) calculated for $[C_{20}H_{16}NO_5F]^+$ requires m/z 369.1013, found m/z 369.1009.

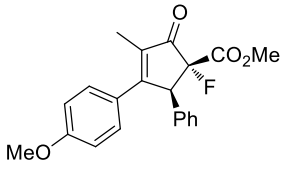


(1*R*,2*S*)-methyl 2-(4-cyanophenyl)-1-fluoro-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2m**). The product **2m** was prepared according to the general procedure above by using **1m** (0.1660 g, 0.50 mmol), NFSI (0.1735 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (8/1-5/1) as the eluent to give (+)-**2m** (0.0910 g, 52% yield) as a white solid. M.p. 206-208 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +358.8 (c = 0.99, $CHCl_3$), 72% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 16.6 (minor), 25.1 (major); IR (neat): 2956, 2923, 2229, 1764, 1713, 1609, 1345, 1241 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.44-7.34 (m, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.02-4.88 (m, 1H), 3.30 (s, 3H), 2.17 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.7 (d, *J* = 18.3 Hz), 165.5 (d, *J* = 29.2 Hz), 164.1 (d, *J* = 4.3 Hz), 140.1 (d, *J* = 2.2 Hz), 137.6, 133.0, 131.9, 130.6, 130.4, 128.9, 128.5, 118.1, 111.9, 96.6 (d, *J* = 203.5 Hz), 56.8 (d, *J* = 24.1 Hz), 52.3, 10.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.2 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{21}H_{16}NO_3F]^+$ requires m/z 349.1114, found m/z 349.1113.



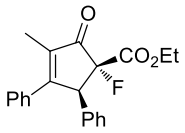
(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-5-phenyl-4-(4-(trifluoromethyl)phenyl)cyclop-ent-3-enecarboxylate (**2n**). The product **2n** was prepared according to the general procedure above by using **1n** (0.1875 g, 0.50 mmol),

NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2 \cdot 3H_2O$ (0.0278 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2n** (0.1785 g, 91% yield) as a white solid. M.p. 145-147 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +335.3 (c = 1.01, $CHCl_3$), 88% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 8.8 (minor), 12.2 (major); IR (neat): 3034, 2956, 1768, 1719, 1615, 1323, 1124 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.24-7.16 (m, 3H), 7.10-7.00 (m, 2H), 4.95-4.82 (m, 1H), 3.26 (s, 3H), 2.16 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.6 (d, *J* = 17.5 Hz), 165.7 (d, *J* = 28.4 Hz), 163.6 (d, *J* = 3.7 Hz), 138.4, 137.1, 133.9 (d, *J* = 1.4 Hz), 131.6 (q, *J* = 32.8 Hz), 129.5, 128.8, 128.4, 128.1, 125.6 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 270.5 Hz), 96.8 (d, *J* = 201.2 Hz), 57.1 (d, *J* = 24.1 Hz), 52.1, 10.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -63.0 (s, 3F), -158.3 (d, *J* = 23.3 Hz, 1F); HRMS (EI) calculated for $[C_{21}H_{16}O_3F_4]^+$ requires m/z 392.1036, found m/z 392.1037.

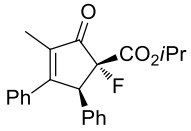


(1*R*,2*S*)-(+)-methyl 1-fluoro-3-(4-methoxyphenyl)-4-methyl-5-oxo-2-phenylcyclopent-3-enecarboxylate (**2o**). The product **2o** was prepared according to the general procedure above by using **1o** (0.1688 g, 0.50 mmol), NFSI (0.1738 g, 0.55 mmol), TIP·$Co(ClO_4)_2 \cdot 3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (8/1-5/1) as the eluent to give (+)-**2o** (0.1691 g, 95% yield) as a colorless oil. Optical Rotation: $[\alpha]_D^{20}$ = +496.9 (c = 1.04, $CHCl_3$), 93% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 10.6 (minor), 17.6 (major); IR (neat): 2954, 2842, 1765, 1706, 1602, 1511, 1346, 1256, 1180 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.24-7.12 (m, 3H), 7.10-7.00 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.92-4.80 (m, 1H), 3.78 (s, 3H), 3.21 (s, 3H), 2.18 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.5 (d, *J* = 17.5 Hz), 166.1 (d, *J* = 29.2 Hz), 165.3 (d, *J* = 3.6 Hz), 161.0, 135.2, 134.9 (d, *J* = 2.2 Hz), 130.7, 129.5, 128.1, 127.6, 125.9, 114.0, 97.0 (d, *J* = 199.0 Hz), 56.9 (d, *J* = 24.1 Hz), 55.2, 51.9 (d, *J* = 1.5 Hz), 10.6; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -157.1 (d, *J* = 25.9 Hz); HRMS (EI)

calculated for $[C_{21}H_{19}O_4F]^+$ requires m/z 354.1267, found m/z 354.1268.

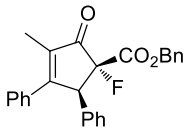


(1*R*,5*S*)-(+)-ethyl 1-fluoro-3-methyl-2-oxo-4,5-diphenylcyclopent-3-enecarboxylate (**2p**). The product **2p** was prepared according to the general procedure above by using **1p** (0.1606 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2p** (0.1582 g, 93% yield) as a white solid. M.p. 71-73 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +461.6 (c = 1.00, $CHCl_3$), 92% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 8.4 (minor), 13.9 (major); IR (neat): 3031, 2984, 1761, 1712, 1619, 1444, 1347, 1218 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.28 (m, 5H), 7.22-7.11 (m, 3H), 7.10-7.00 (m, 2H), 4.96-4.82 (m, 1H), 3.85-3.73 (m, 1H), 3.68-3.55 (m, 1H), 2.16 (d, *J* = 2.4 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.0 (d, *J* = 17.5 Hz), 165.7 (d, *J* = 28.5 Hz), 165.6 (d, *J* = 4.4 Hz), 136.9, 134.6 (d, *J* = 2.2 Hz), 133.7, 130.1, 129.7, 128.64, 128.61, 128.2, 127.7, 96.7 (d, *J* = 201.2 Hz), 61.8, 57.1 (d, *J* = 24.0 Hz), 13.5, 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -157.5 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{21}H_{19}O_3F]^+$ requires m/z 338.1318, found m/z 338.1319.

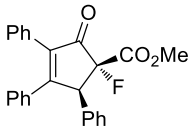


(1*R*,5*S*)-(+)-*iso*propyl 1-fluoro-3-methyl-2-oxo-4,5-diphenylcyclopent-3-enecarboxylate (**2q**). The product **2q** was prepared according to the general procedure above by using **1q** (0.1675 g, 0.50 mmol), NFSI (0.1735 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0275 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2q** (0.1603 g, 91% yield) as a white solid. M.p. 134-136 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +471.8 (c = 1.03, $CHCl_3$), 88% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 6.7 (minor), 15.2 (major); IR (neat): 3061, 2925, 1756, 1712, 1619, 1453, 1347 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.29 (m, 5H), 7.22-7.00 (m, 5H),

4.95-4.80 (m, 1H), 4.68-4.53 (m, 1H), 2.15 (d, *J* = 2.0 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.2 (d, *J* = 17.5 Hz), 165.8 (d, *J* = 4.4 Hz), 165.2 (d, *J* = 27.0 Hz), 136.8, 134.6 (d, *J* = 2.2 Hz), 133.7, 130.0, 129.9, 128.60, 128.57, 128.2, 127.6, 96.5 (d, *J* = 202.0 Hz), 70.2, 57.0 (d, *J* = 24.1 Hz), 21.1, 21.0, 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -157.0 (d, *J* = 25.9 Hz); HRMS (EI) calculated for $[C_{22}H_{21}O_3F]^+$ requires m/z 352.1472, found m/z 352.1475.

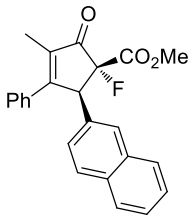


(1*R*,5*S*)-(+)-benzyl 1-fluoro-3-methyl-2-oxo-4,5-diphenylcyclopent-3-enecarboxylate (**2r**). The product **2r** was prepared according to the general procedure above by using **1r** (0.1915 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2$·$3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^{o}C for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2r** (0.1880 g, 94% yield) as a white solid. M.p. 120-122 ^{o}C; Optical Rotation: $[\alpha]_D^{20}$ = +349.6 (c = 1.02, $CHCl_3$), 89% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 14.1 (minor), 18.8 (major); IR (neat): 3061, 2925, 1756, 1712, 1619, 1453, 1347, 1105 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.45-7.22 (m, 8H), 7.18-6.95 (m, 7H), 4.90 (d, *J* = 24.4 Hz, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 2.14 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.8 (d, *J* = 17.5 Hz), 165.7 (d, *J* = 5.9 Hz), 165.5 (d, *J* = 28.4 Hz), 136.9, 134.4 (d, *J* = 1.4 Hz), 134.3, 133.6, 130.1, 129.6, 128.61, 128.59, 128.4, 128.3, 128.2, 128.1, 127.7, 97.0 (d, *J* = 200.5 Hz), 67.2, 57.1 (d, *J* = 23.3 Hz), 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.2 (d, *J* = 24.8 Hz); HRMS (EI) calculated for $[C_{22}H_{21}O_3F]^+$ requires m/z 352.1475, found m/z 352.1475.



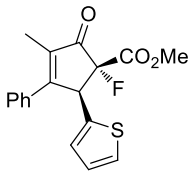
(1*R*,5*S*)-(+)-methyl 1-fluoro-2-oxo-3,4,5-triphenylcyclopent-3-enecarboxylate (**2s**). The product **2s** was prepared according to the general procedure above by using **1s** (0.1850 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2$·$3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^{o}C for 15 h, the crude reaction mixture was purified by

flash column chromatography using PE/EA (12/1-8/1) as the eluent to give (+)-**2s** (0.1701 g, 88% yield) as a white solid. M.p. 142-144 ^{o}C; Optical Rotation: $[\alpha]_D^{20}$ = +207.0 (c = 1.02, $CHCl_3$), 77% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 8.5 (major), 9.3 (minor); (**2s** with 94% ee could be obtained after recrystallization from CH_2Cl_2 and PE, Optical Rotation: $[\alpha]_D^{20}$ = +293.6 (c = 1.00, $CHCl_3$), 94% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 8.4 (major), 9.2 (minor)); IR (neat): 3060, 2954, 1767, 1715, 1444, 1352, 1078 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.32-7.27 (m, 2H), 7.25-7.05 (m, 10H), 5.00 (d, *J* = 24.4 Hz, 1H), 3.29 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.0 (d, *J* = 17.5 Hz), 166.3 (d, *J* = 3.6 Hz), 165.9 (d, *J* = 29.1 Hz), 139.7, 134.3 (d, *J* = 2.2 Hz), 133.0, 130.6, 130.4, 129.6, 129.3, 128.7, 128.6, 128.4, 128.3, 127.8, 97.4 (d, *J* = 199.8 Hz), 57.2 (d, *J* = 24.1 Hz), 52.1; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -157.0 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{25}H_{19}O_3F]^+$ requires m/z 386.1318, found m/z 386.1314.

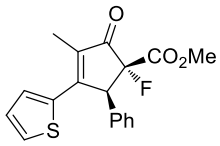


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-5-(naphthalen-2-yl)-2-oxo-4-phenylcyclopent-3-enecarboxylate (**2t**). The product **2t** was prepared according to the general procedure above by using **1t** (0.1785 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2$·$3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^{o}C for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2t** (0.1752 g, 94% yield) as a white solid. M.p. 140-142 ^{o}C; Optical Rotation: $[\alpha]_D^{20}$ = +411.4 (c = 0.96, $CHCl_3$), 91% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 9.8 (minor), 13.6 (major); IR (neat): 3058, 2953, 1765, 1713, 1615, 1439, 1347, 1238, 1089 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75-7.66 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.50-7.38 (m, 4H), 7.36-7.25 (m, 3H), 7.11 (d, *J* = 8.8 Hz, 1H), 5.06 (d, *J* = 24.4 Hz, 1H), 3.12 (s, 3H), 2.20 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.8 (d, *J* = 17.5 Hz), 165.9 (d, *J* = 28.4 Hz), 165.7 (d, *J* = 3.6 Hz), 137.0, 133.6, 132.9, 132.5, 132.1 (d, *J* = 2.2 Hz), 130.1, 129.2, 128.7, 128.6, 127.81, 127.77, 127.5, 126.7, 126.28, 126.25, 97.0 (d, *J* = 200.6 Hz), 57.2 (d, *J* = 23.3 Hz), 52.0, 10.5; ^{19}F NMR:

(376 MHz, $CDCl_3$) δ -157.7 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{24}H_{19}O_3F]^+$ requires m/z 374.1318, found m/z 374.1321.

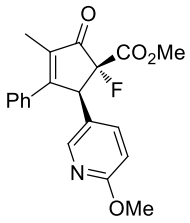


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-4-phenyl-5-(thiophen-2-yl)cyclopent-3-enecarboxylate (**2u**). The product **2u** was prepared according to the general procedure above by using **1u** (0.1566 g, 0.50 mmol), NFSI (0.1735 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-6/1) as the eluent to give (+)-**2u** (0.1160 g, 70% yield) as a white solid. M.p. 115-117 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +364.0 (c = 1.00, $CHCl_3$), 76% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 8.1 (minor), 10.3 (major); IR (neat): 2954, 2925, 1766, 1714, 1618, 1437, 1346, 1219, 1089 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.50-7.34 (m, 5H), 7.12 (d, *J* = 5.2 Hz, 1H), 6.82 (dd, *J* = 3.6, 5.2 Hz, 1H), 6.74 (d, *J* = 3.6 Hz, 1H), 5.22-5.08 (m, 1H), 3.41 (s, 3H), 2.13 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.0 (d, *J* = 17.5 Hz), 165.7 (d, *J* = 29.2 Hz), 164.9 (d, *J* = 4.3 Hz), 136.6, 136.5, 133.3, 130.2, 128.6, 128.4, 126.6, 125.9, 96.8 (d, *J* = 201.3 Hz), 52.4, 52.1 (d, *J* = 25.5 Hz), 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -159.3 (d, *J* = 21.8 Hz); HRMS (EI) calculated for $[C_{18}H_{15}O_3FS]^+$ requires m/z 330.0726, found m/z 330.0729.

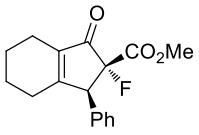


(1*R*,5*S*)-(+)-methyl 1-fluoro-3-methyl-2-oxo-5-phenyl-4-(thiophen-2-yl)cyclopent-3-enecarboxylate (**2v**). The product **2v** was prepared according to the general procedure above by using **1v** (0.1566 g, 0.50 mmol), NFSI (0.1736 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2v** (0.1474 g, 89% yield) as a white solid. M.p. 142-144 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +158.8 (c = 1.00, $CHCl_3$), 87% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, *n* = 220 nm, t_r 9.0 (minor),

12.2 (major); IR (neat): 2953, 2925, 1759, 1702, 1584, 1413, 1348, 1225, 1081 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 0.8, 5.2 Hz, 1H), 7.32-7.22 (m, 3H), 7.20-7.06 (m, 3H), 7.04 (dd, *J* = 4.0, 5.2 Hz, 1H), 4.84-4.72 (m, 1H), 3.20 (s, 3H), 2.30 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.7 (d, *J* = 17.5 Hz), 166.1 (d, *J* = 29.9 Hz), 157.8 (d, *J* = 2.9 Hz), 136.8, 135.4 (d, *J* = 3.7 Hz), 134.0, 132.4, 131.9, 129.2, 128.4, 128.1, 127.9, 96.5 (d, *J* = 197.6 Hz), 57.6 (d, *J* = 25.6 Hz), 51.9, 10.8; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -153.6 (d, *J* = 24.8 Hz); HRMS (EI) calculated for $[C_{18}H_{15}O_3FS]^+$ requires m/z 330.0726, found m/z 330.0727.

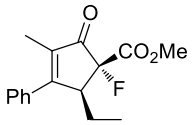


(1*R*,2*R*)-(+)-methyl 1-fluoro-2-(6-methoxypyridin-3-yl)-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2w**). The product **2w** was prepared according to the general procedure above by using **1w** (0.1689 g, 0.50 mmol), NFSI (0.1738 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^oC for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (5/1) as the eluent to give (+)-**2w** (0.0954 g, 54% yield) as a white solid. M.p. 113-115 ^oC; Optical Rotation: $[\alpha]_D^{20}$ = +377.1 (c = 0.97, $CHCl_3$), 79% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, *n* = 220 nm, t_r 10.0 (minor), 13.6 (major); IR (neat): 2953, 2925, 1766, 1714, 1607, 1493, 1394, 1294, 1090 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.0 Hz, 1H), 7.44-7.32 (m, 5H), 7.20 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 1H), 4.92-4.76 (m, 1H), 3.83 (s, 3H), 3.37 (s, 3H), 2.15 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.3 (d, *J* = 18.2 Hz), 165.8 (d, *J* = 29.1 Hz), 165.1 (d, *J* = 4.4 Hz), 163.5, 147.9, 139.3, 137.2, 133.1, 130.3, 128.8, 128.6, 122.9 (d, *J* = 2.2 Hz), 110.4, 96.8 (d, *J* = 201.3 Hz), 54.0 (d, *J* = 24.1 Hz), 53.4, 52.3, 10.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -159.2 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{20}H_{18}NO_4F]^+$ requires m/z 355.1220, found m/z 355.1220.



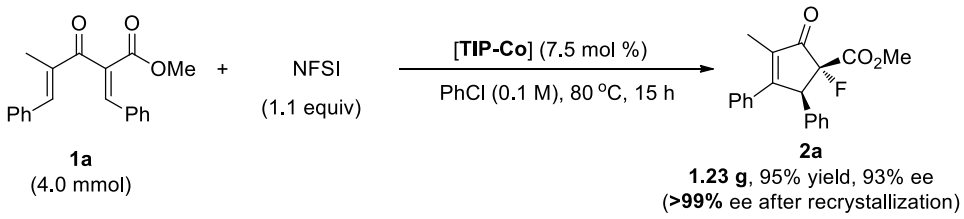
(2*R*,3*S*)-(+)-methyl 2-fluoro-1-oxo-3-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indene-2-carboxylate (**2x**). The product **2x** was prepared according to the general procedure above by using **1x** (0.1358 g, 0.50 mmol), NFSI (0.1735 g, 0.55 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.0276 g,

0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^{o}C for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2x** (0.0721 g, 50% yield) as a white solid. M.p. 115-117 ^{o}C; Optical Rotation: $[\alpha]_D^{20}$ = +20.8 (c = 0.98, $CHCl_3$), 73% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 7.8 (minor), 9.2 (major); IR (neat): 3032, 2931, 1765, 1716, 1639, 1436, 1236, 1098 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40-7.25 (m, 3H), 7.17-7.04 (m, 2H), 4.23 (d, *J* = 23.6 Hz, 1H), 3.24 (s, 3H), 2.55-2.28 (m, 3H), 2.25-2.08 (m, 1H), 1.95-1.68 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.7 (d, *J* = 18.2 Hz), 172.4 (d, *J* = 4.4 Hz), 166.2 (d, *J* = 28.4 Hz), 139.5, 133.9 (d, *J* = 2.1 Hz), 129.3, 128.4, 128.1, 96.9 (d, *J* = 200.6 Hz), 58.6 (d, *J* = 24.1 Hz), 51.8 (d, *J* = 1.5 Hz), 26.9, 21.8, 21.2, 20.2; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -158.4 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{17}H_{17}O_3F]^+$ requires m/z 288.1162, found m/z 288.1160.



(1*R*,2*S*)-(+)-methyl 2-ethyl-1-fluoro-4-methyl-5-oxo-3-phenylcyclopent-3-enecarboxylate (**2y**). The product **2y** was prepared according to the general procedure above by using **1y** (0.1299 g, 0.50 mmol), NFSI (0.1738 g, 0.55 mmol), TIP·$Co(ClO_4)_2$·$3H_2O$ (0.0276 g, 0.0375 mmol) and chlorobenzene (5 mL). After heated to 80 ^{o}C for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give (+)-**2y** (0.0665 g, 48% yield) as a colorless oil. Optical Rotation: $[\alpha]_D^{20}$ = +172.6 (c = 1.00, $CHCl_3$), 44% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 5.8 (minor), 7.8 (major); IR (neat): 2957, 2883, 1765, 1713, 1621, 1441, 1348, 1289, 1128 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55-7.40 (m, 3H), 7.38-7.30 (m, 2H), 3.84 (s, 3H), 3.54-3.32 (m, 1H), 1.88 (d, *J* = 2.4 Hz, 3H), 1.73-1.58 (m, 1H), 1.48-1.30 (m, 1H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 198.0 (d, *J* = 17.5 Hz), 170.2 (d, *J* = 5.1 Hz), 167.1 (d, *J* = 28.4 Hz), 134.7, 133.9, 129.8, 128.7, 127.6, 96.5 (d, *J* = 199.8 Hz), 53.3 (d, *J* = 21.9 Hz), 52.7, 21.4, 12.3, 9.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -160.7 (d, *J* = 24.4 Hz); HRMS (EI) calculated for $[C_{16}H_{17}O_3F]^+$ requires m/z 276.1162, found m/z 276.1161.

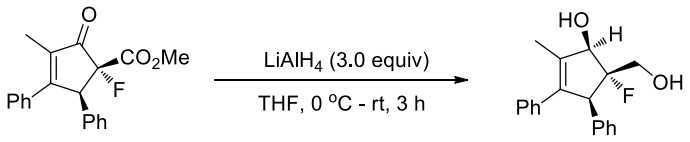
V. Gram Scale Reaction and Further Derivatizations



1a
(4.0 mmol)

2a
1.23 g, 95% yield, 93% ee
(**>99%** ee after recrystallization)

Gram scale reaction was conducted according to the general procedure above by using **1a** (1.2261 g, 4.0 mmol), NFSI (1.3876 g, 4.4 mmol), TIP·$Co(ClO_4)_2·3H_2O$ (0.2208 g, 0.3 mmol) and chlorobenzene (40 mL). After heated to 80 °C for 15 h, the crude reaction mixture was purified by flash column chromatography using PE/EA (10/1-8/1) as the eluent to give (+)-**2a** (1.2309 g, 95% yield) as a white solid. Optical Rotation: $[\alpha]_D^{20}$ = +486.1 (c = 0.98, $CHCl_3$), 93% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 8.5 (minor), 12.8 (major); **2a** with >99% ee could be obtained after recrystallization from CH_2Cl_2 and PE, Optical Rotation: $[\alpha]_D^{20}$ = +527.1 (c = 0.98, $CHCl_3$), >99% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 8.4 (minor), 12.6 (major).

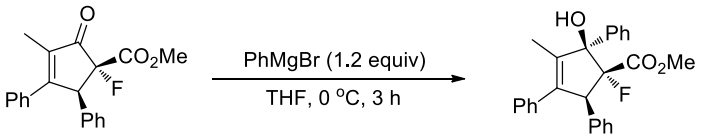


2a (>99% ee)

5a

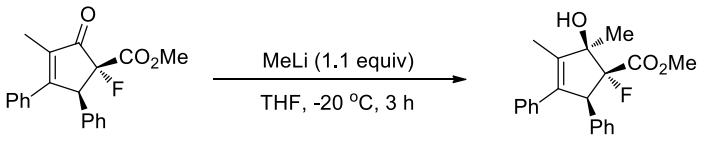
To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, $LiAlH_4$ (0.0230 g, 0.60 mmol) and THF (1 mL) were added. **2a** (0.0651 g, 0.20 mmol) (dissolved in 2 mL THF) was added dropwisely to the mixture at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 3 hours. After carefully quenched with water (20 mL), the aqueous layer was extracted with ether (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography on silica gel using PE/EA (3/1) as the eluent to give (+)-**5a** (0.0434 g, 73% yield, *dr* > 20:1) as a white solid. M.p. 79-81 °C; Optical Rotation: $[\alpha]_D^{20}$ = +133.8 (c = 1.02, $CHCl_3$), >99% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 9.1 (major), 9.9 (minor); IR (neat): 3424, 3060, 2916, 2883, 1602, 1495, 1621, 1447, 1261, 1025

cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.30-7.10 (m, 10H), 4.74 (dd, *J* = 2.8, 19.2 Hz, 1H), 4.38-4.20 (m, 1H), 3.62-3.50 (m, 1H), 3.41 (dd, *J* = 11.2, 34.0 Hz, 1H), 3.26 (br, 1H), 2.48 (br, 1H), 2.05 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.7, 137.2 (d, *J* = 8.0 Hz), 135.7, 135.1, 129.3, 128.5, 128.4, 128.0, 127.3, 127.2, 104.9 (d, *J* = 176.4 Hz), 85.0 (d, *J* = 35.7 Hz), 63.8 (d, *J* = 21.9 Hz), 62.2 (d, *J* = 27.0 Hz), 13.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -149.1--149.6 (m) (for decoupling spectrum, see: ^{19}F NMR: (376 MHz, $CDCl_3$) δ -149.3); HRMS (ESI) calculated for $[C_{19}H_{20}O_2F]^+$ $[M+H]^+$ requires m/z 299.1447, found m/z 299.1433.



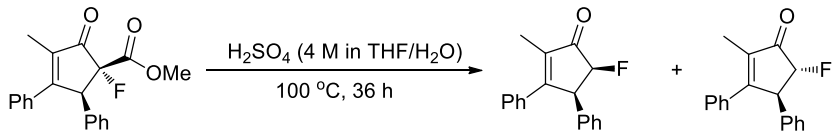
2a (>99% ee) **6a**

To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, **2a** (0.0652 g, 0.20 mmol) and THF (2 mL) were added. Then phenylmagnesium bromide (96 μL, 0.24 mmol, 2.5 M in Et_2O) was added dropwisely to the mixture at 0 °C. The reaction mixture was left to stir at 0 ℃ for 3 hours and quenched with saturated NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography on silica gel using PE/EA (15/1-10/1) as the eluent to give (+)-**6a** (0.0507 g, 63% yield, *dr* > 20:1) as a white solid. M.p. 148-150 °C; Optical Rotation: $[\alpha]_D^{20}$ = +233.0 (c = 1.00, $CHCl_3$), >99% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 7.8 (minor), 10.3 (major); IR (neat): 3520, 2955, 2924, 1756, 1724, 1493, 1447, 1312, 1057 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.45-7.39 (m, 2H), 7.38-7.32 (m, 1H), 7.31-7.18 (m, 5H), 7.17-7.03 (m, 5H), 4.75-4.60 (m, 1H), 4.33 (s, 1H), 3.33 (s, 3H), 1.88 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 169.9 (d, *J* = 27.7 Hz), 139.7, 137.3 (d, *J* = 4.4 Hz), 137.2 (d, *J* = 4.4 Hz), 136.1 (d, *J* = 2.2 Hz), 135.2, 129.8, 128.5, 128.22, 128.16, 128.0, 127.9, 127.3 (d, *J* = 2.9 Hz), 127.2 (d, *J* = 2.1 Hz), 105.6 (d, *J* = 211.4 Hz), 89.8 (d, *J* = 21.1 Hz), 60.1 (d, *J* = 24.0 Hz), 52.3, 12.2; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -157.4 (d, *J* = 23.3 Hz); HRMS (ESI) calculated for $[C_{26}H_{23}O_3FNa]^+$ $[M+Na]^+$ requires m/z 425.1529, found m/z 425.1529.



2a (>99% ee) **7a**

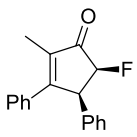
To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, **2a** (0.0651 g, 0.20 mmol) and THF (2 mL) were added. Then methyllithium (140 μL, 0.22 mmol, 1.6 M in Et_2O) was added dropwisely to the mixture at -20 °C. The reaction mixture was left to stir at -20 ℃ for 3 hours and quenched with water (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography on silica gel using PE/EA (10/1-8/1) as the eluent to give (+)-**7a** (0.0463 g, 68% yield, *dr* > 20:1) as a white solid. M.p. 117-119 °C; Optical Rotation: $[\alpha]_D^{20}$ = +144.8 (c = 0.98, $CHCl_3$), 98% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 5.5 (minor), 6.7 (major); IR (neat): 3480, 2953, 1759, 1726, 1441, 1314, 1235, 1076 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 7.17-7.05 (m, 8H), 4.70-4.53 (m, 1H), 3.53 (s, 1H), 2.93 (s, 3H), 1.97 (d, *J* = 2.4 Hz, 3H), 1.50 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 169.5 (d, *J* = 26.9 Hz), 140.2 (d, *J* = 2.2 Hz), 136.3 (d, *J* = 2.1 Hz), 135.4, 133.9 (d, *J* = 4.4 Hz), 129.7, 128.4, 128.0, 127.9, 127.2, 127.0, 106.4 (d, *J* = 208.5 Hz), 85.4 (d, *J* = 21.8 Hz), 59.7 (d, *J* = 24.1 Hz), 52.1, 19.9 (d, *J* = 11.0 Hz), 11.0; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -164.0 (dq, *J* = 5.3, 23.3 Hz); HRMS (EI) calculated for $[C_{21}H_{21}O_3F]^+$ requires m/z 340.1475, found m/z 340.1473.



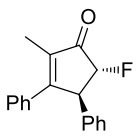
2a (>99% ee) **8a** **9a**

To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, **2a** (0.0652 g, 0.20 mmol), THF (1.5 mL) and H_2O (0.5 mL) were added. Then H_2SO_4 (conc.) (0.44 mL, 8.0 mmol) was added dropwisely to the mixture at room temperature. Then the reaction mixture was heated to reflux at 100 ℃ for 36 hours. After cooled down to room temperature, the reaction was carefully neutralized with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with

brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography on silica gel using PE/EA (12/1-10/1) as the eluent to give separable diastereoisomers (+)-**8a** (0.0277 g, 52% yield) and (+)-**9a** (0.0090 g, 17% yield). (**8a**/**9a** = 5/1, determined by crude ^{1}H NMR analysis).

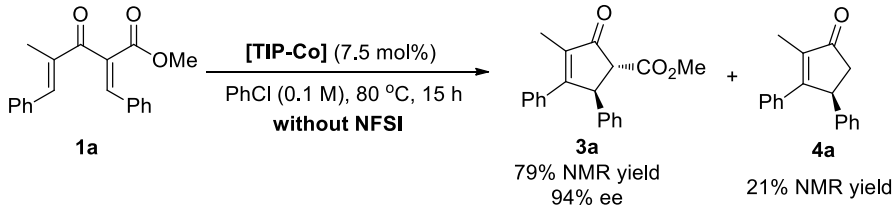


(4*S*,5*S*)-(+)-5-fluoro-2-methyl-3,4-diphenylcyclopent-2-enone (**8a**). Colorless oil. Optical Rotation: $[\alpha]_D^{20}$ = +170.2 (c = 0.98, $CHCl_3$), >99% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 7.5 (minor), 7.9 (major); IR (neat): 3030, 2922, 1713, 1608, 1447, 1383, 1331, 1128, 1029 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.42-7.20 (m, 8H), 7.18-7.07 (m, 2H), 5.30 (dd, *J* = 3.2, 52.0 Hz, 1H), 4.69 (d, *J* = 2.8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 202.6 (d, *J* = 15.3 Hz), 164.1 (d, *J* = 1.5 Hz), 135.7 (d, *J* = 1.4 Hz) 135.4 (d, *J* = 5.1 Hz), 134.5, 130.0, 128.8, 128.7, 128.6, 128.3, 127.8, 89.7 (d, *J* = 197.6 Hz), 51.8 (d, *J* = 18.2 Hz), 10.1; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -199.1 (d, *J* = 51.9 Hz); HRMS (EI) calculated for $[C_{18}H_{15}OF]^+$ requires m/z 266.1107, found m/z 266.1108.

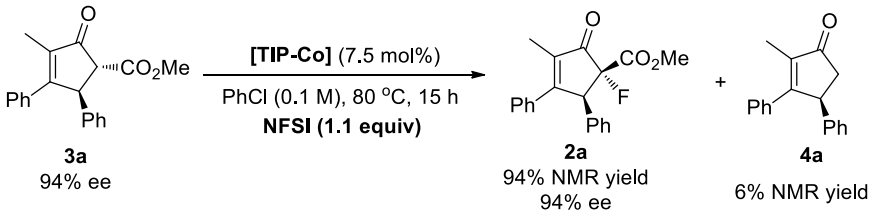


(4*S*,5*R*)-(+)-5-fluoro-2-methyl-3,4-diphenylcyclopent-2-enone (**9a**). Colorless oil. Optical Rotation: $[\alpha]_D^{20}$ = +515.0 (c = 0.50, $CHCl_3$), 96% ee, determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 6.0 (minor), 6.6 (major); IR (neat): 3029, 2922, 1715, 1616, 1447, 1331, 1075, 1003 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.27-7.13 (m, 3H), 7.12-7.04 (m, 2H), 4.90 (dd, *J* = 2.8, 51.2 Hz, 1H), 4.60-4.45 (m, 1H), 2.08 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 201.8 (d, *J* = 14.6 Hz), 165.5 (d, *J* = 5.1 Hz), 139.1, 136.0, 133.8, 129.8, 129.0, 128.7, 128.5, 127.9, 127.3, 96.1 (d, *J* = 193.2 Hz), 53.4 (d, *J* = 19.7 Hz), 10.1; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -189.9 (dd, *J* = 21.8, 51.5 Hz); HRMS (EI) calculated for $[C_{18}H_{15}OF]^+$ requires m/z 266.1107, found m/z 266.1110.

VI. Control Experiments



To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, TIP·Co(ClO_4)$_2$·3H_2O (0.0276 g, 7.5 mol %), **1a** (0.1533 g, 0.50 mmol) and chlorobenzene (5 mL) were added. Then the flask was sealed with a screw cap and heated to 80 °C for 15 h. After cooled down to room temperature, the mixture was filtered through a pad of silica gel and washed with ether. The filtrate was concentrated under reduced pressure and directly determined by NMR analysis. The results of NMR analysis showed that the corresponding product **3a** was obtained in 79% yield with excellent diastereoselectivity (>20/1). The enantioselectivity of product **3a** (94% ee) was determined by HPLC according to our previously reported HPLC conditions[3]: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 11.2 (minor), 17.9 (major).



To a 25 mL flame-dried Schlenk flask cooled under the atmosphere of nitrogen, TIP·Co(ClO_4)$_2$·3H_2O (0.0110 g, 7.5 mol %), **3a** (0.0612 g, 0.20 mmol) (obtained from the above experiment), NFSI (0.0695 g, 0.22 mmol) and chlorobenzene (2 mL) were added. Then the flask was sealed with a screw cap and heated to 80 °C for 15 h. After cooled down to room temperature, the mixture was filtered through a pad of silica gel and washed with ether. The filtrate was concentrated under reduced pressure and directly determined by NMR analysis. The results of NMR analysis showed that the corresponding product **2a** was obtained in 94% yield with excellent diastereoselectivity (>20/1). The enantioselectivity of product **2a** (94% ee) was determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, *n* = 220 nm, t_r 8.4 (minor), 12.7 (major).

VII. Reference

[1] Brégeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J. C.; Gaumont, A. C. *Amino Acids* **2008**, *35*, 175.

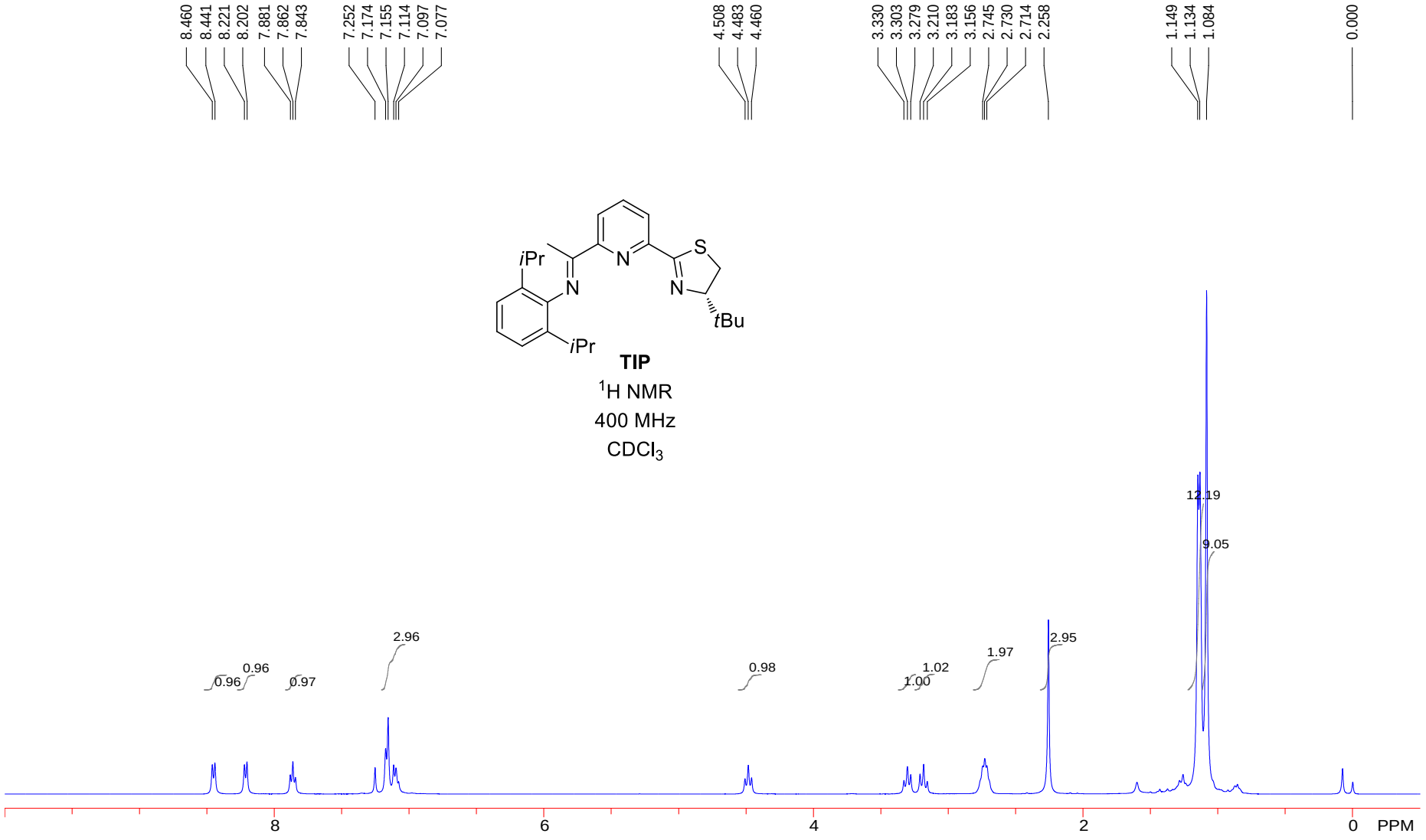
[2] (a) Chen, J.-H.; Xi, T.; Ren, X.; Guo, J.; Cheng, B.; Lu, Z. *Org. Chem. Front.* **2014**, *1*, 1306. (b) Chen, J.-H.; Xi, T.; Lu, Z. *Org. Lett*. **2014**, *16*, 6452 .(c) Xi, T.; Mei, Y.-C.; Lu, Z. *Org. Lett.* **2015**, *17*, 5939.

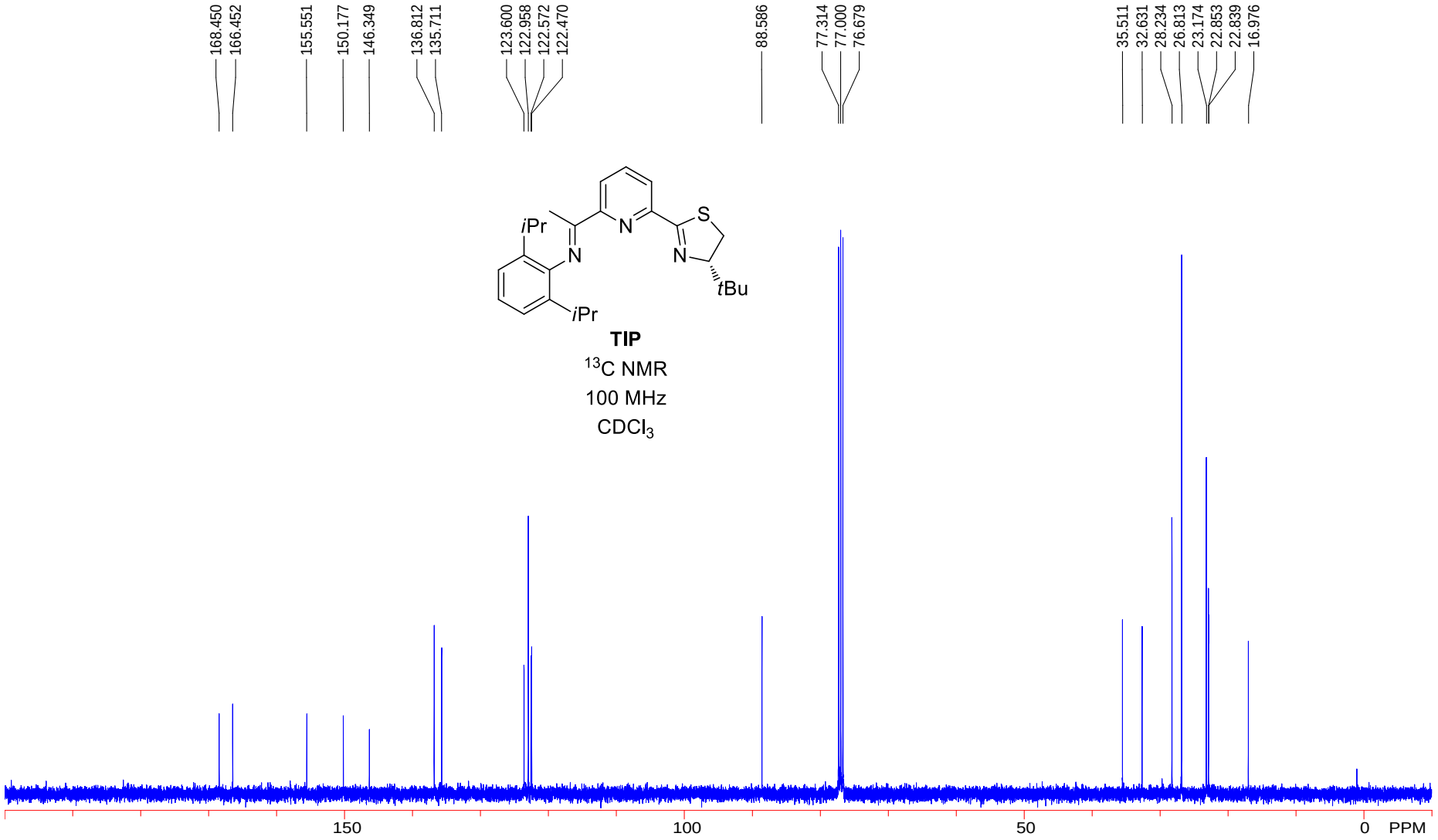
[3] Zhang, H.-Y.; Lu, Z. *Org. Chem. Front.* **2018**, *5*, 1763.

[4] Kerwat, D.; Grätz, S.; Kretz, J.; Seidel, M.; Kunert, M.; Weston, J. B.; Süssmuth, R. D. *ChemMedChem* **2016**, *11*, 1899.

[5] Aggarwal, V. K.; Belfield, A. J. *Org. Lett.* **2003**, *5*, 5075.

VIII. NMR Spectra

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77.314
77.000
76.679
35.511
32.631
28.234
26.813
23.174
22.853
22.839
16.976
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S
N
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iPr
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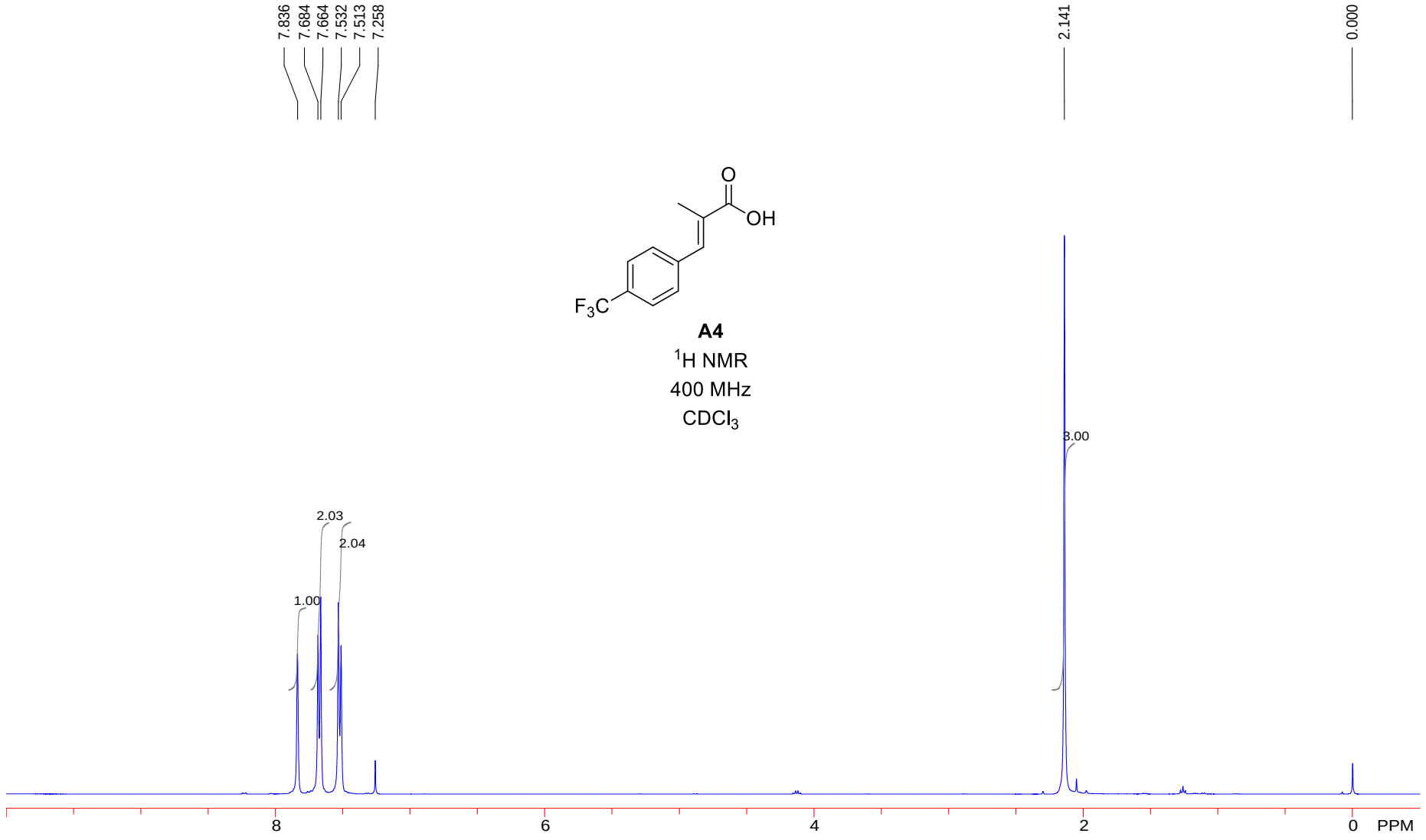
CDCl3
150
100
50
0
PPM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CDCl3
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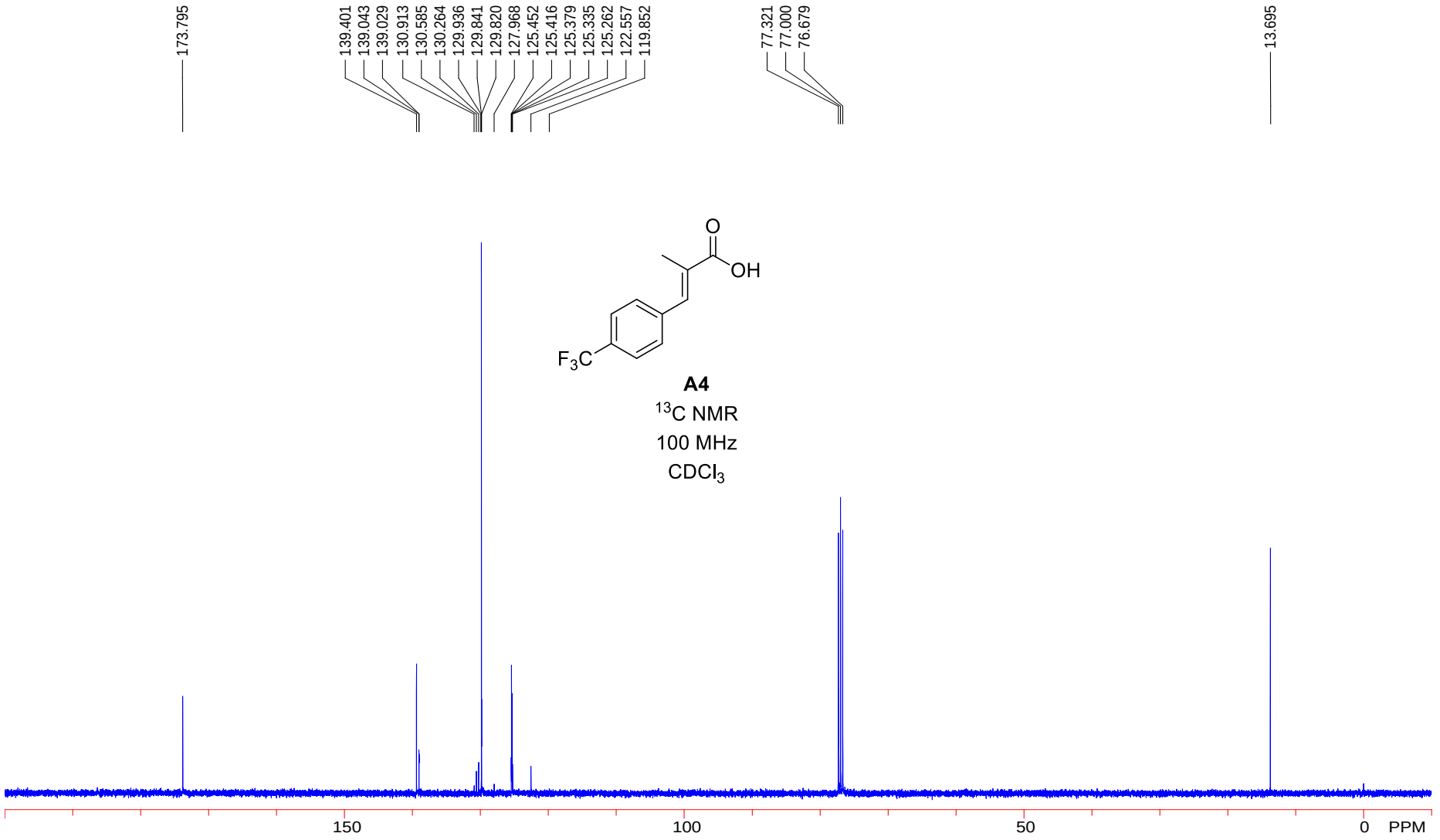
2.04
1.00
8
6
4
2
0
PPM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129.841
129.820
127.968
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125.416
125.379
125.335
125.262
122.557
119.852
77.321
77.000
76.679
13.695
O
OH
F3C
A4
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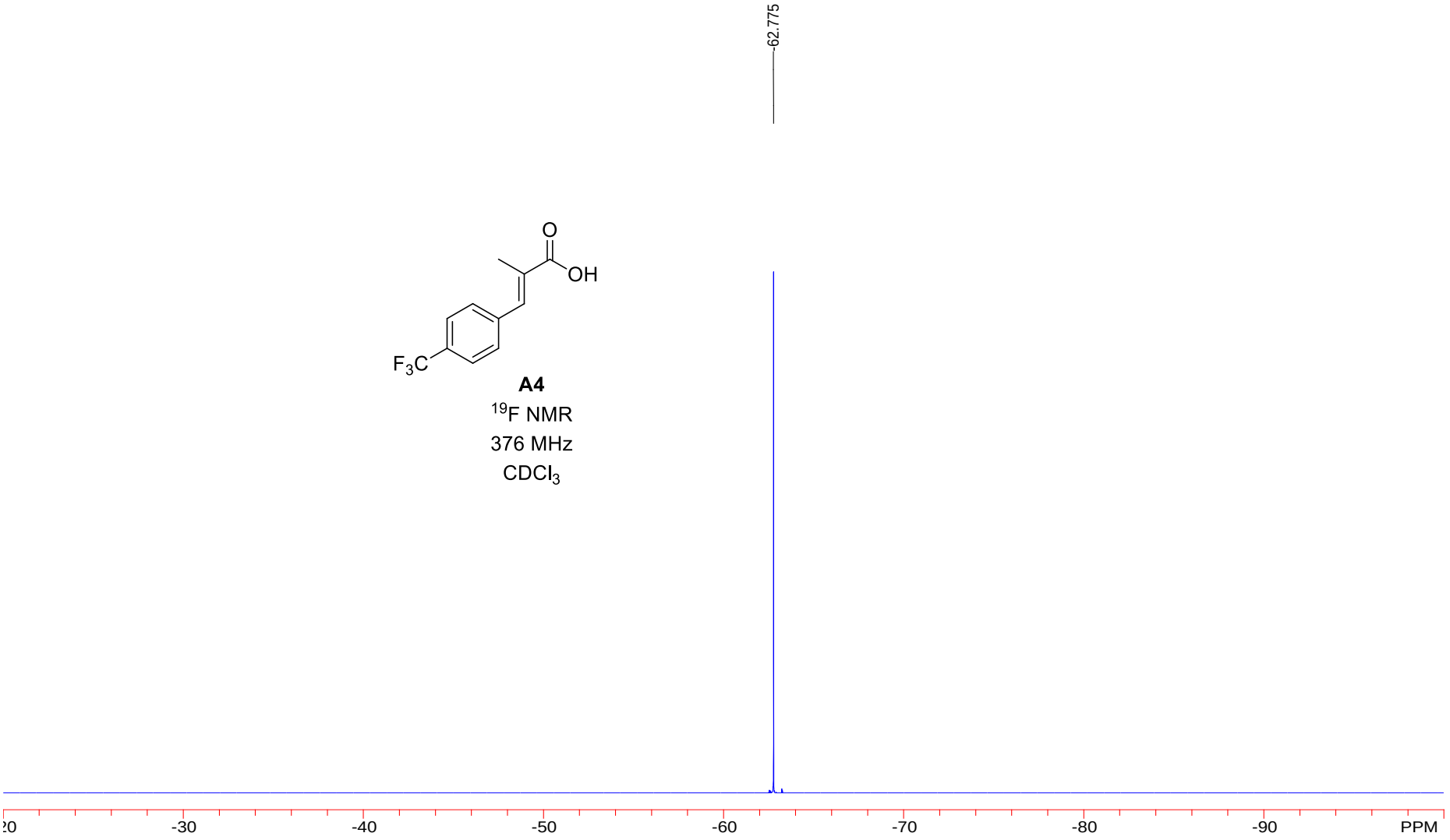
100 MHz
CDCl3
150
100
50
0
PPM

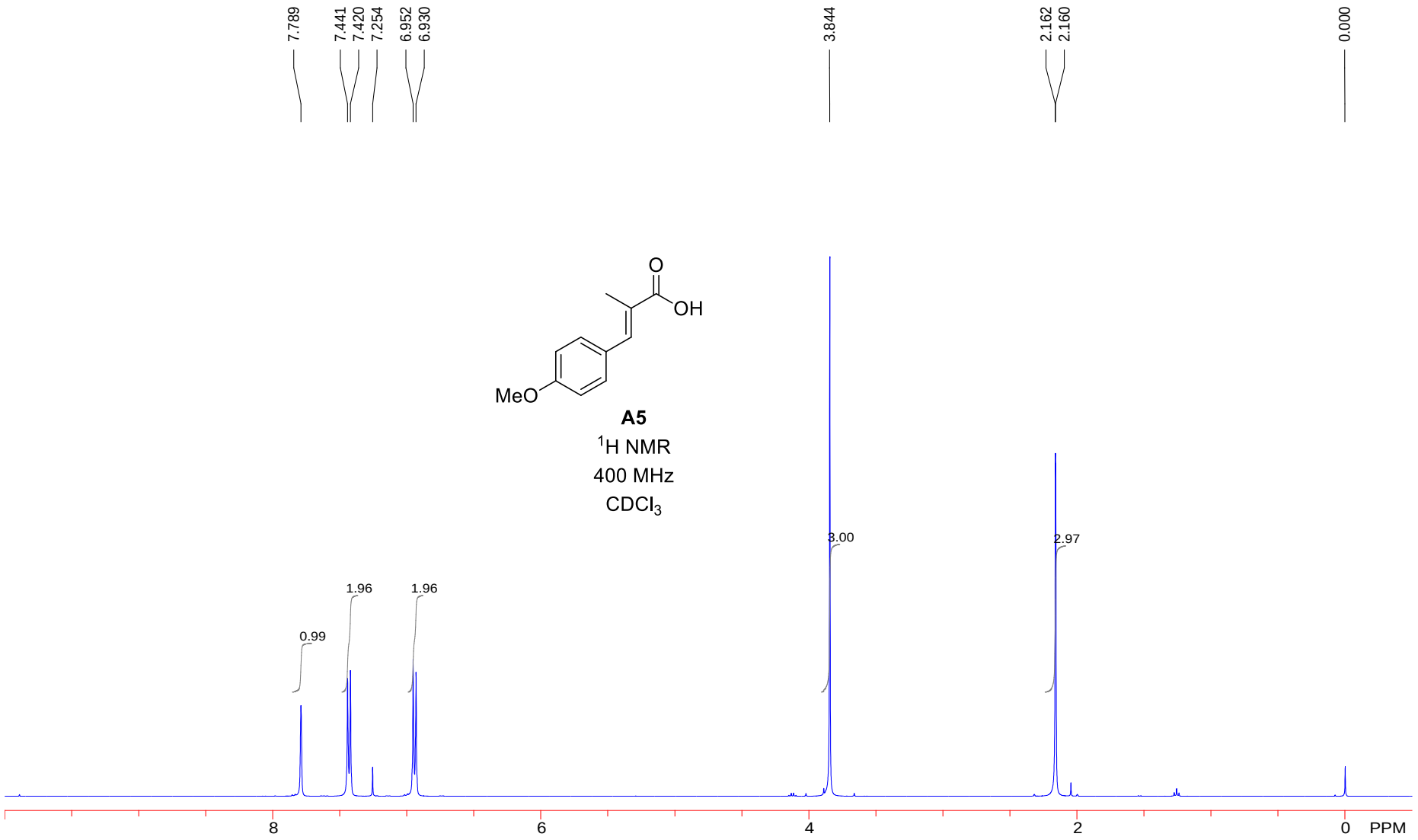
A4

^{19}F NMR

376 MHz

$CDCl_3$

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0.000
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CDCl3
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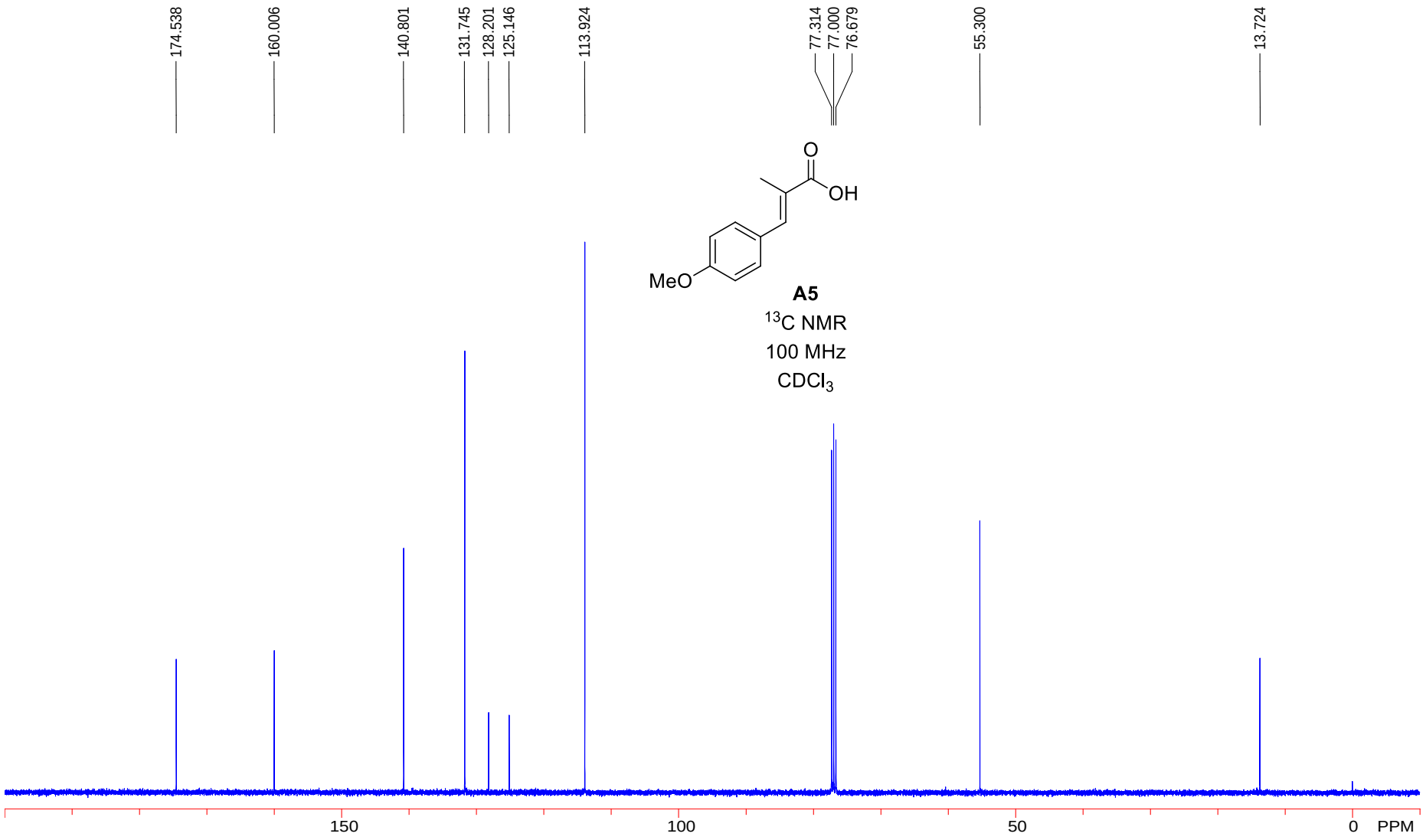
3.00
2.97
8
6
4
2
0
PPM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O
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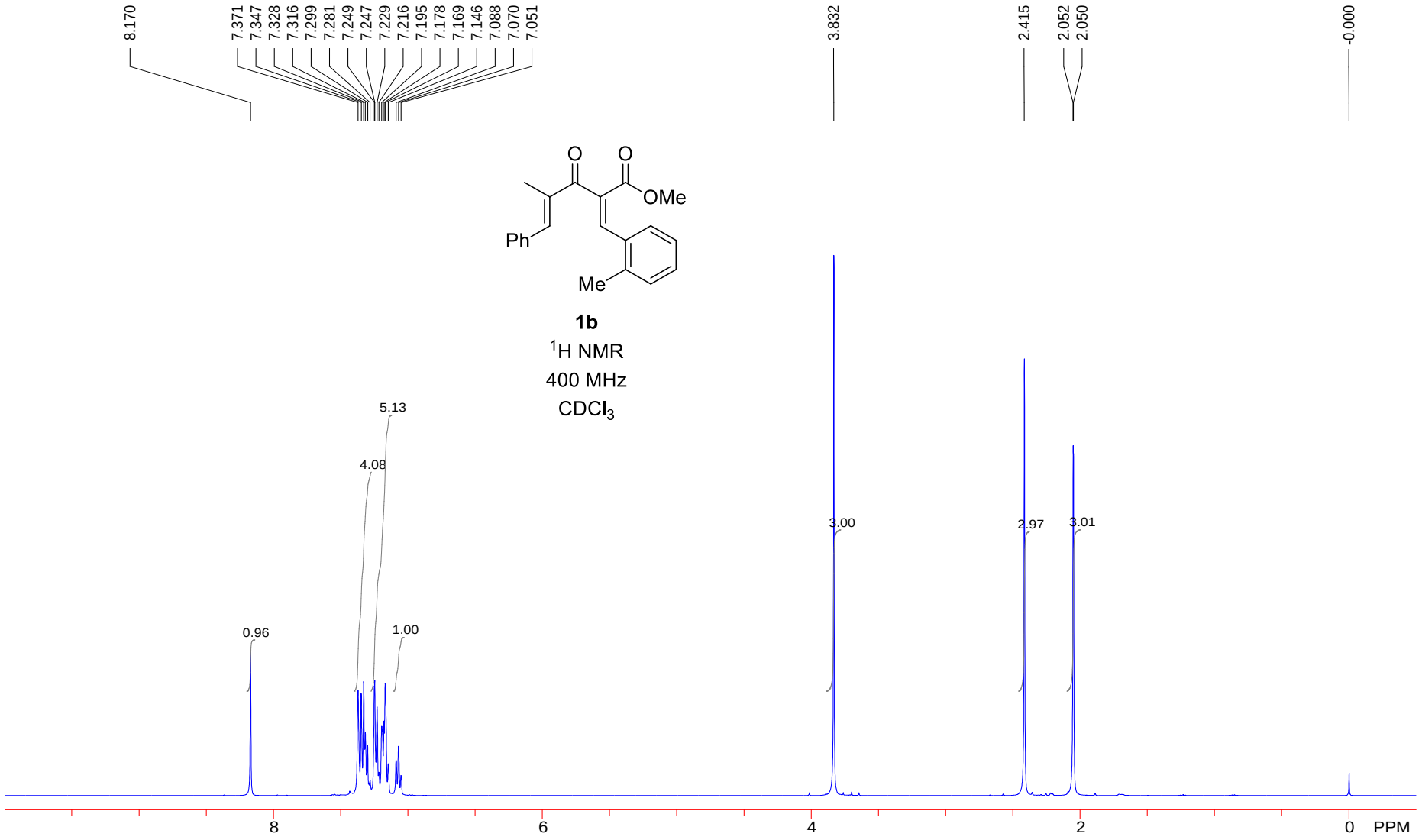
PPM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7.249
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7.178
7.169
7.146
7.088
7.070
7.051
3.832
2.415
2.052
2.050
-0.000
O
O
OMe
Ph
Me
1b
1H NMR
400 MHz
CDCl3
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4.08
3.00
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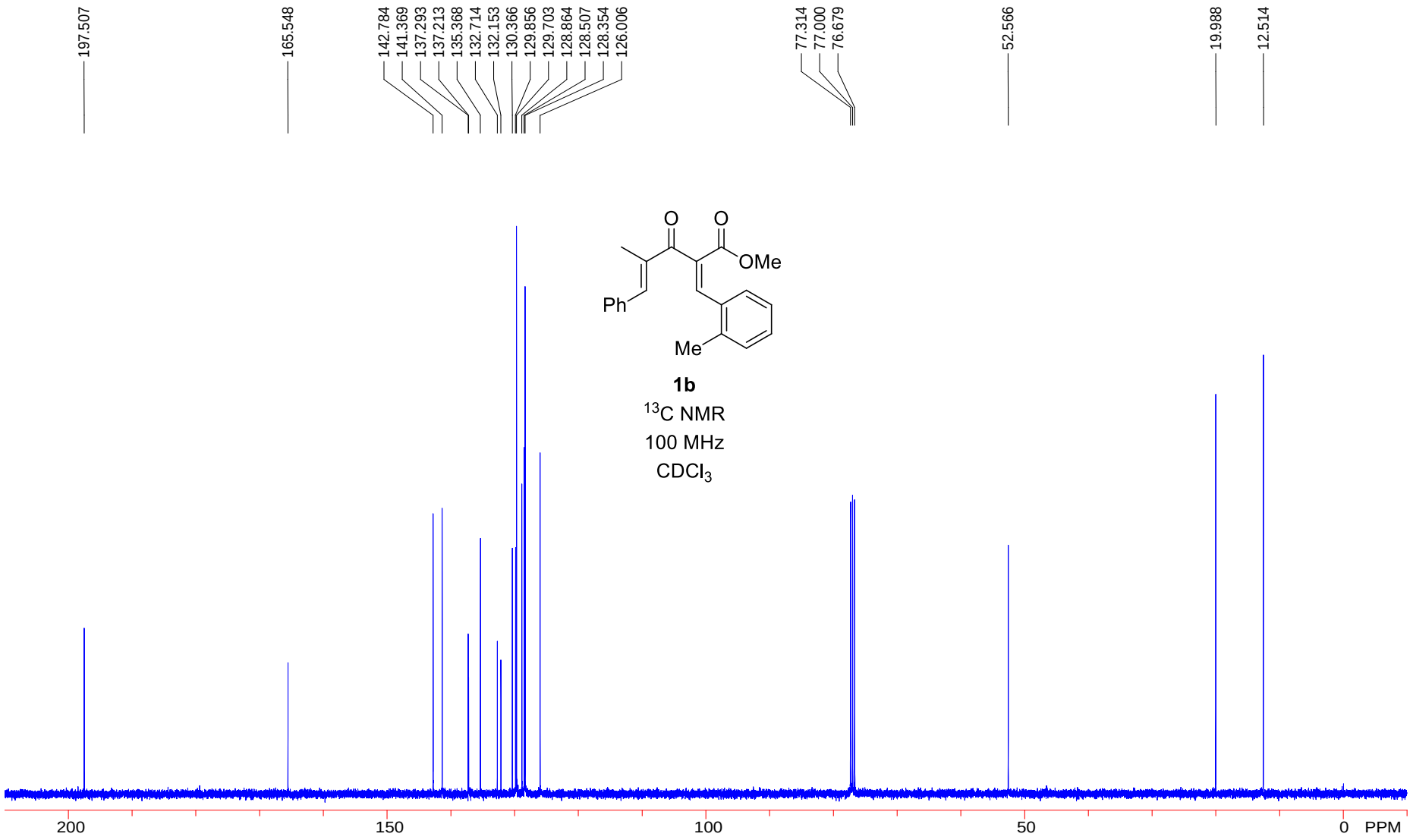
0.96
1.00
8
6
4
2
0
PPM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128.864
128.507
128.354
126.006
77.314
77.000
76.679
52.566
19.988
12.514
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O
OMe
Ph
Me
1b
13C NMR
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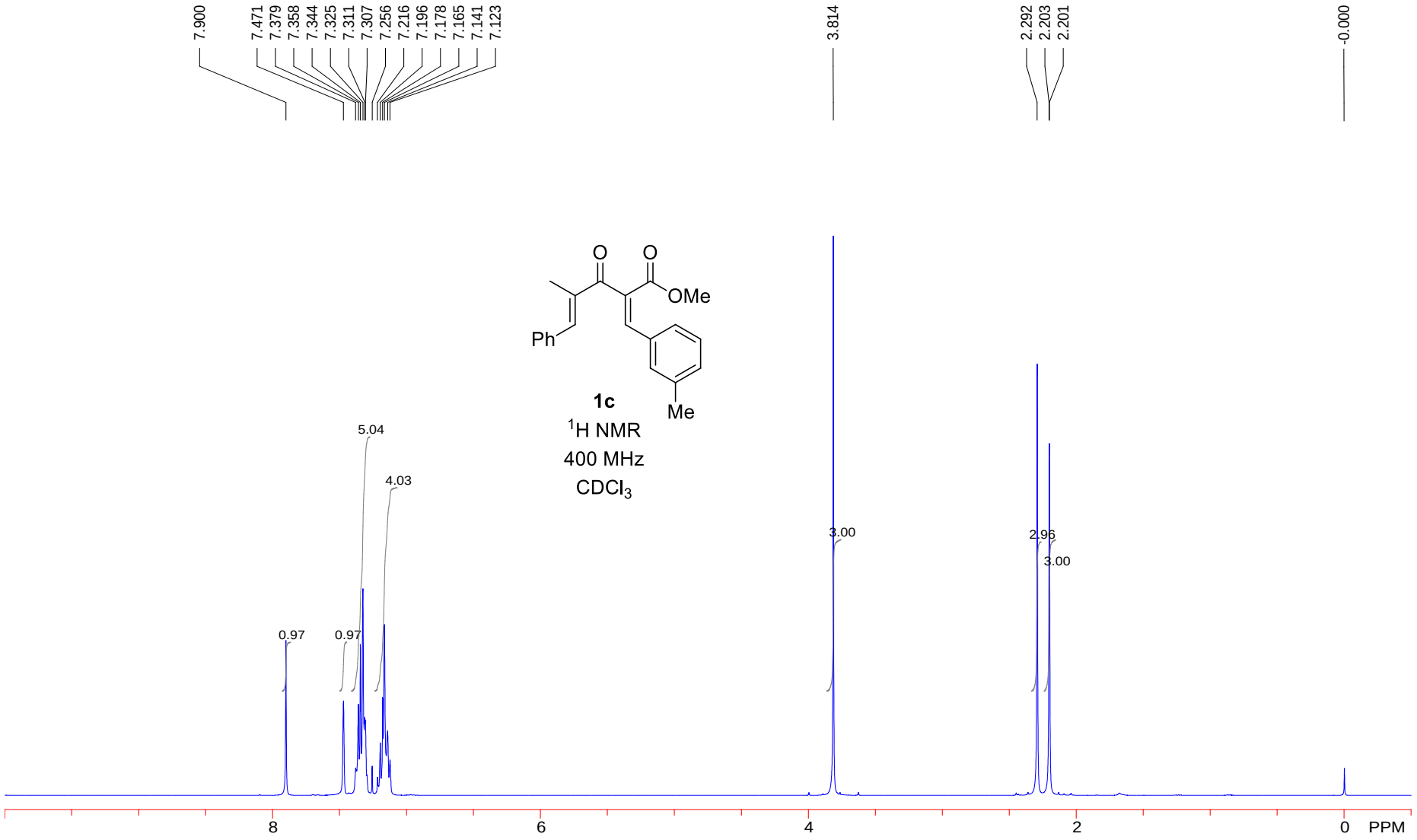
CDCl3
200
150
100
50
0
PPM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7.165
7.141
7.123
3.814
2.292
2.203
2.201
-0.000
O
O
OMe
Ph
Me
1c
1H NMR
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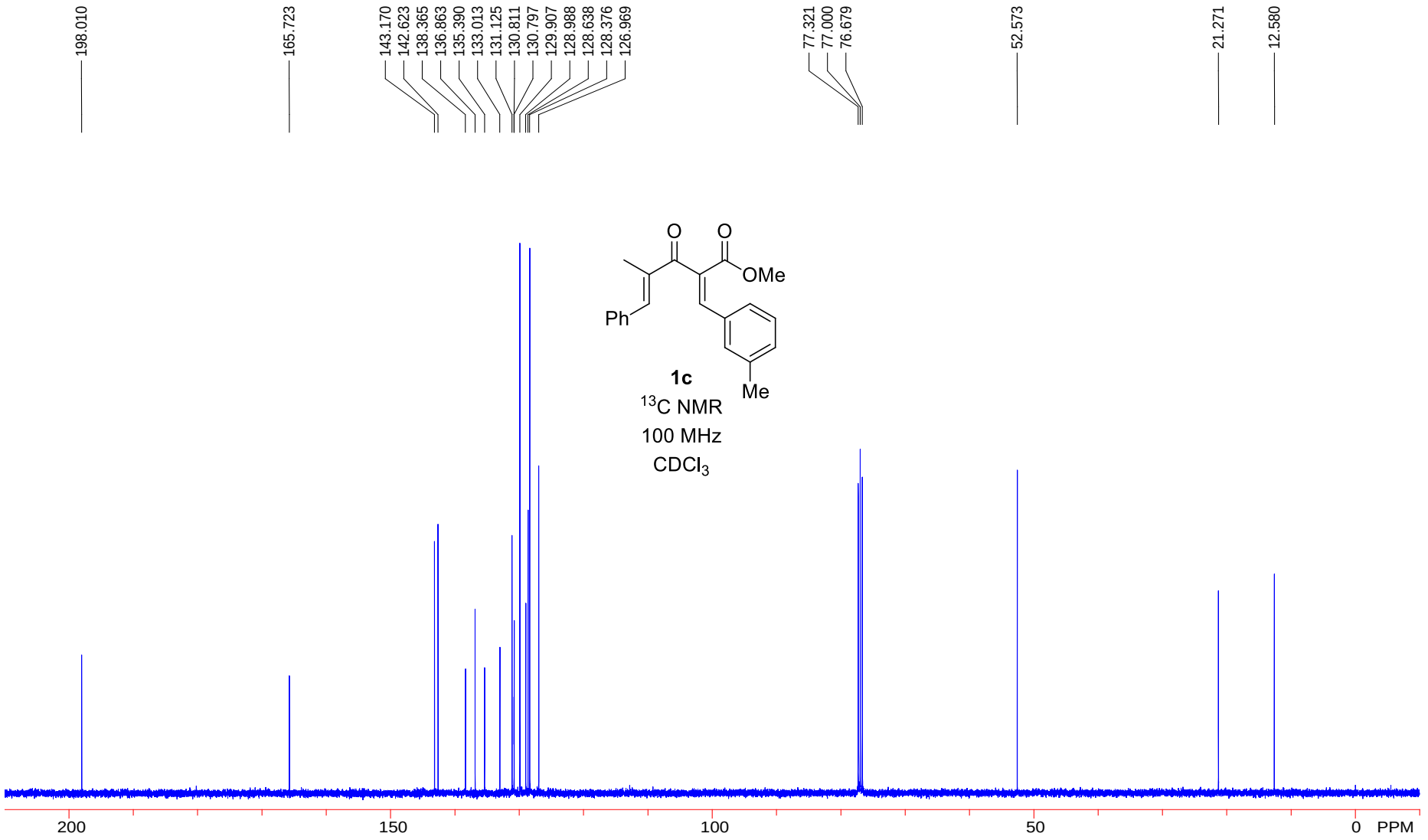
3.00
8
6
4
2
0
PPM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128.638
128.376
126.969
77.321
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76.679
52.573
21.271
12.580
O
O
OMe
Ph
Me
1c
13C NMR
100 MHz
CDCl3
200
150
100
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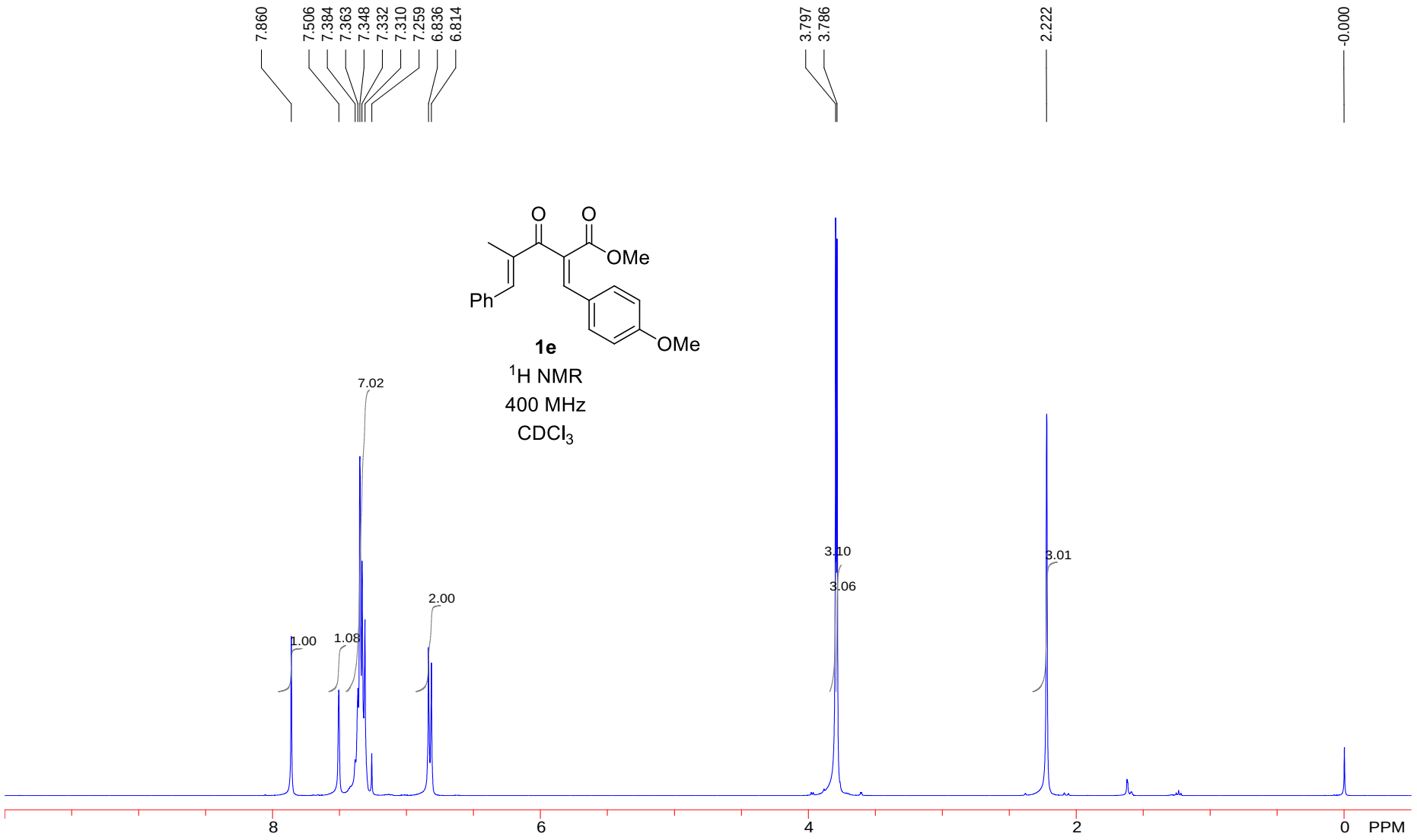
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6.814
3.797
3.786
2.222
-0.000
O
O
OMe
Ph
OMe
1e
1H NMR
400 MHz
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1.08
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3.06
3.01
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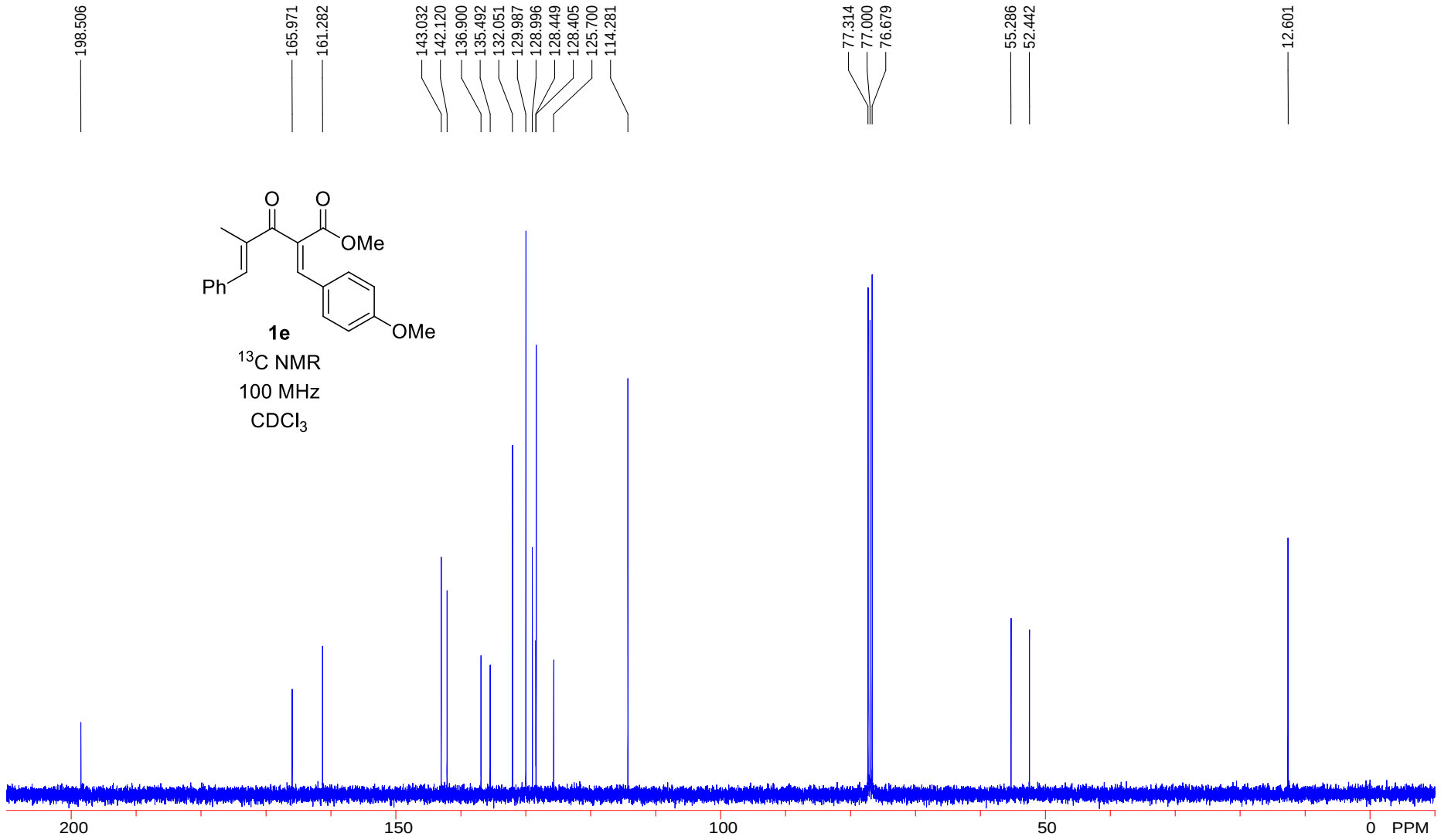
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135.492
132.051
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128.996
128.449
128.405
125.700
114.281
77.314
77.000
76.679
55.286
52.442
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Ph
OMe
1e
13C NMR
100 MHz
CDCl3
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150
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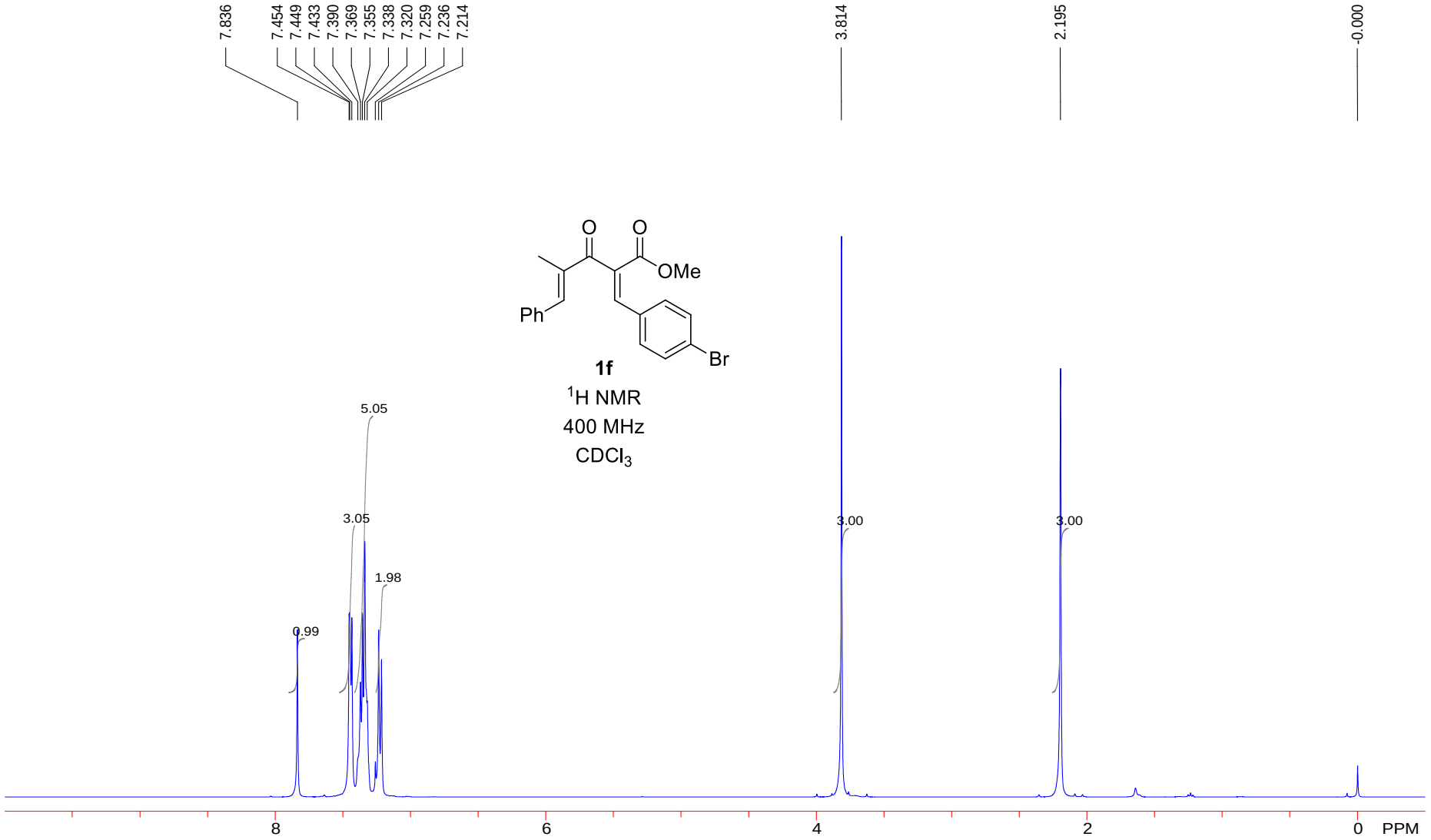
PPM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7.338
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7.259
7.236
7.214
3.814
2.195
-0.000
O
O
OMe
Ph
Br
1f
1H NMR
400 MHz
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5.05
3.05
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3.00
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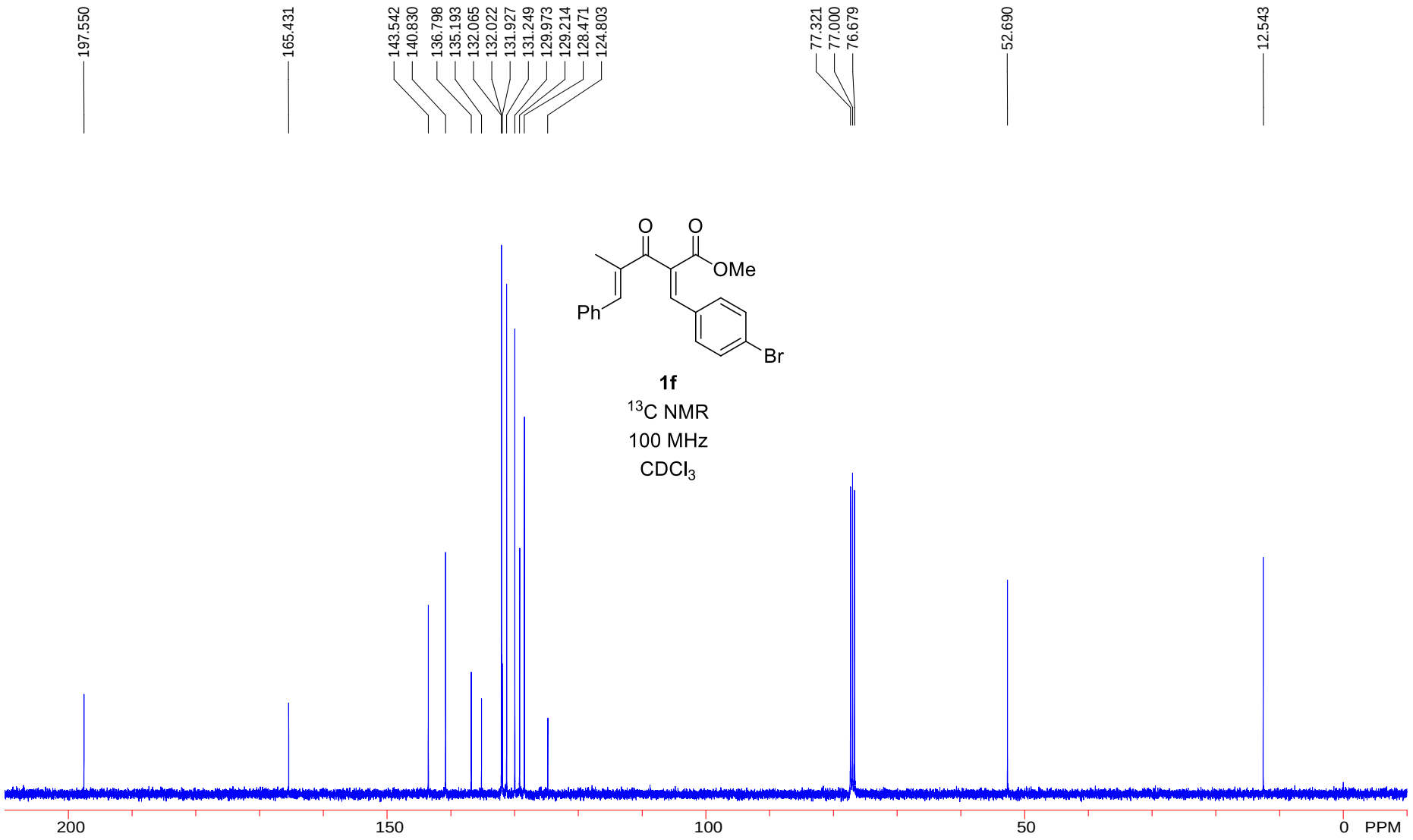
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129.214
128.471
124.803
77.321
77.000
76.679
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OMe
Ph
Br
1f
13C NMR
100 MHz
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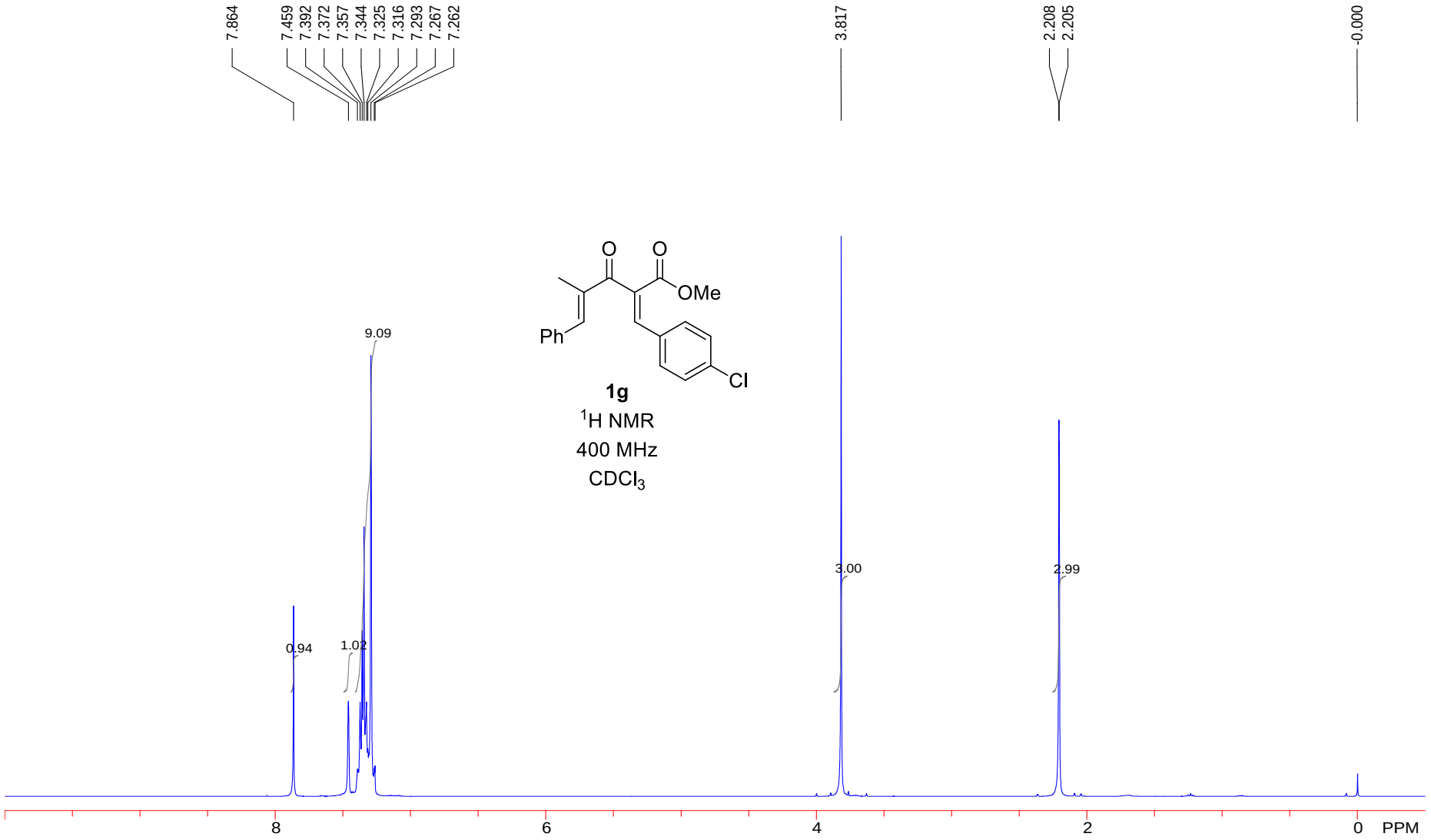
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7.293
7.267
7.262
3.817
2.208
2.205
-0.000
O
O
OMe
Ph
Cl
1g
1H NMR
400 MHz
CDCl3
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1.02
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6
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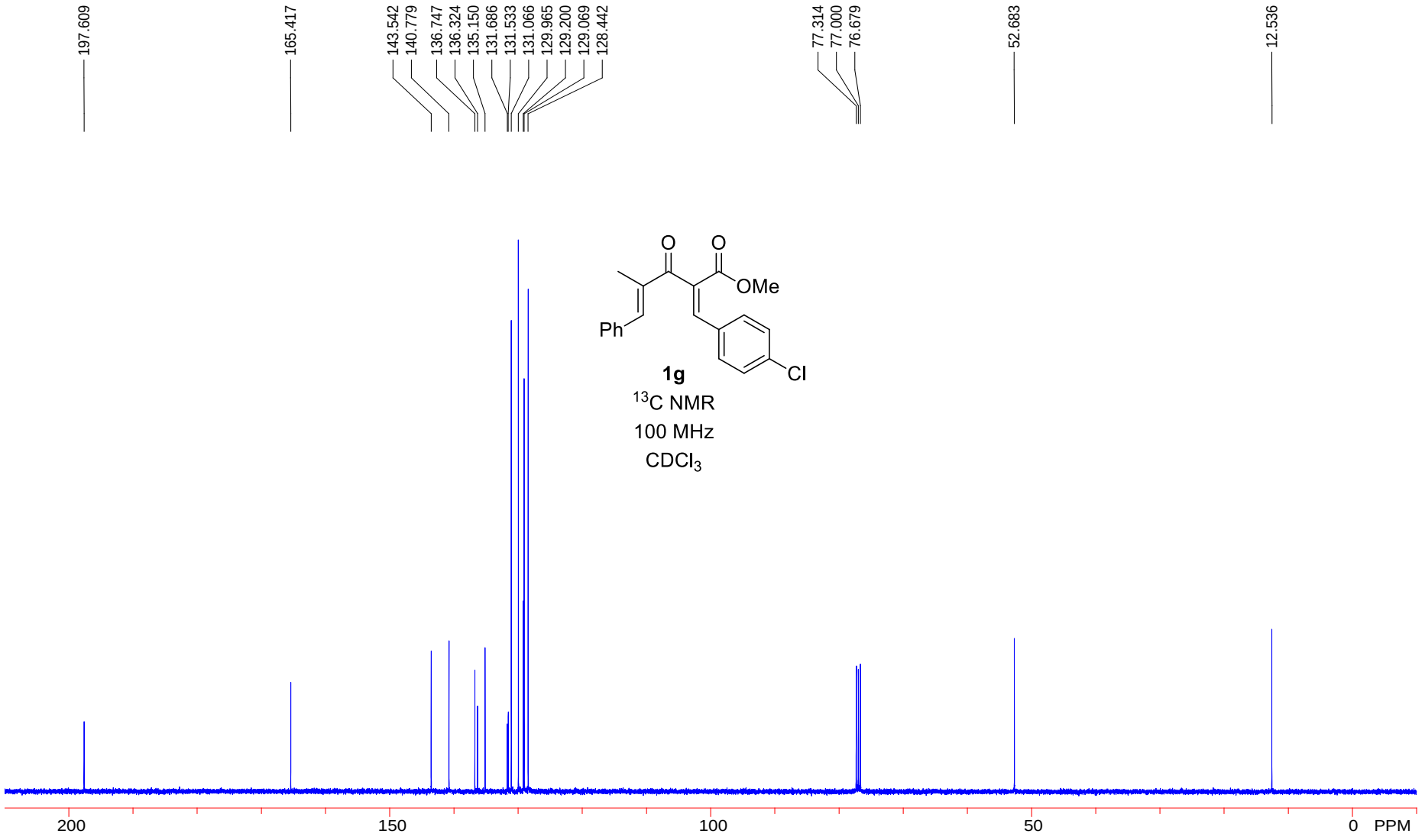
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128.442
77.314
77.000
76.679
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OMe
Ph
Cl
1g
13C NMR
100 MHz
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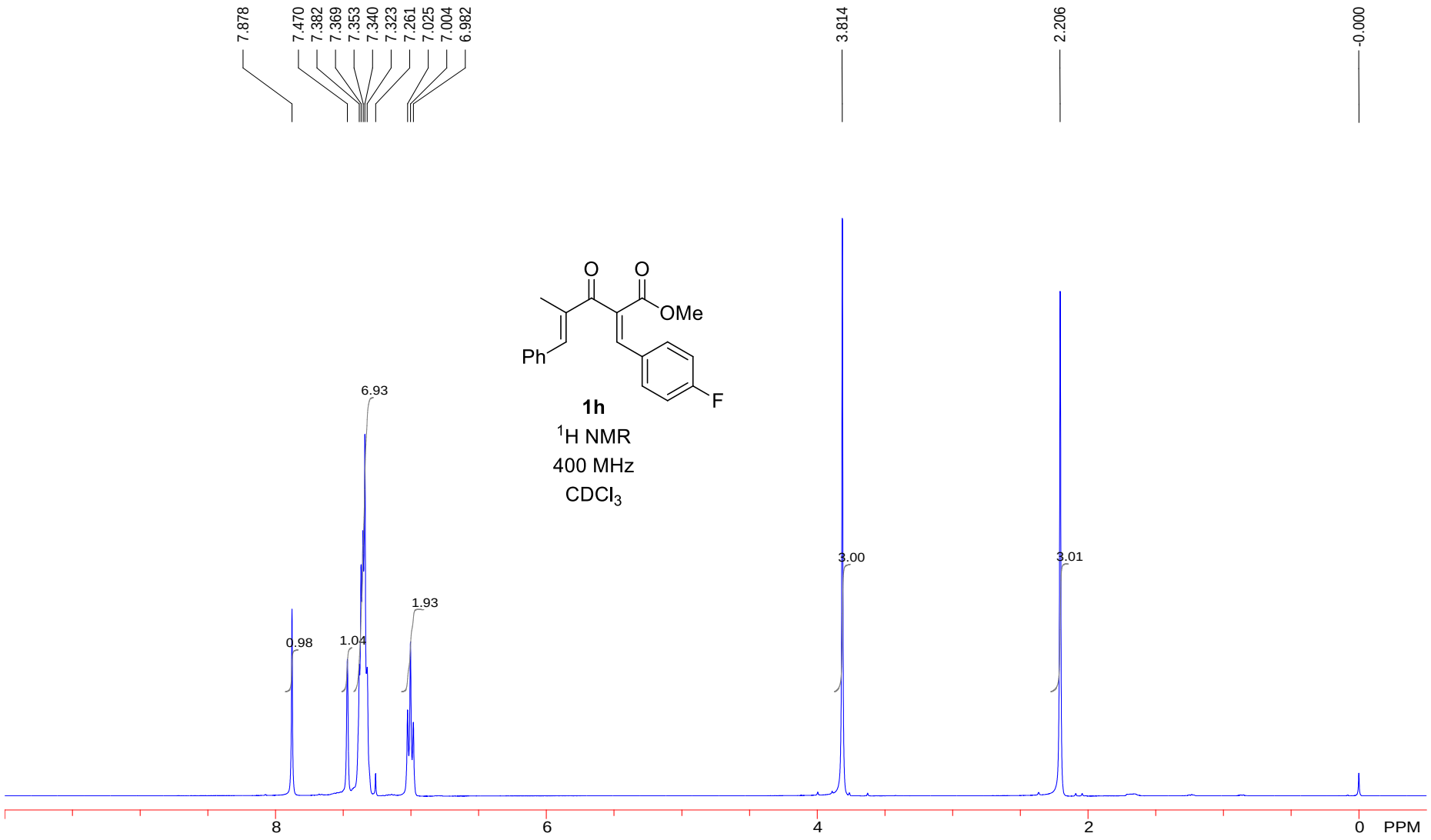
200
150
100
50
0
PPM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7.369
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7.340
7.323
7.261
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7.004
6.982
3.814
2.206
-0.000
O
O
OMe
Ph
F
1h
1H NMR
400 MHz
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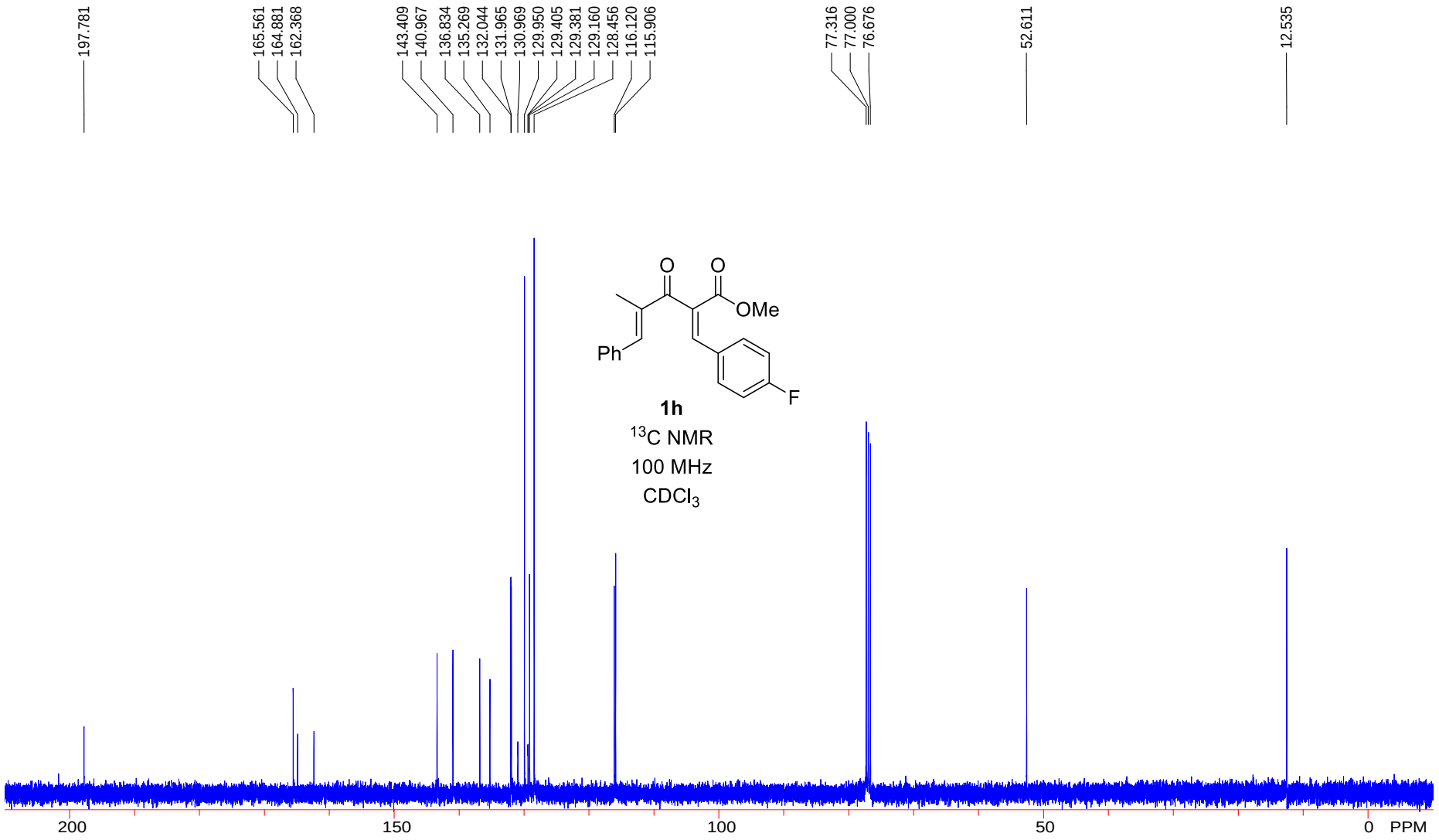
6.93
0.98
1.04
1.93
3.00
3.01
8
6
4
2
0
PPM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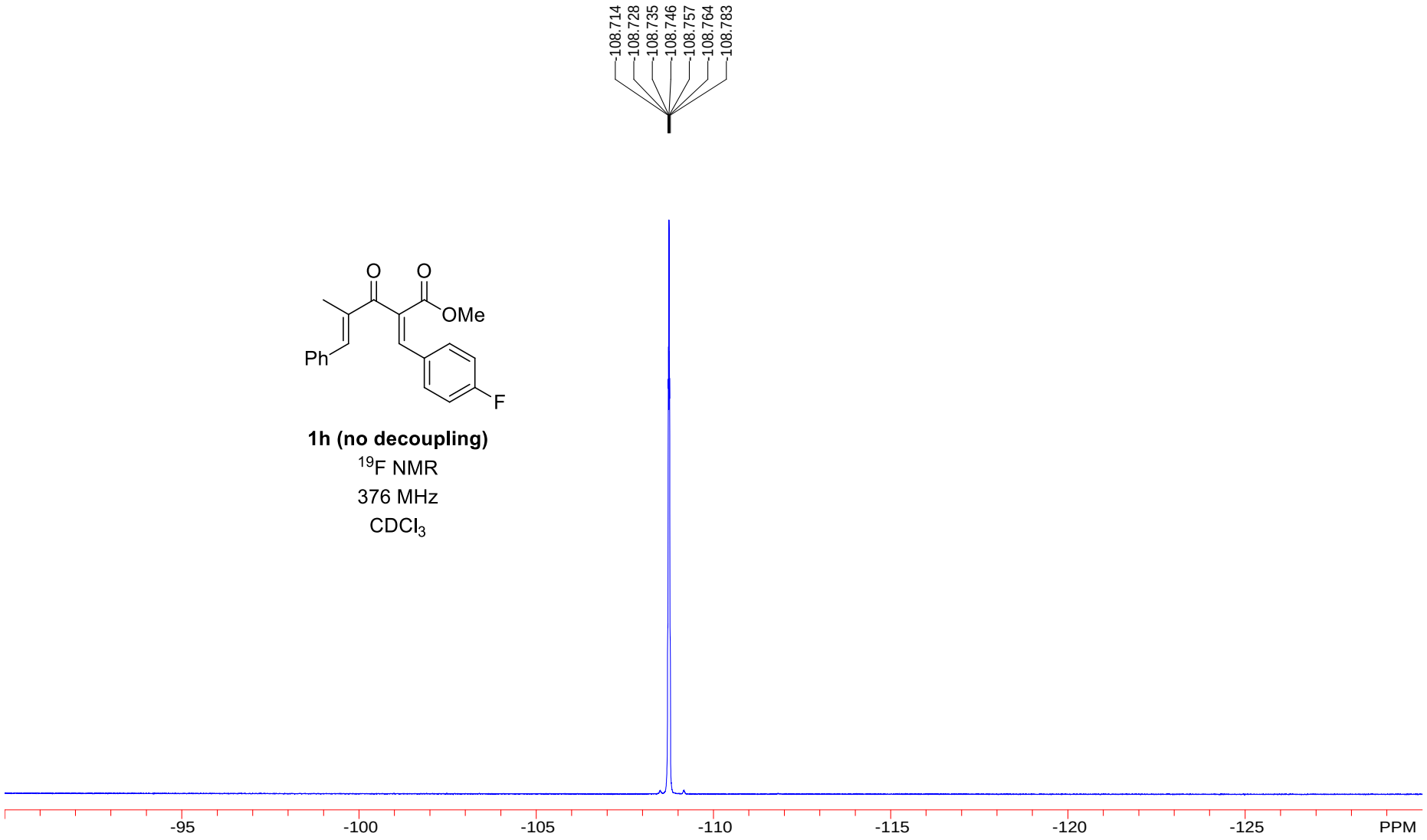
140.967
136.834
135.269
132.044
131.965
130.969
129.950
129.405
129.381
129.160
128.456
116.120
115.906
77.316
77.000
76.676
52.611
12.535
O
O
OMe
Ph
F
1h
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

1h

^{19}F NMR

376 MHz

$CDCl_3$

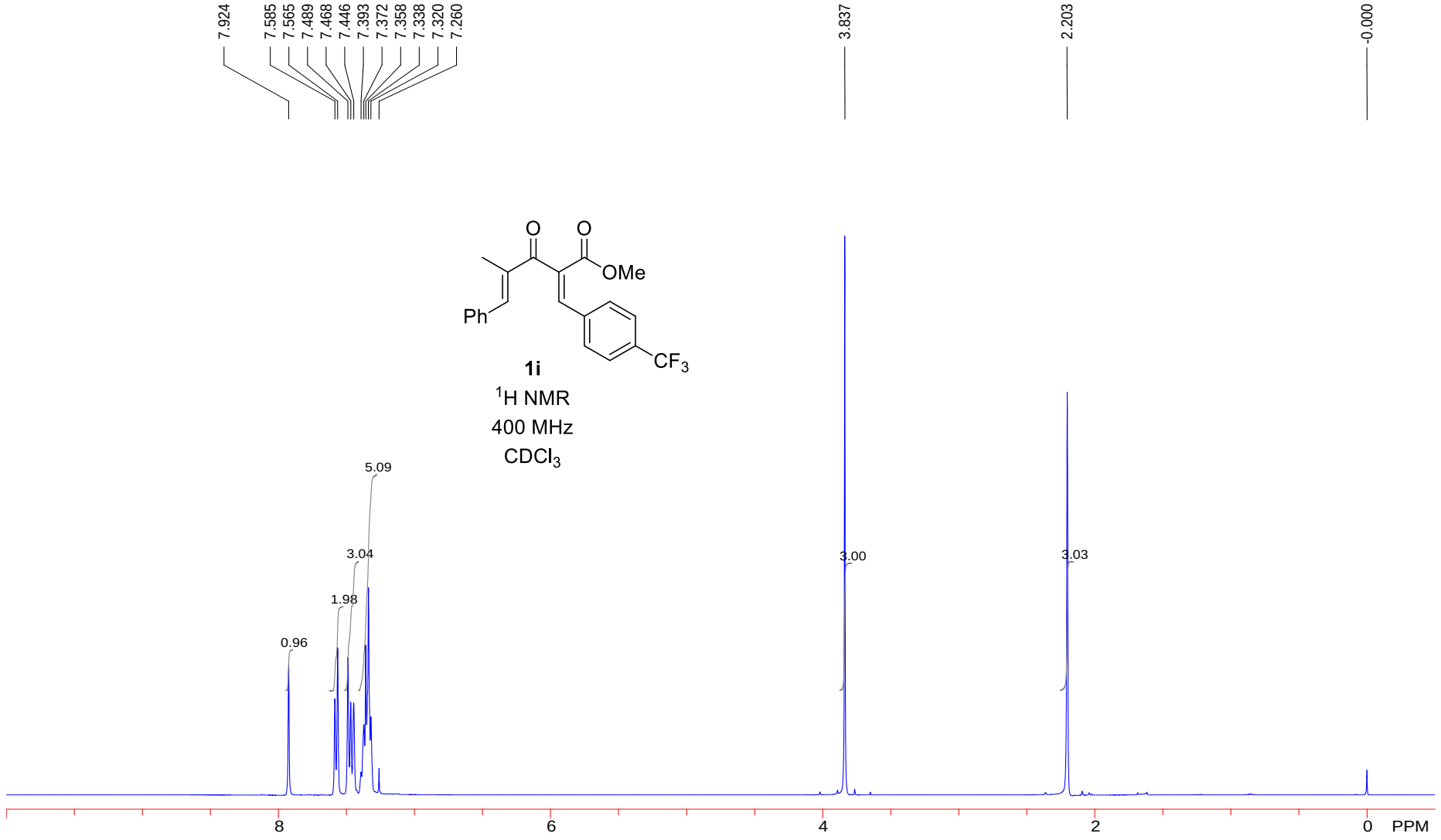


1h (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$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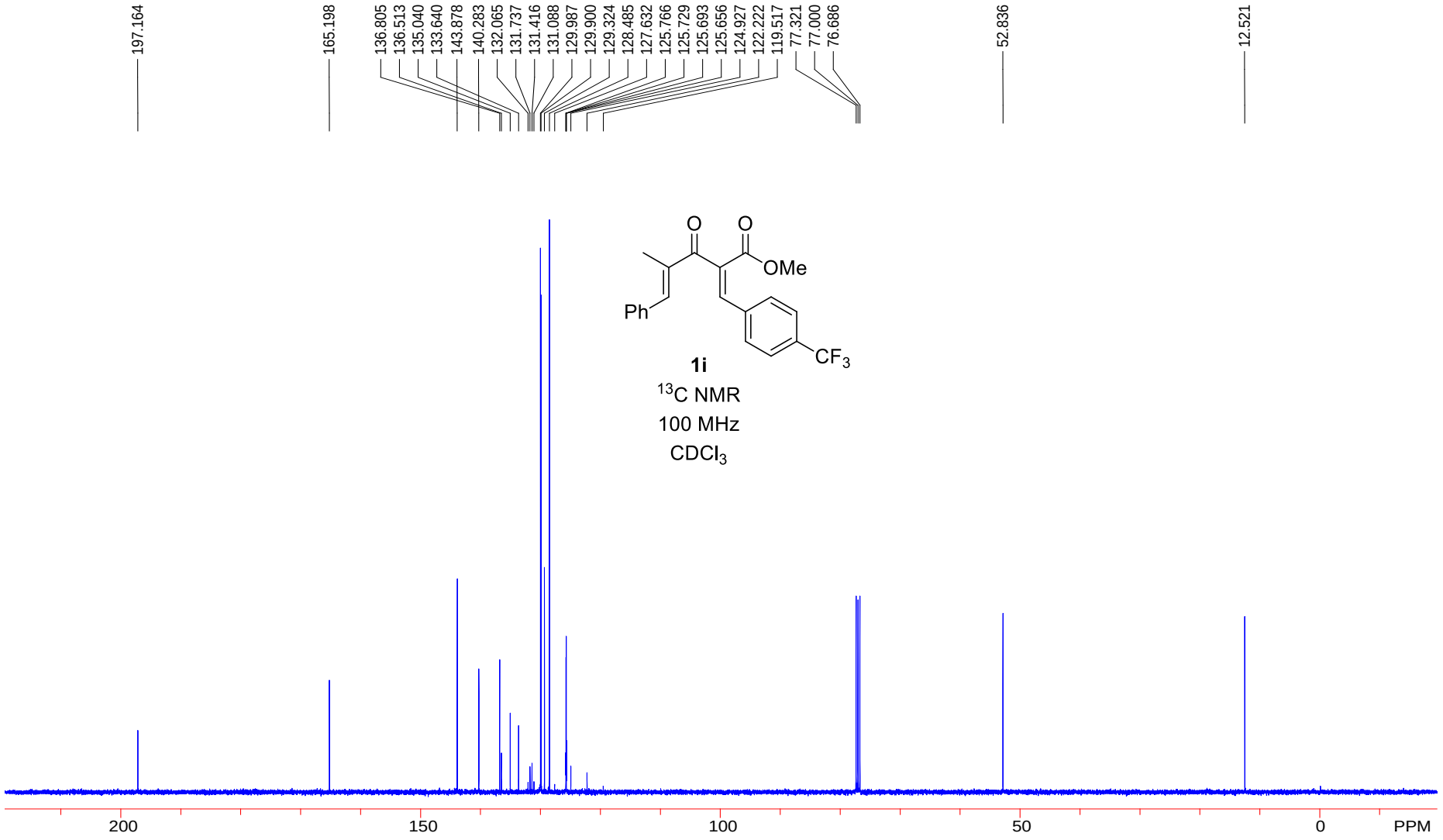
7.565
7.489
7.468
7.446
7.393
7.372
7.358
7.338
7.320
7.260
3.837
2.203
-0.000
O
O
OMe
Ph
CF3
1i
1H NMR
400 MHz
CDCl3
5.09
3.04
1.98
0.96
3.00
3.03
8
6
4
2
0
PPM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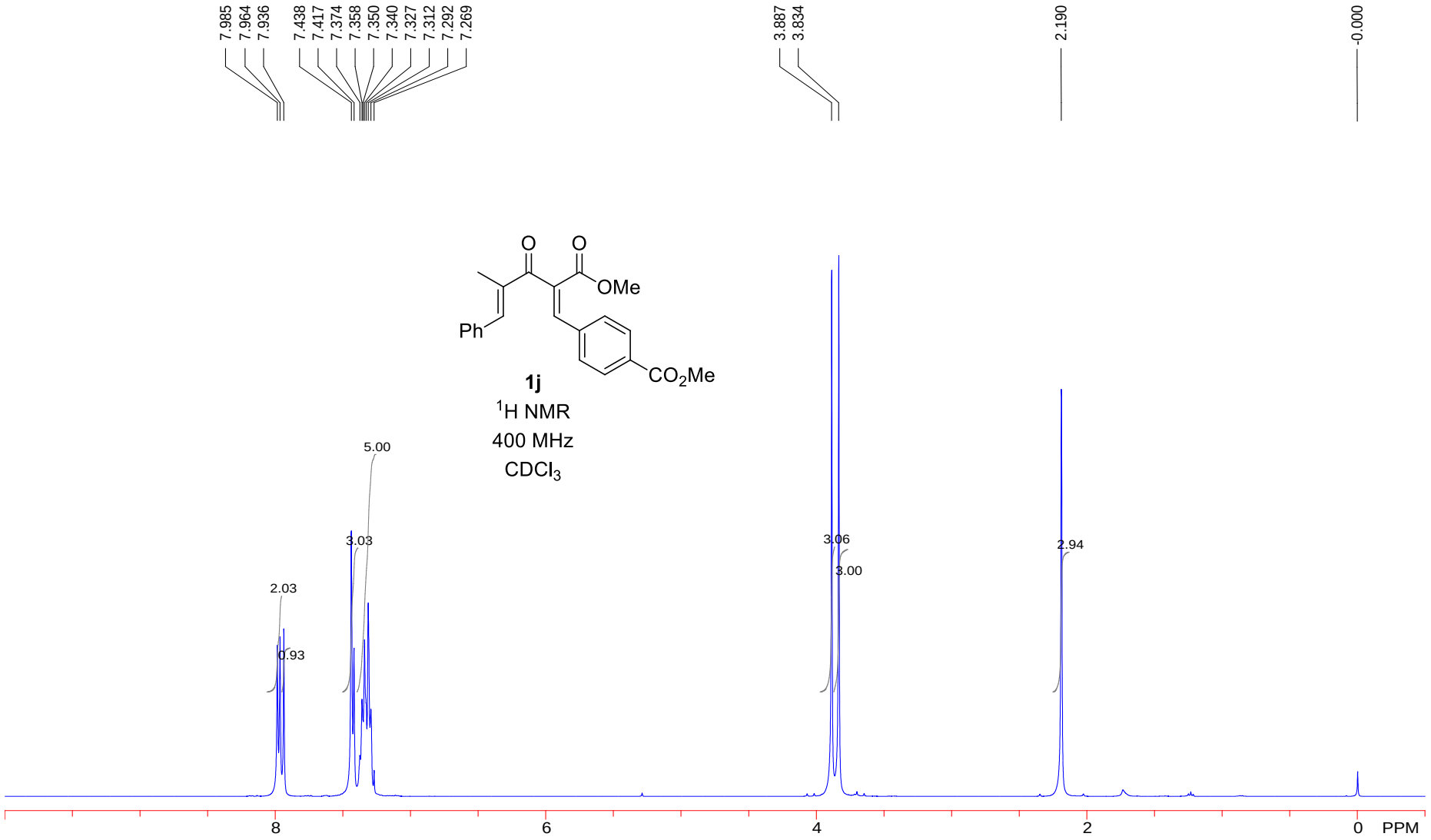
165.198
136.805
136.513
135.040
133.640
143.878
140.283
132.065
131.737
131.416
131.088
129.987
129.900
129.324
128.485
127.632
125.766
125.729
125.693
125.656
124.927
122.222
119.517
77.321
77.000
76.686
52.836
12.521
O
O
OMe
Ph
CF3
1i
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

-62.981
O
O
OMe
Ph
CF3
1i
19F NMR
376 MHz
CDCl3
-30
-40
-50
-60
-70
-80
-90
PPM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7.936
7.438
7.417
7.374
7.358
7.350
7.340
7.327
7.312
7.292
7.269
3.887
3.834
2.190
-0.000
O
O
OMe
Ph
CO2Me
1j
1H NMR
400 MHz
CDCl3
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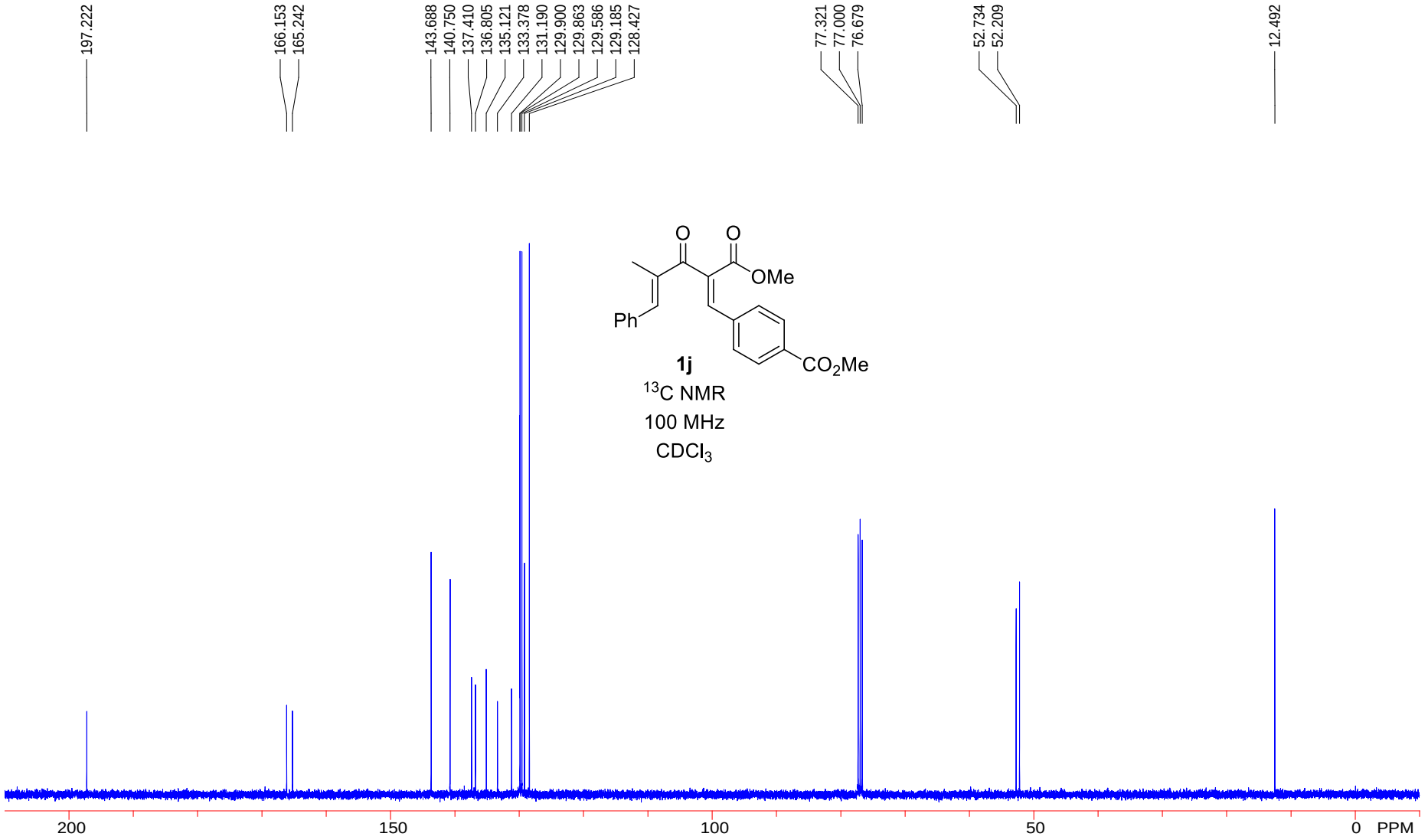
3.03
2.03
0.93
3.06
3.00
2.94
8
6
4
2
0
PPM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165.242
143.688
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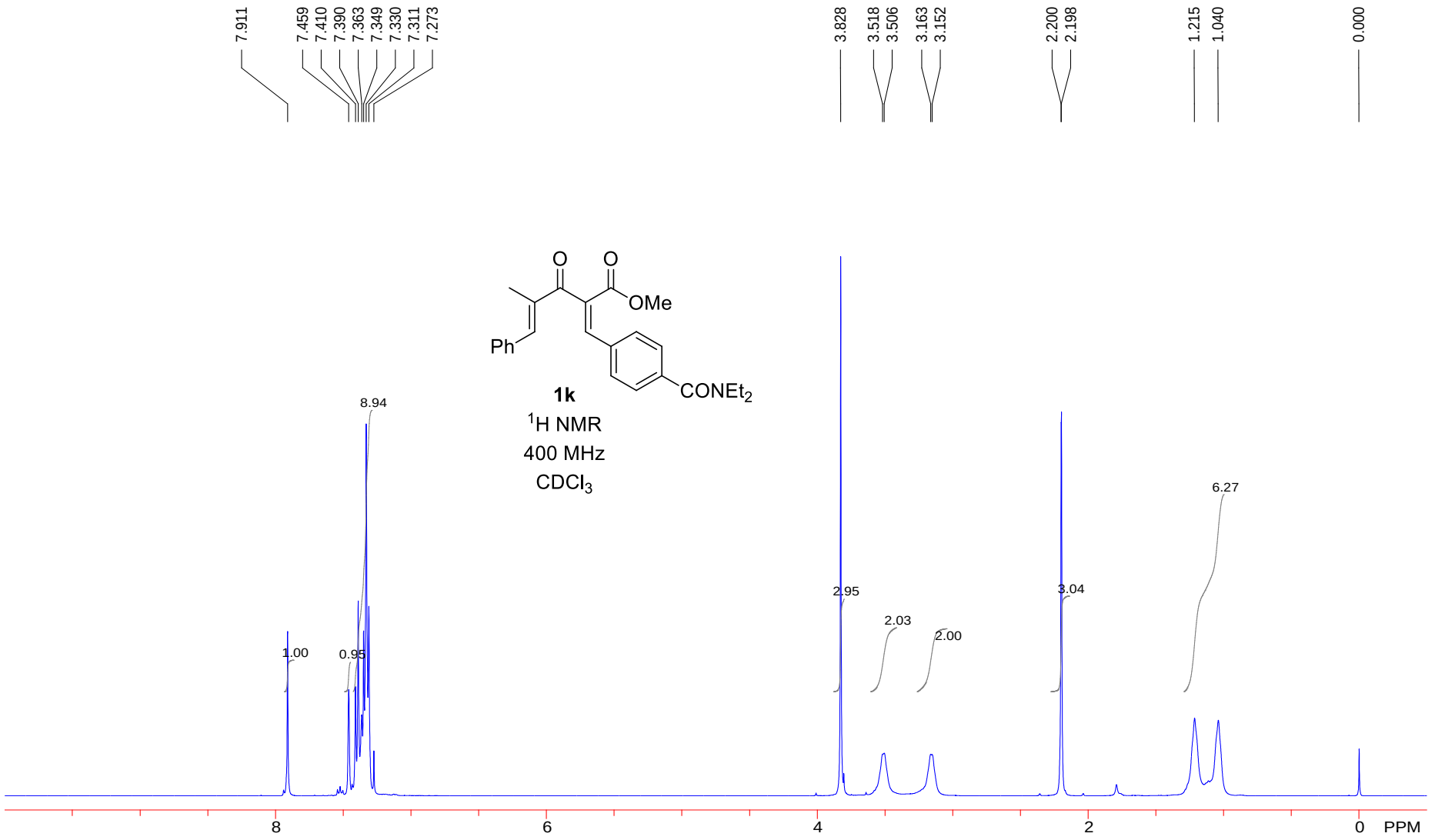
137.410
136.805
135.121
133.378
131.190
129.900
129.863
129.586
129.185
128.427
77.321
77.000
76.679
52.734
52.209
12.492
O
O
OMe
Ph
CO2Me
1j
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM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7.410
7.390
7.363
7.349
7.330
7.311
7.273
3.828
3.518
3.506
3.163
3.152
2.200
2.198
1.215
1.040
0.000
O
O
OMe
Ph
CONEt2
1k
1H NMR
400 MHz
CDCl3
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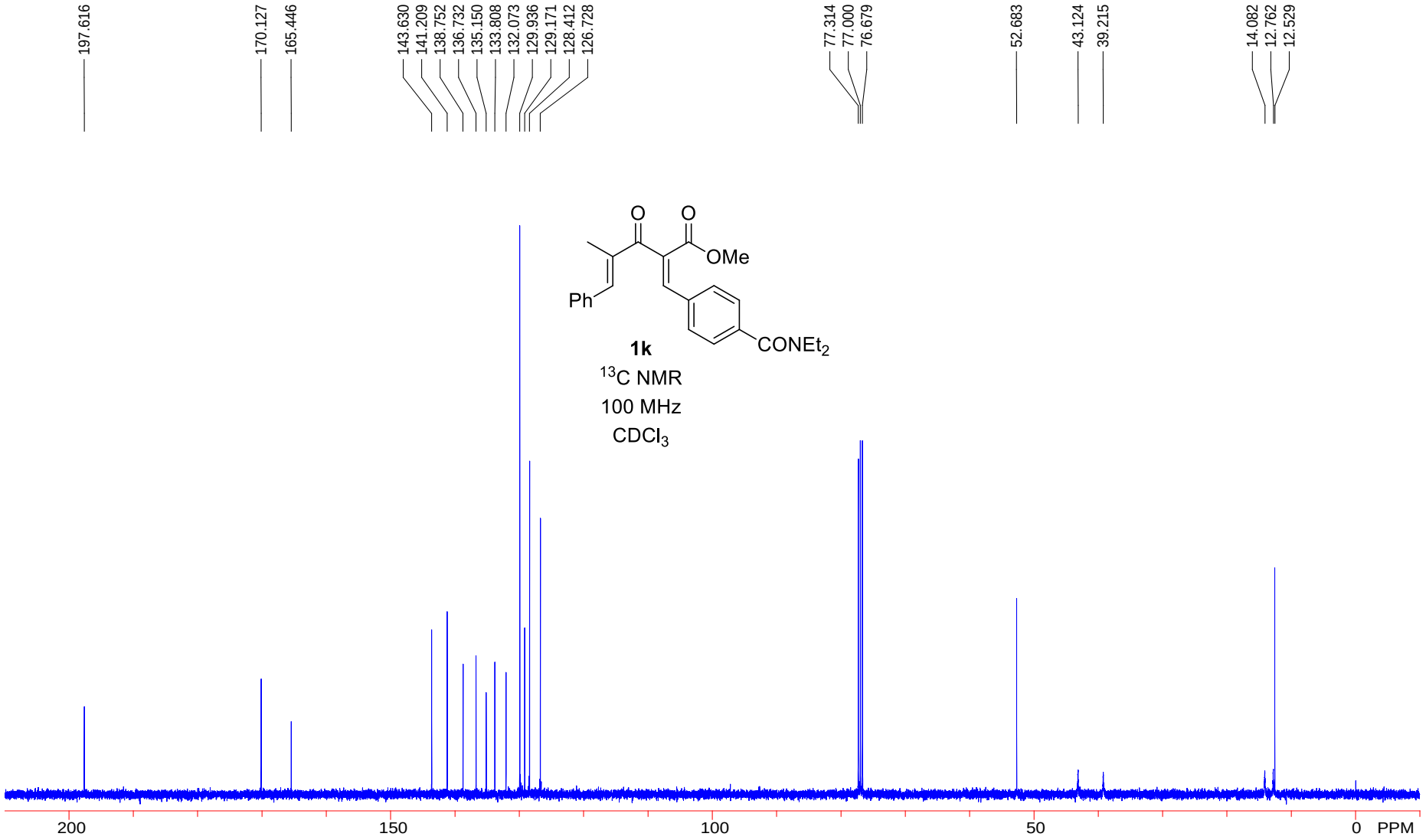
1.00
0.95
2.95
2.03
2.00
3.04
6.27
8
6
4
2
0
PPM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138.752
136.732
135.150
133.808
132.073
129.936
129.171
128.412
126.728
77.314
77.000
76.679
52.683
43.124
39.215
14.082
12.762
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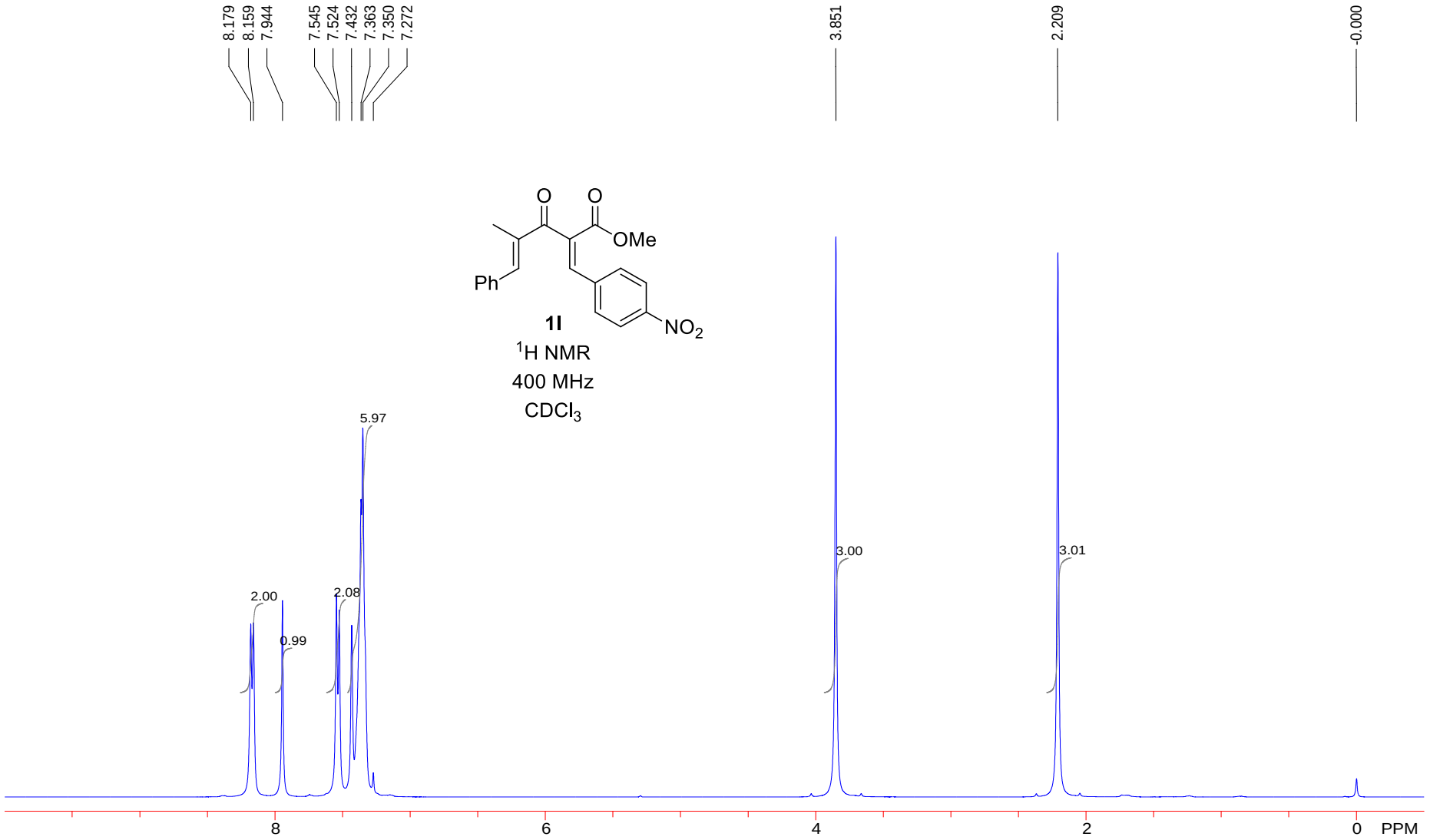
O
O
OMe
Ph
CONEt2
1k
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM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8.159
7.944
7.545
7.524
7.432
7.363
7.350
7.272
3.851
2.209
-0.000
O
O
OMe
Ph
NO2
1l
1H NMR
400 MHz
CDCl3
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2.00
0.99
2.08
3.00
3.01
8
6
4
2
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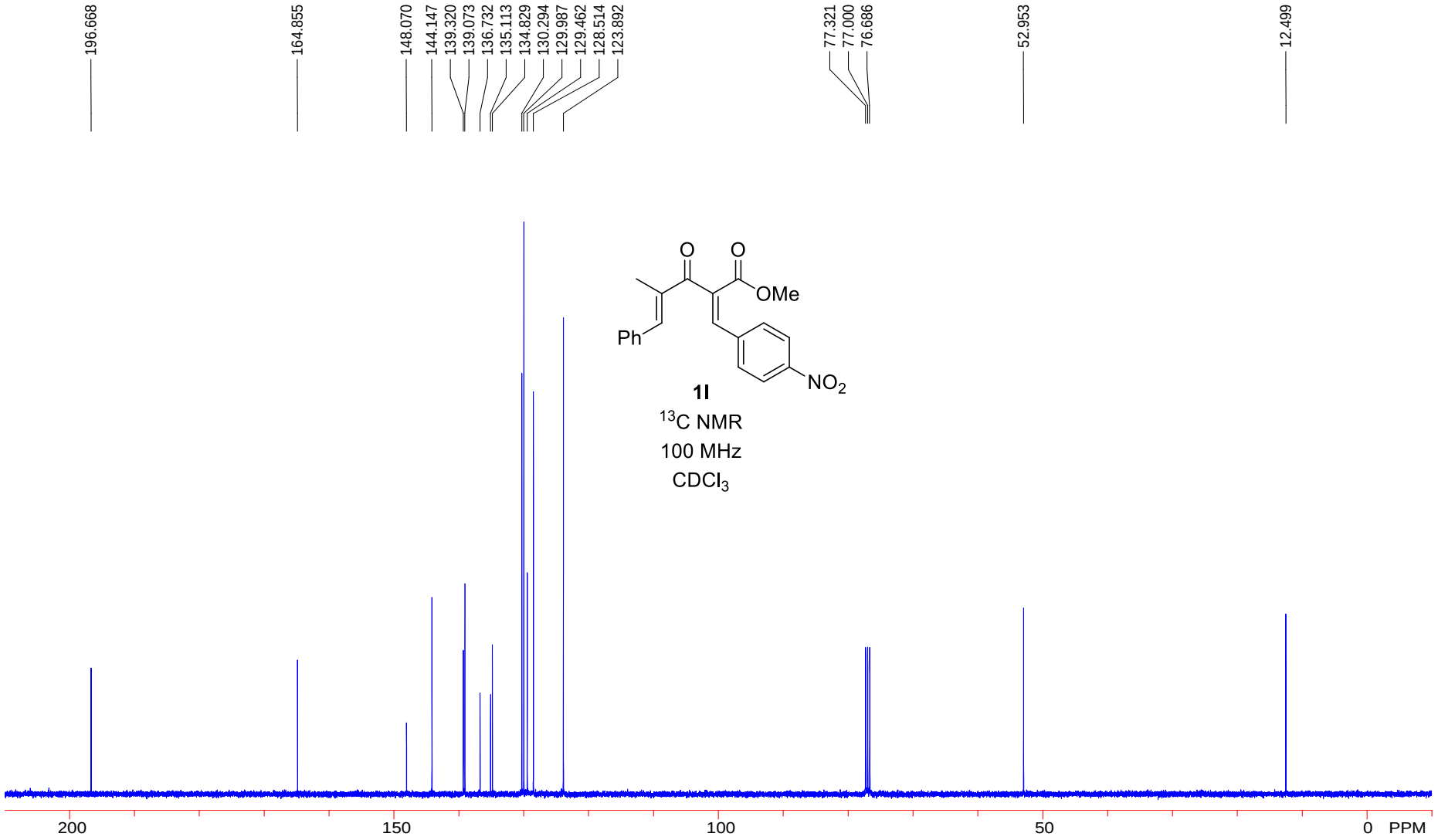
PPM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135.113
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129.987
129.462
128.514
123.892
77.321
77.000
76.686
52.953
12.499
O
O
OMe
Ph
NO2
1l
13C NMR
100 MHz
CDCl3
200
150
100
50
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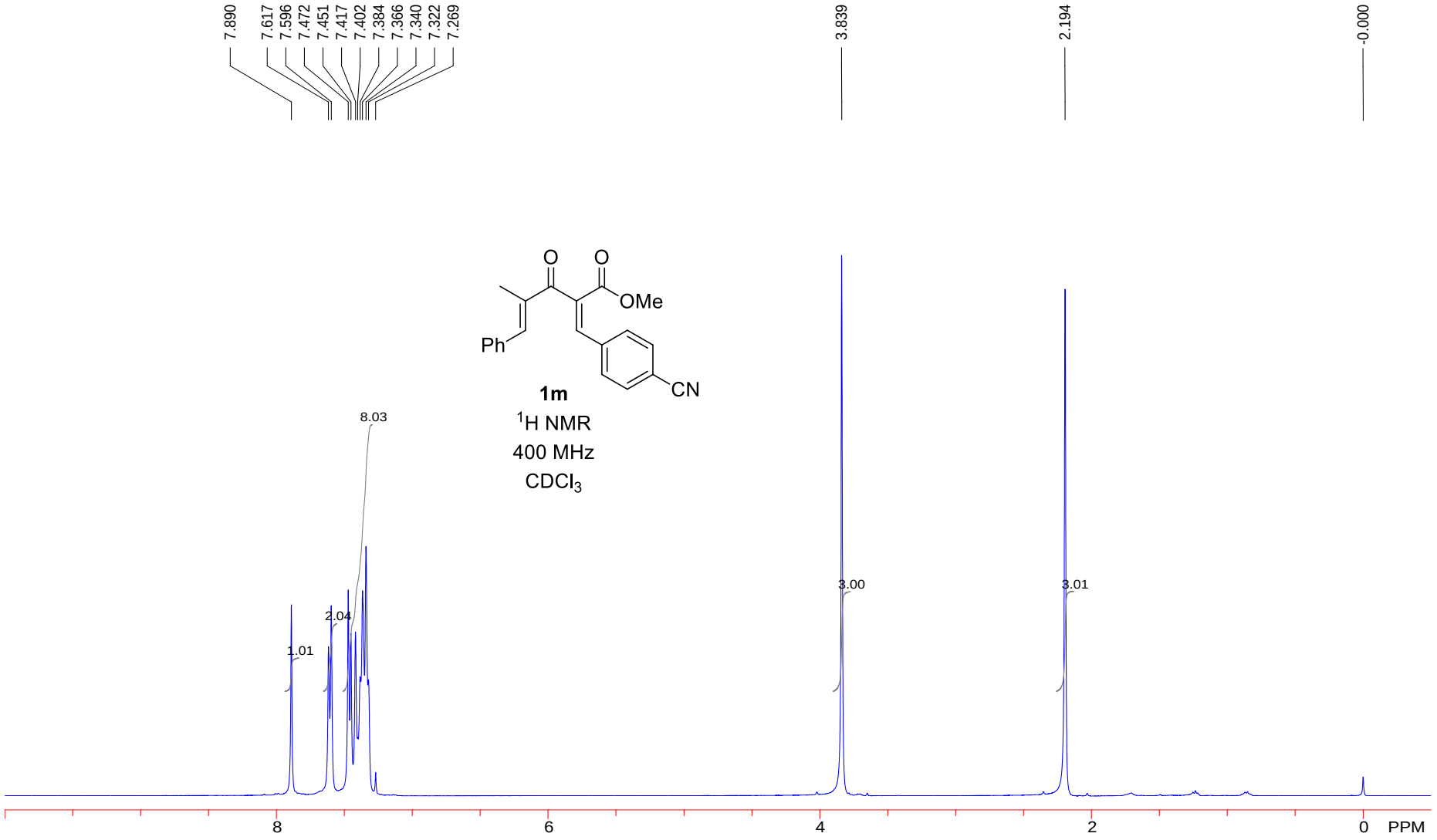
PPM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7.472
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7.340
7.322
7.269
3.839
2.194
-0.000
O
O
OMe
Ph
CN
1m
1H NMR
400 MHz
CDCl3
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2.04
3.00
3.01
8
6
4
2
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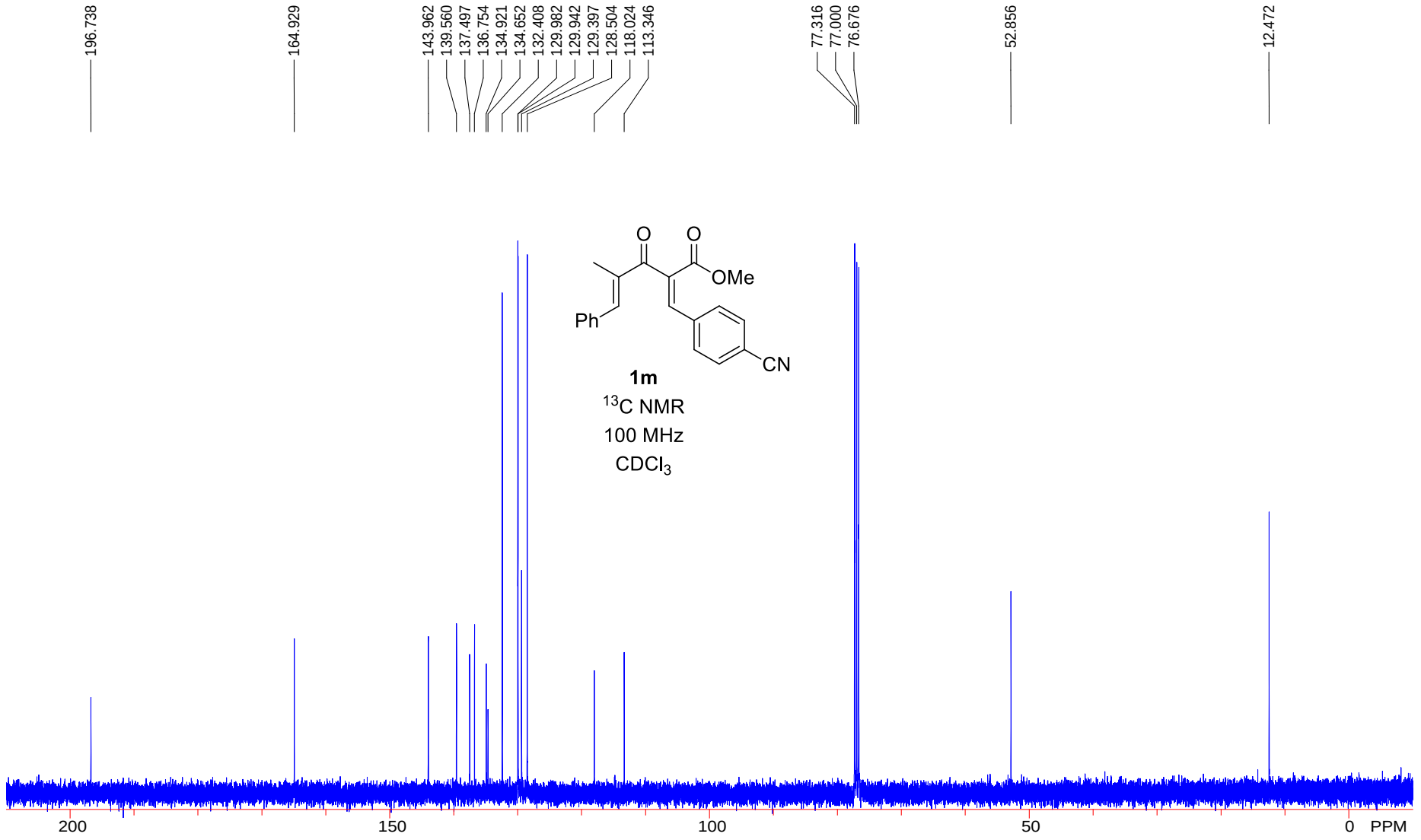
PPM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129.397
128.504
118.024
113.346
77.316
77.000
76.676
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O
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OMe
Ph
CN
1m
13C NMR
100 MHz
CDCl3
200
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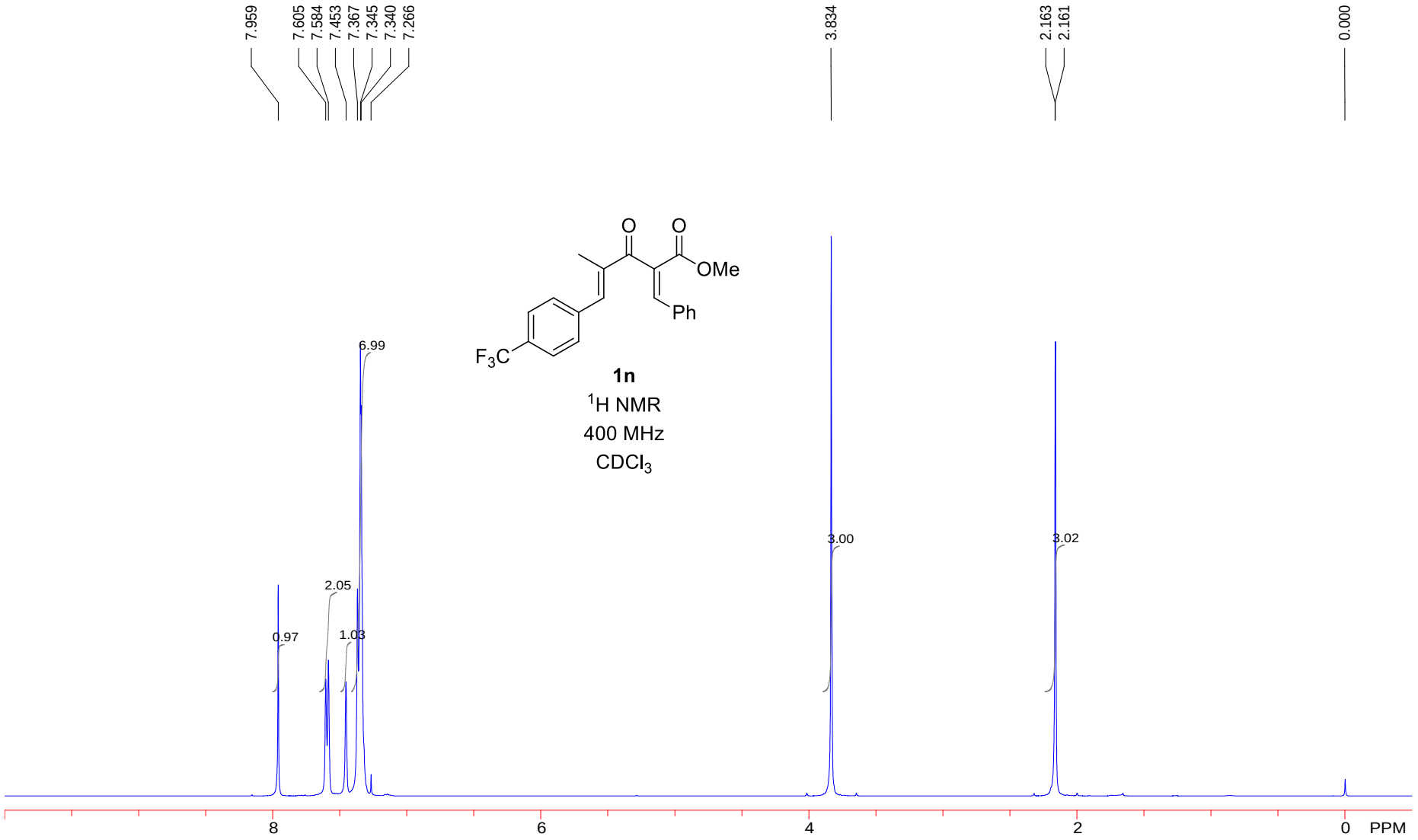
PPM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7.266
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2.161
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O
O
OMe
Ph
F3C
1n
1H NMR
400 MHz
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3.02
8
6
4
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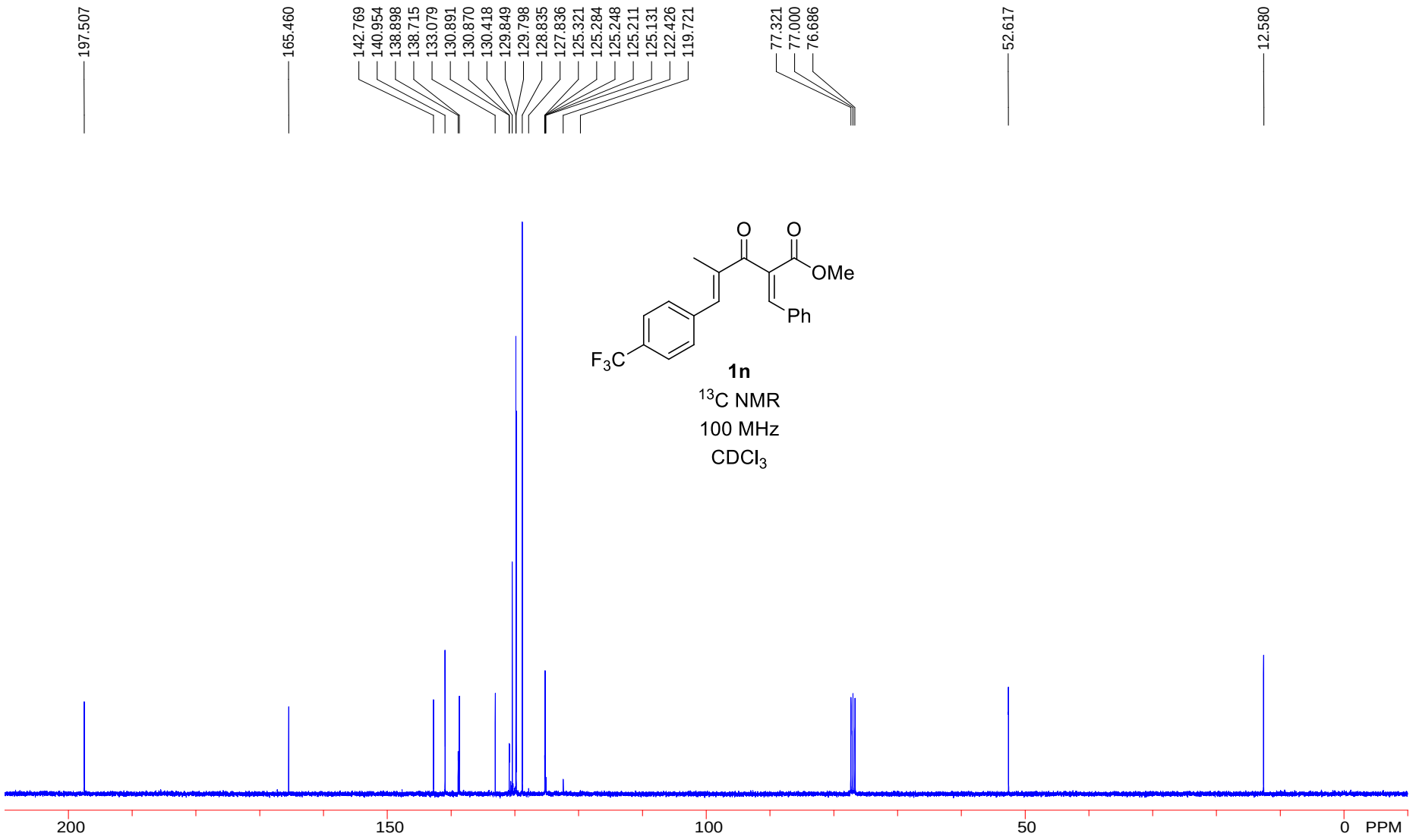
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128.835
127.836
125.321
125.284
125.248
125.211
125.131
122.426
119.721
77.321
77.000
76.686
52.617
12.580
O
O
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Ph
F3C
1n
13C NMR
100 MHz
CDCl3
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150
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50
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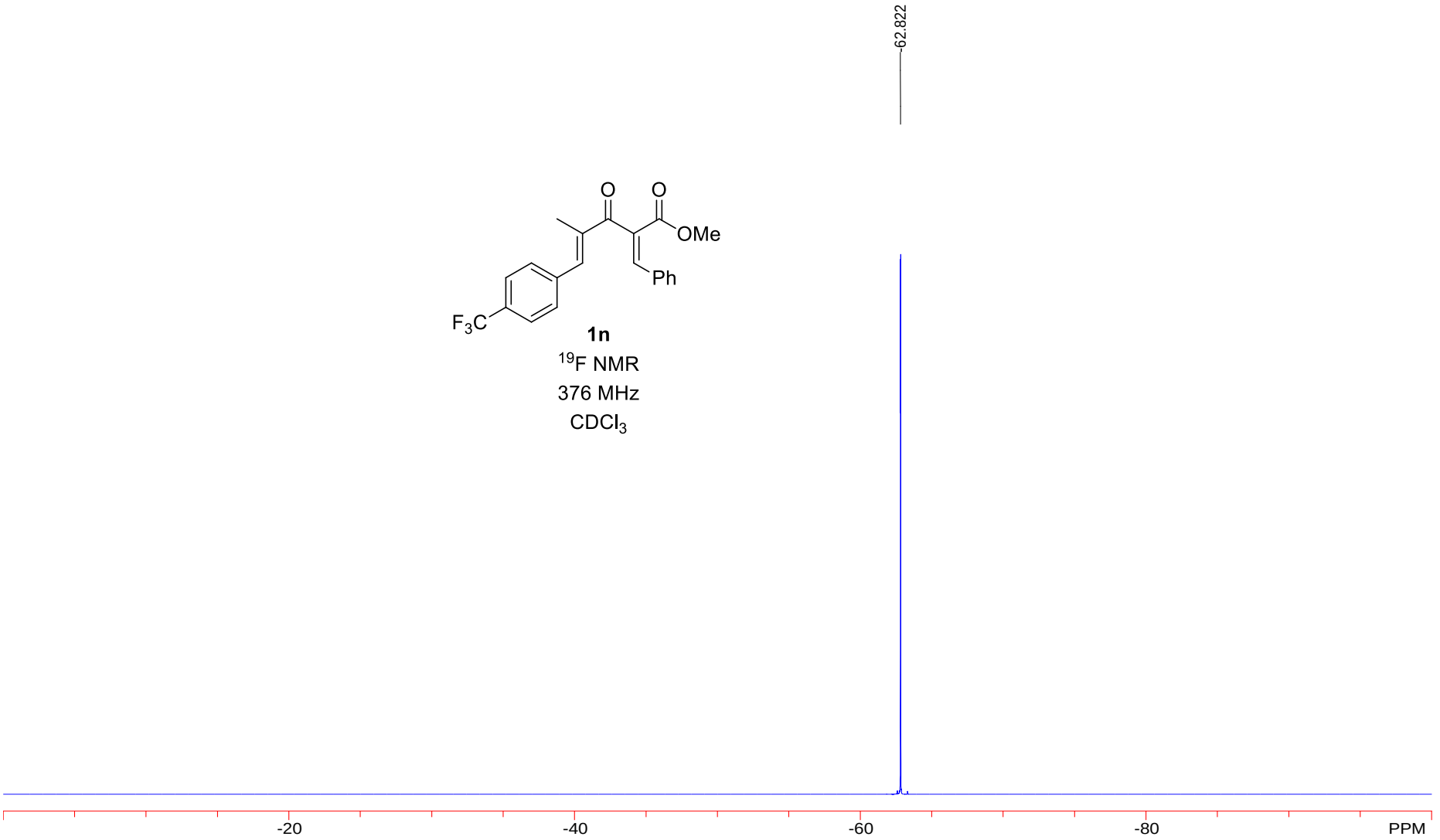
PPM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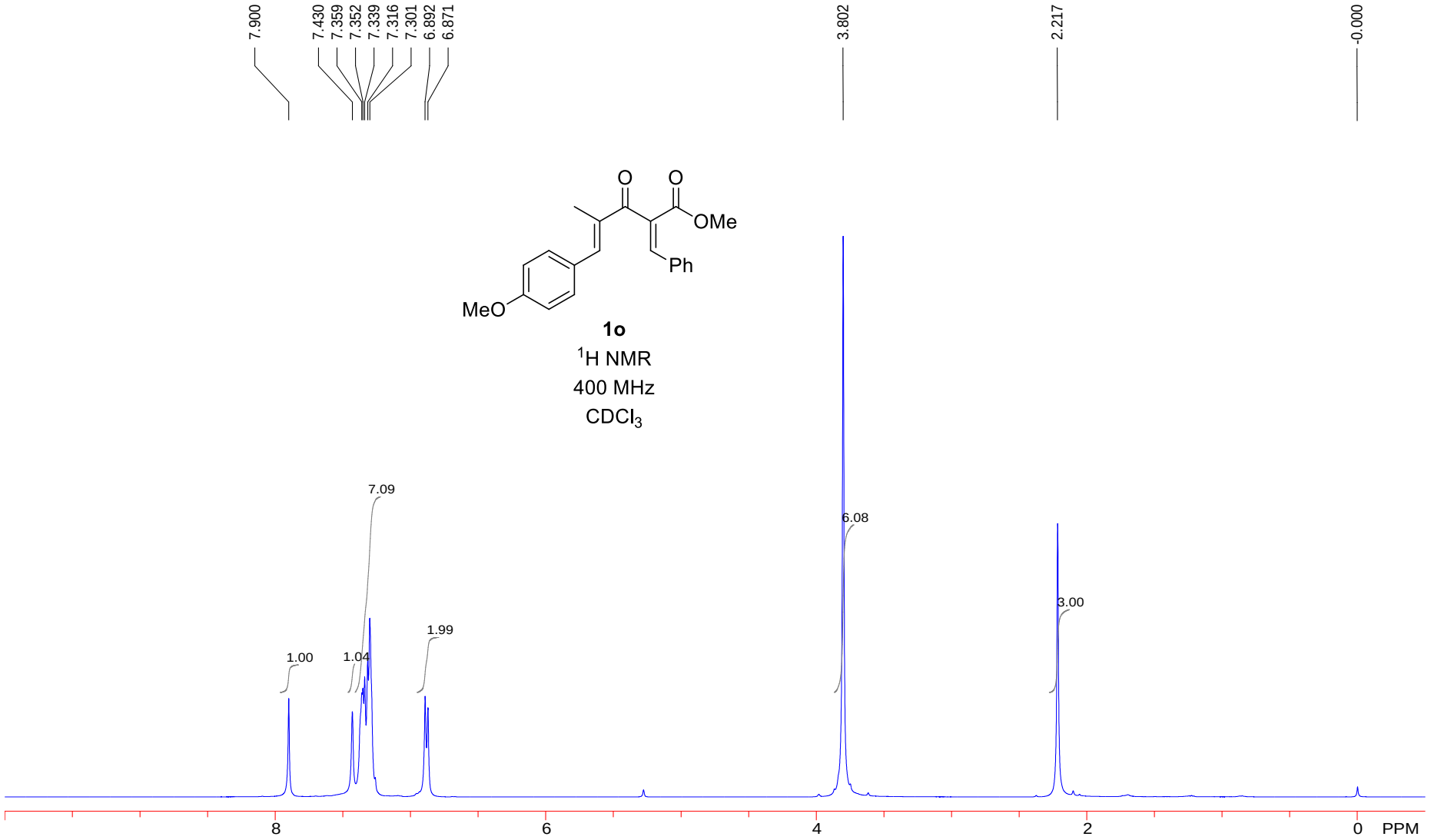
Ph
F3C
1n
19F NMR
376 MHz
CDCl3
-20
-40
-60
-80
PPM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7.316
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6.892
6.871
3.802
2.217
-0.000
O
O
OMe
Ph
MeO
1o
1H NMR
400 MHz
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1.04
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6
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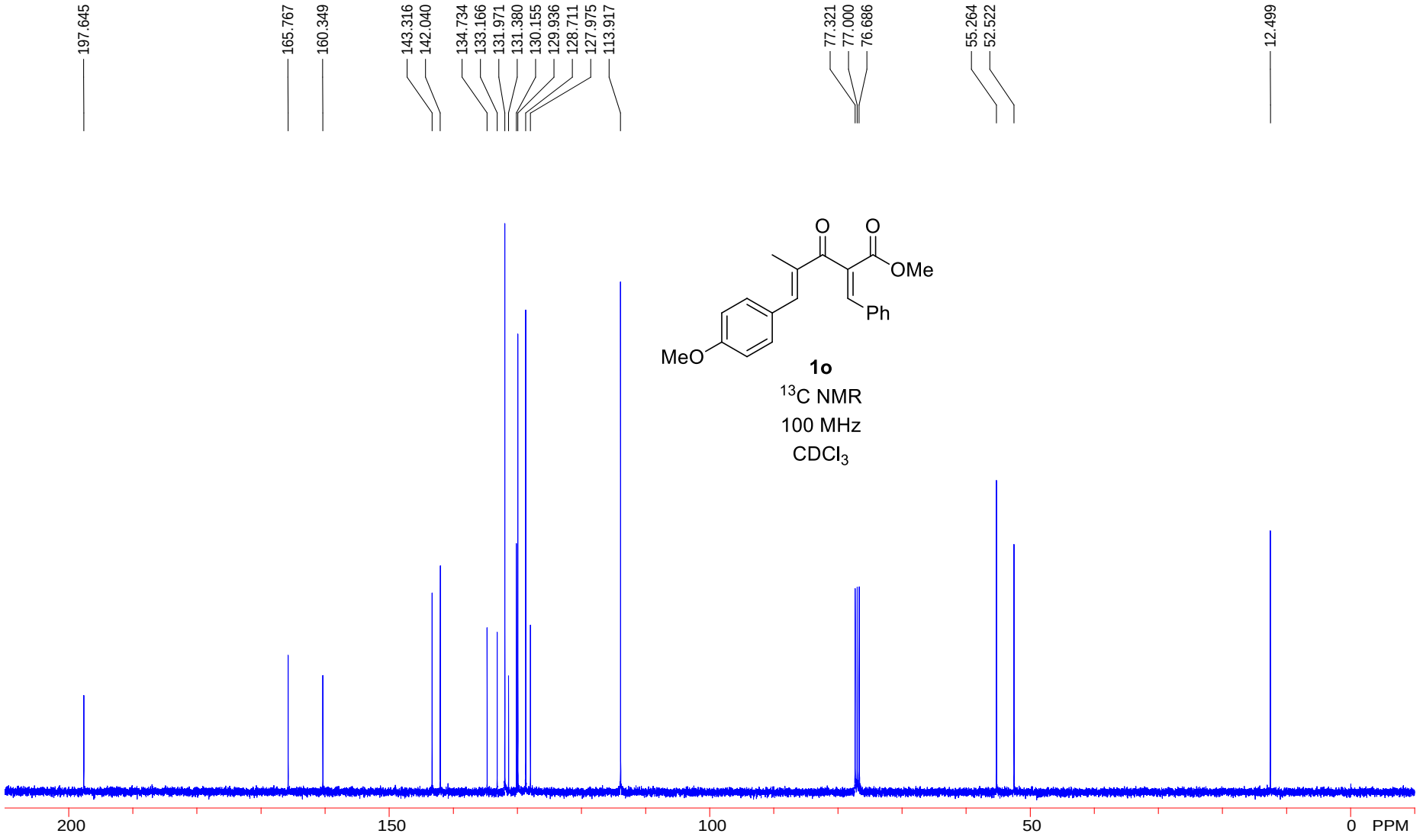
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113.917
77.321
77.000
76.686
55.264
52.522
12.499
O
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OMe
Ph
MeO
1o
13C NMR
100 MHz
CDCl3
200
150
100
50
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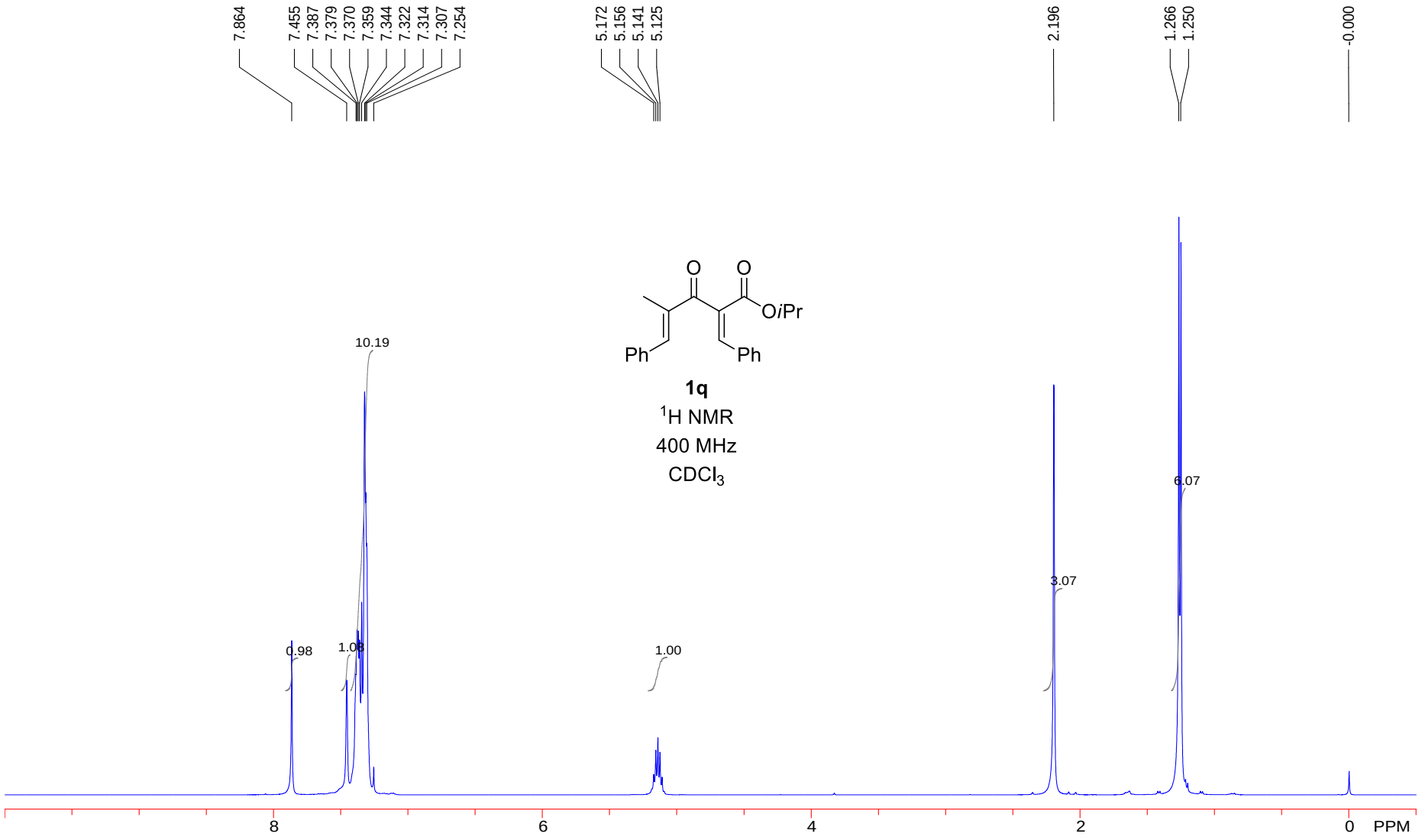
PPM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7.359
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7.322
7.314
7.307
7.254
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5.156
5.141
5.125
2.196
1.266
1.250
-0.000
O
O
OiPr
Ph
Ph
1q
1H NMR
400 MHz
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1.00
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6
4
2
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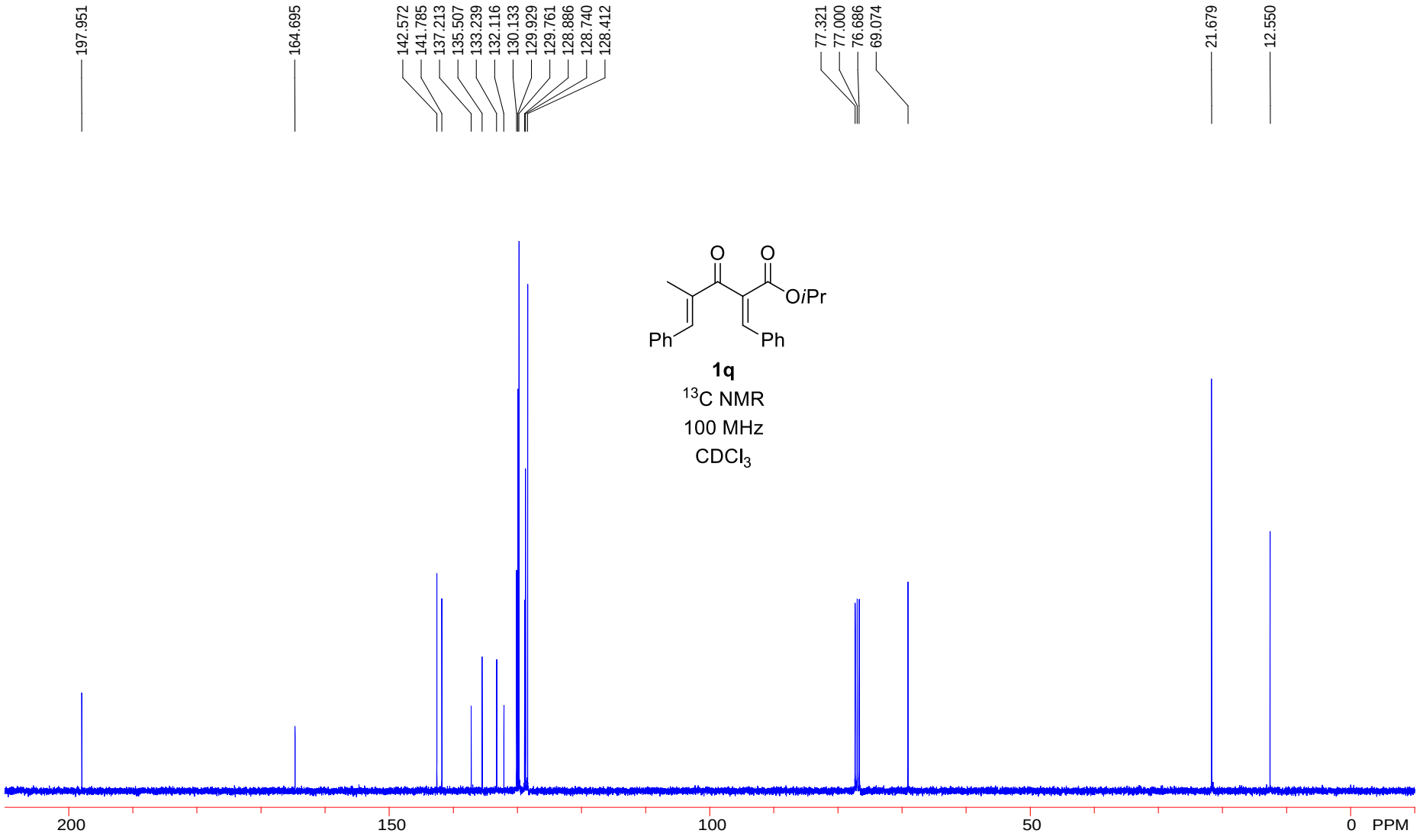
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128.740
128.412
77.321
77.000
76.686
69.074
21.679
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OiPr
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Ph
1q
13C NMR
100 MHz
CDCl3
200
150
100
50
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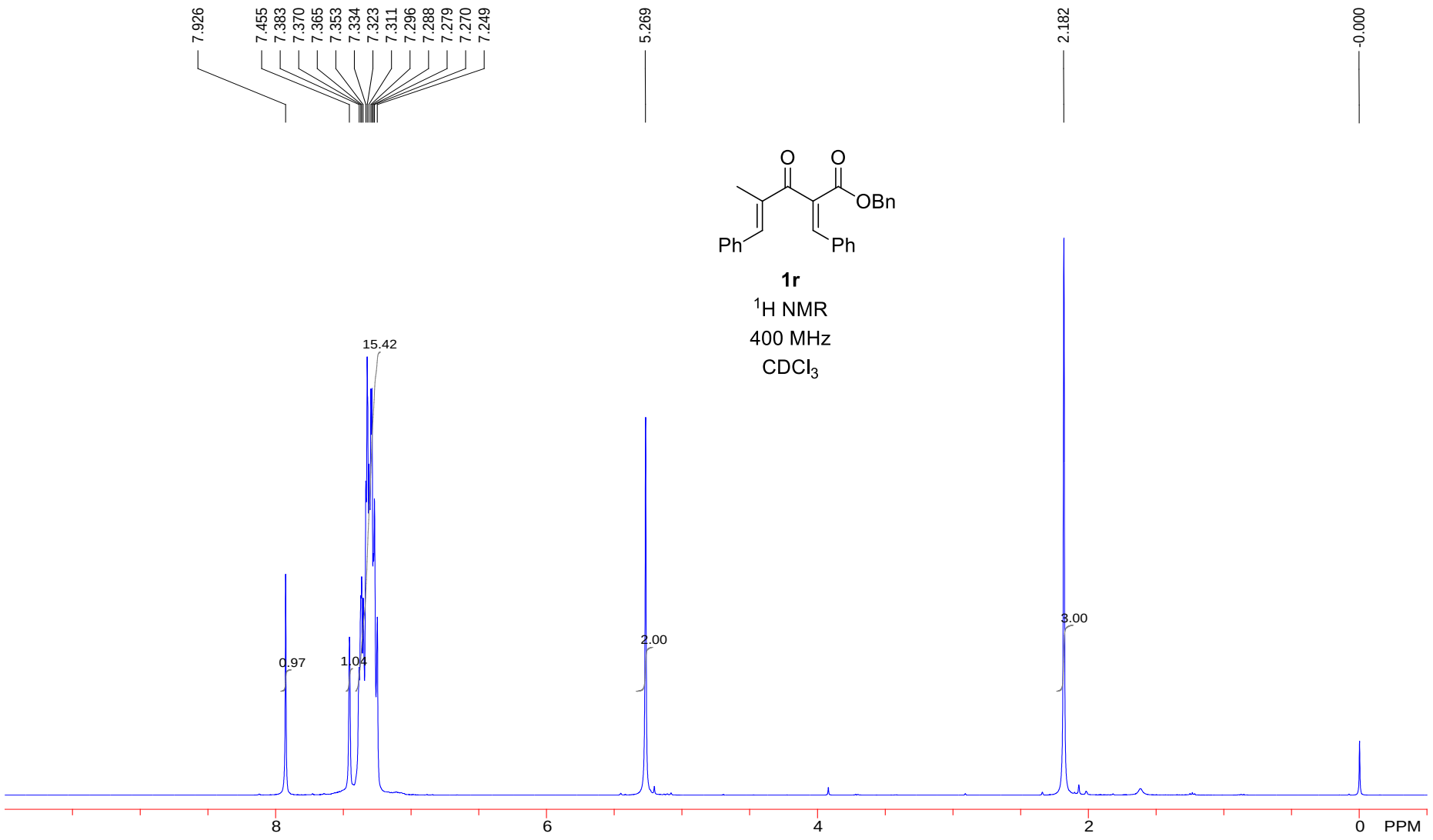
PPM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7.323
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7.296
7.288
7.279
7.270
7.249
5.269
2.182
-0.000
O
O
OBn
Ph
Ph
1r
1H NMR
400 MHz
CDCl3
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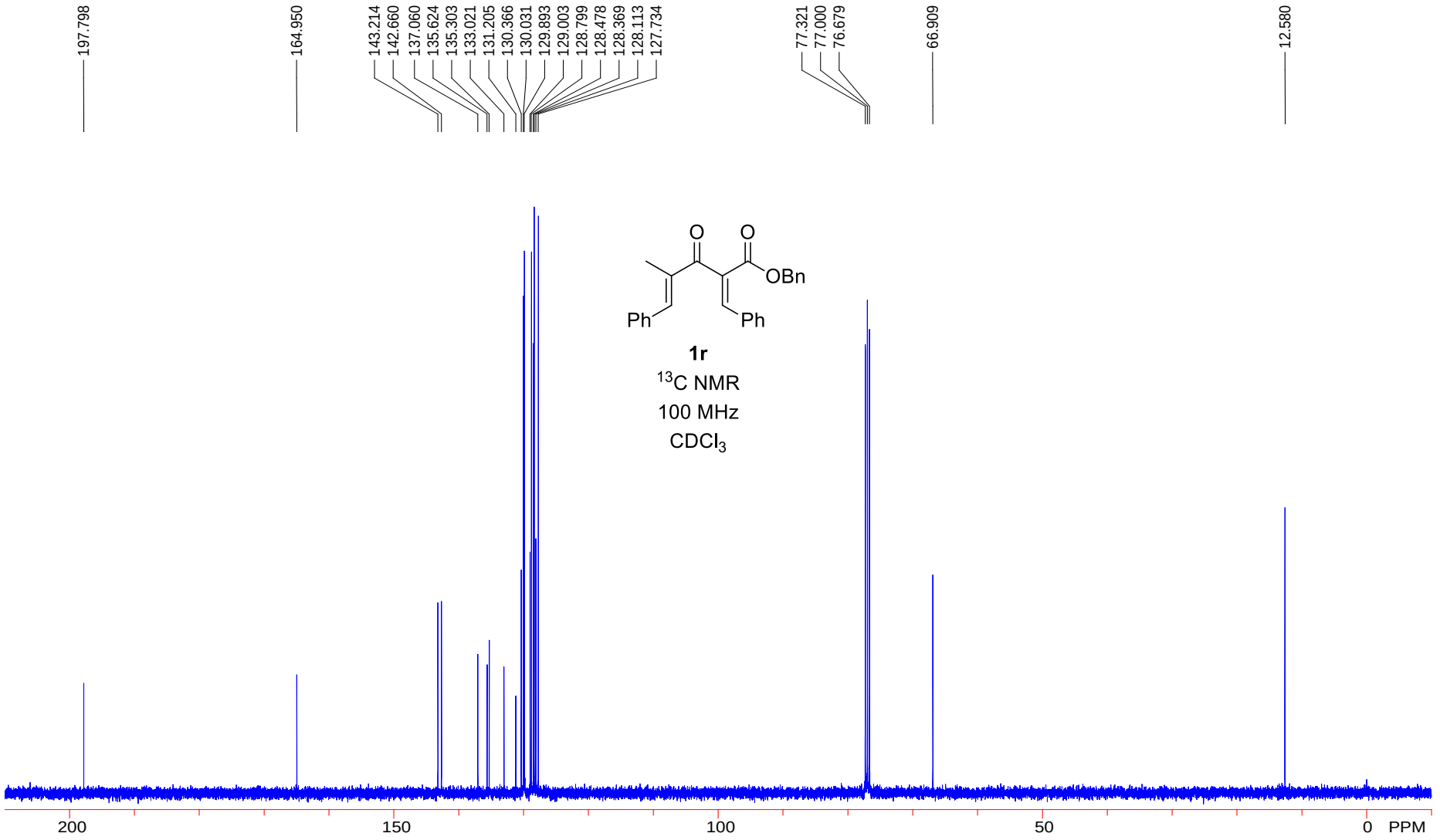
2.00
3.00
8
6
4
2
0
PPM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143.214
142.660
137.060
135.624
135.303
133.021
131.205
130.366
130.031
129.893
129.003
128.799
128.478
128.369
128.113
127.734
77.321
77.000
76.679
66.909
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Ph
1r
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100 MHz
CDCl3
200
150
100
50
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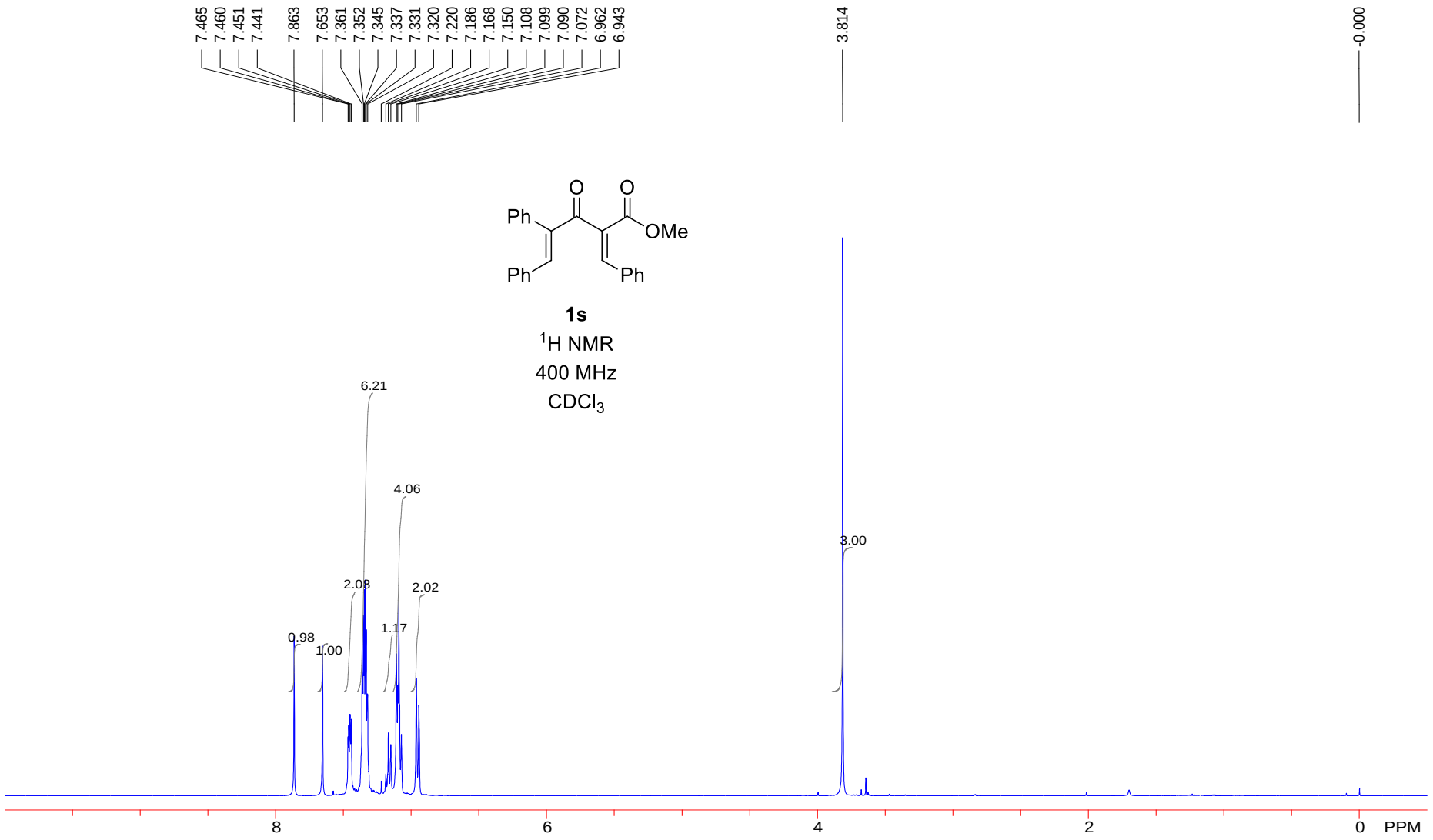
PPM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7.451
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7.352
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7.337
7.331
7.320
7.220
7.186
7.168
7.150
7.108
7.099
7.090
7.072
6.962
6.943
3.814
-0.000
O
O
Ph
OMe
Ph
Ph
1s
1H NMR
400 MHz
CDCl3
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2.08
2.02
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1.00
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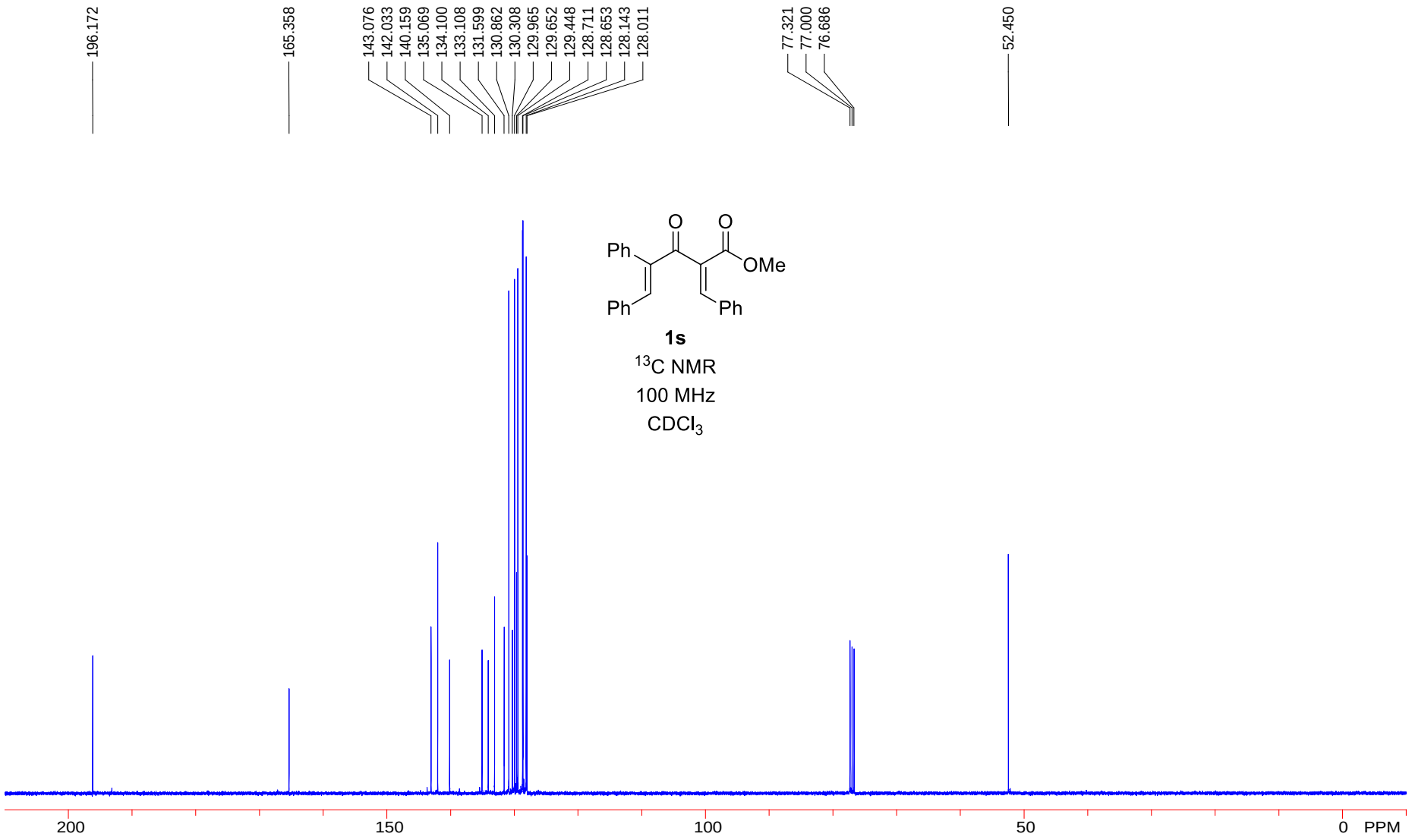
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134.100
133.108
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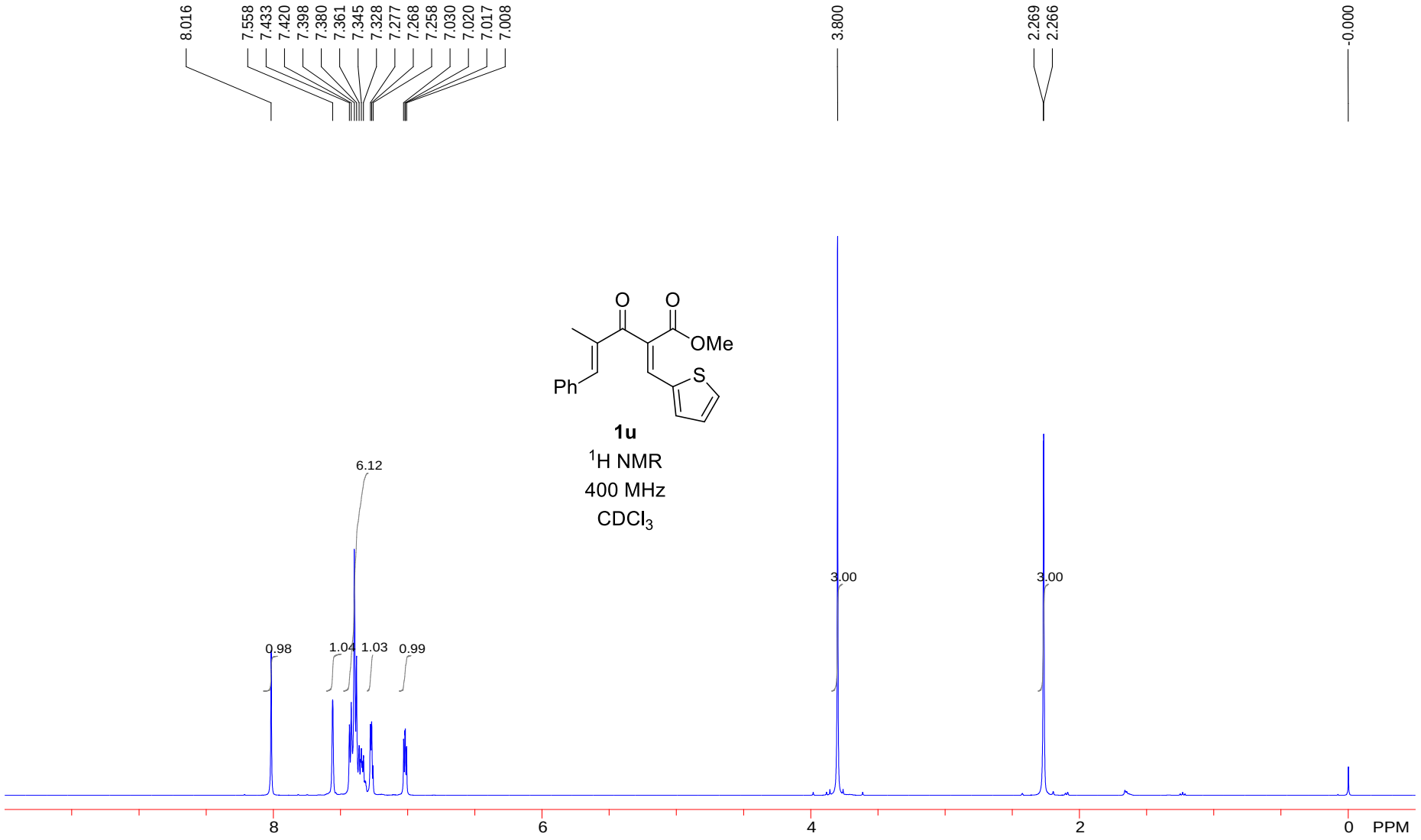
130.862
130.308
129.965
129.652
129.448
128.711
128.653
128.143
128.011
77.321
77.000
76.686
52.450
O
O
Ph
OMe
Ph
Ph
1s
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM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7.558
7.433
7.420
7.398
7.380
7.361
7.345
7.328
7.277
7.268
7.258
7.030
7.020
7.017
7.008
3.800
2.269
2.266
-0.000
O
O
OMe
Ph
S
1u
1H NMR
400 MHz
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0.98
1.04
1.03
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3.00
3.00
8
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4
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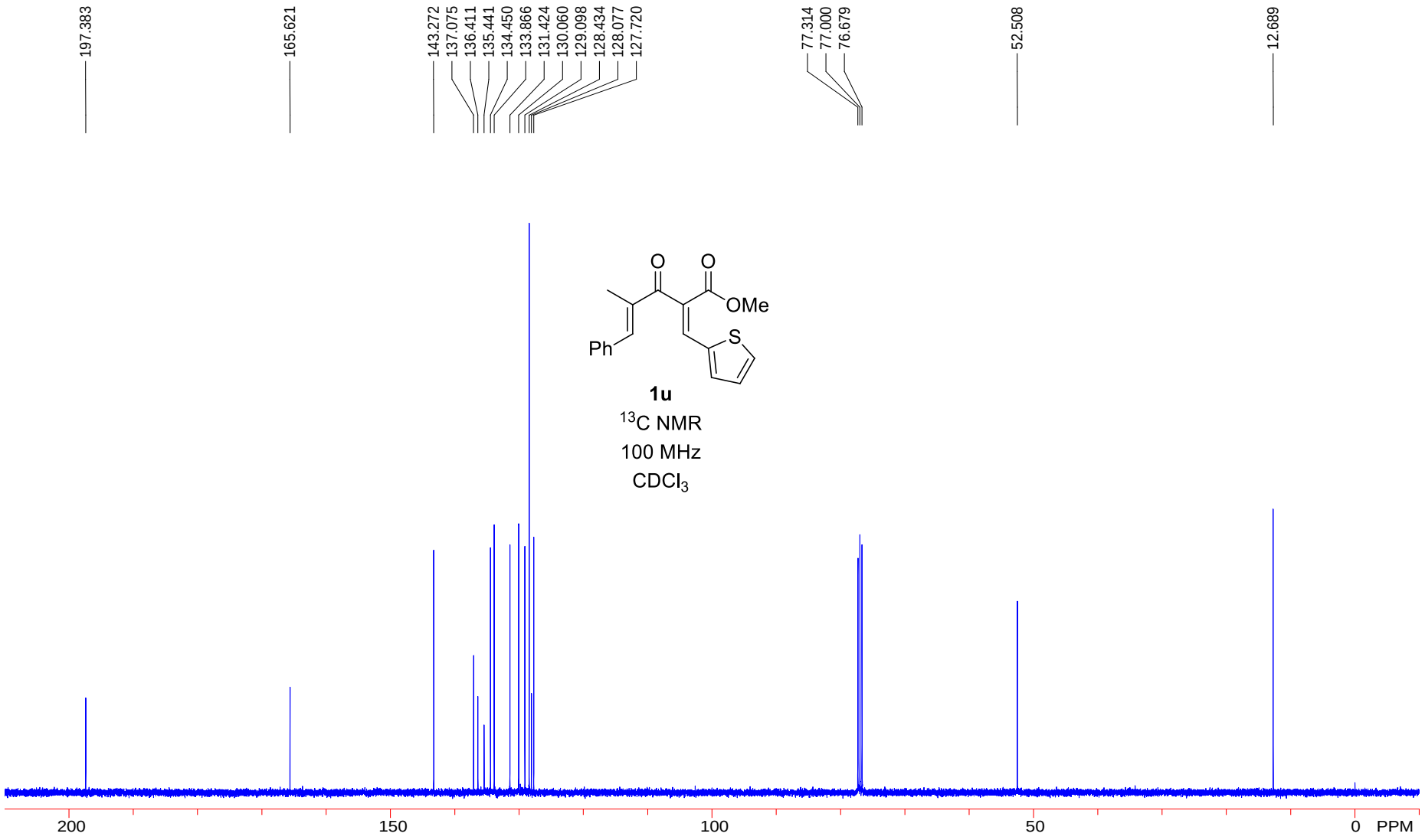
0
PPM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143.272
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136.411
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134.450
133.866
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130.060
129.098
128.434
128.077
127.720
77.314
77.000
76.679
52.508
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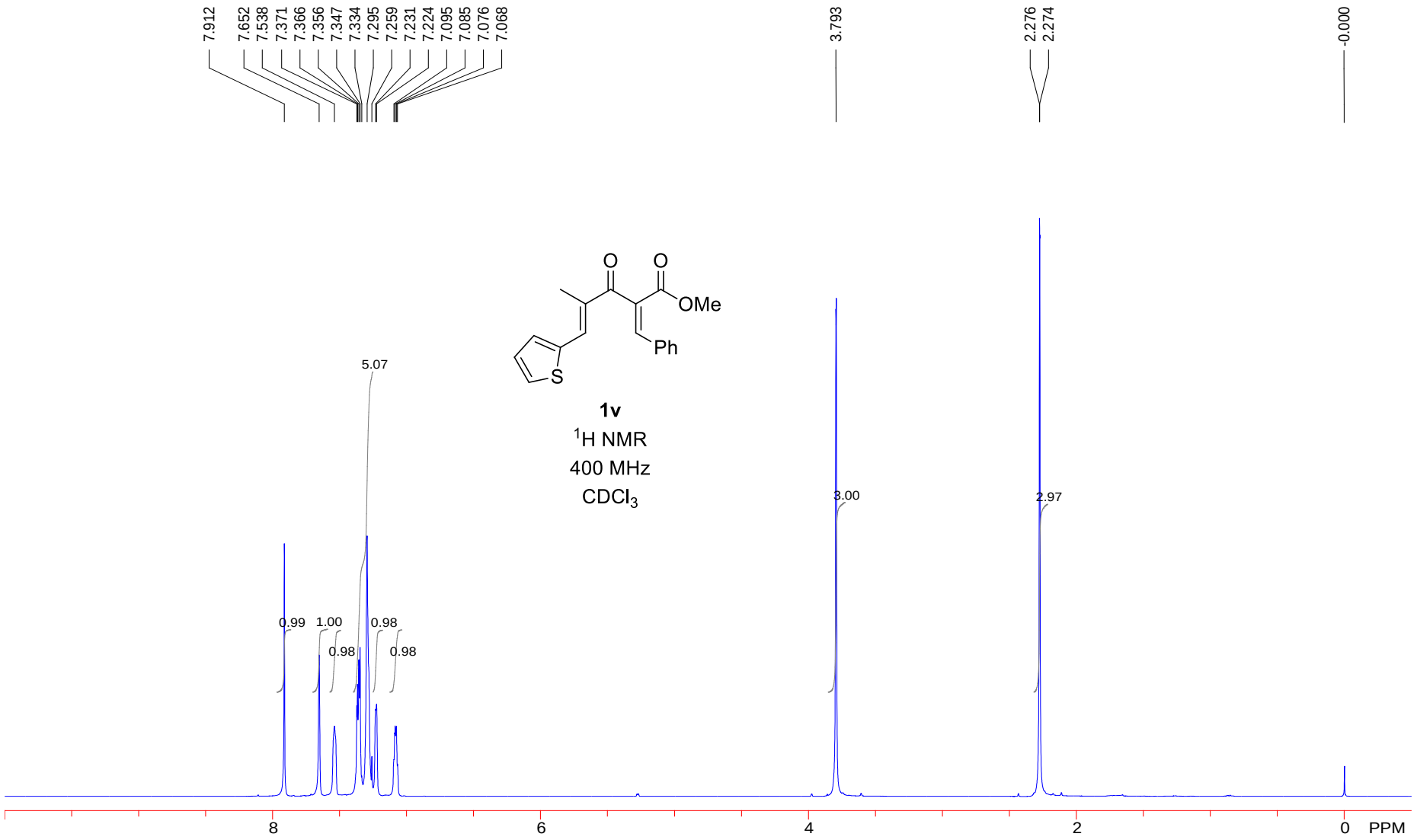
O
OMe
Ph
S
1u
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM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7.652
7.538
7.371
7.366
7.356
7.347
7.334
7.295
7.259
7.231
7.224
7.095
7.085
7.076
7.068
3.793
2.276
2.274
-0.000
O
O
OMe
Ph
S
1v
1H NMR
400 MHz
CDCl3
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2.97
0.99
1.00
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0.98
0.98
8
6
4
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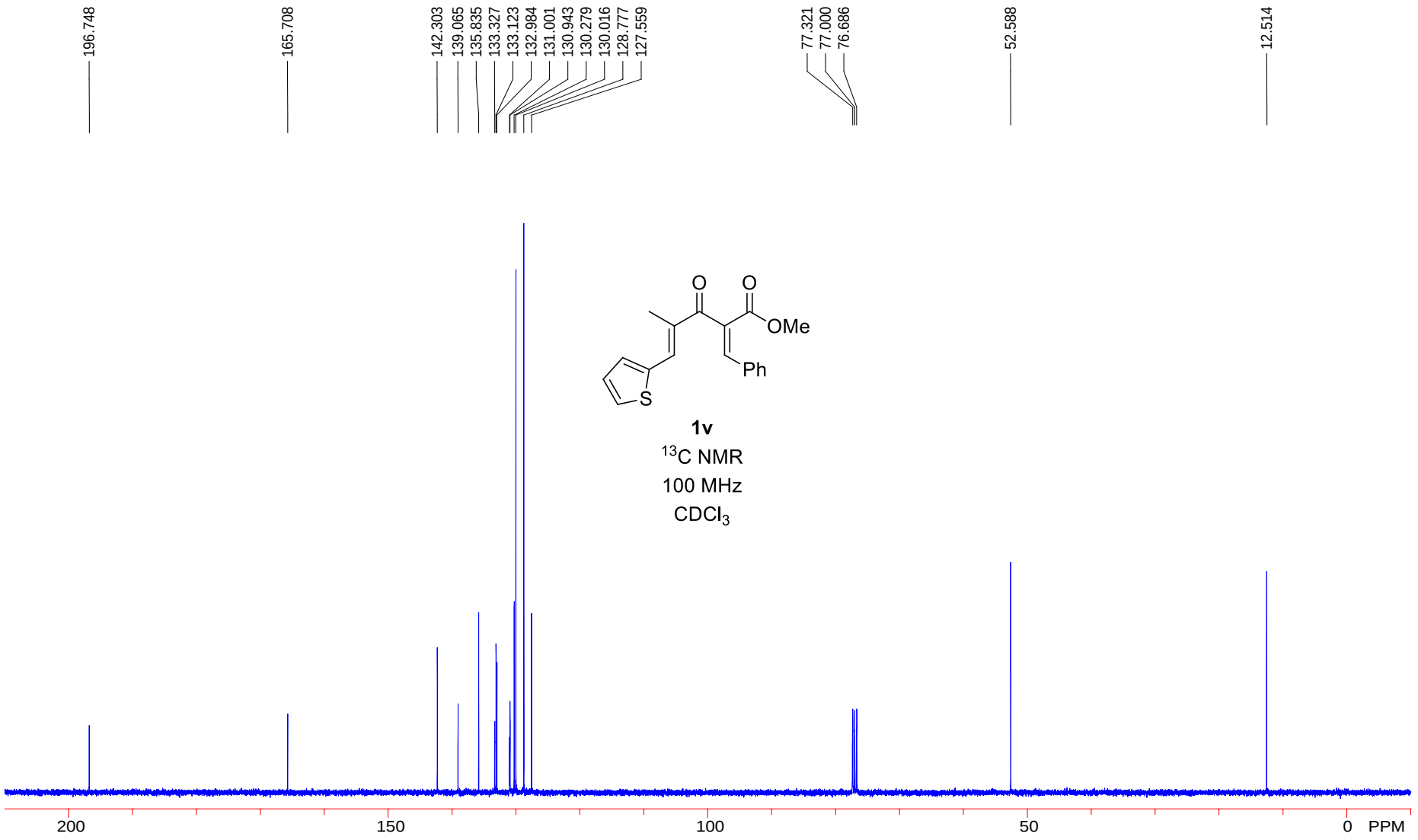
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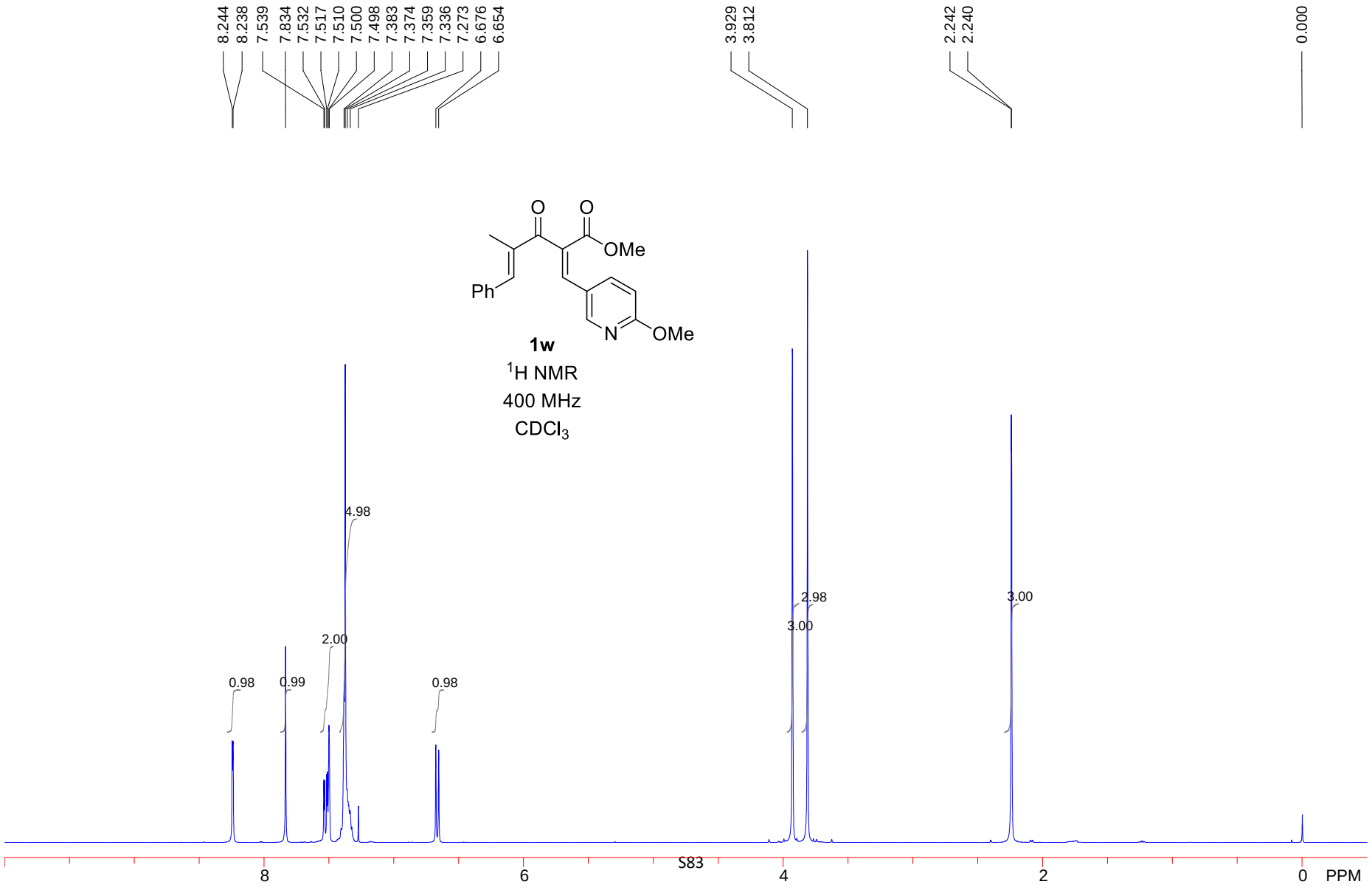
142.303
139.065
135.835
133.327
133.123
132.984
131.001
130.943
130.279
130.016
128.777
127.559
77.321
77.000
76.686
52.588
12.514
O
O
OMe
Ph
S
1v
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM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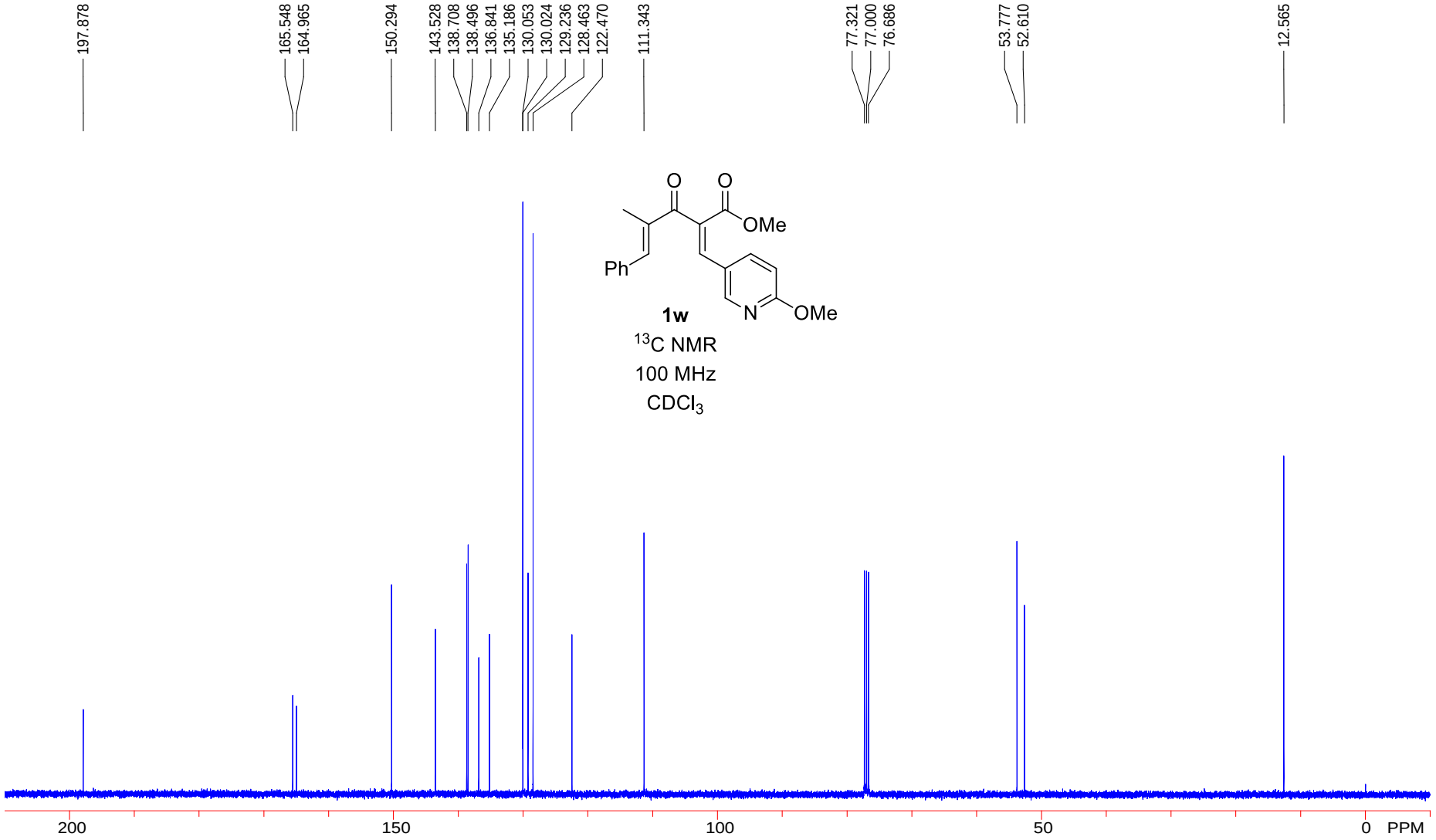
8.238
7.539
7.834
7.532
7.517
7.510
7.500
7.498
7.383
7.374
7.359
7.336
7.273
6.676
6.654
3.929
3.812
2.242
2.240
0.000
O
O
OMe
Ph
N
OMe
1w
1H NMR
400 MHz
CDCl3
4.98
2.98
3.00
3.00
2.00
0.98
0.99
0.98
8
6
4
2
0
PPM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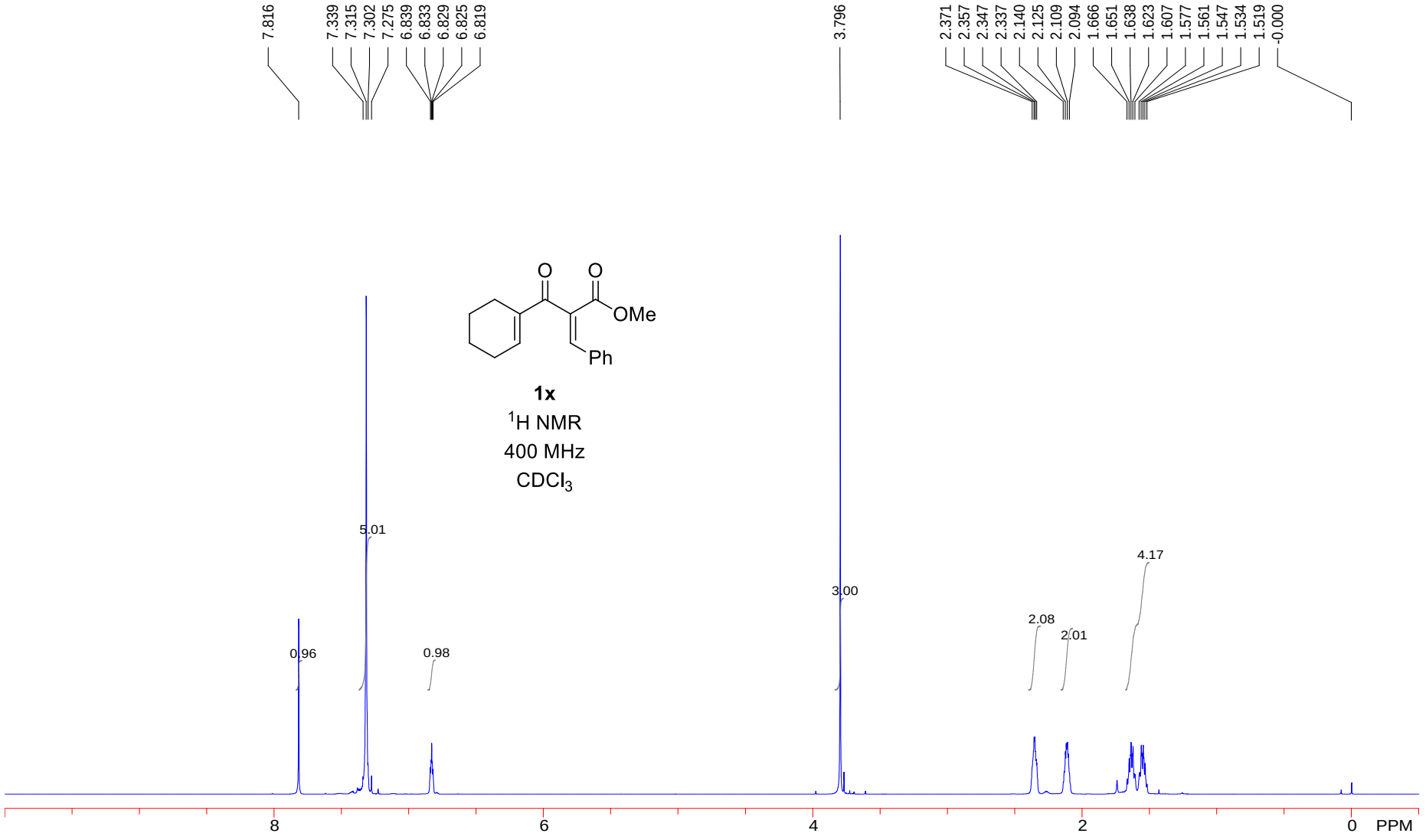
164.965
150.294
143.528
138.708
138.496
136.841
135.186
130.053
130.024
129.236
128.463
122.470
111.343
77.321
77.000
76.686
53.777
52.610
12.565
O
O
OMe
Ph
N
OMe
1w
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM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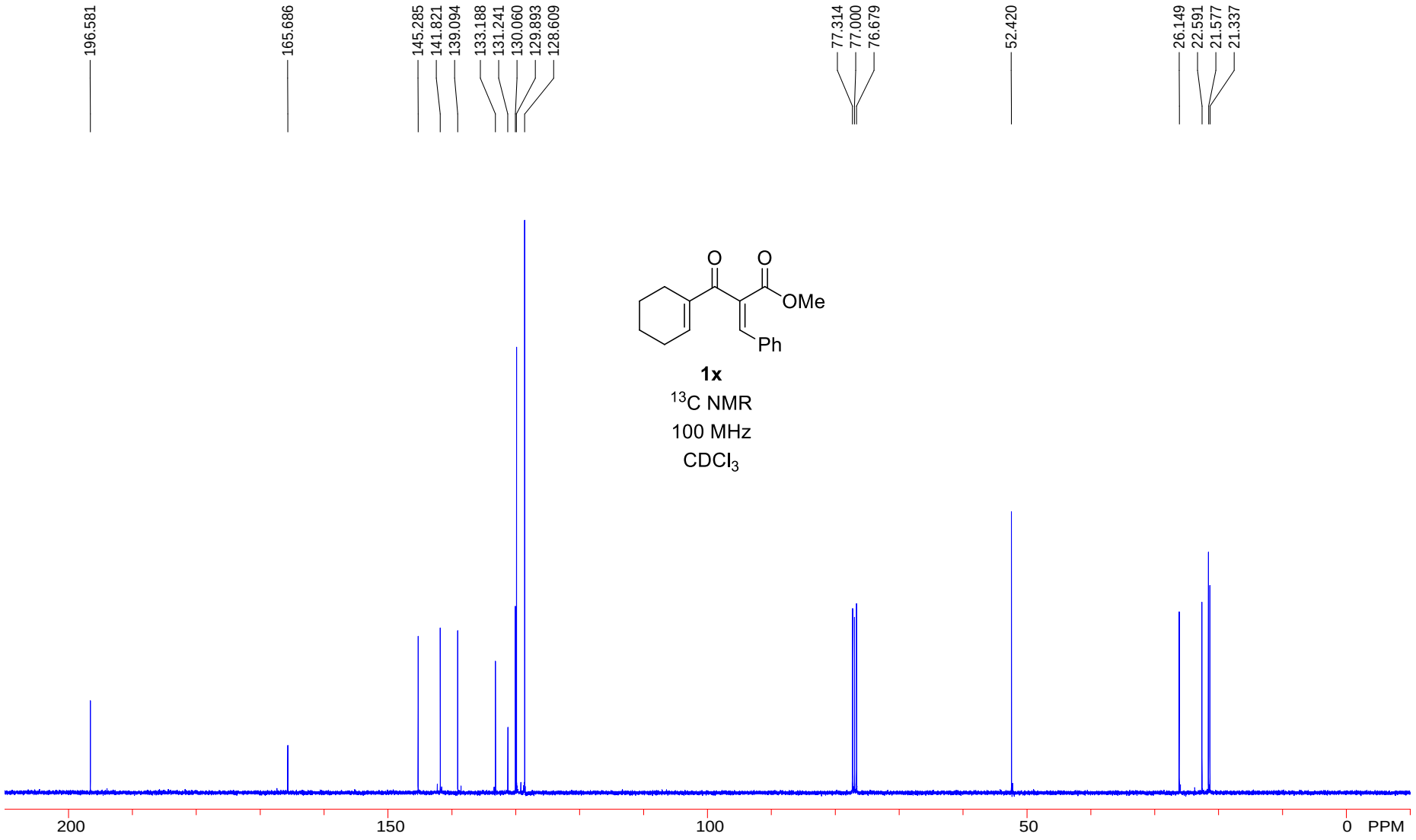
7.339
7.315
7.302
7.275
6.839
6.833
6.829
6.825
6.819
3.796
2.371
2.357
2.347
2.337
2.140
2.125
2.109
2.094
1.666
1.651
1.638
1.623
1.607
1.577
1.561
1.547
1.534
1.519
-0.000
O
O
OMe
Ph
1x
1H NMR
400 MHz
CDCl3
5.01
0.96
0.98
3.00
2.08
2.01
4.17
8
6
4
2
0
PPM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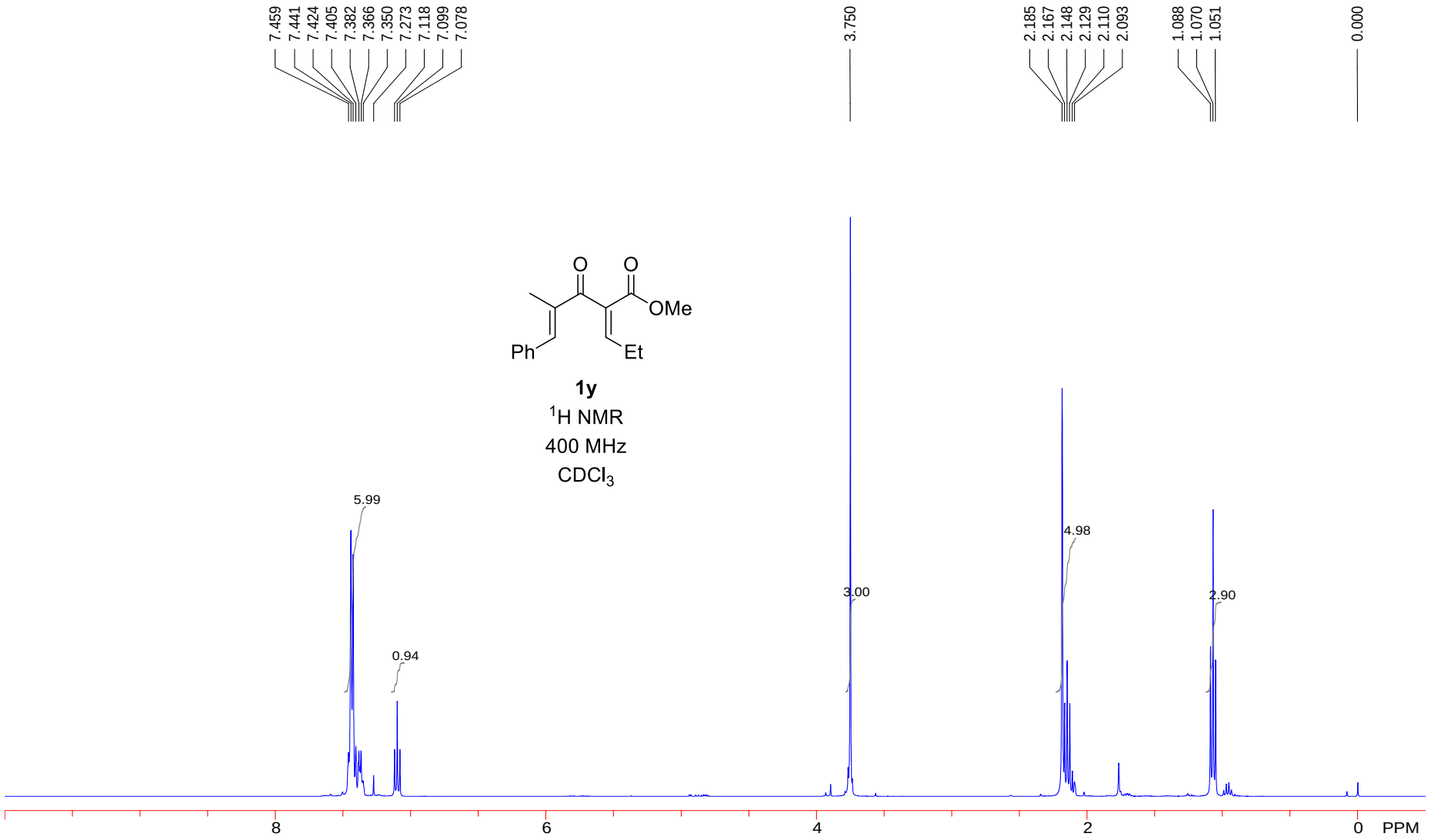
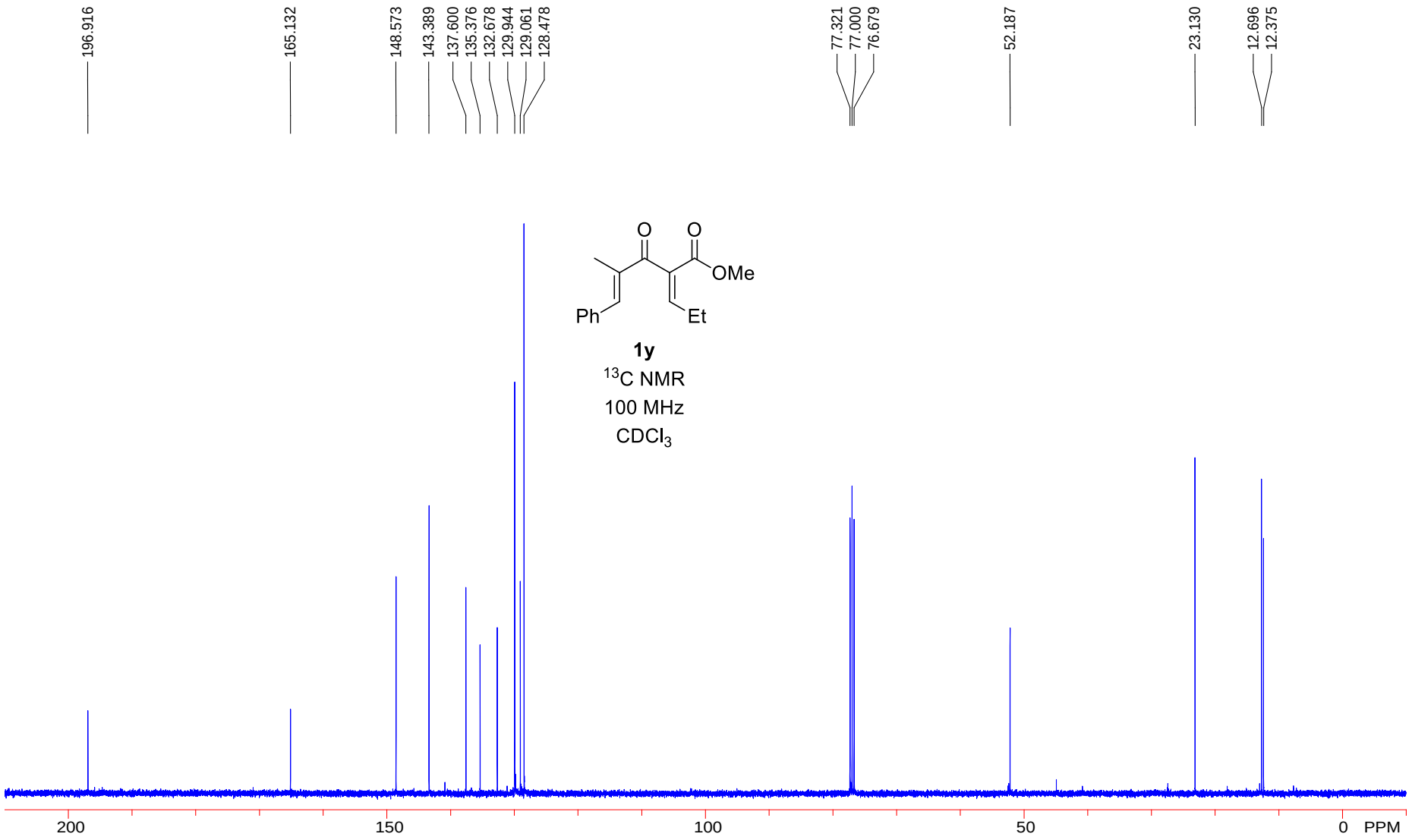
165.686
145.285
141.821
139.094
133.188
131.241
130.060
129.893
128.609
77.314
77.000
76.679
52.420
26.149
22.591
21.577
21.337
O
O
OMe
Ph
1x
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM


7.459
7.441
7.424
7.405
7.382
7.366
7.350
7.273
7.118
7.099
7.078
3.750
2.185
2.167
2.148
2.129
2.110
2.093
1.088
1.070
1.051
0.000
O
O
OMe
Ph
Et
1y
1H NMR
400 MHz
CDCl3
5.99
0.94
3.00
4.98
2.90
8
6
4
2
0
PPM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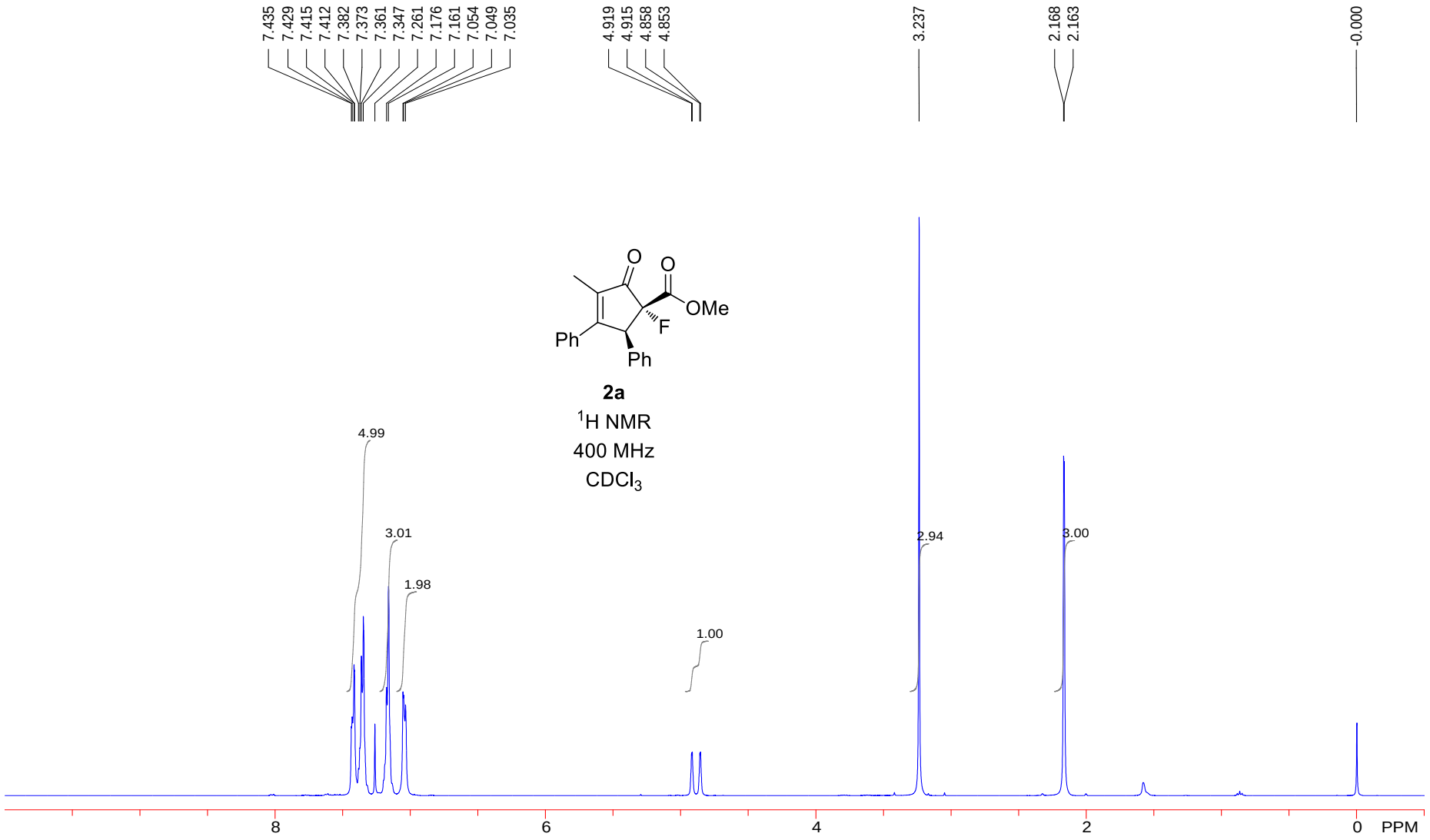
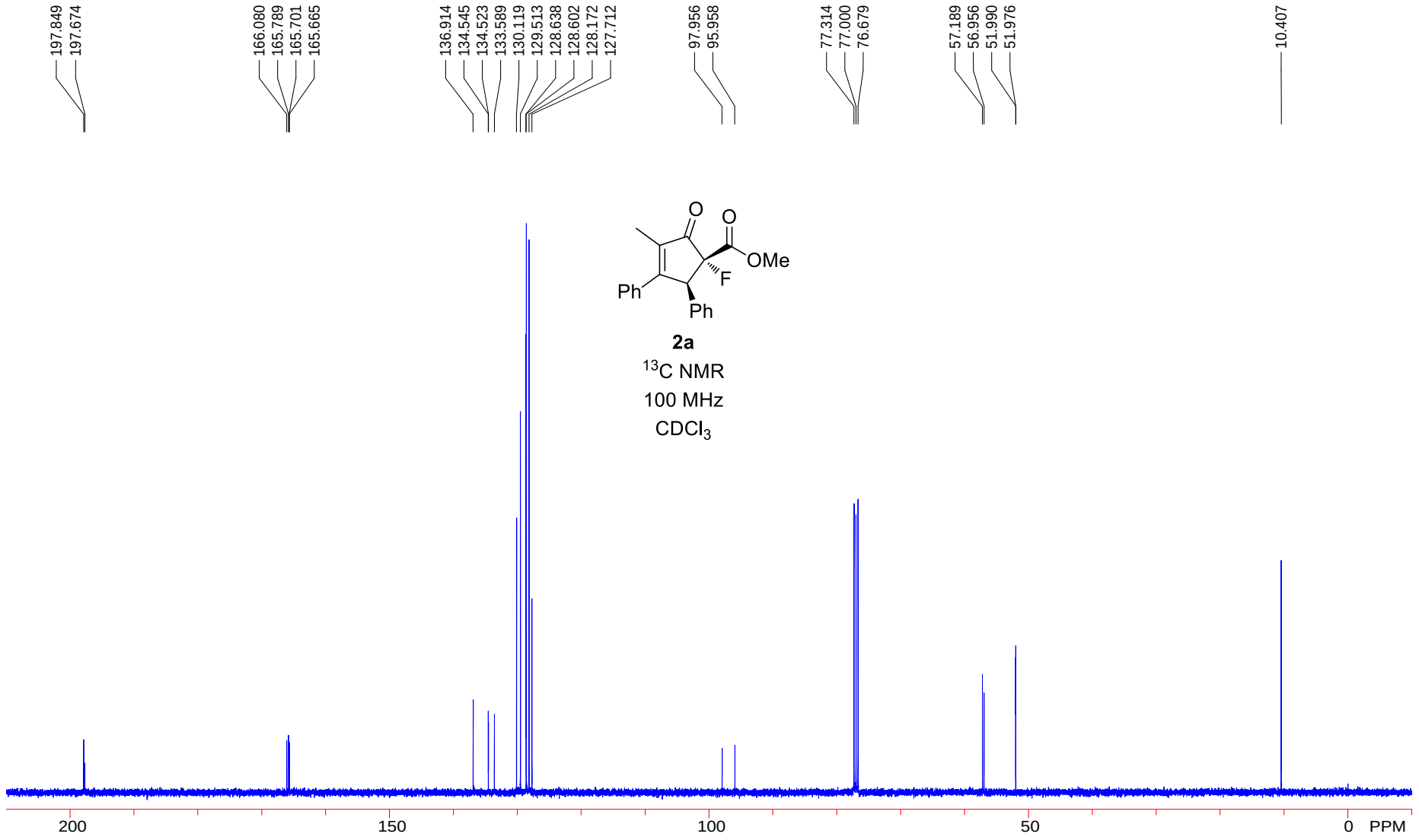
148.573
143.389
137.600
135.376
132.678
129.944
129.061
128.478
77.321
77.000
76.679
52.187
23.130
12.696
12.375
O
O
OMe
Ph
Et
1y
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM


7.435
7.429
7.415
7.412
7.382
7.373
7.361
7.347
7.261
7.176
7.161
7.054
7.049
7.035
4.919
4.915
4.858
4.853
3.237
2.168
2.163
-0.000
O
O
OMe
F
Ph
Ph
2a
1H NMR
400 MHz
CDCl3
4.99
3.01
1.98
1.00
2.94
3.00
8
6
4
2
0
PPM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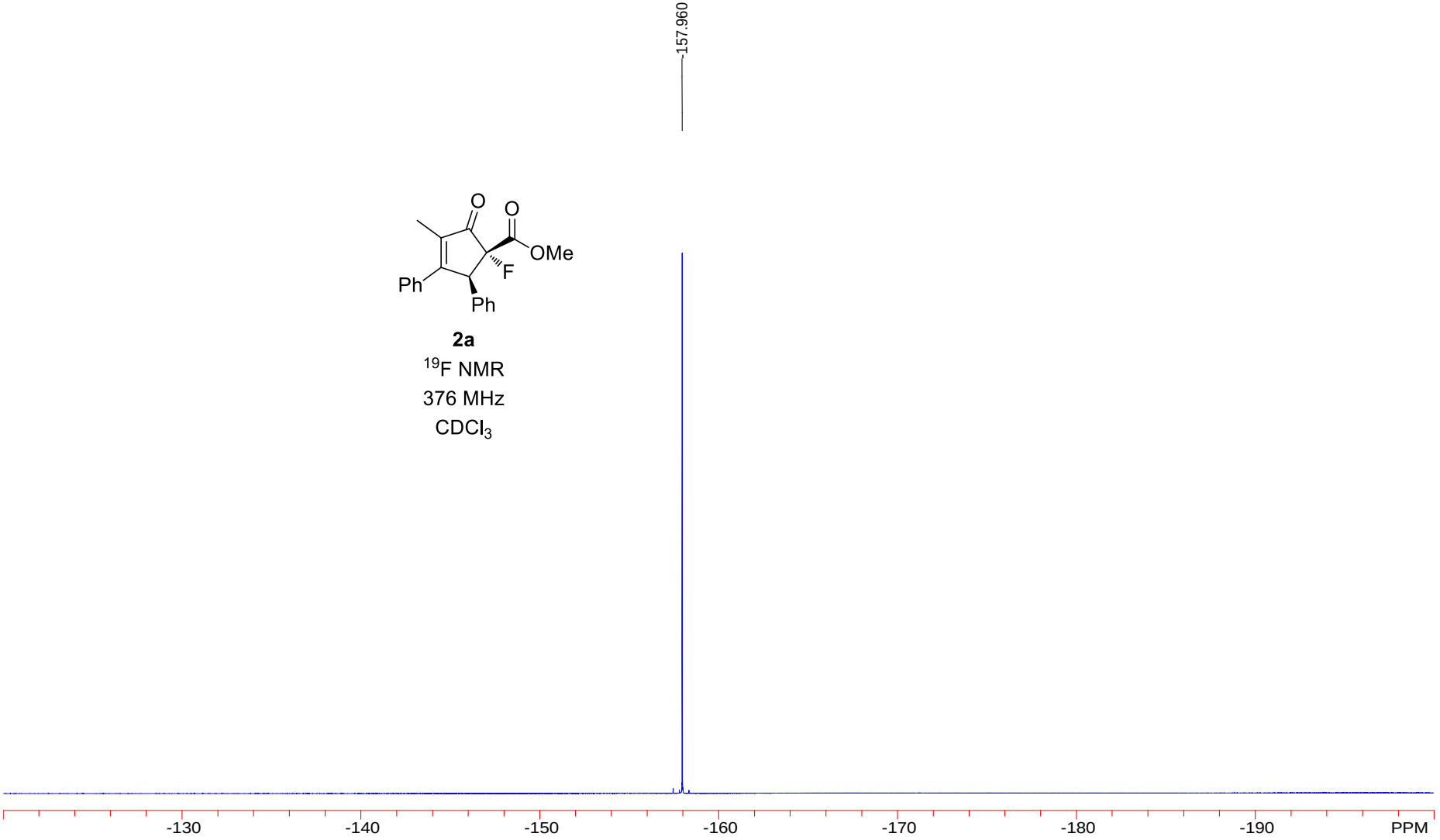
197.674
166.080
165.789
165.701
165.665
136.914
134.545
134.523
133.589
130.119
129.513
128.638
128.602
128.172
127.712
97.956
95.958
77.314
77.000
76.679
57.189
56.956
51.990
51.976
10.407
O
O
OMe
F
Ph
Ph
2a
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

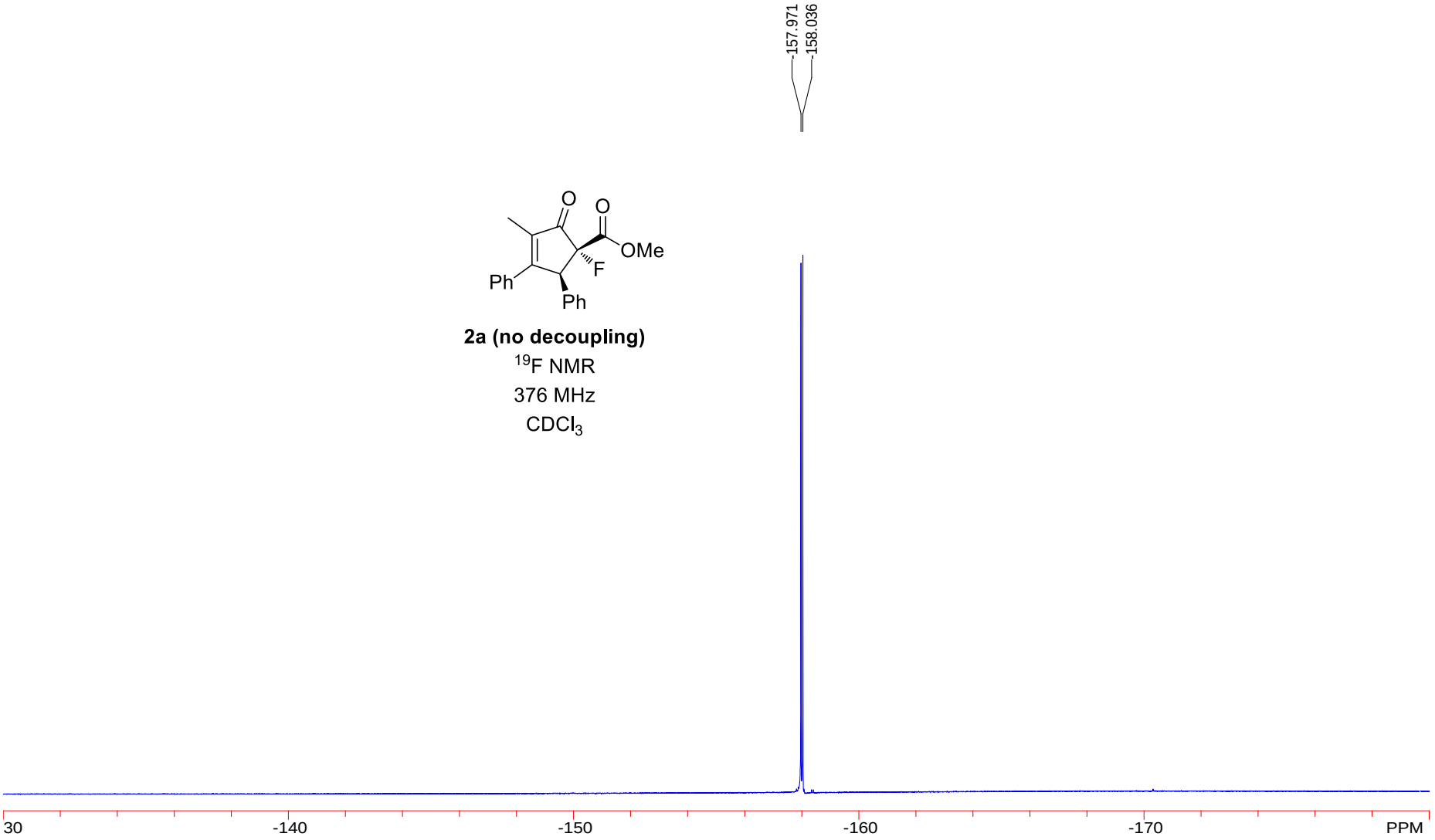
2a

^{19}F NMR

376 MHz

$CDCl_3$



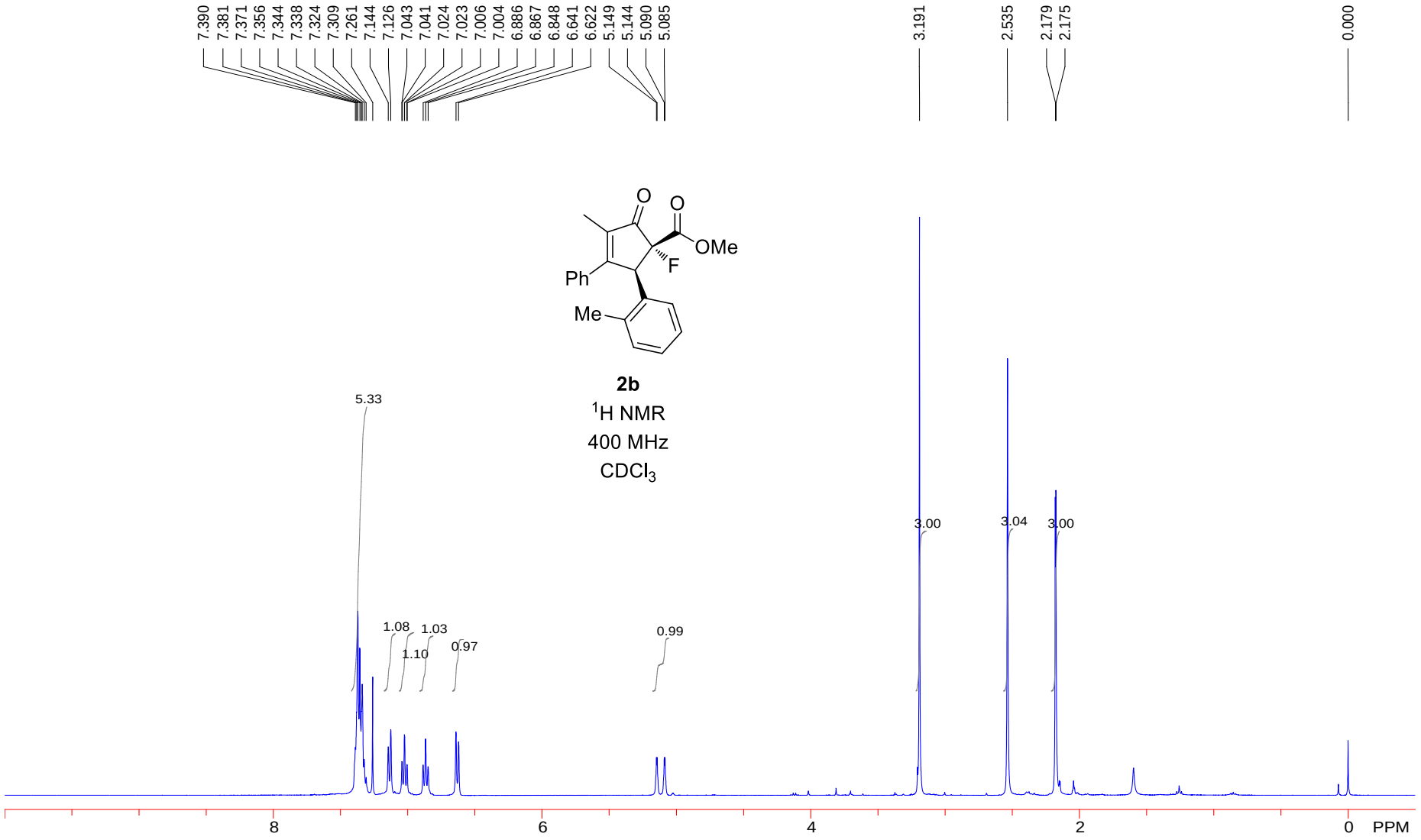


2a (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$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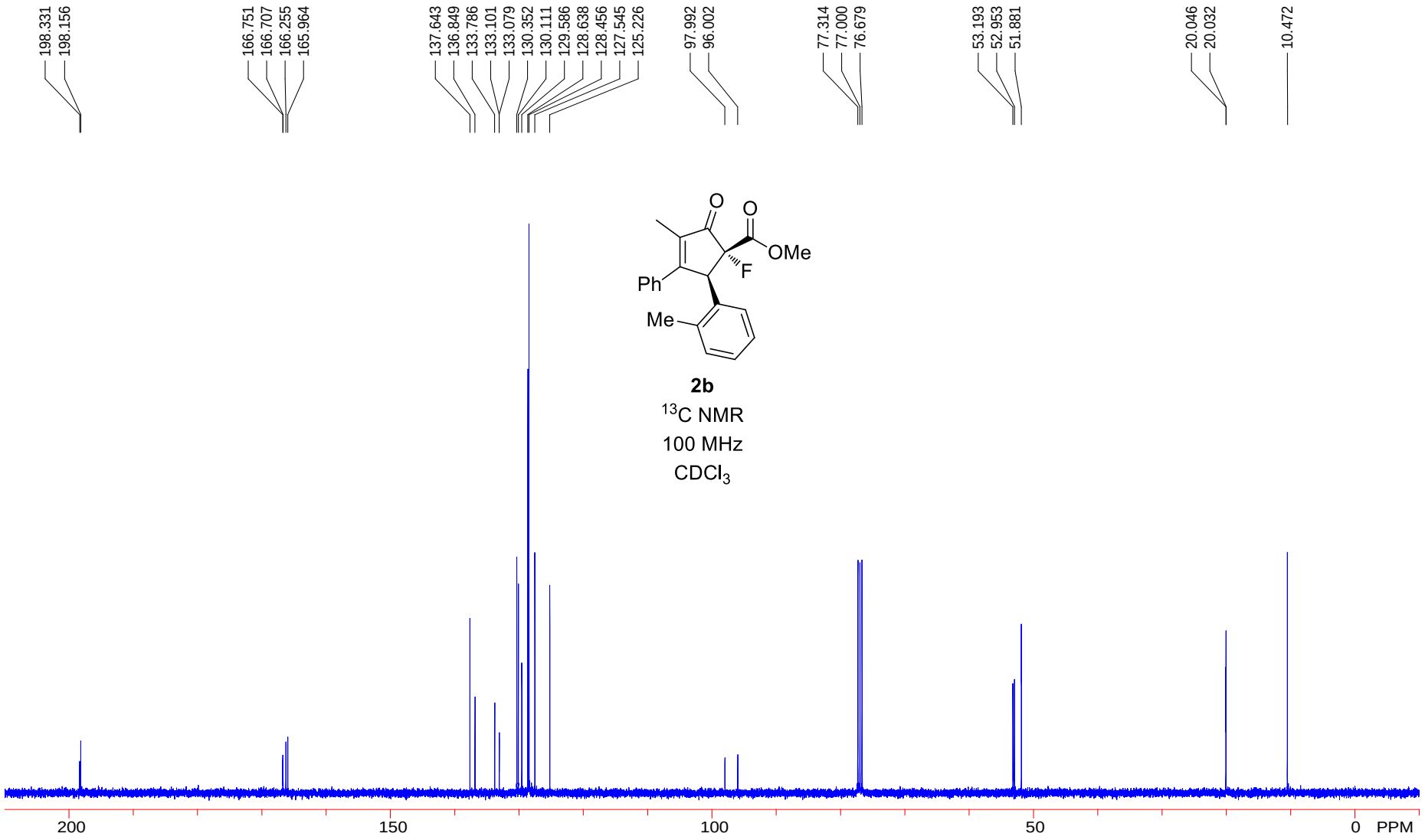
7.381
7.371
7.356
7.344
7.338
7.324
7.309
7.261
7.144
7.126
7.043
7.041
7.024
7.023
7.006
7.004
6.886
6.867
6.848
6.641
6.622
5.149
5.144
5.090
5.085
3.191
2.535
2.179
2.175
0.000
O
O
OMe
F
Ph
Me
2b
1H NMR
400 MHz
CDCl3
5.33
1.08
1.10
1.03
0.97
0.99
3.00
3.04
3.00
8
6
4
2
0
PPM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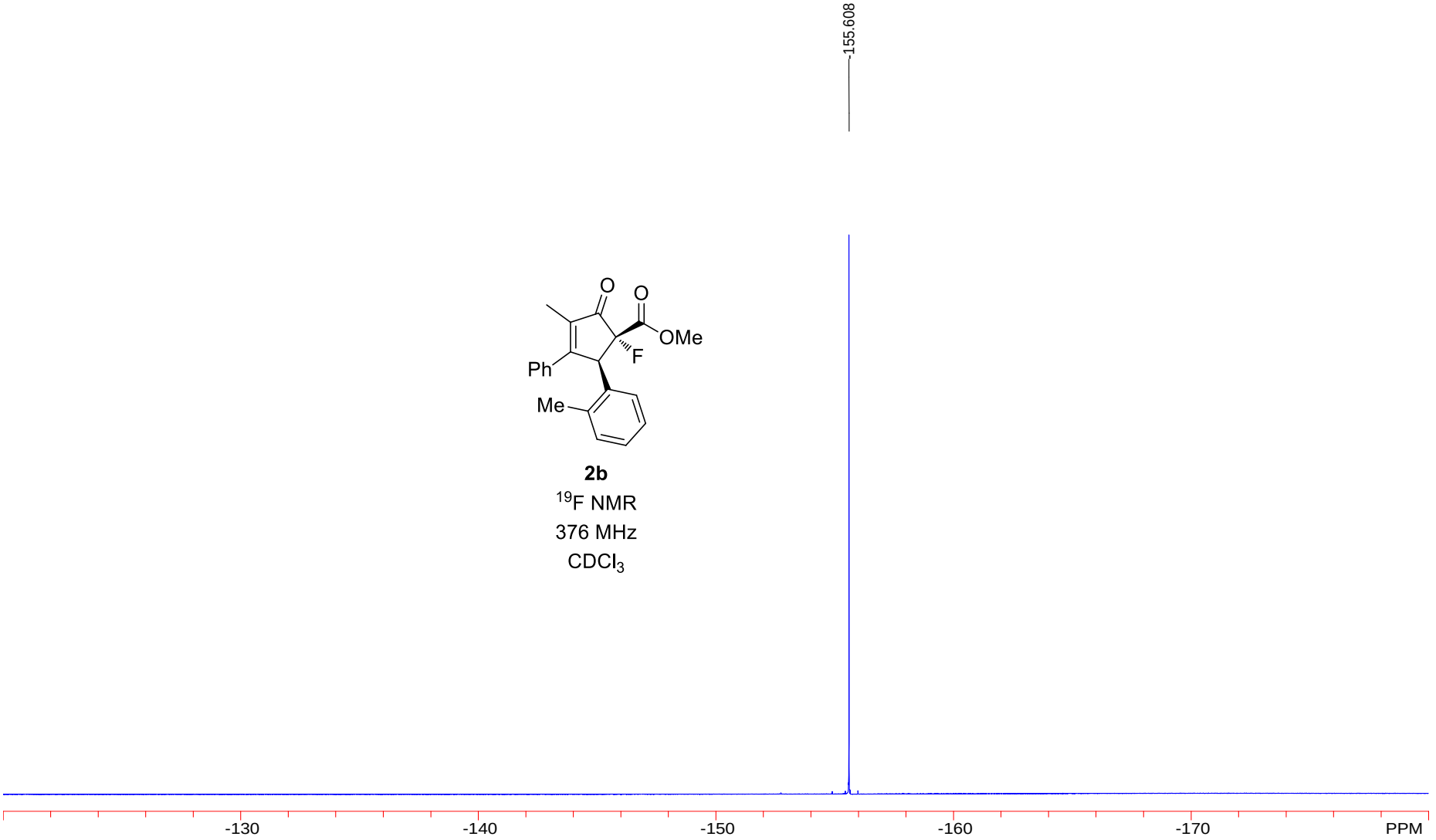
166.707
166.255
165.964
137.643
136.849
133.786
133.101
133.079
130.352
130.111
129.586
128.638
128.456
127.545
125.226
97.992
96.002
77.314
77.000
76.679
53.193
52.953
51.881
20.046
20.032
10.472
O
O
OMe
F
Ph
Me
2b
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

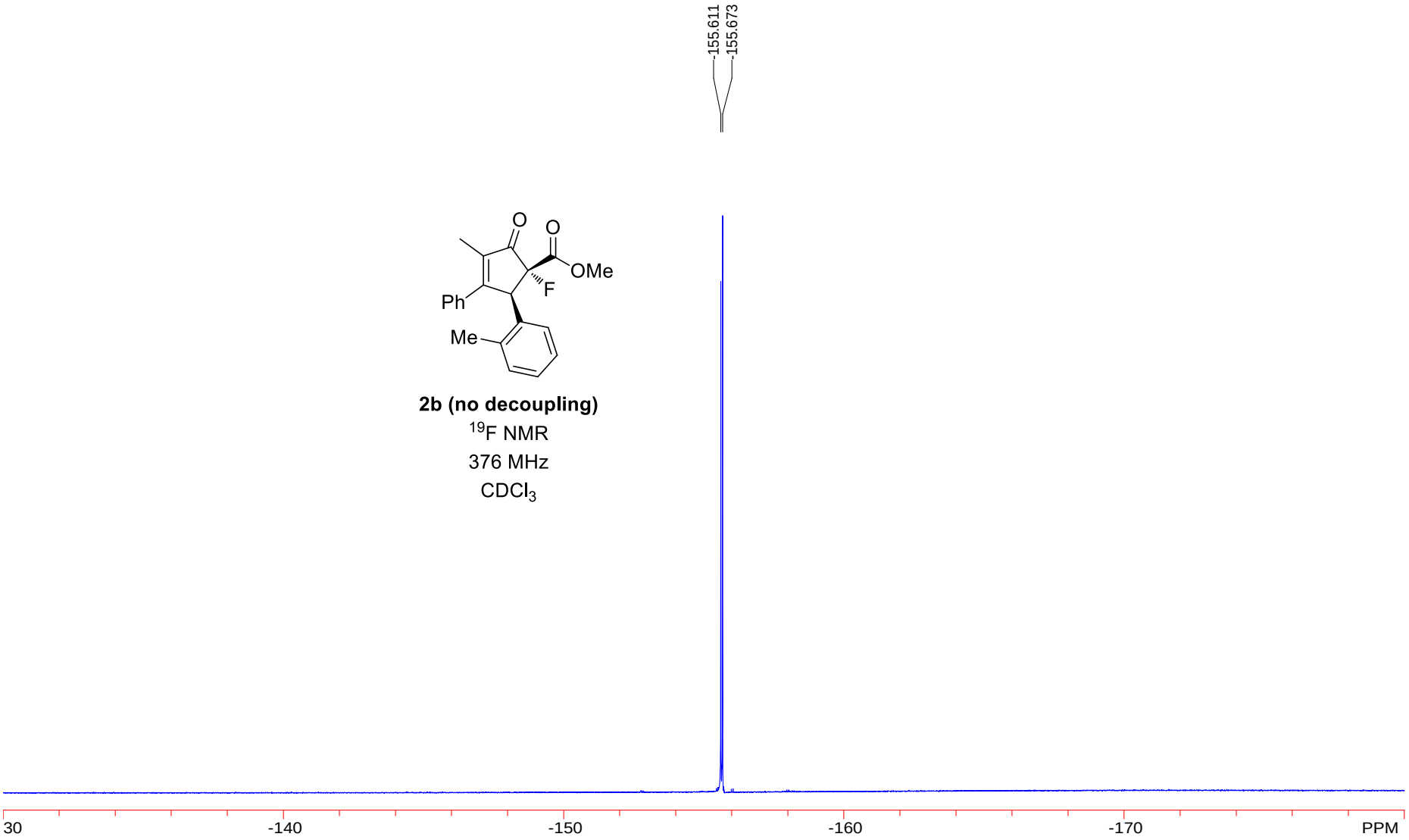


2b

^{19}F NMR

376 MHz

$CDCl_3$

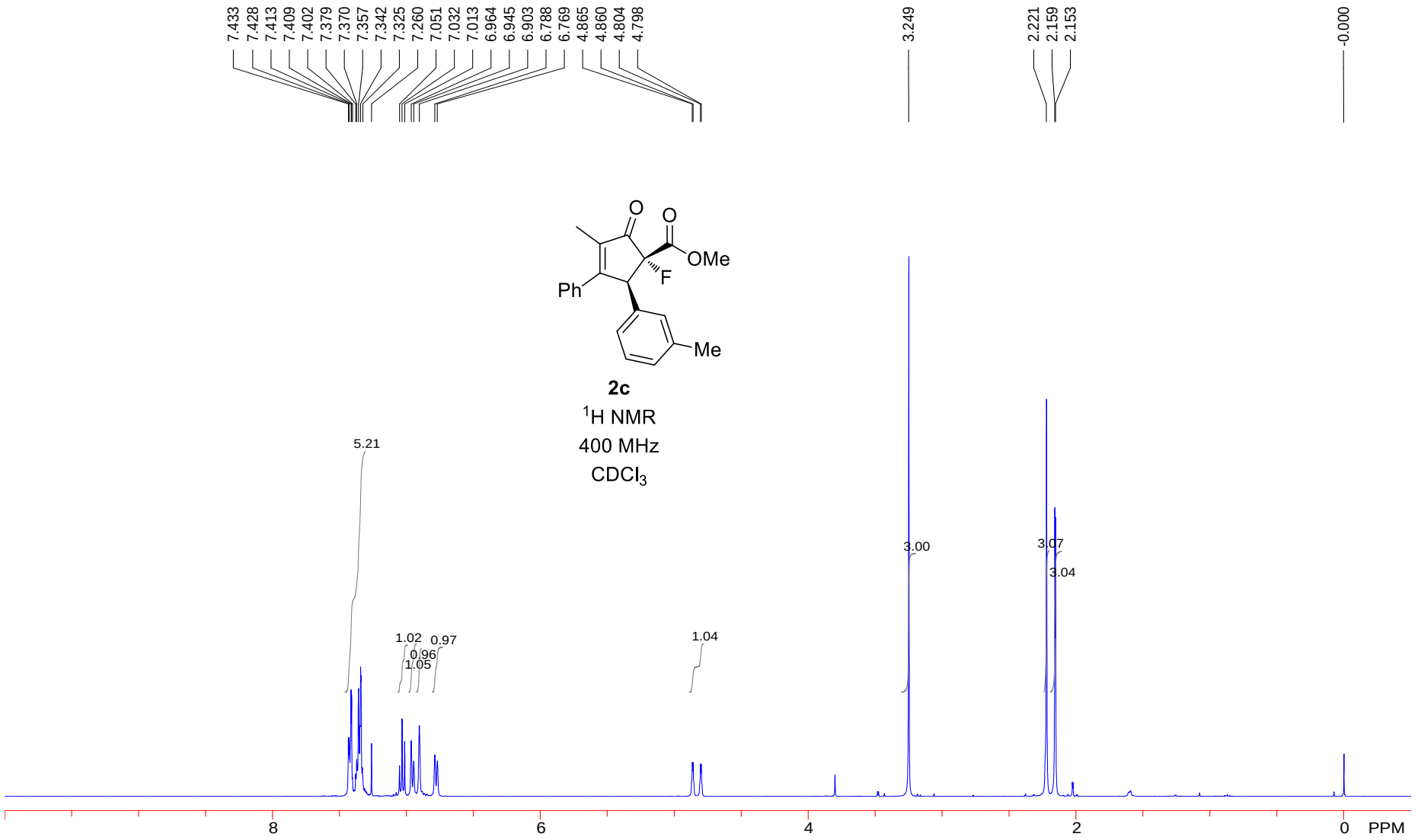


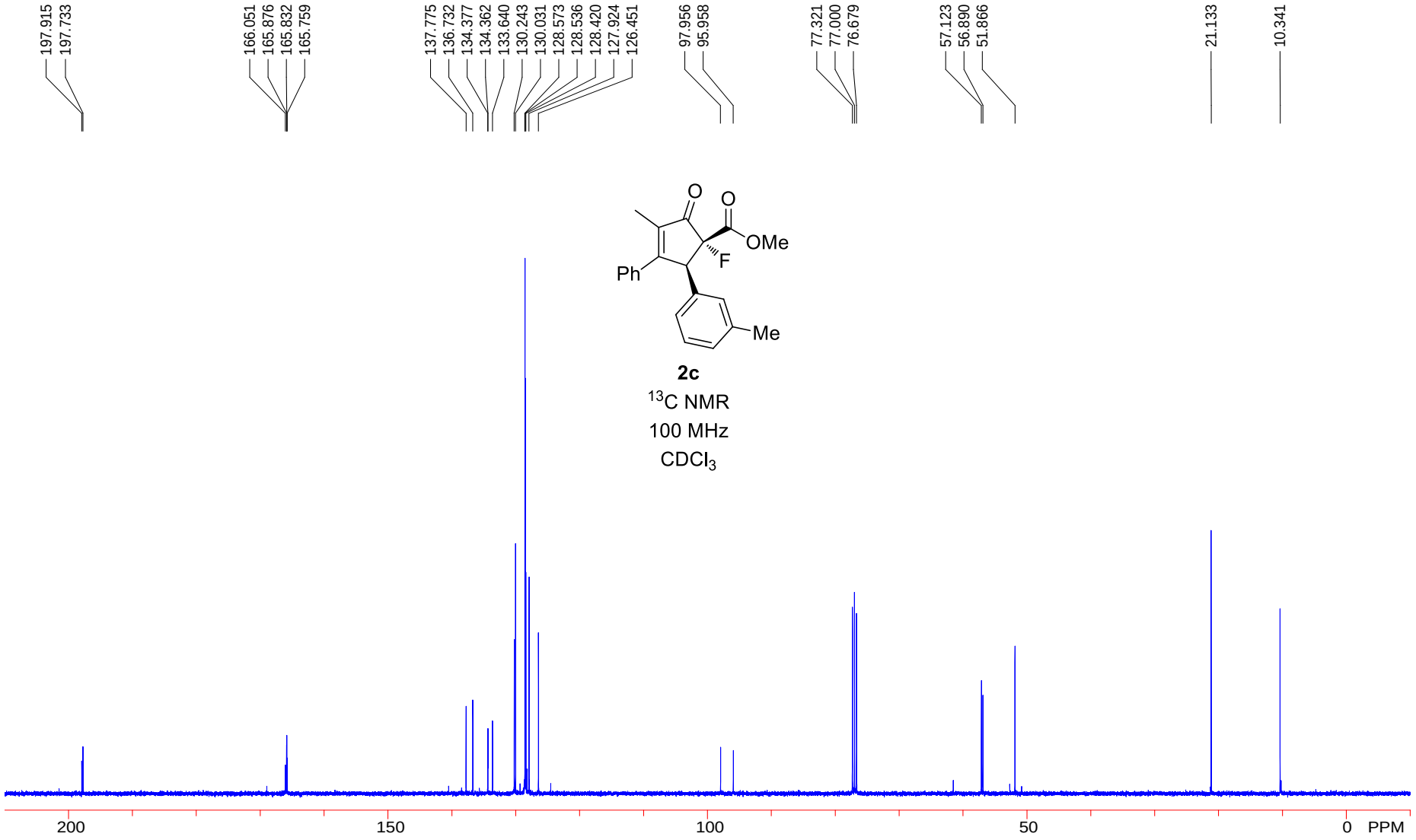
2b (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$


7.433
7.428
7.413
7.409
7.402
7.379
7.370
7.357
7.342
7.325
7.260
7.051
7.032
7.013
6.964
6.945
6.903
6.788
6.769
4.865
4.860
4.804
4.798
3.249
2.221
2.159
2.153
-0.000
O
O
OMe
F
Ph
Me
2c
1H NMR
400 MHz
CDCl3
5.21
1.02
0.96
1.05
0.97
1.04
3.00
3.07
3.04
8
6
4
2
0
PPM

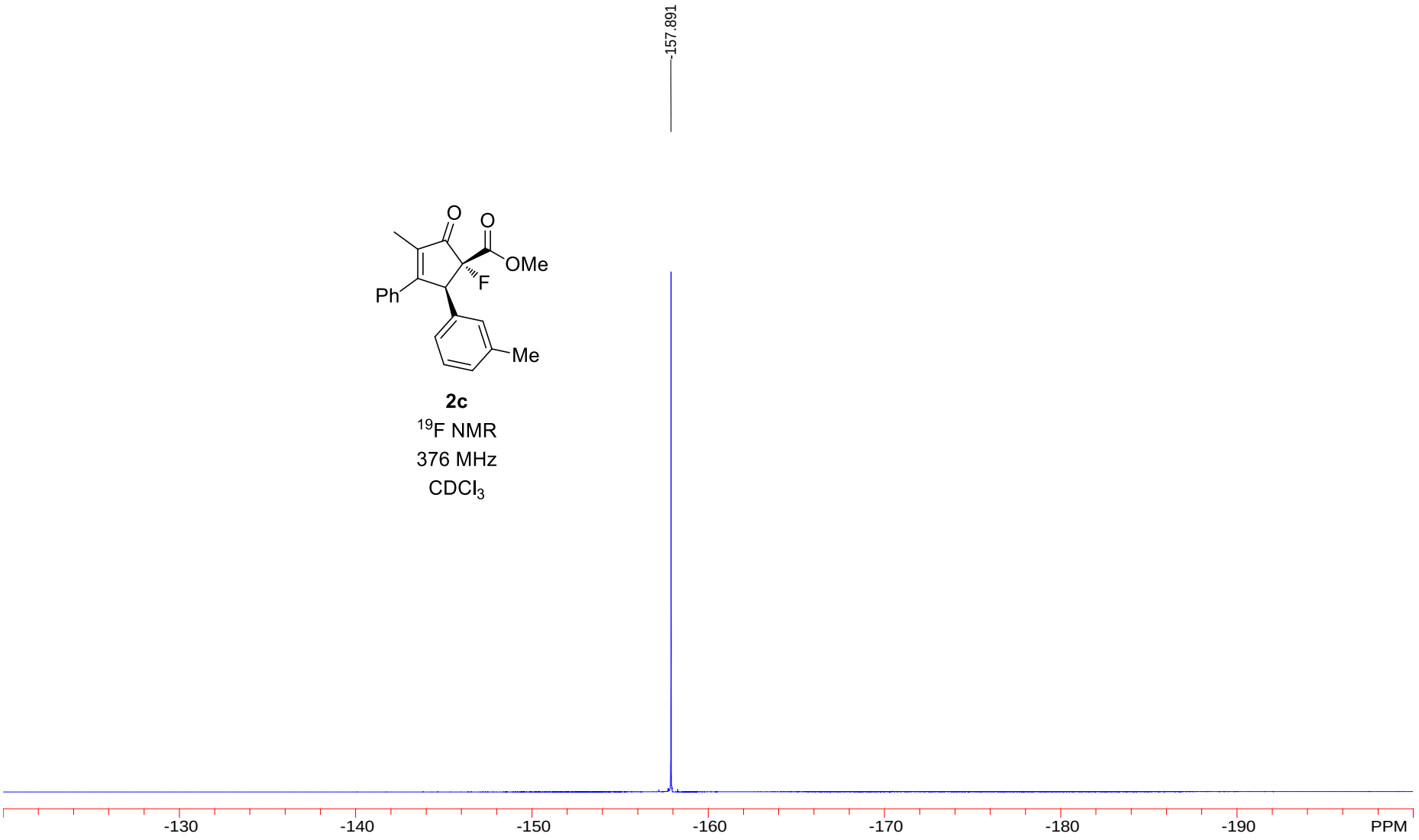

197.915
197.733
166.051
165.876
165.832
165.759
137.775
136.732
134.377
134.362
133.640
130.243
130.031
128.573
128.536
128.420
127.924
126.451
97.956
95.958
77.321
77.000
76.679
57.123
56.890
51.866
21.133
10.341
O
O
OMe
F
Ph
Me
2c
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

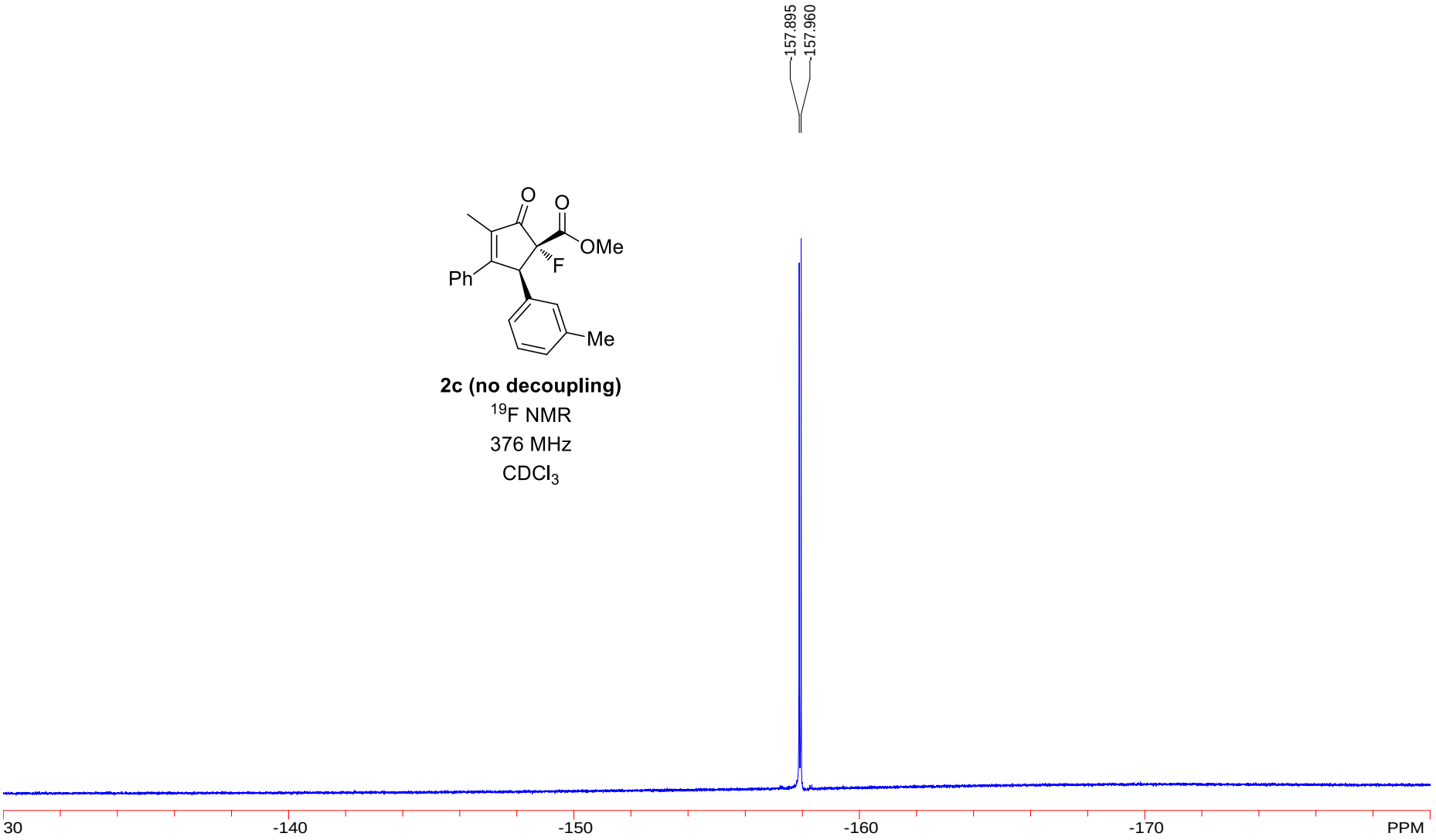
2c

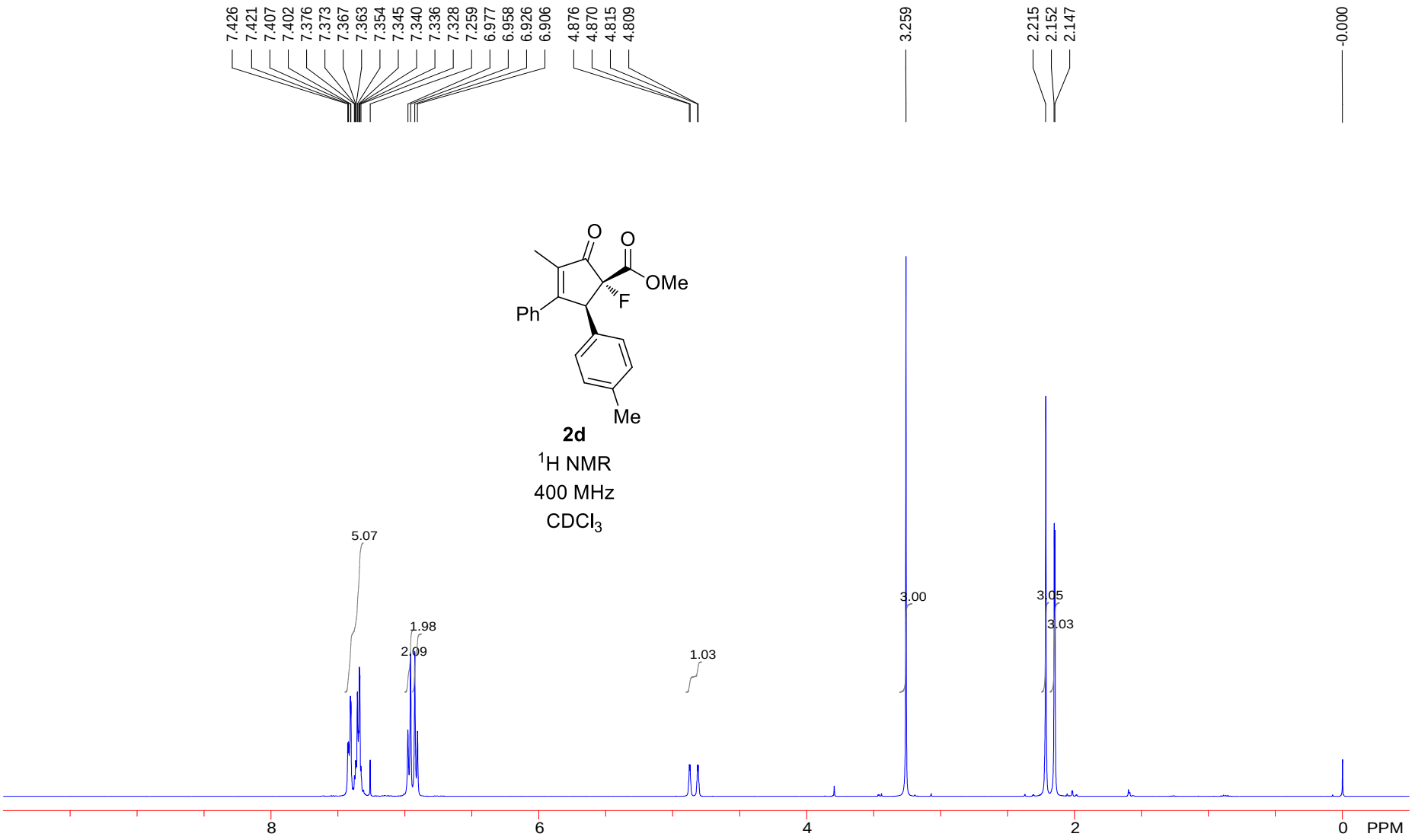
^{19}F NMR

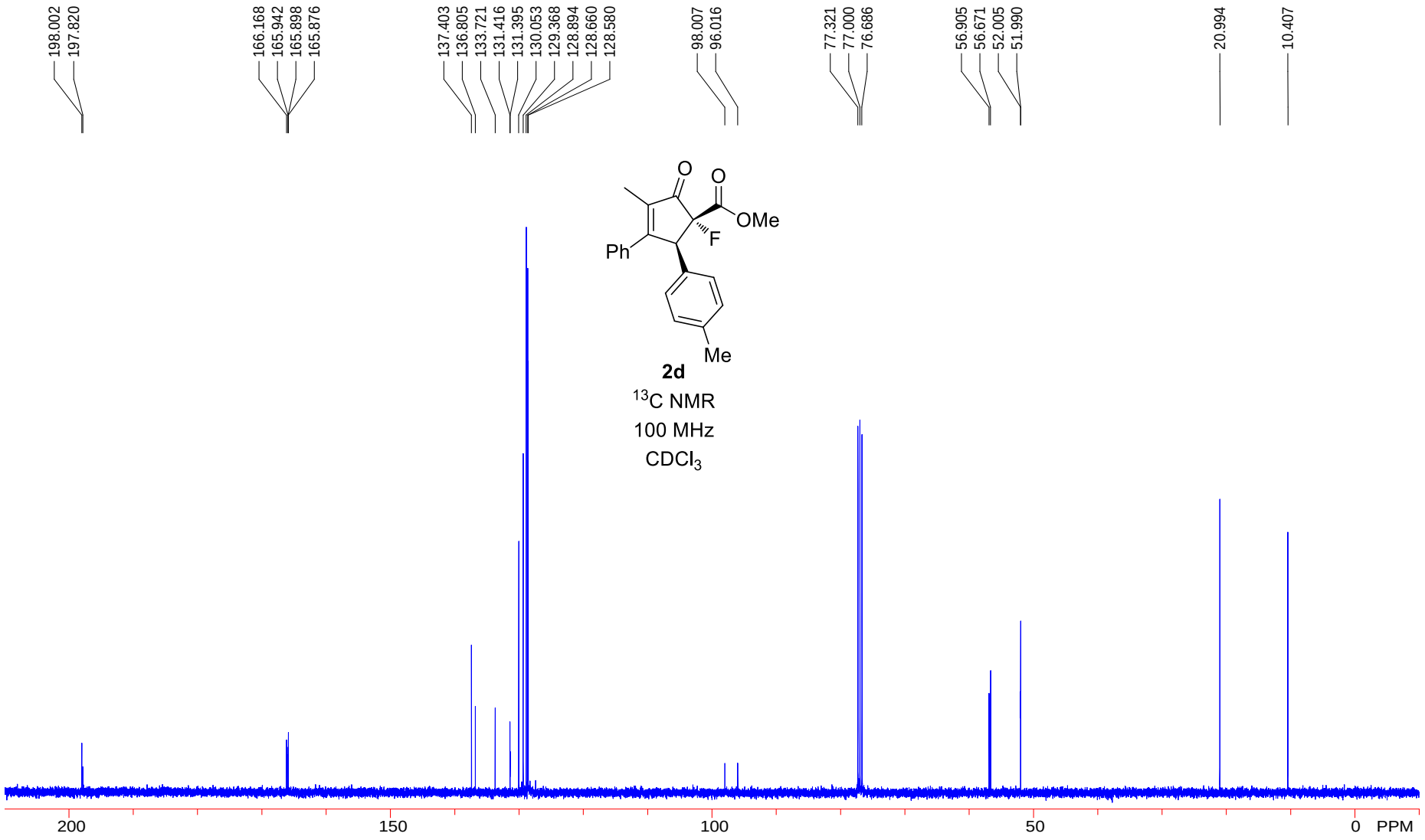
376 MHz

$CDCl_3$




157.895
157.960
O
O
OMe
F
Ph
Me
2c (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.426
7.421
7.407
7.402
7.376
7.373
7.367
7.363
7.354
7.345
7.340
7.336
7.328
7.259
6.977
6.958
6.926
6.906
4.876
4.870
4.815
4.809
3.259
2.215
2.152
2.147
-0.000
O
O
OMe
F
Ph
Me
2d
1H NMR
400 MHz
CDCl3
5.07
1.98
2.09
1.03
3.00
3.05
3.03
8
6
4
2
0
PPM

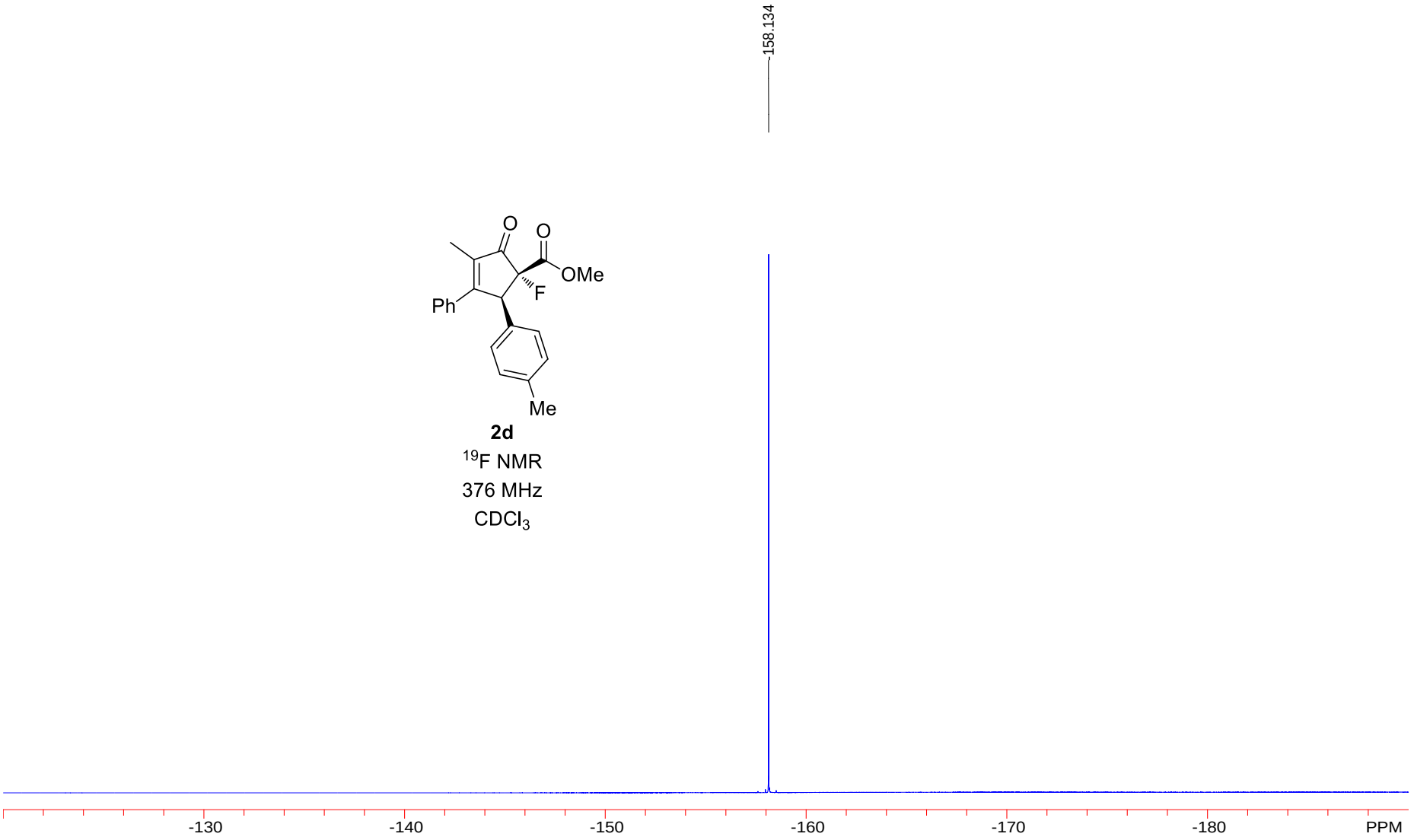

198.002
197.820
166.168
165.942
165.898
165.876
137.403
136.805
133.721
131.416
131.395
130.053
129.368
128.894
128.660
128.580
98.007
96.016
77.321
77.000
76.686
56.905
56.671
52.005
51.990
20.994
10.407
O
O
OMe
F
Ph
Me
2d
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

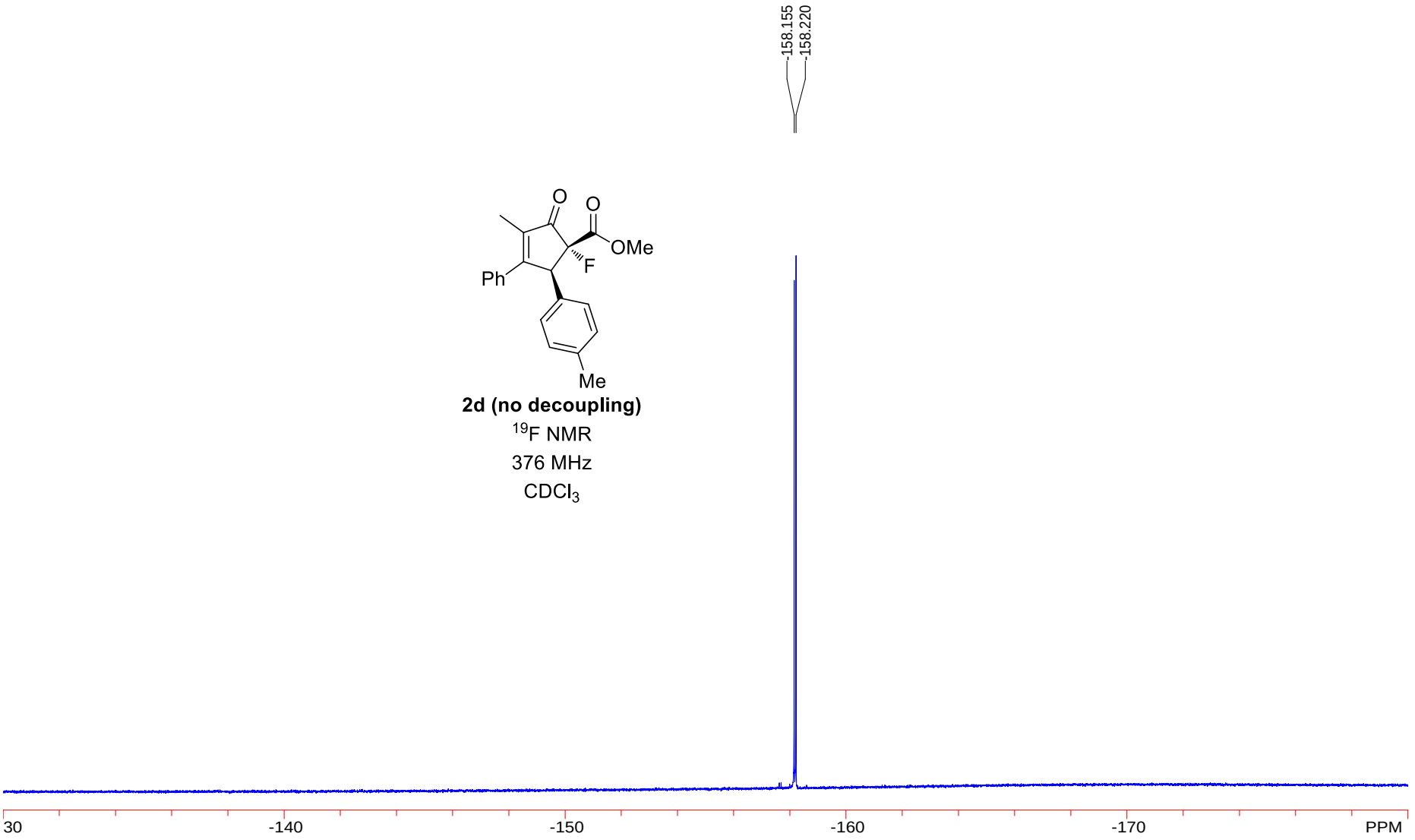
2d

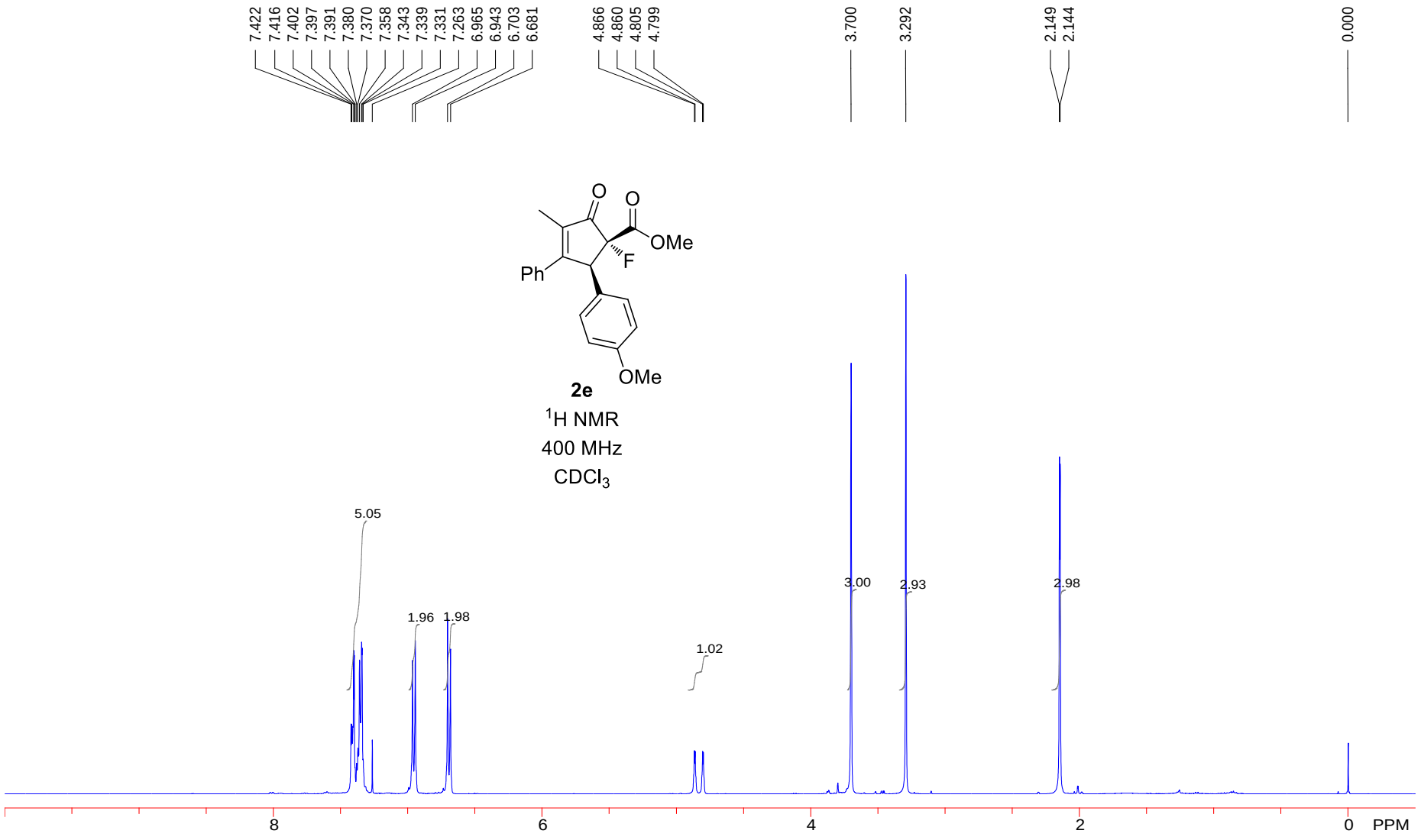
^{19}F NMR

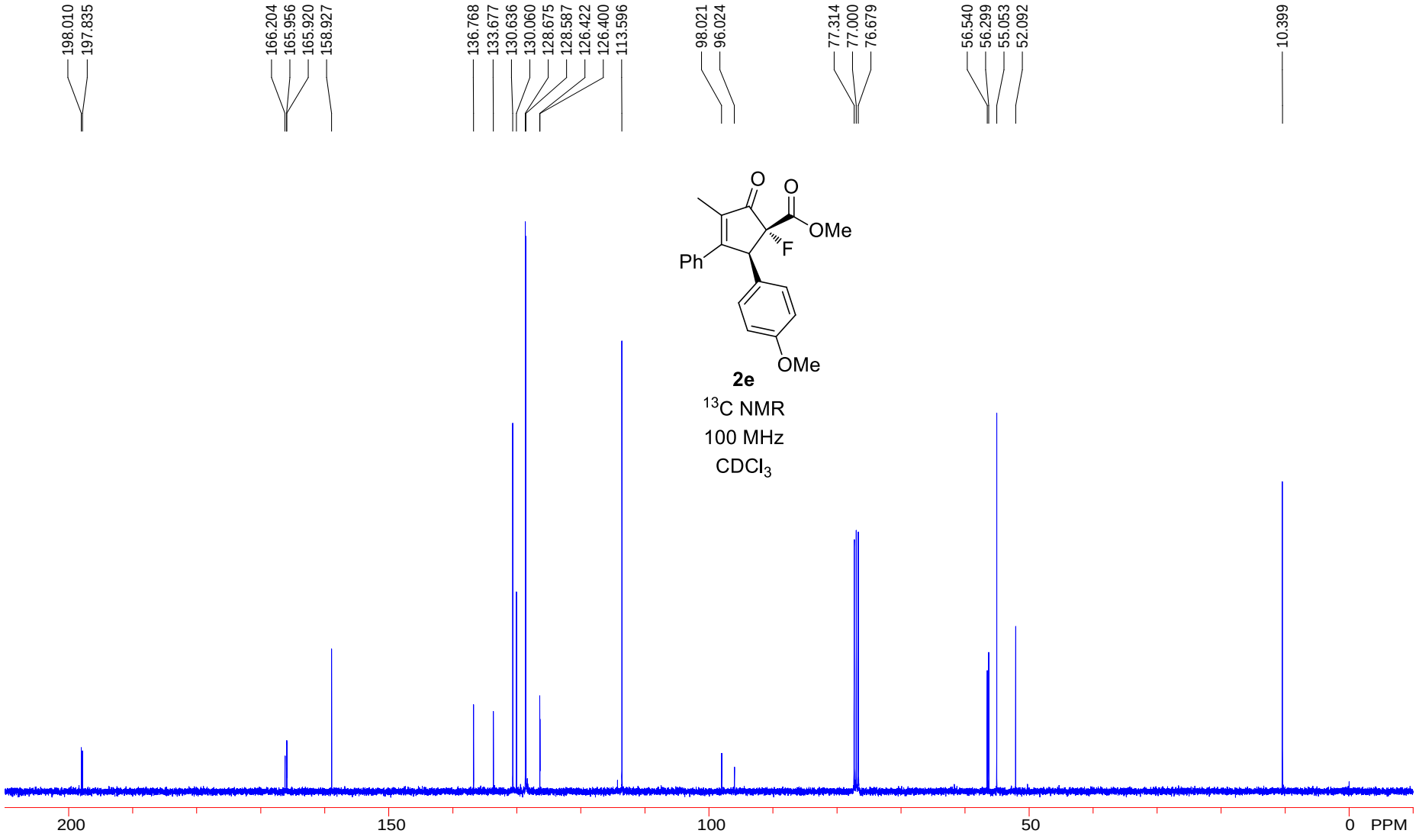
376 MHz

$CDCl_3$




158.155
158.220
O
O
OMe
F
Ph
Me
2d (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.422
7.416
7.402
7.397
7.391
7.380
7.370
7.358
7.343
7.339
7.331
7.263
6.965
6.943
6.703
6.681
4.866
4.860
4.805
4.799
3.700
3.292
2.149
2.144
0.000
O
O
OMe
F
Ph
OMe
2e
1H NMR
400 MHz
CDCl3
5.05
1.96
1.98
1.02
3.00
2.93
2.98
8
6
4
2
0
PPM

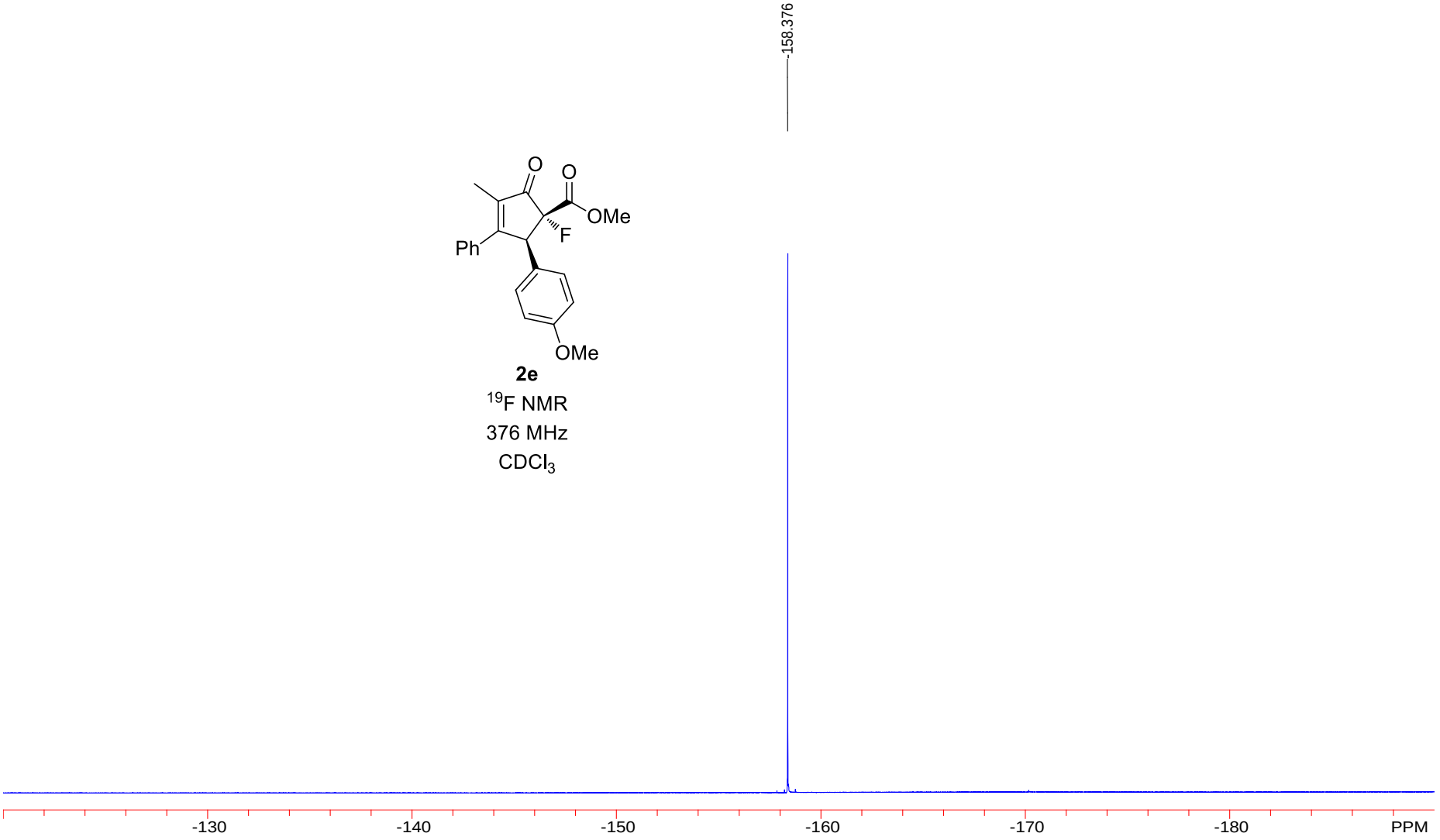

198.010
197.835
166.204
165.956
165.920
158.927
136.768
133.677
130.636
130.060
128.675
128.587
126.422
126.400
113.596
98.021
96.024
77.314
77.000
76.679
56.540
56.299
55.053
52.092
10.399
O
O
OMe
F
Ph
OMe
2e
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

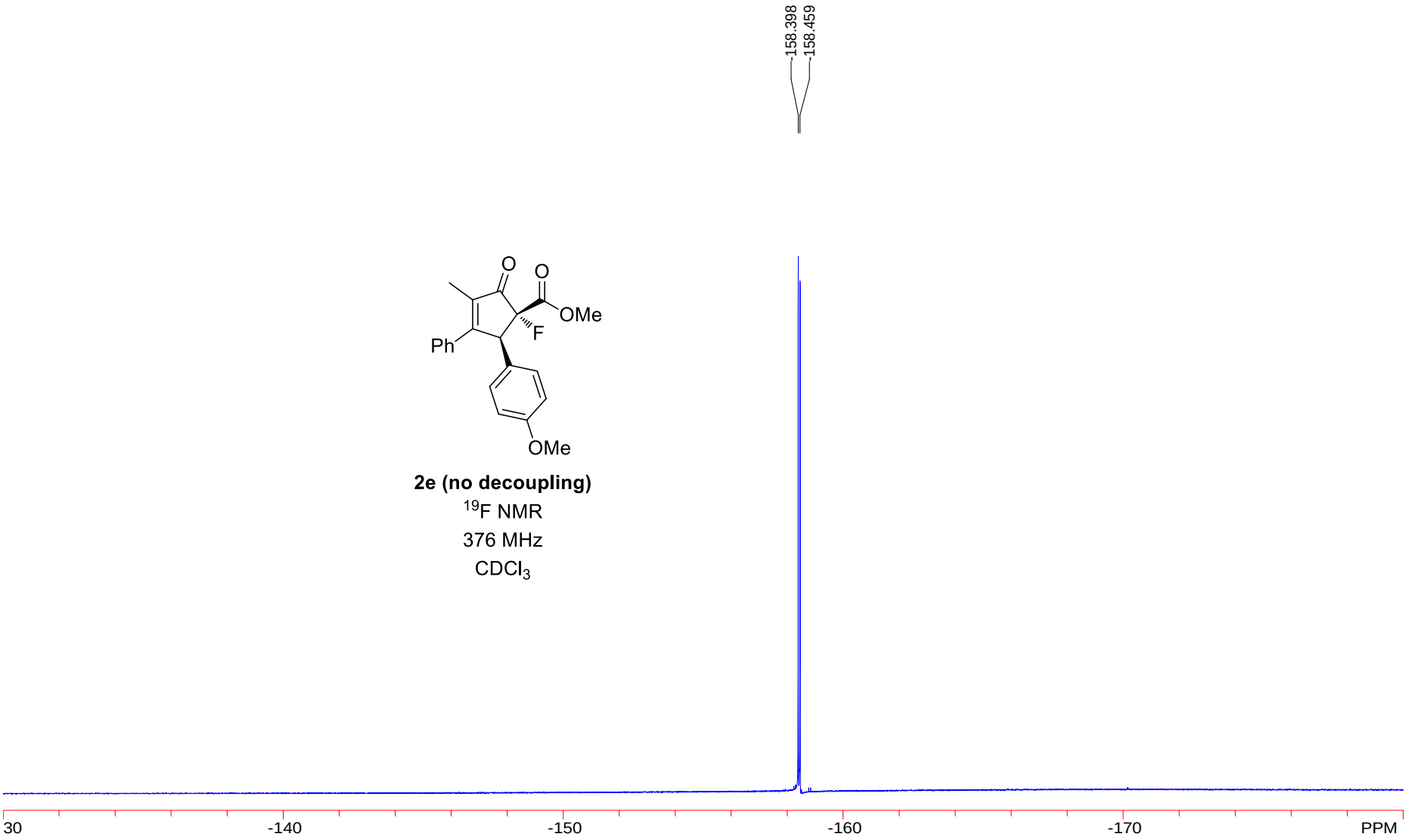
2e

^{19}F NMR

376 MHz

$CDCl_3$



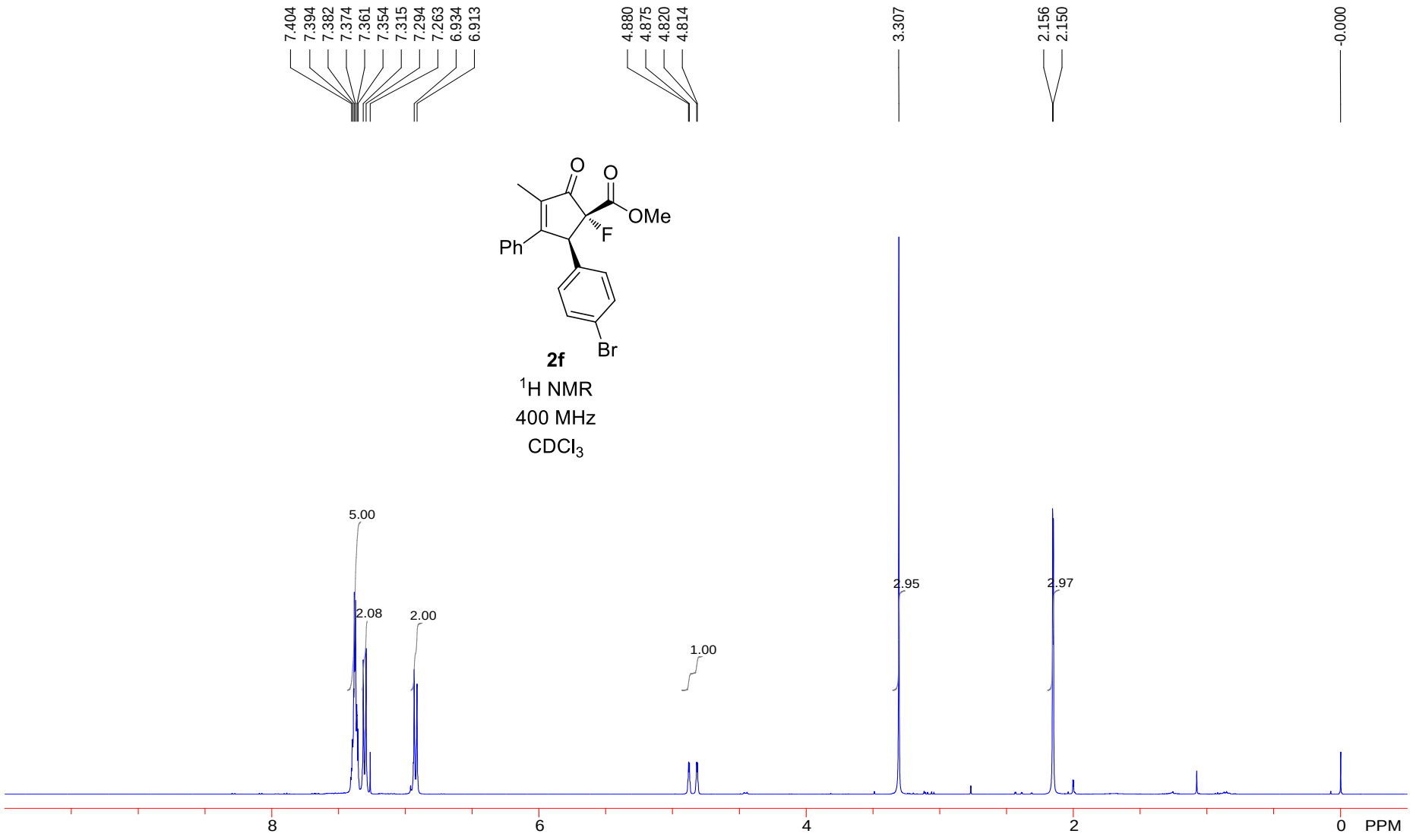


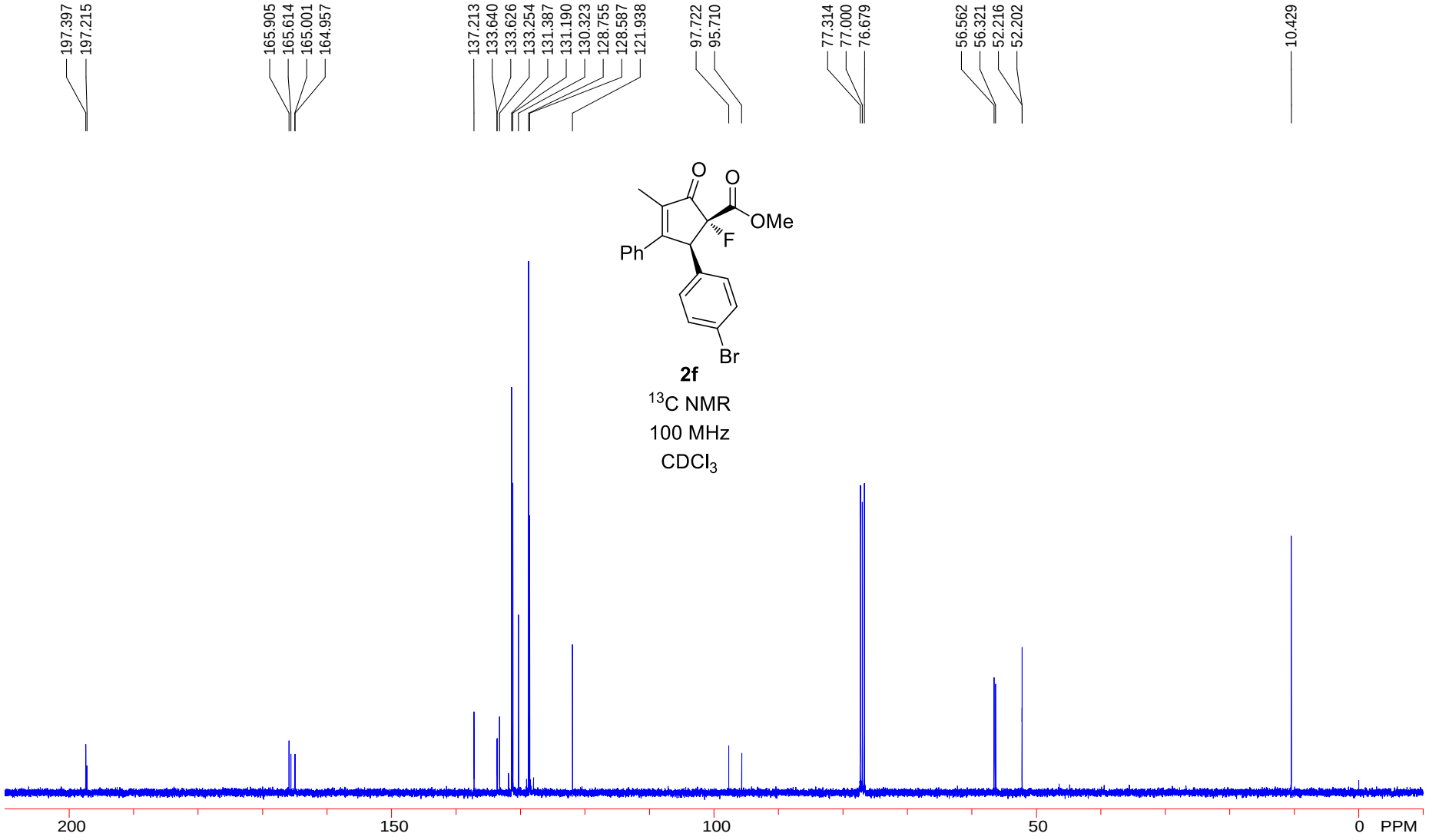
2e (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$


7.404
7.394
7.382
7.374
7.361
7.354
7.315
7.294
7.263
6.934
6.913
4.880
4.875
4.820
4.814
3.307
2.156
2.150
-0.000
O
O
OMe
F
Ph
Br
2f
1H NMR
400 MHz
CDCl3
5.00
2.08
2.00
1.00
2.95
2.97
8
6
4
2
0
PPM

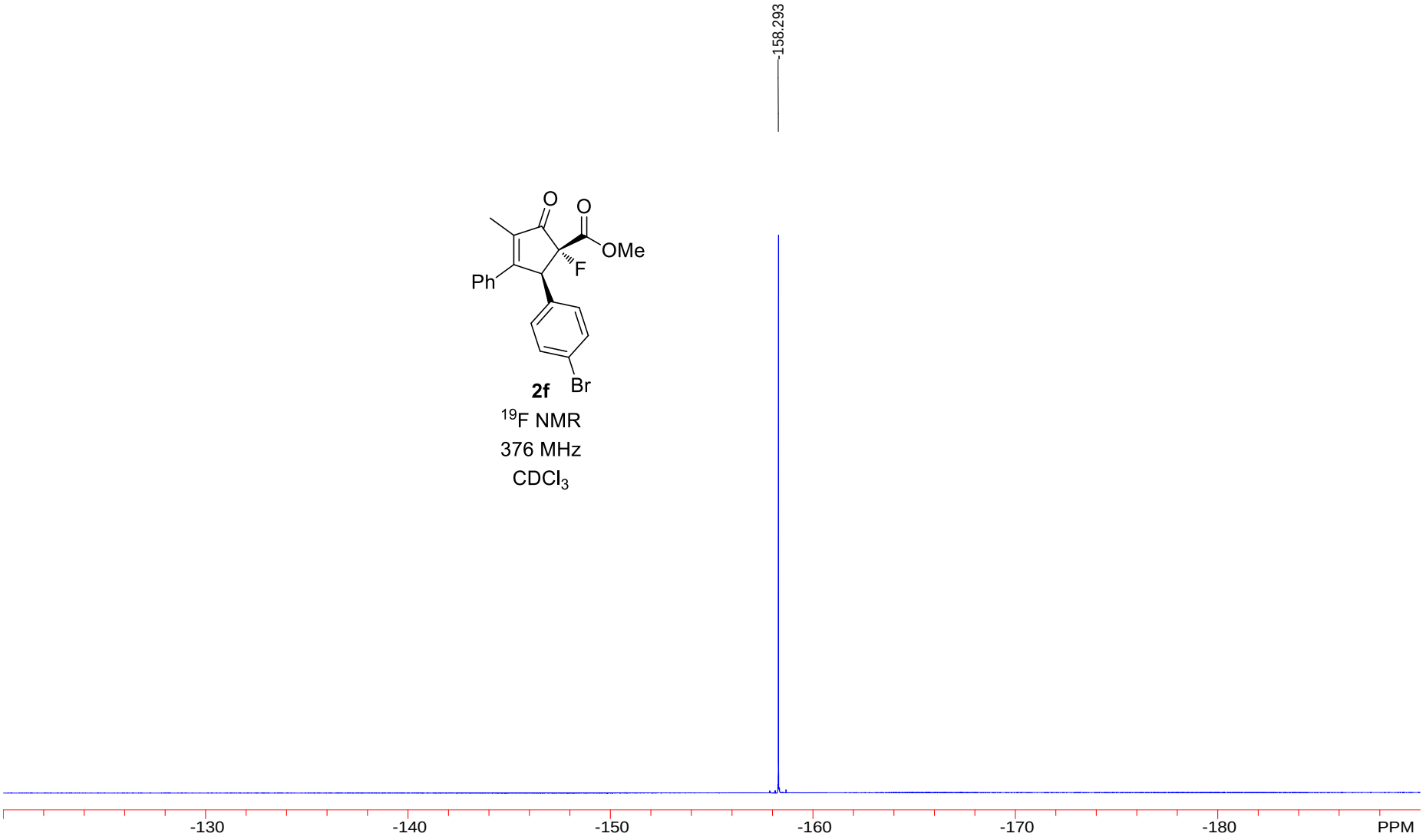

197.397
197.215
165.905
165.614
165.001
164.957
137.213
133.640
133.626
133.254
131.387
131.190
130.323
128.755
128.587
121.938
97.722
95.710
77.314
77.000
76.679
56.562
56.321
52.216
52.202
10.429
O
O
OMe
F
Ph
Br
2f
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

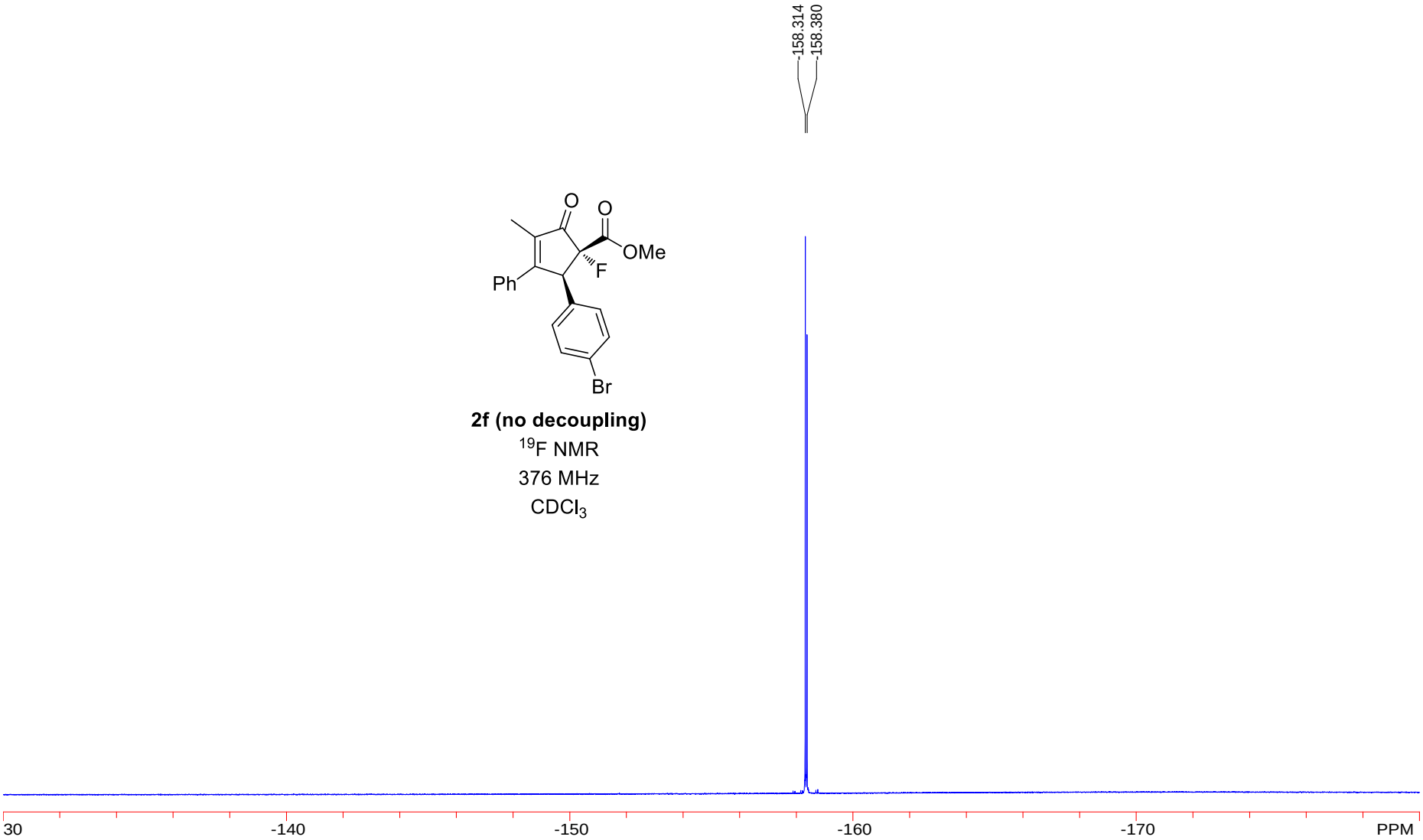
2f

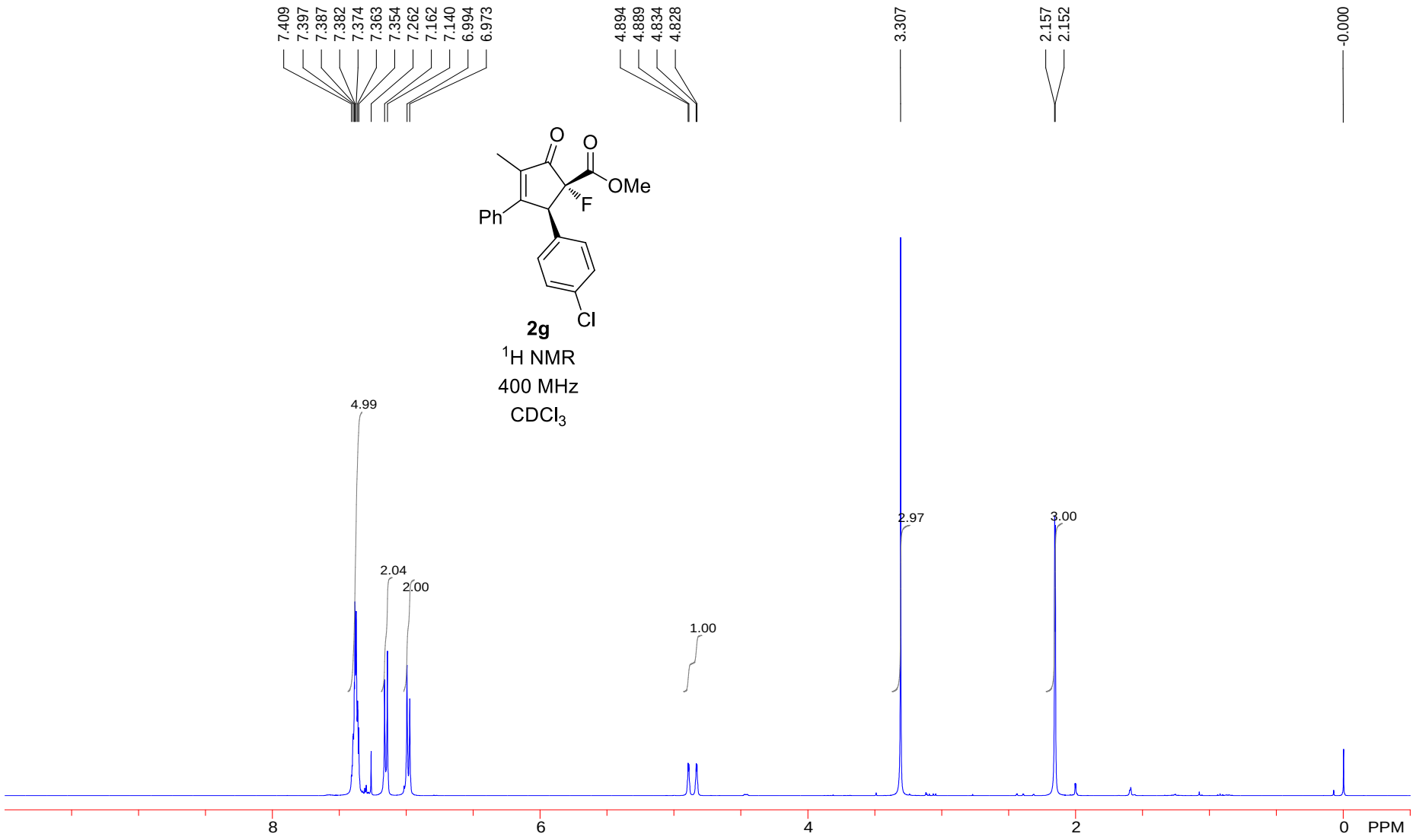
^{19}F NMR

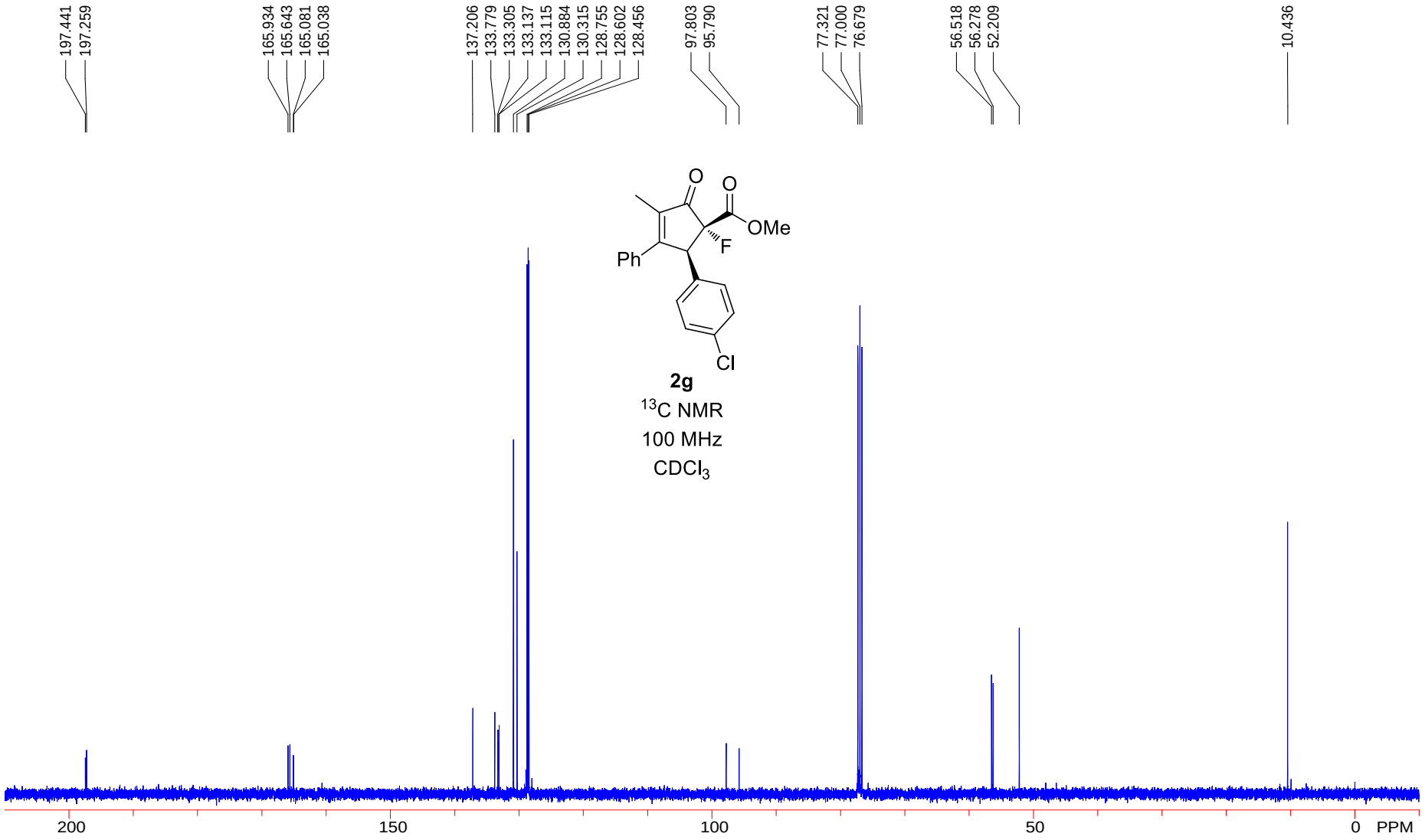
376 MHz

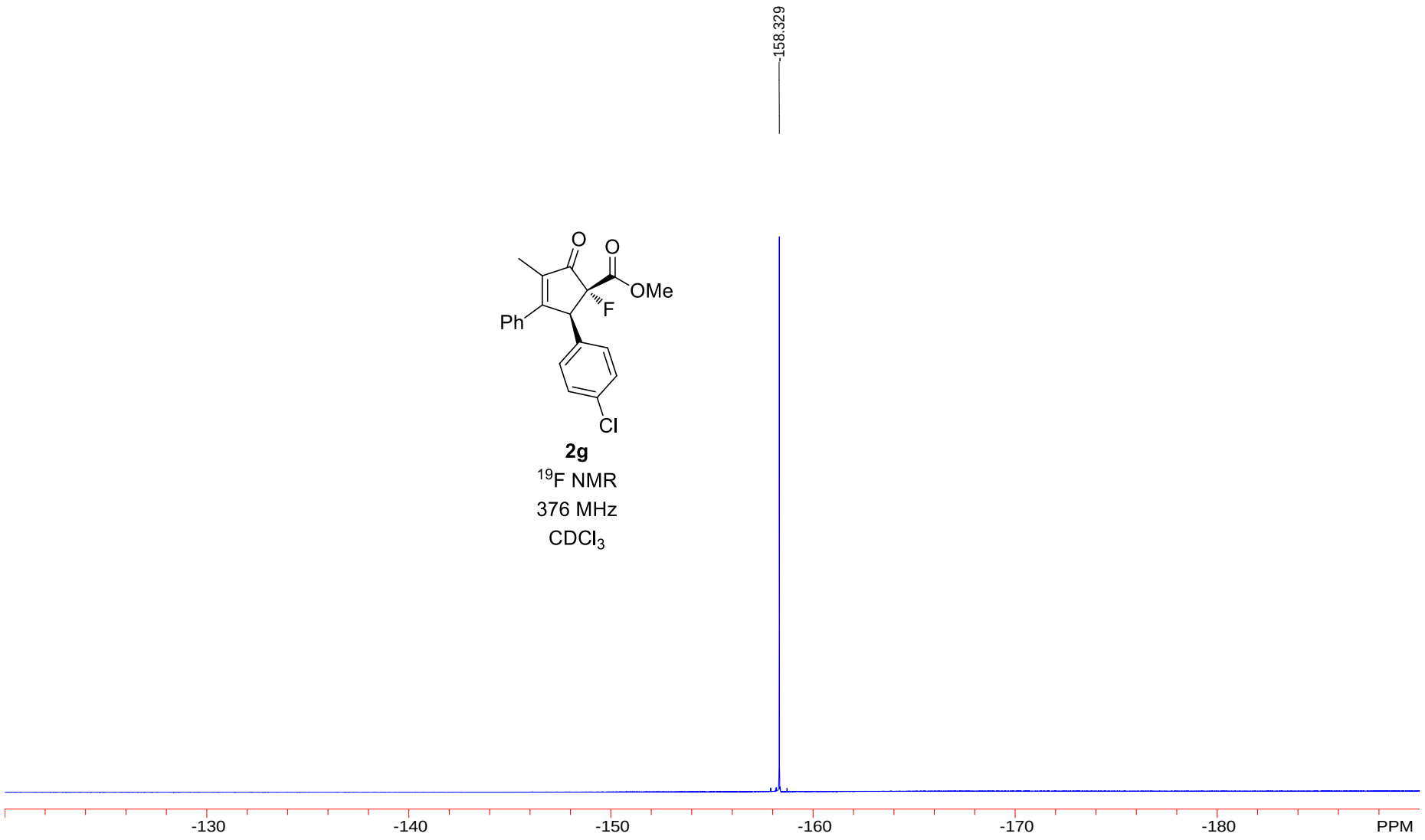
$CDCl_3$




158.314
158.380
O
O
OMe
F
Ph
Br
2f (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.409
7.397
7.387
7.382
7.374
7.363
7.354
7.262
7.162
7.140
6.994
6.973
4.894
4.889
4.834
4.828
3.307
2.157
2.152
-0.000
O
O
OMe
F
Ph
Cl
2g
1H NMR
400 MHz
CDCl3
4.99
2.04
2.00
1.00
2.97
3.00
8
6
4
2
0
PPM


197.441
197.259
165.934
165.643
165.081
165.038
137.206
133.779
133.305
133.137
133.115
130.884
130.315
128.755
128.602
128.456
97.803
95.790
77.321
77.000
76.679
56.518
56.278
52.209
10.436
O
O
OMe
F
Ph
Cl
2g
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

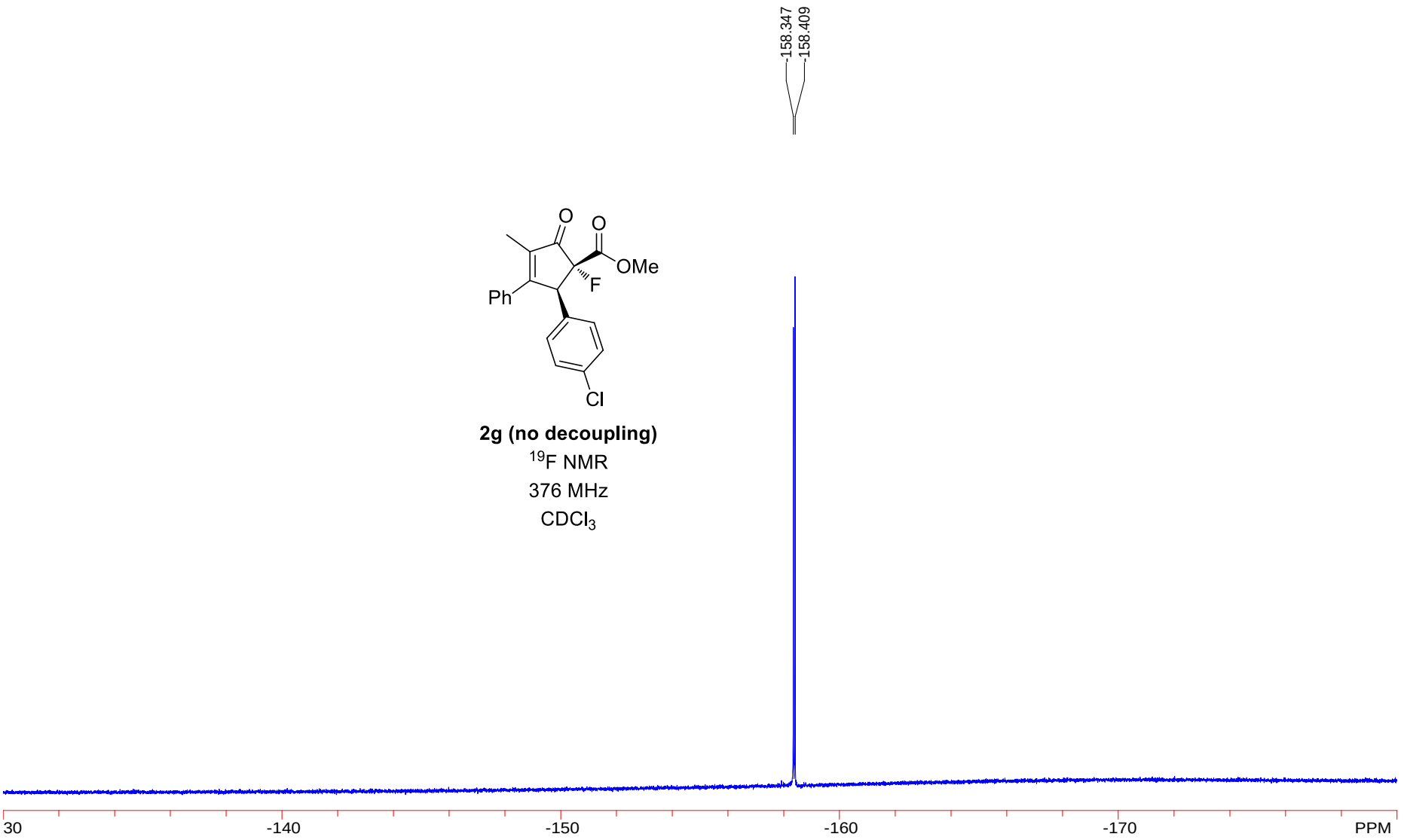


2g

^{19}F NMR

376 MHz

$CDCl_3$

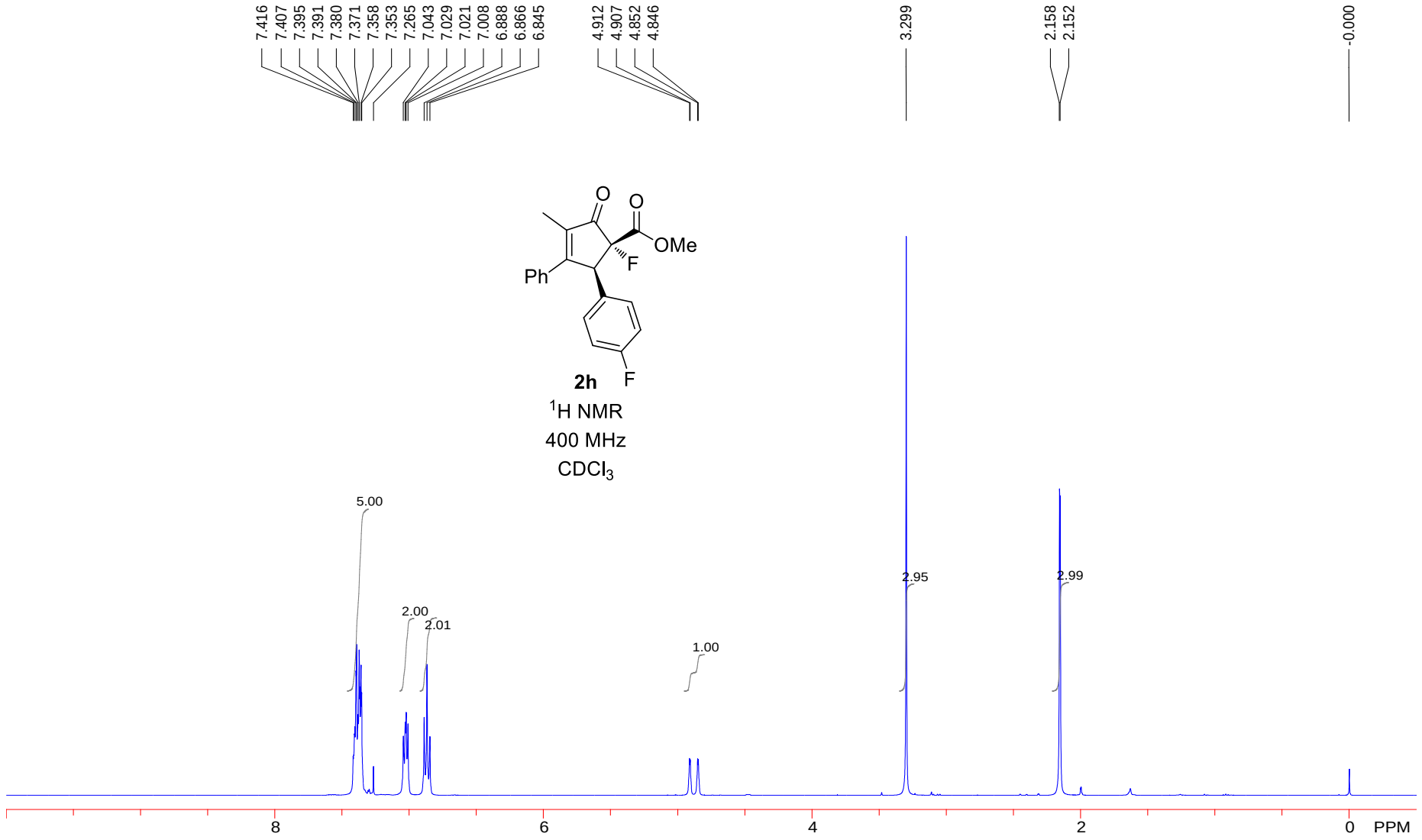


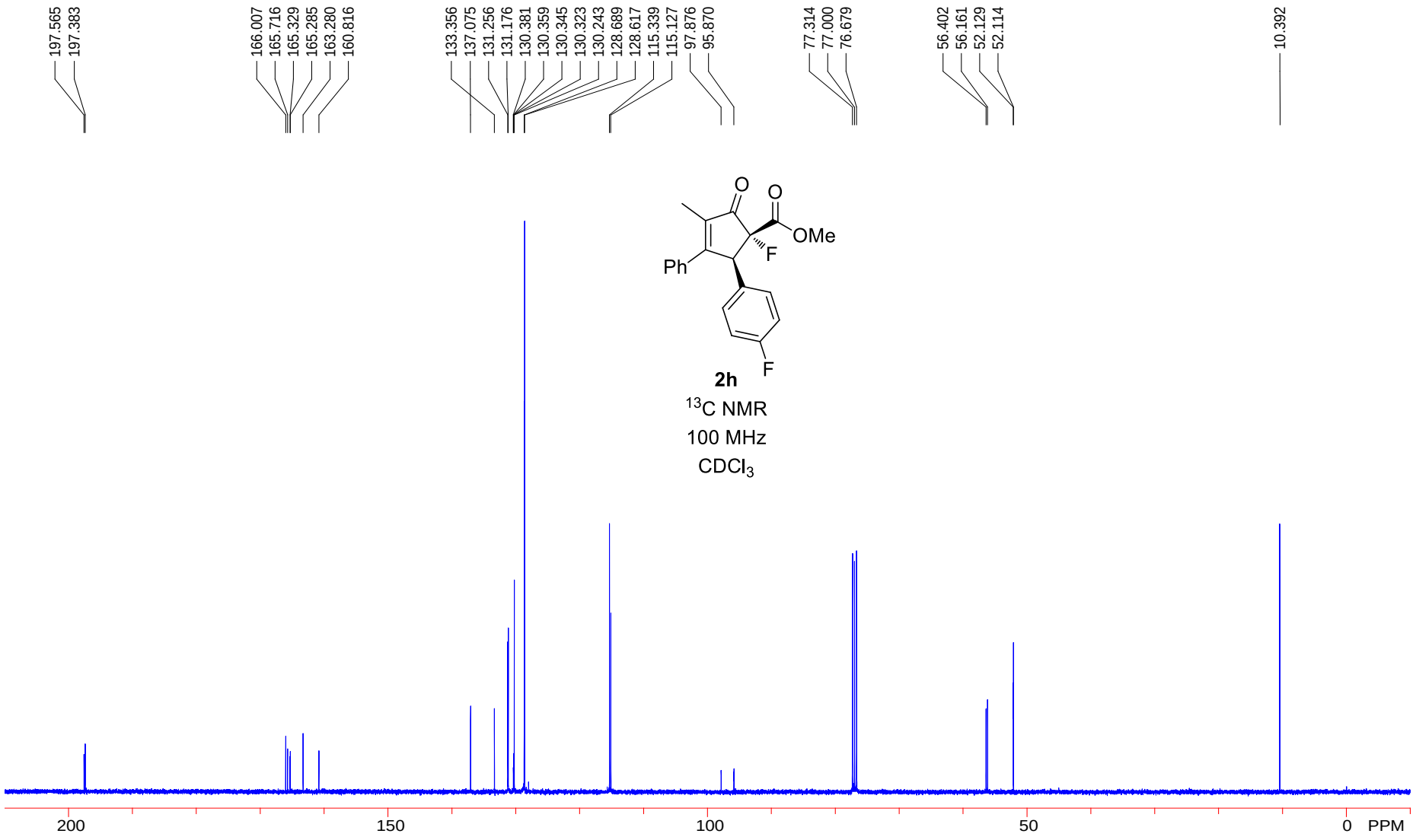
2g (no decoupling)

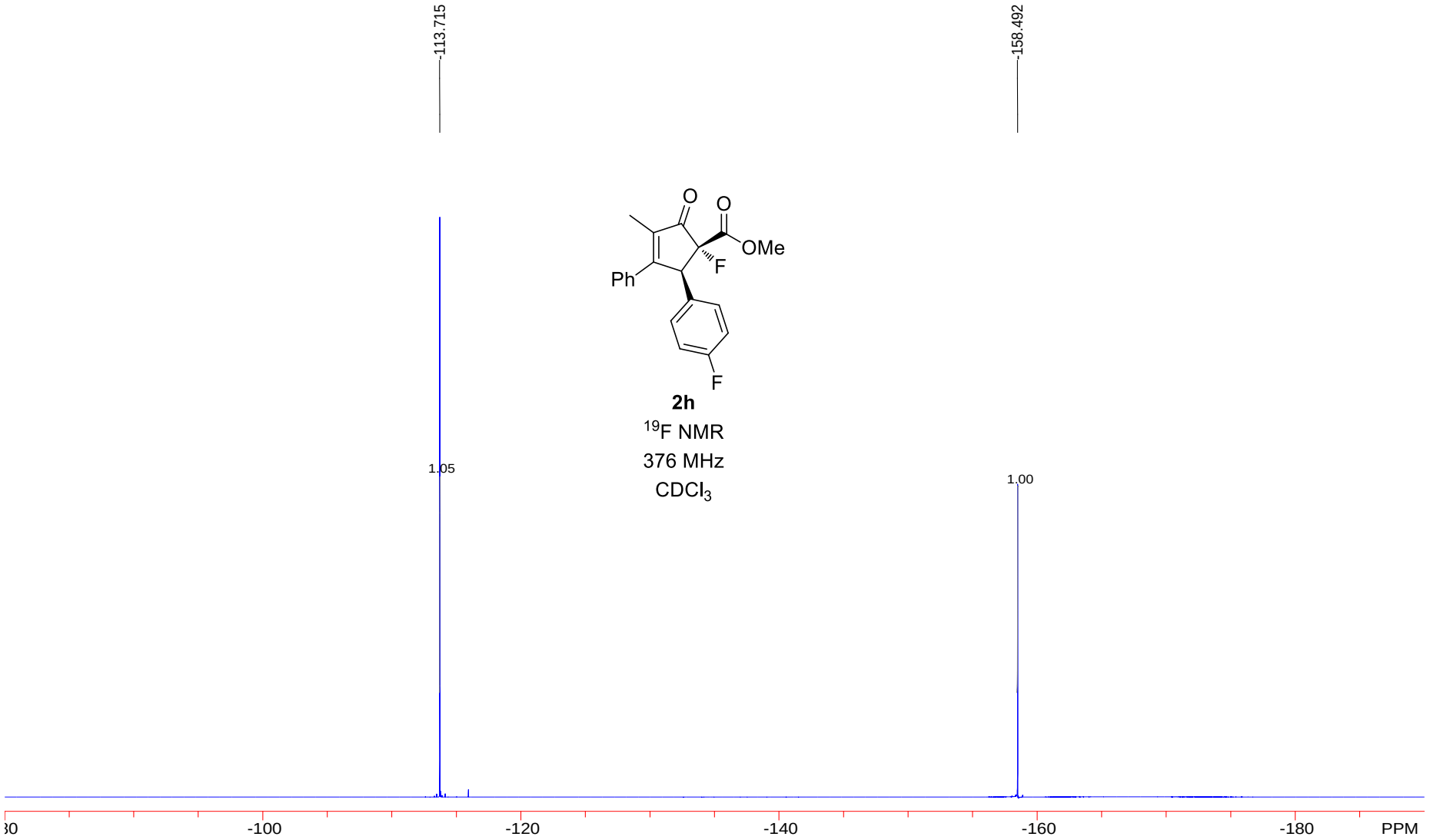
^{19}F NMR

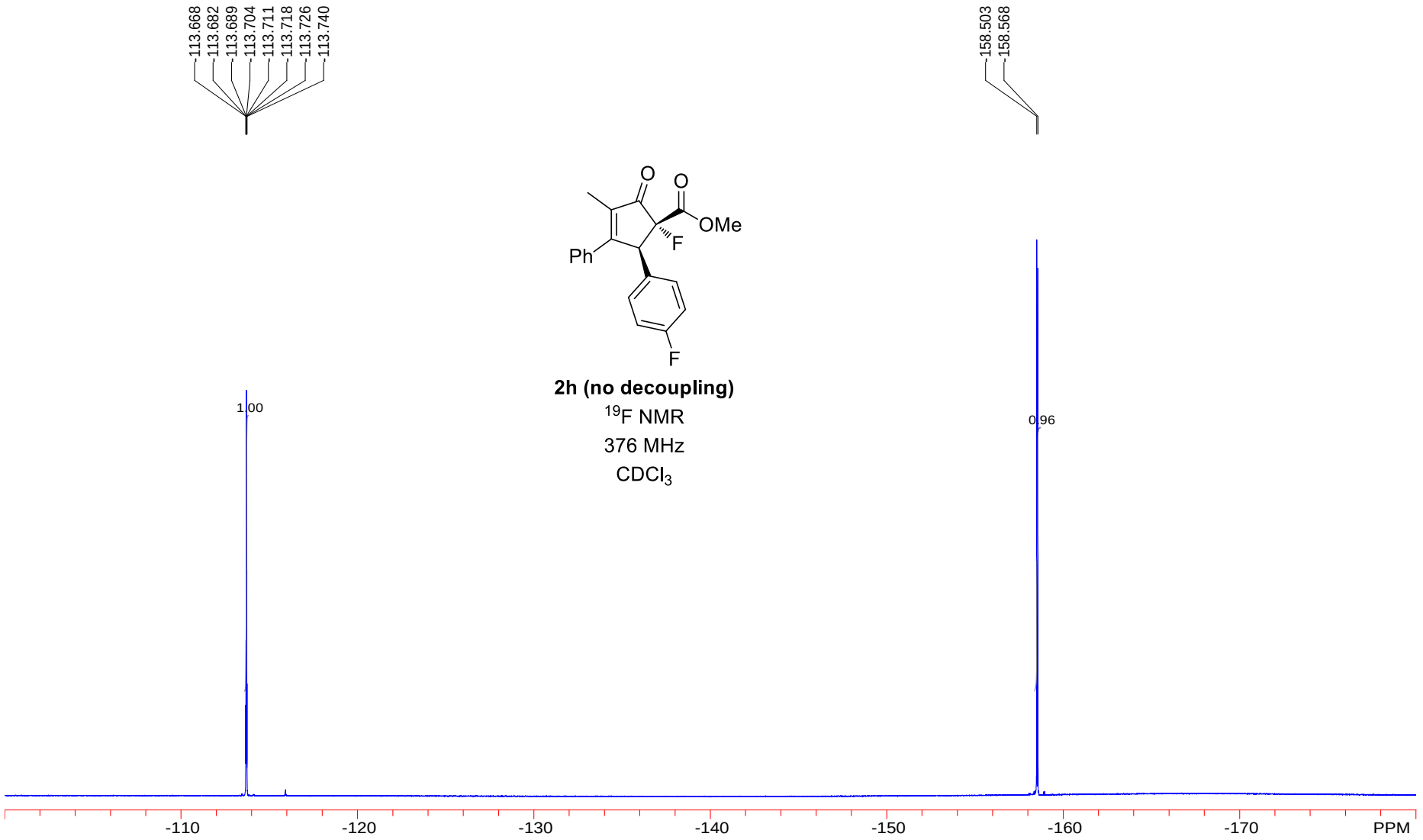
376 MHz

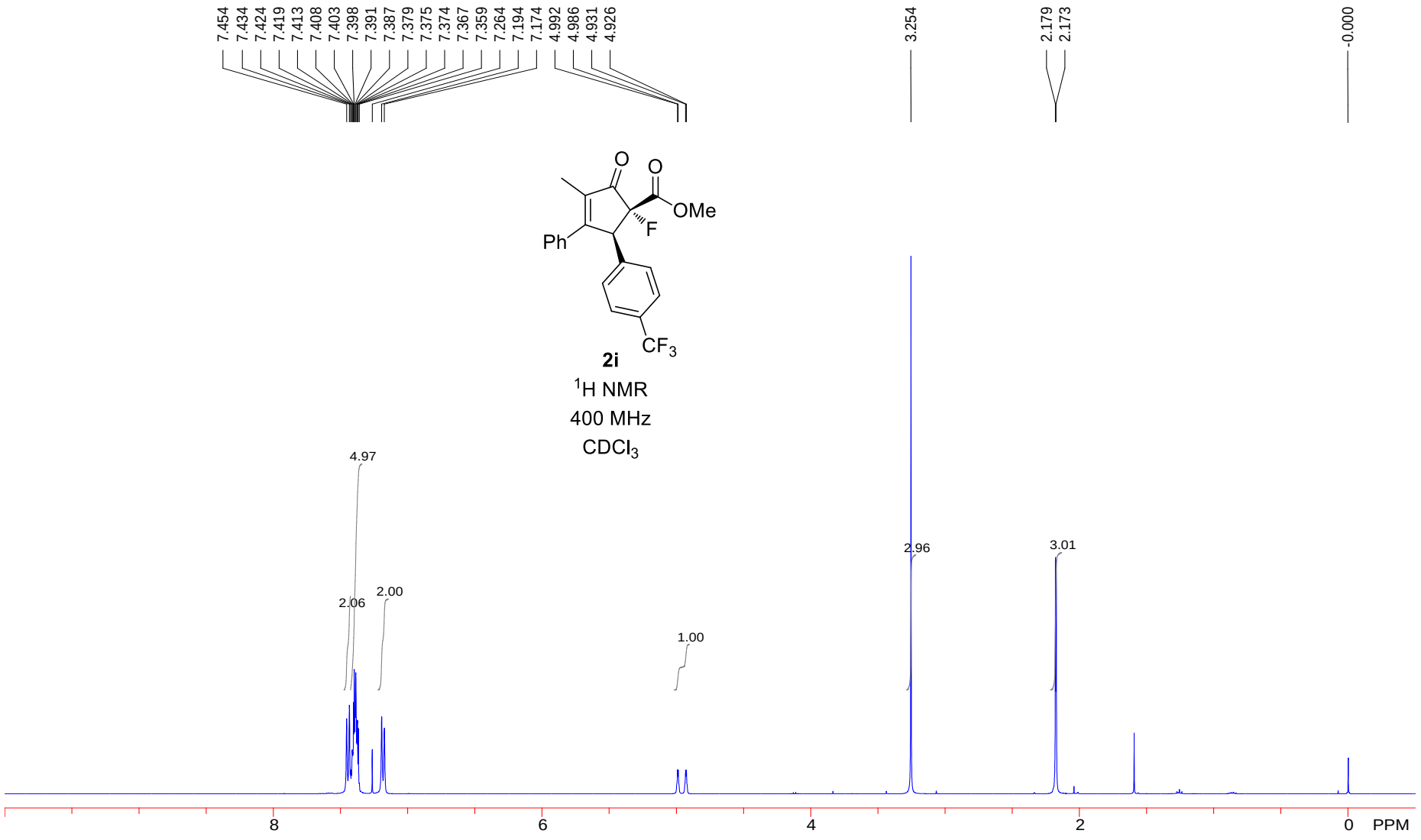
$CDCl_3$

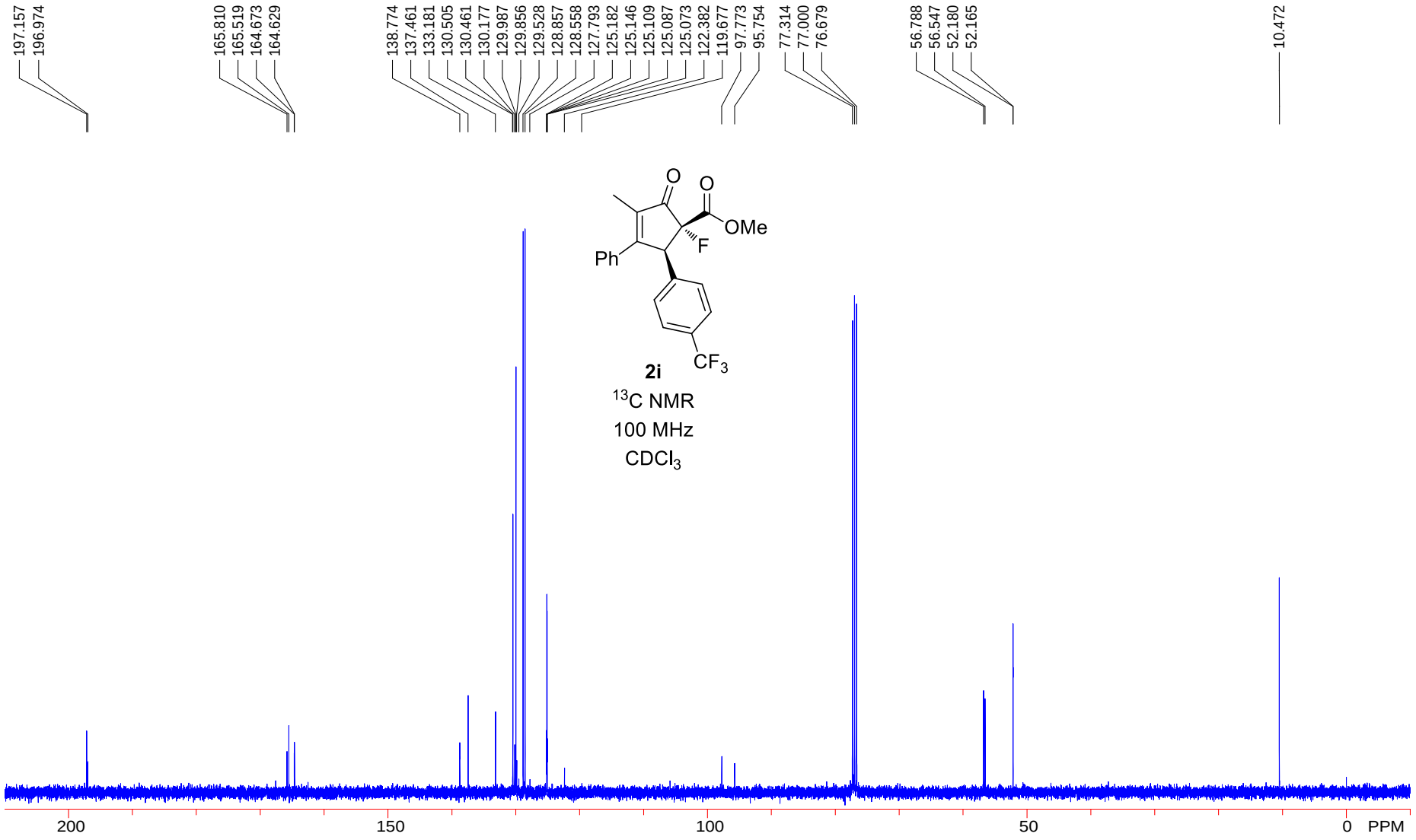

7.416
7.407
7.395
7.391
7.380
7.371
7.358
7.353
7.265
7.043
7.029
7.021
7.008
6.888
6.866
6.845
4.912
4.907
4.852
4.846
3.299
2.158
2.152
-0.000
O
O
OMe
F
Ph
F
2h
1H NMR
400 MHz
CDCl3
5.00
2.00
2.01
1.00
2.95
2.99
8
6
4
2
0
PPM

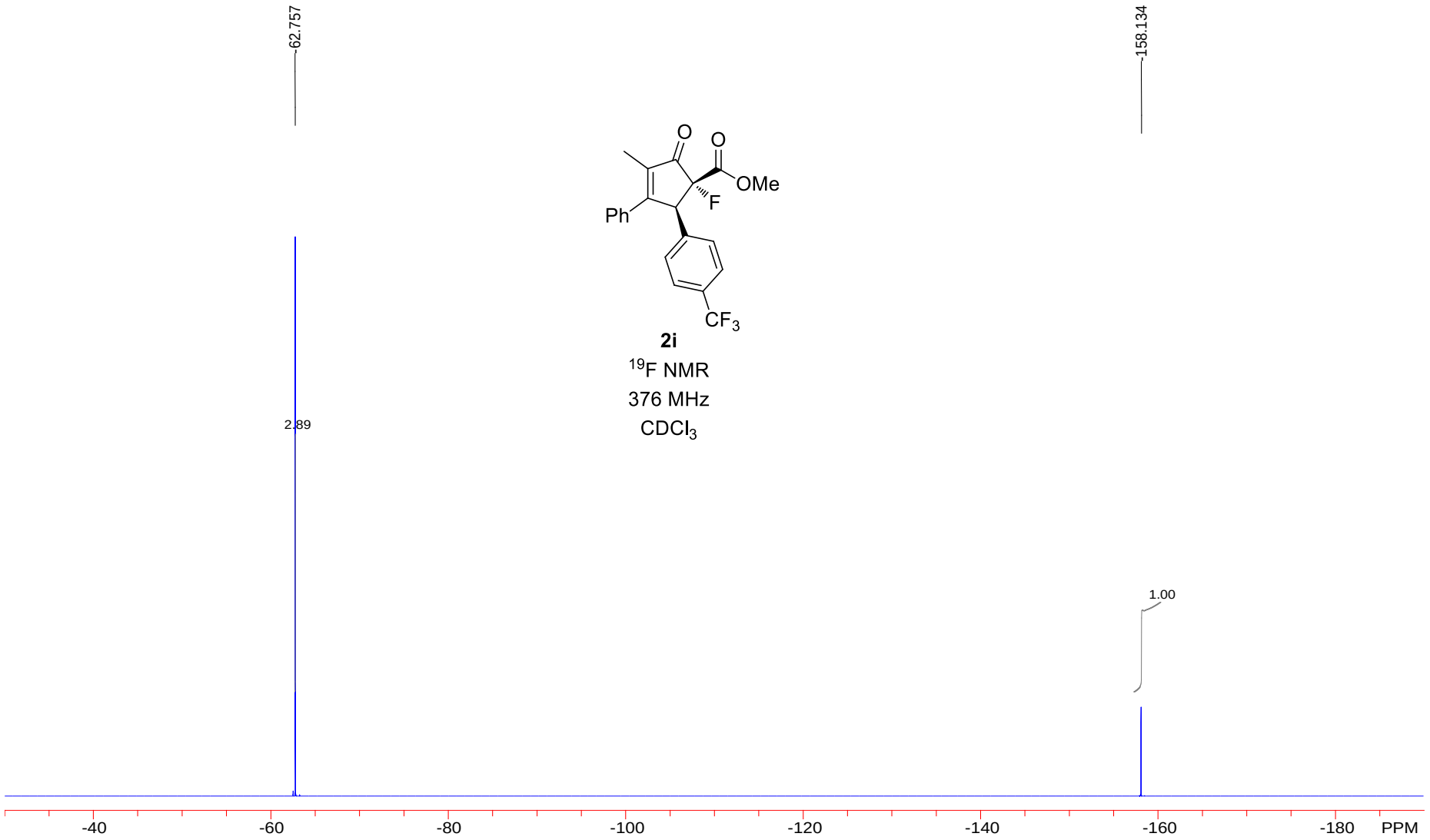

197.565
197.383
166.007
165.716
165.329
165.285
163.280
160.816
133.356
137.075
131.256
131.176
130.381
130.359
130.345
130.323
130.243
128.689
128.617
115.339
115.127
97.876
95.870
77.314
77.000
76.679
56.402
56.161
52.129
52.114
10.392
O
O
OMe
F
Ph
F
2h
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

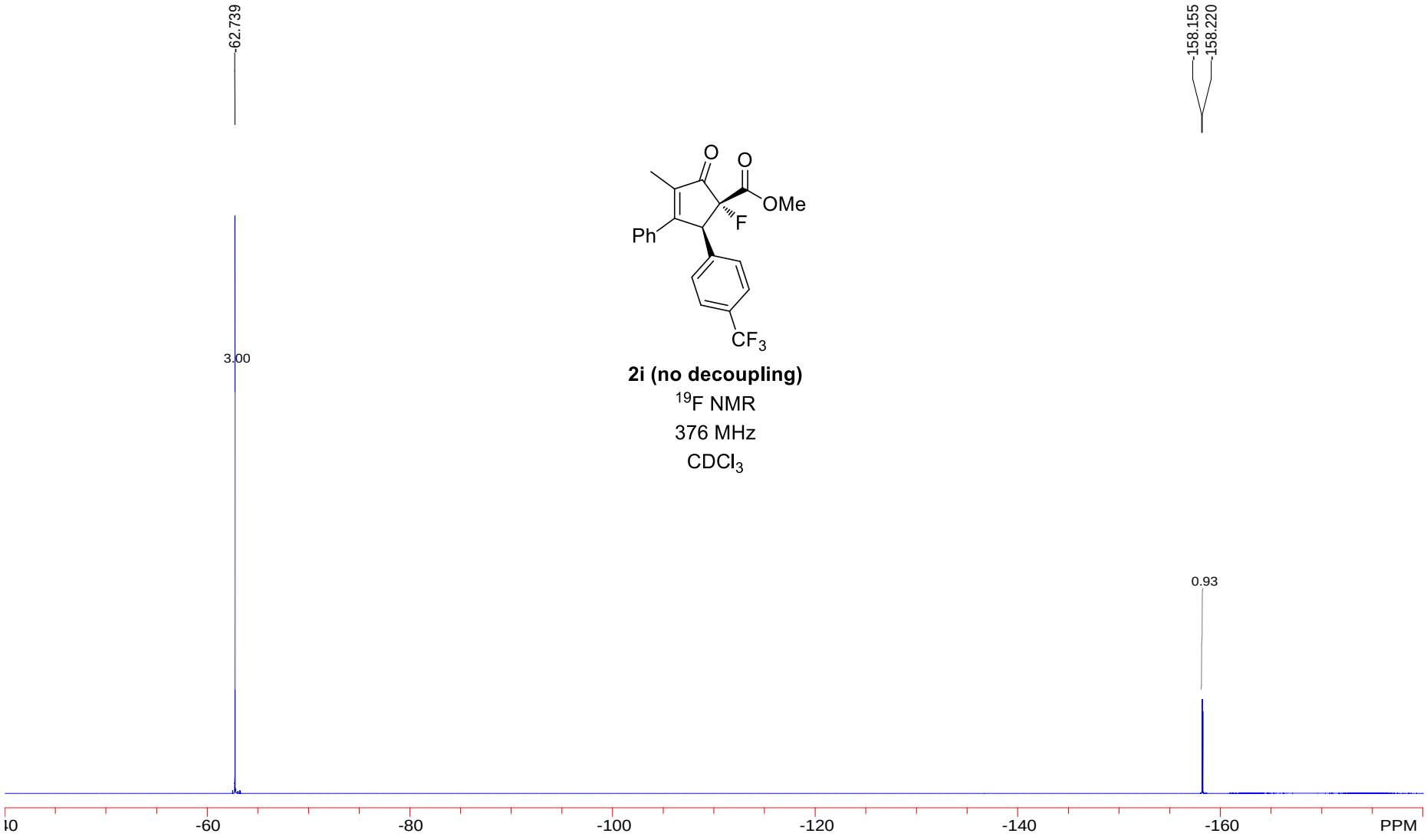

-113.715
-158.492
O
O
OMe
F
Ph
F
2h
19F NMR
376 MHz
CDCl3
1.05
1.00
-100
-120
-140
-160
-180
PPM


113.668
113.682
113.689
113.704
113.711
113.718
113.726
113.740
158.503
158.568
O
O
OMe
F
Ph
F
2h (no decoupling)
19F NMR
376 MHz
CDCl3
1.00
0.96
-110
-120
-130
-140
-150
-160
-170
PPM


7.454
7.434
7.424
7.419
7.413
7.408
7.403
7.398
7.391
7.387
7.379
7.375
7.374
7.367
7.359
7.264
7.194
7.174
4.992
4.986
4.931
4.926
3.254
2.179
2.173
-0.000
O
O
OMe
F
Ph
CF3
2i
1H NMR
400 MHz
CDCl3
4.97
2.06
2.00
1.00
2.96
3.01
8
6
4
2
0
PPM


197.157
196.974
165.810
165.519
164.673
164.629
138.774
137.461
133.181
130.505
130.461
130.177
129.987
129.856
129.528
128.857
128.558
127.793
125.182
125.146
125.109
125.087
125.073
122.382
119.677
97.773
95.754
77.314
77.000
76.679
56.788
56.547
52.180
52.165
10.472
O
O
OMe
F
Ph
CF3
2i
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM


62.757
158.134
O
O
OMe
F
Ph
CF3
2i
19F NMR
376 MHz
CDCl3
2.89
1.00
-40
-60
-80
-100
-120
-140
-160
-180
PPM

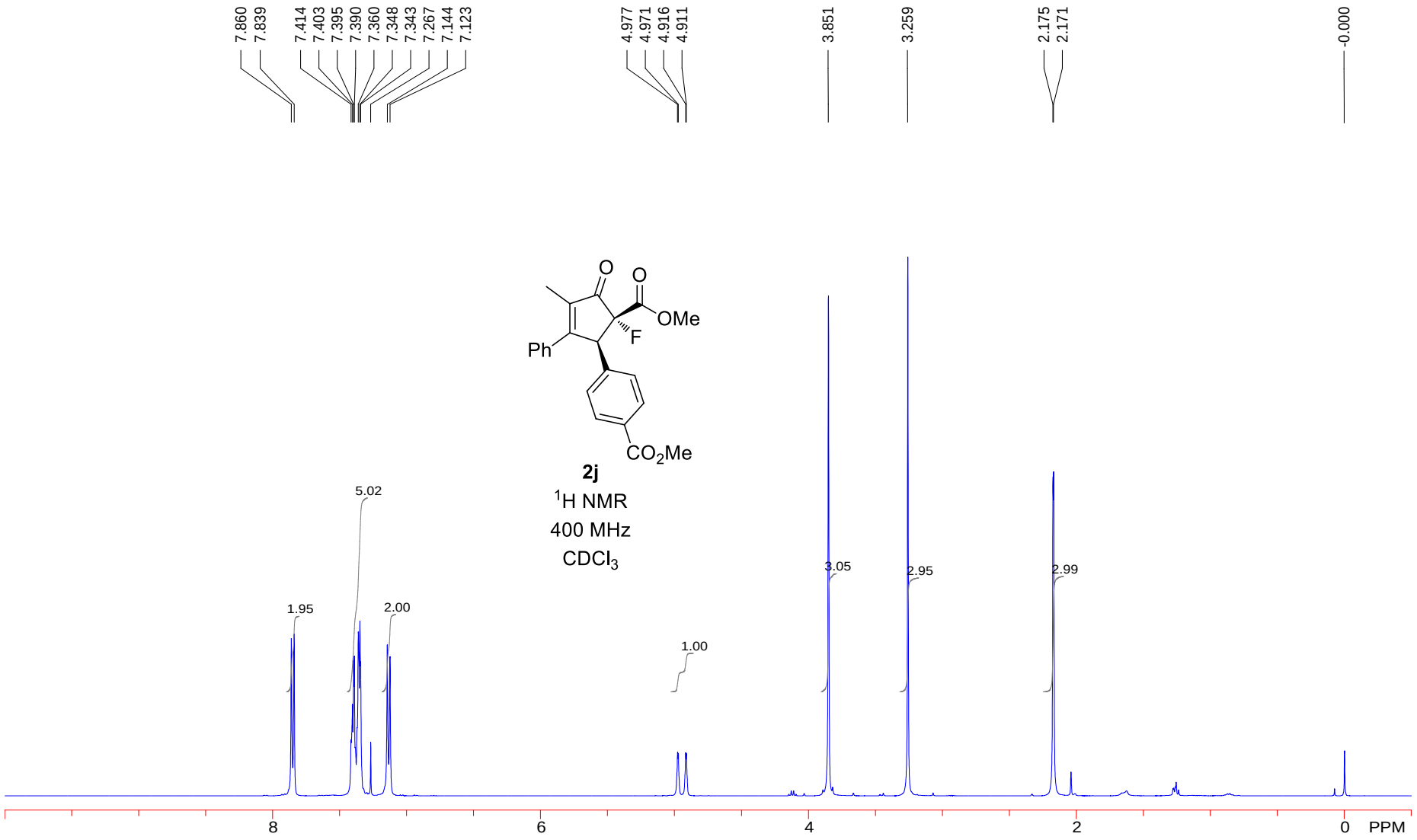


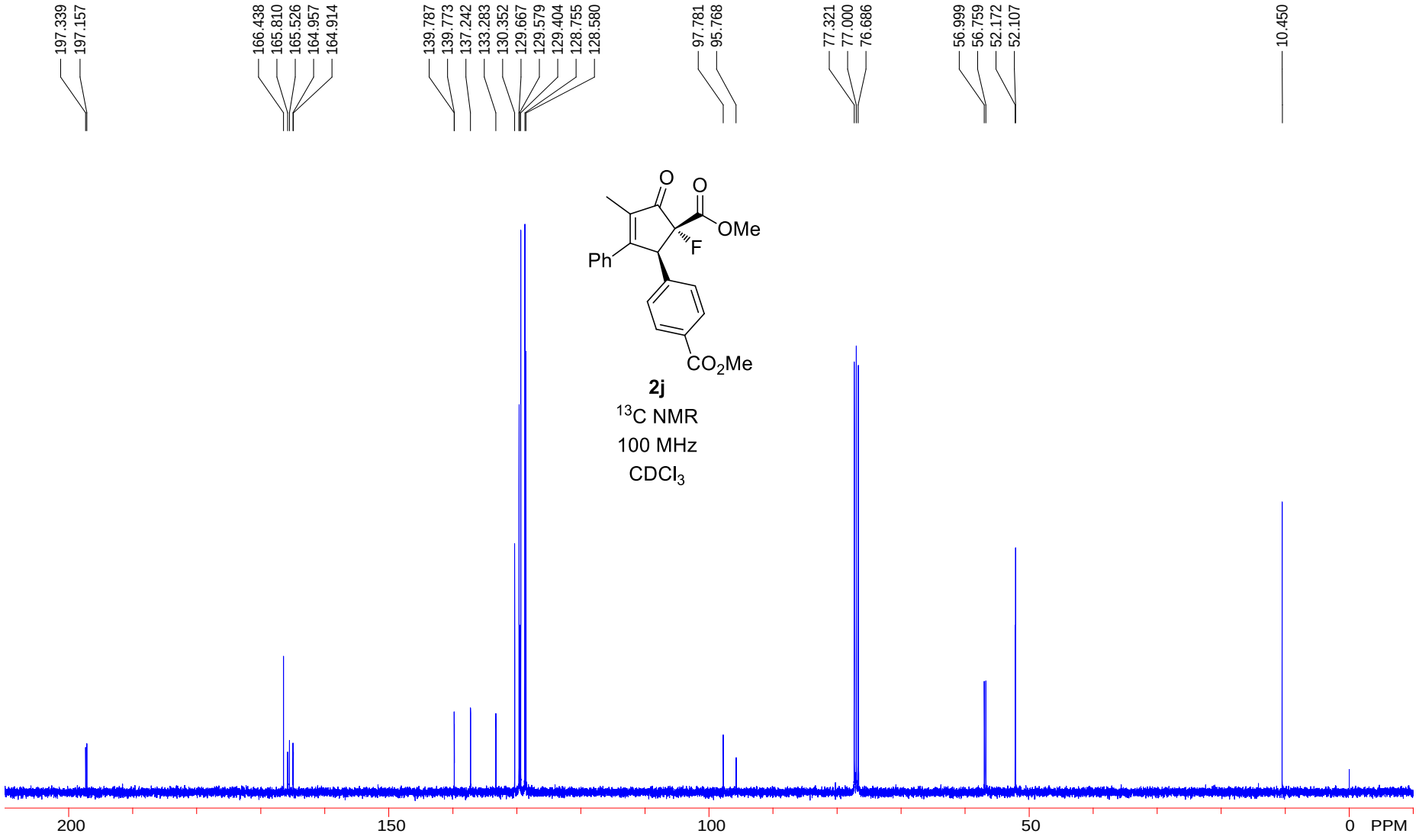
2i (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$


7.860
7.839
7.414
7.403
7.395
7.390
7.360
7.348
7.343
7.267
7.144
7.123
4.977
4.971
4.916
4.911
3.851
3.259
2.175
2.171
-0.000
O
O
OMe
F
Ph
CO2Me
2j
1H NMR
400 MHz
CDCl3
5.02
1.95
2.00
1.00
3.05
2.95
2.99
8
6
4
2
0
PPM

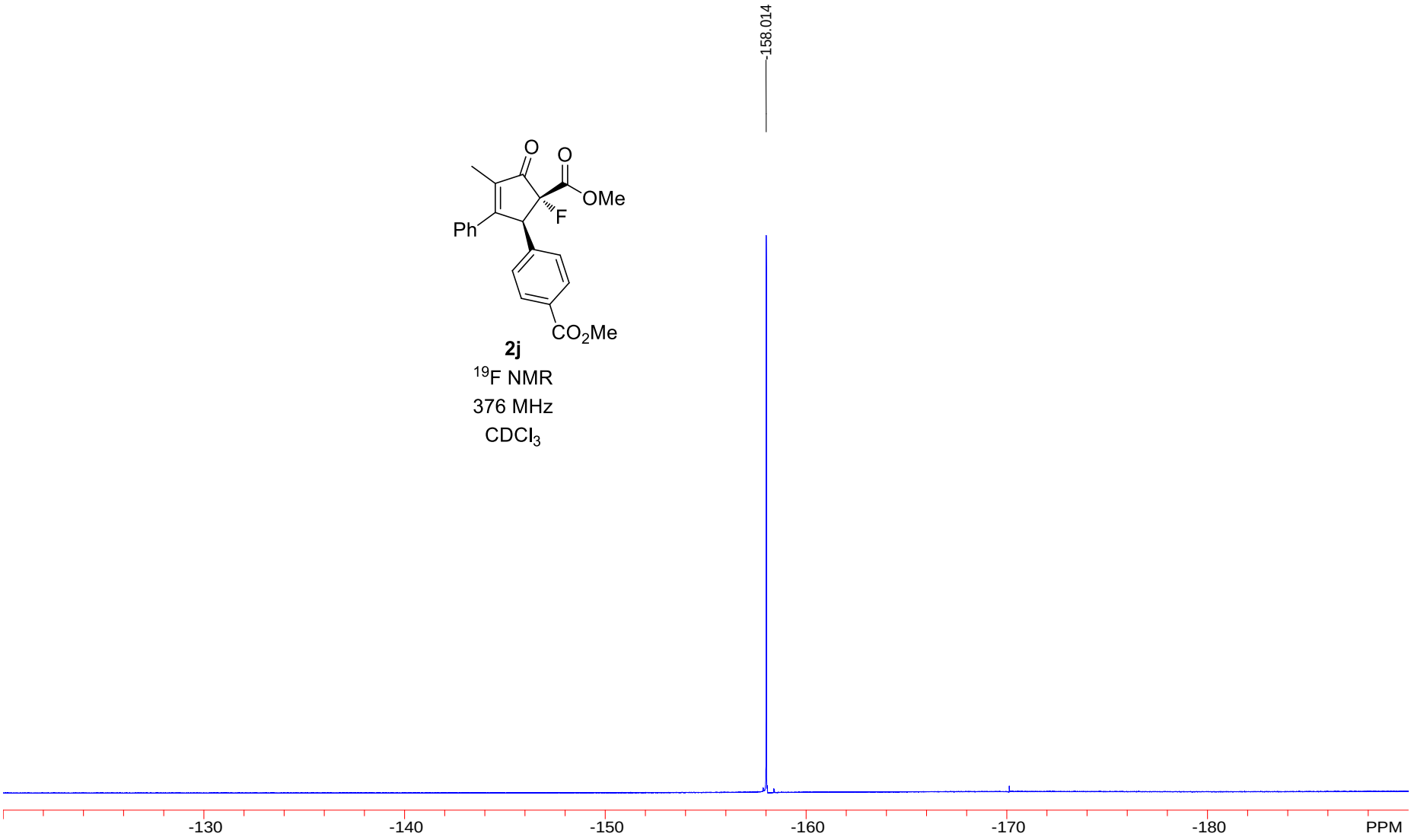

197.339
197.157
166.438
165.810
165.526
164.957
164.914
139.787
139.773
137.242
133.283
130.352
129.667
129.579
129.404
128.755
128.580
97.781
95.768
77.321
77.000
76.686
56.999
56.759
52.172
52.107
10.450
O
O
OMe
F
Ph
CO2Me
2j
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

2j

^{19}F NMR

376 MHz

$CDCl_3$

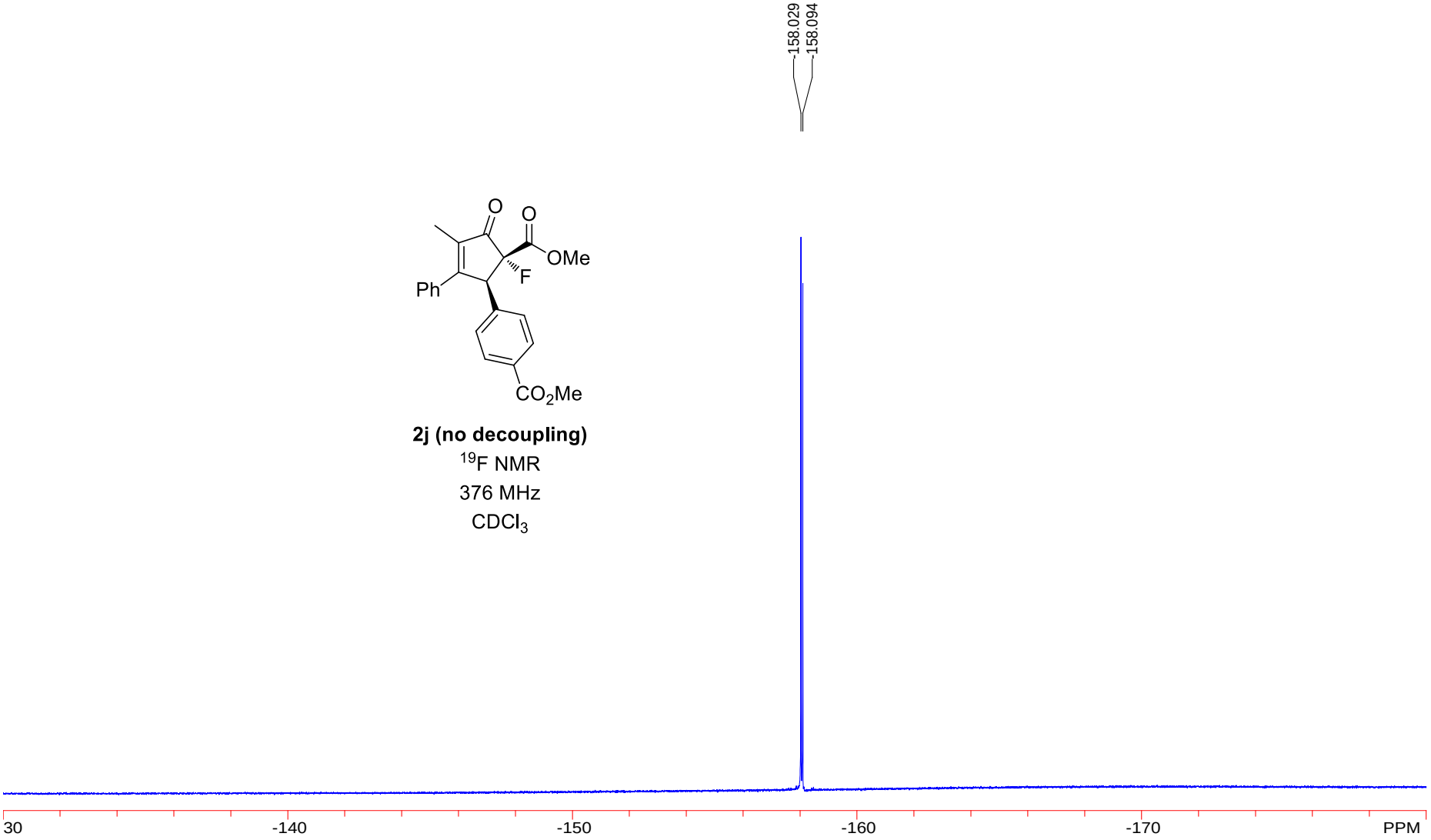


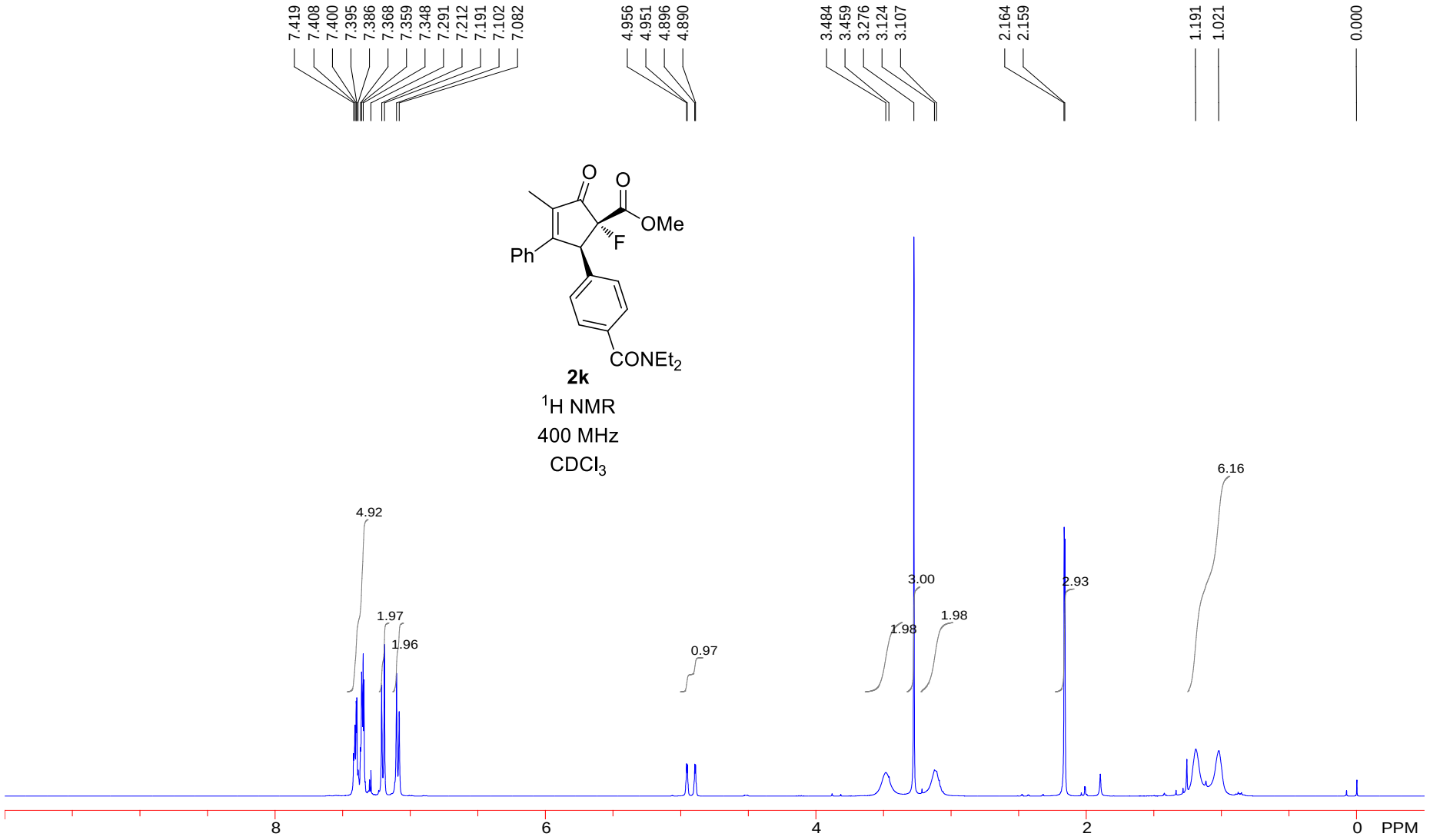
2j (no decoupling)

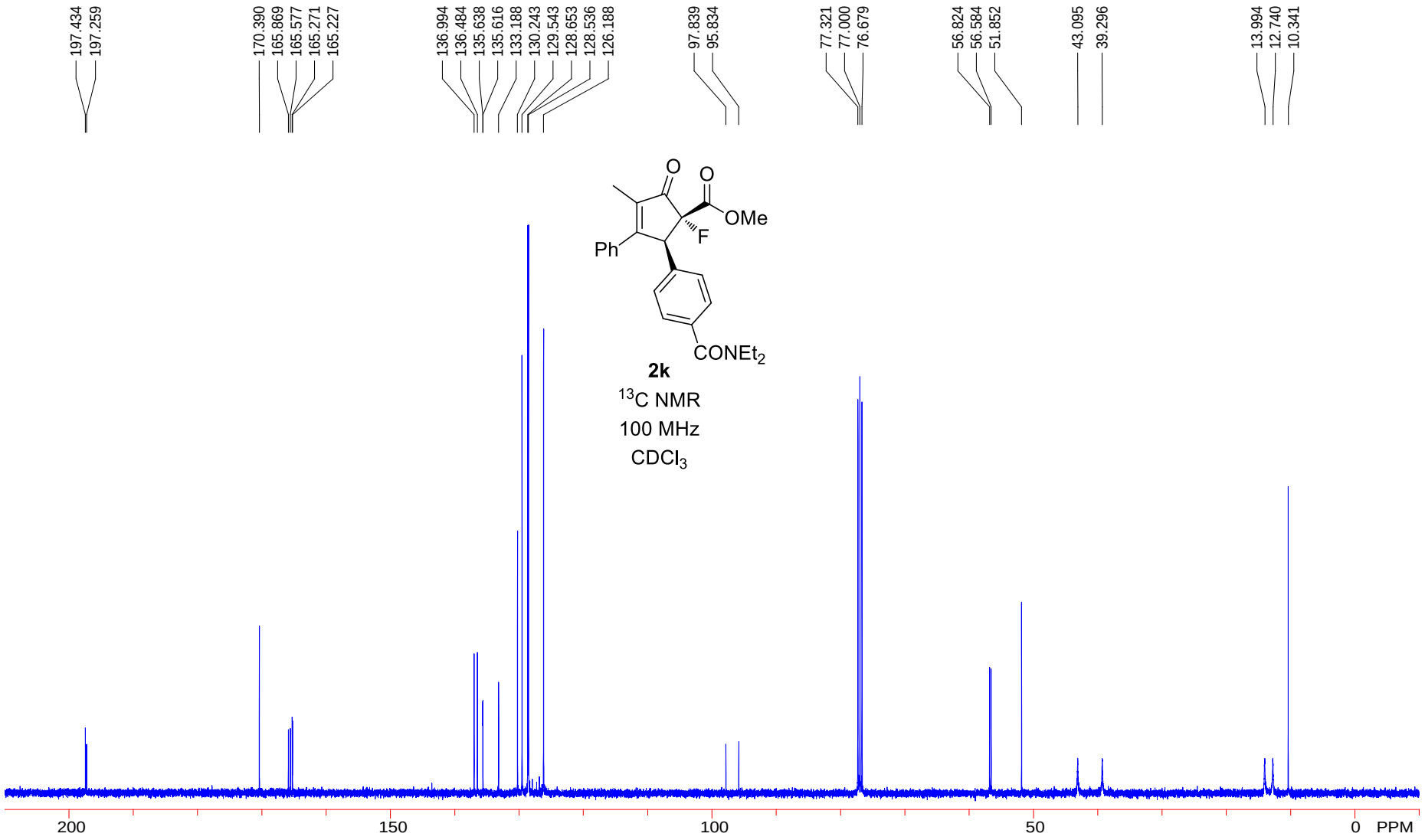
^{19}F NMR

376 MHz

$CDCl_3$




7.419
7.408
7.400
7.395
7.386
7.368
7.359
7.348
7.291
7.212
7.191
7.102
7.082
4.956
4.951
4.896
4.890
3.484
3.459
3.276
3.124
3.107
2.164
2.159
1.191
1.021
0.000
O
O
OMe
F
Ph
CONEt2
2k
1H NMR
400 MHz
CDCl3
4.92
1.97
1.96
0.97
1.98
3.00
1.98
2.93
6.16
8
6
4
2
0
PPM

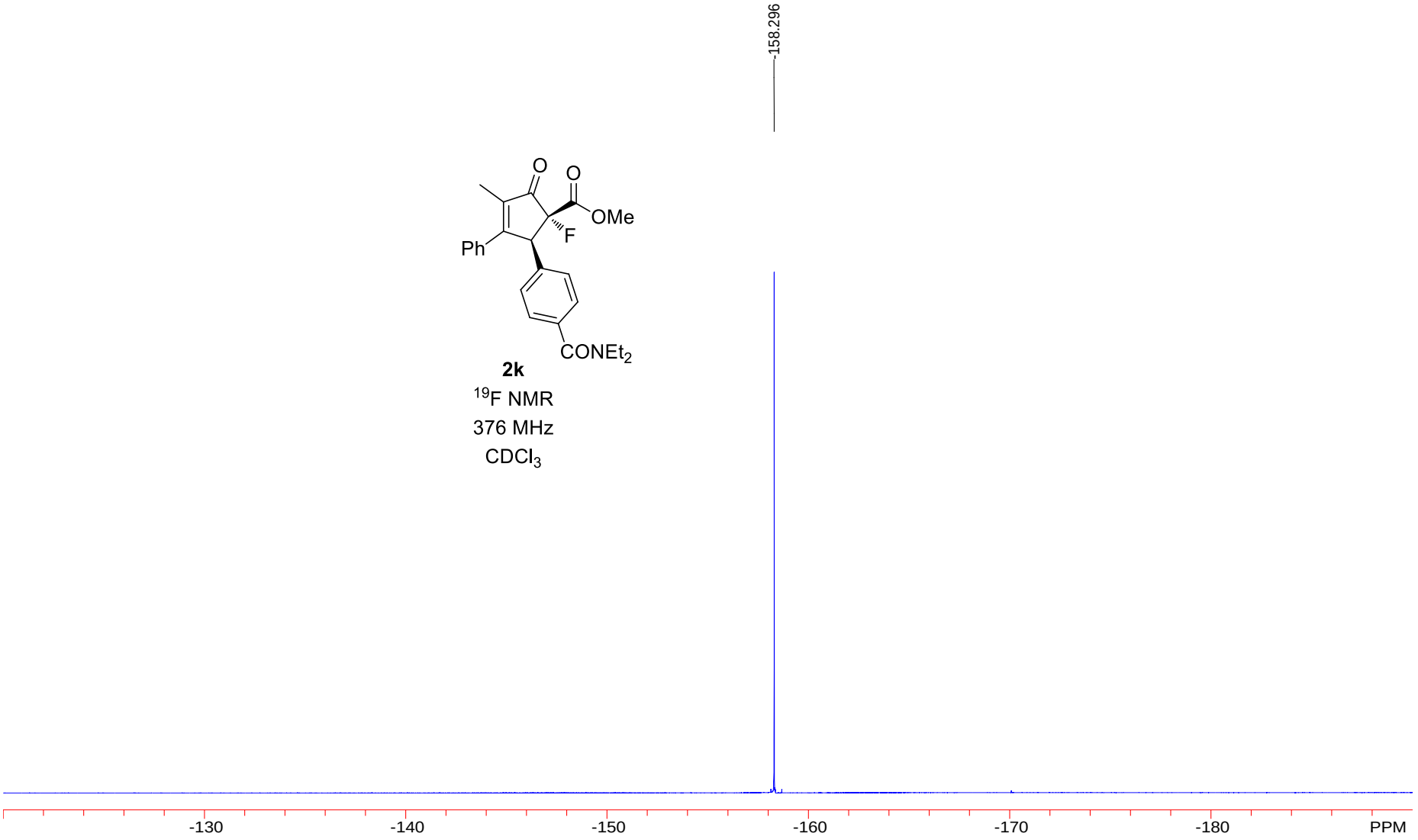

197.434
197.259
170.390
165.869
165.577
165.271
165.227
136.994
136.484
135.638
135.616
133.188
130.243
129.543
128.653
128.536
126.188
97.839
95.834
77.321
77.000
76.679
56.824
56.584
51.852
43.095
39.296
13.994
12.740
10.341
O
O
OMe
F
Ph
CONEt2
2k
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

2k

^{19}F NMR

376 MHz

$CDCl_3$

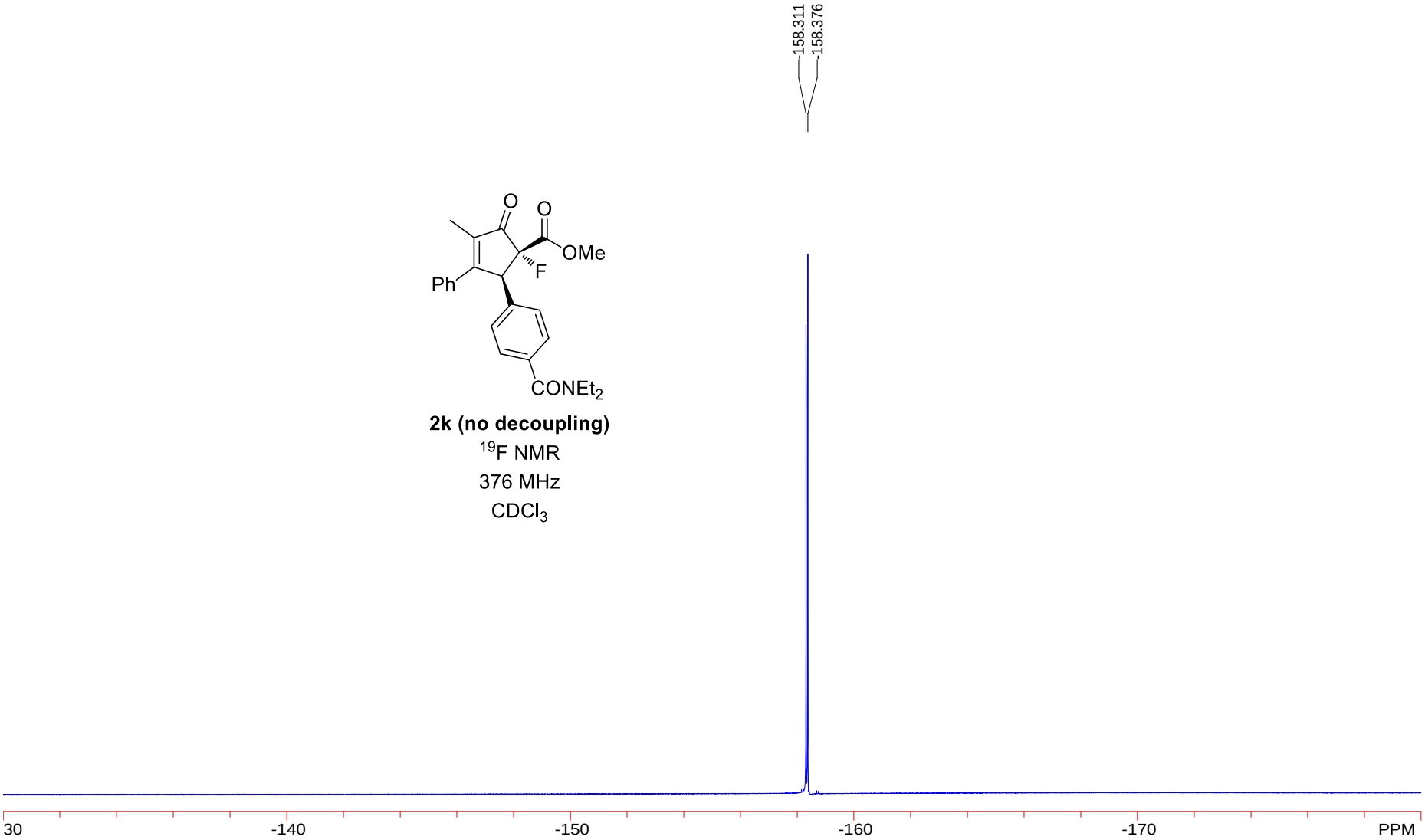


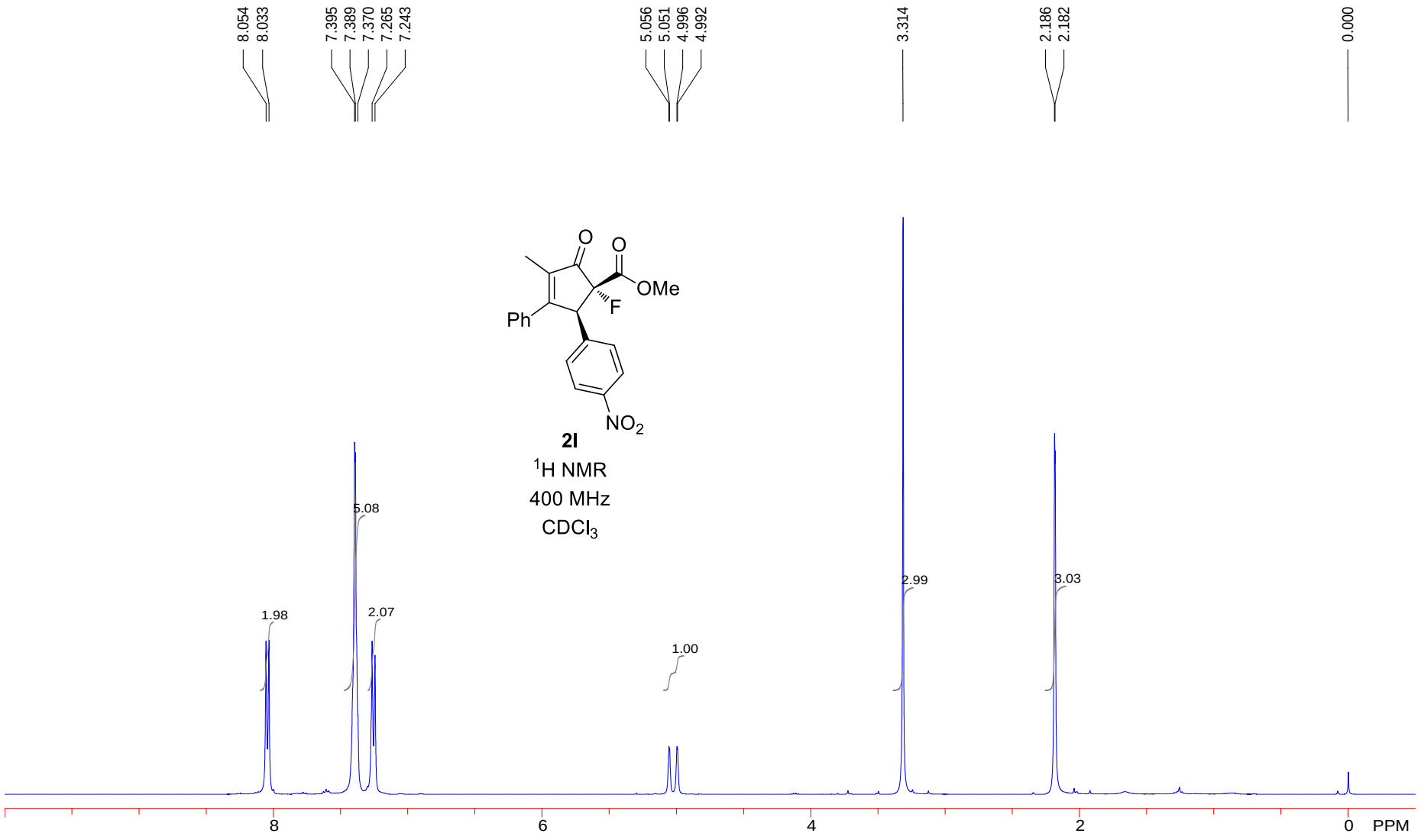
2k (no decoupling)

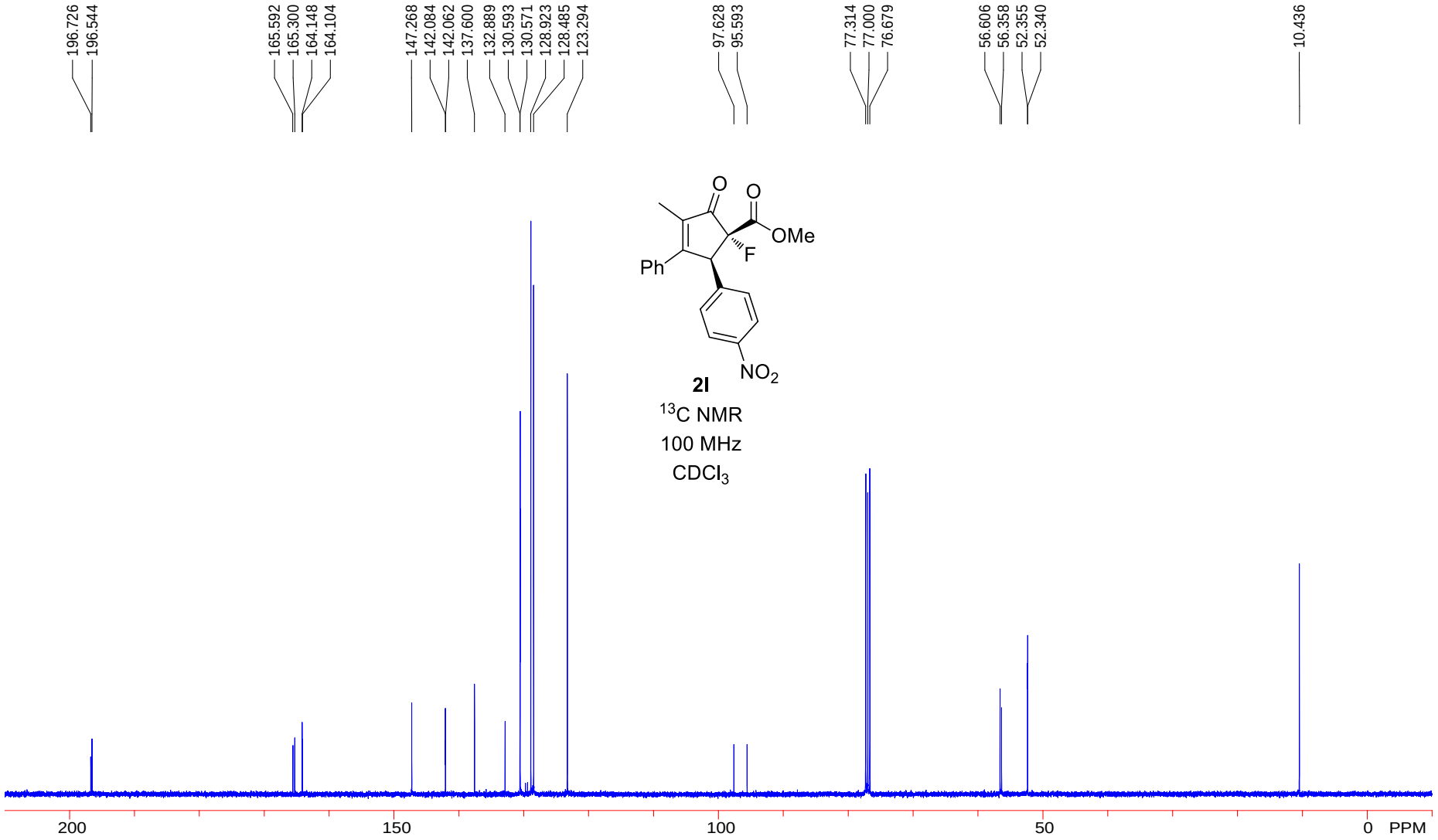
^{19}F NMR

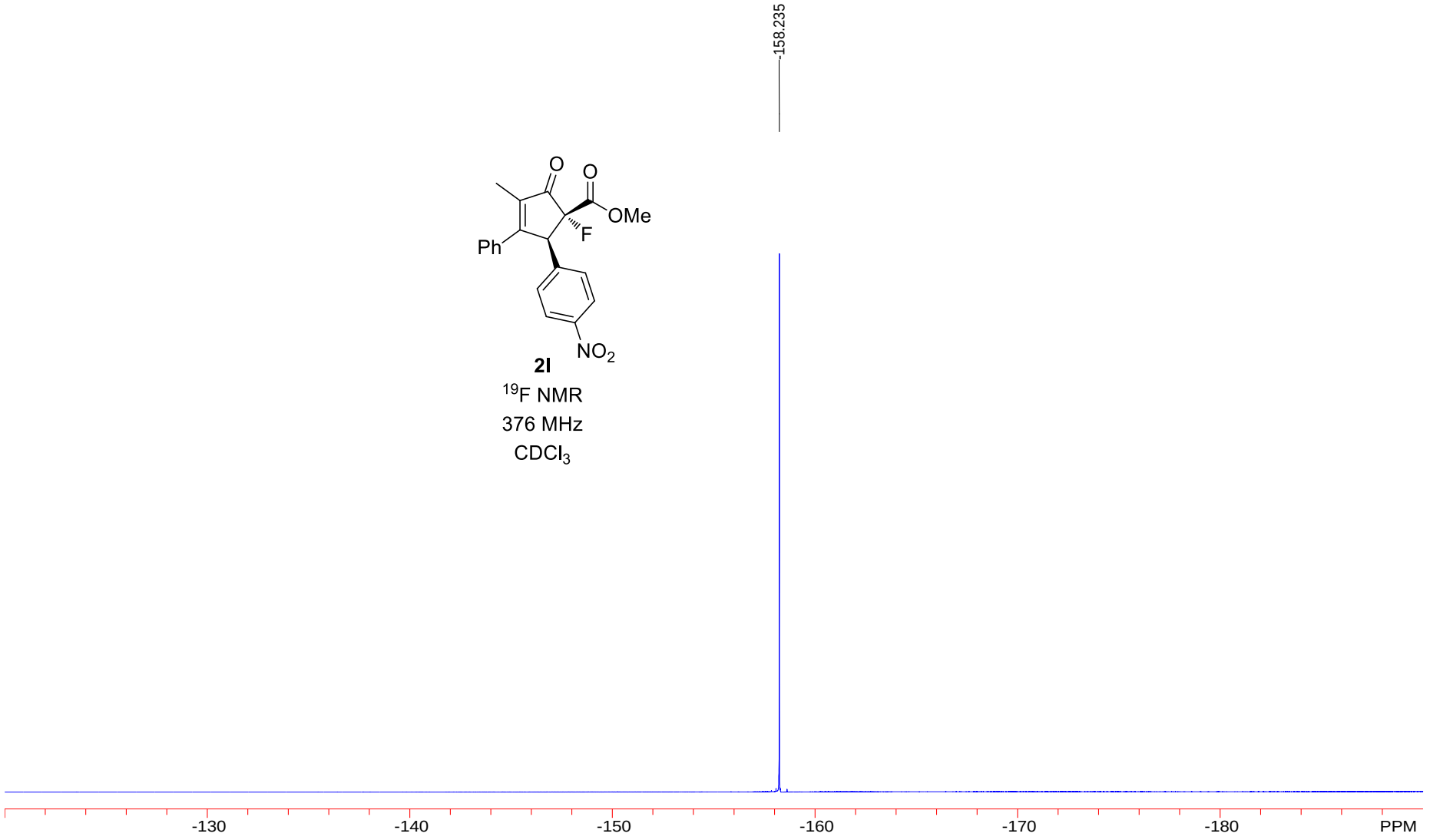
376 MHz

$CDCl_3$




8.054
8.033
7.395
7.389
7.370
7.265
7.243
5.056
5.051
4.996
4.992
3.314
2.186
2.182
0.000
O
O
OMe
F
Ph
NO2
2l
1H NMR
400 MHz
CDCl3
5.08
1.98
2.07
1.00
2.99
3.03
8
6
4
2
0
PPM


196.726
196.544
165.592
165.300
164.148
164.104
147.268
142.084
142.062
137.600
132.889
130.593
130.571
128.923
128.485
123.294
97.628
95.593
77.314
77.000
76.679
56.606
56.358
52.355
52.340
10.436
O
O
OMe
F
Ph
NO2
2l
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

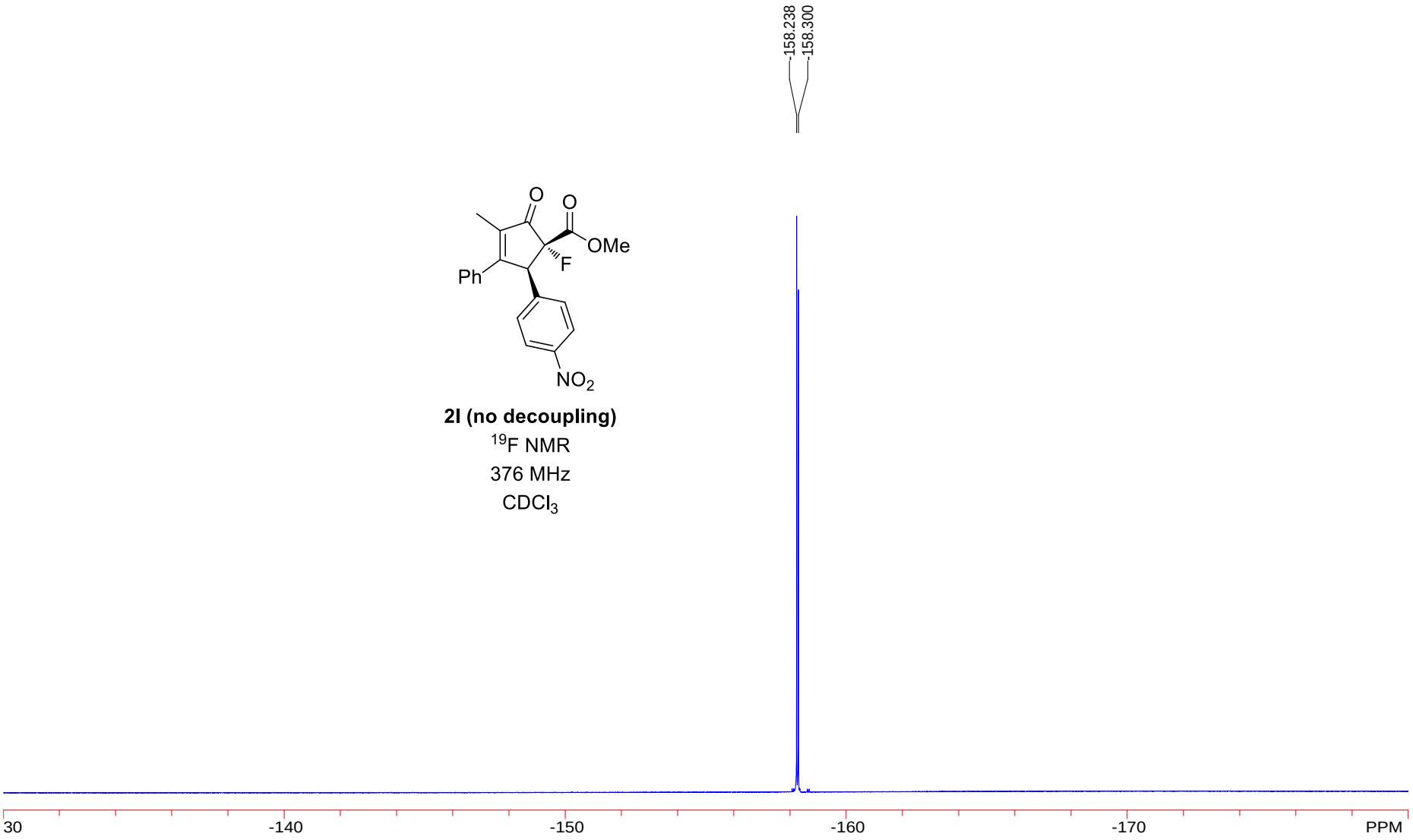


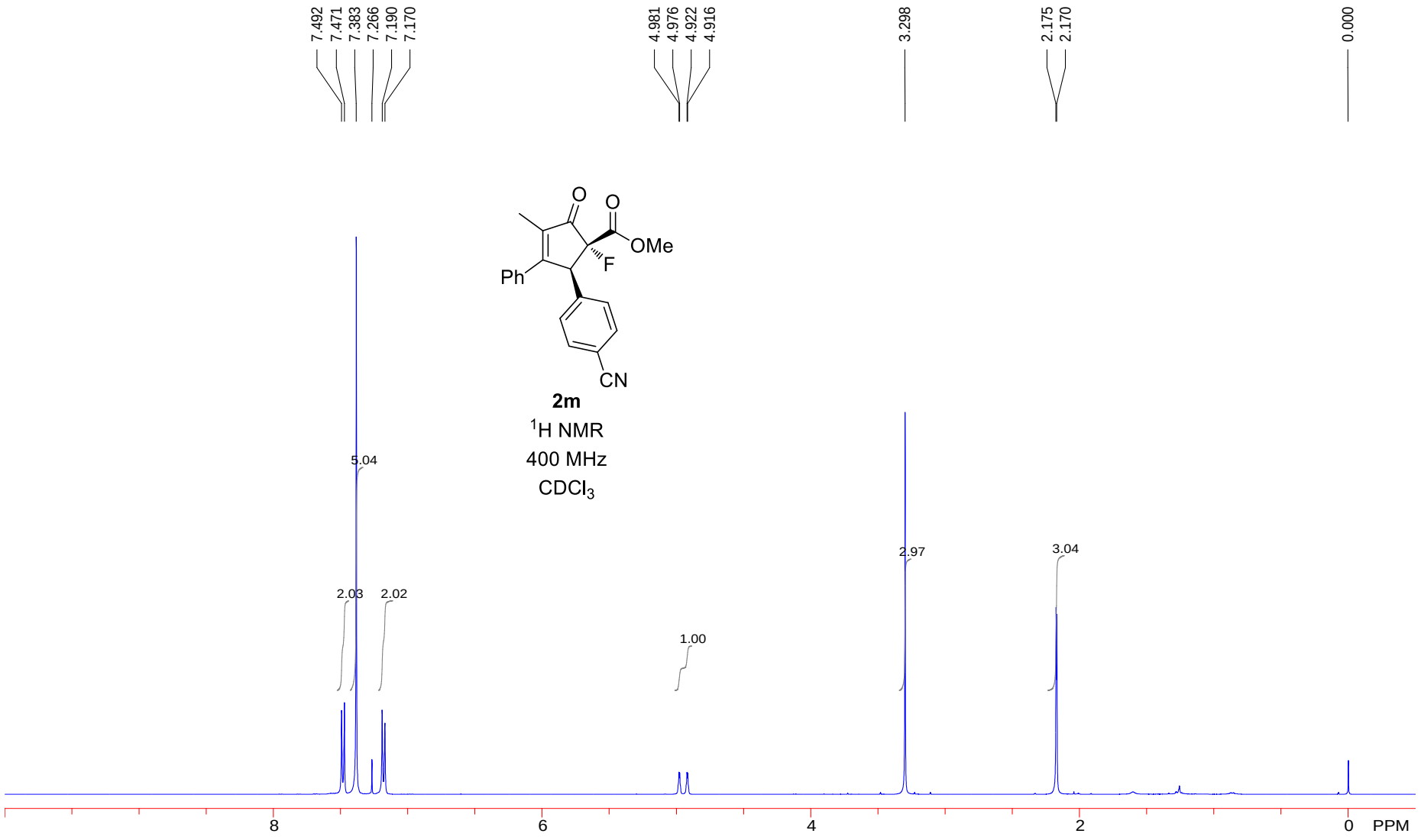
2l

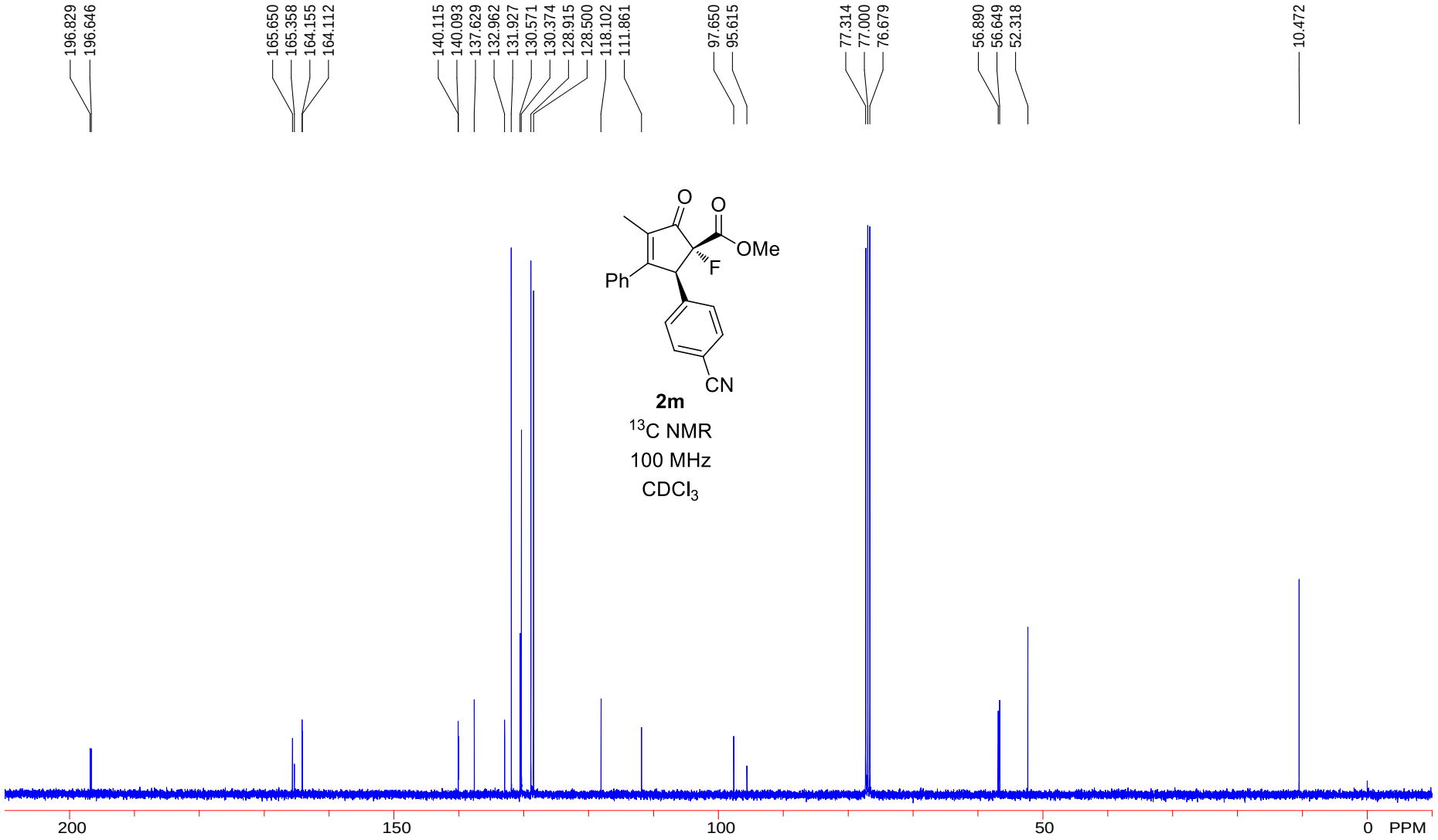
^{19}F NMR

376 MHz

$CDCl_3$


158.238
158.300
O
O
OMe
F
Ph
NO2
2l (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.492
7.471
7.383
7.266
7.190
7.170
4.981
4.976
4.922
4.916
3.298
2.175
2.170
0.000
O
O
OMe
F
Ph
CN
2m
1H NMR
400 MHz
CDCl3
5.04
2.03
2.02
1.00
2.97
3.04
8
6
4
2
0
PPM

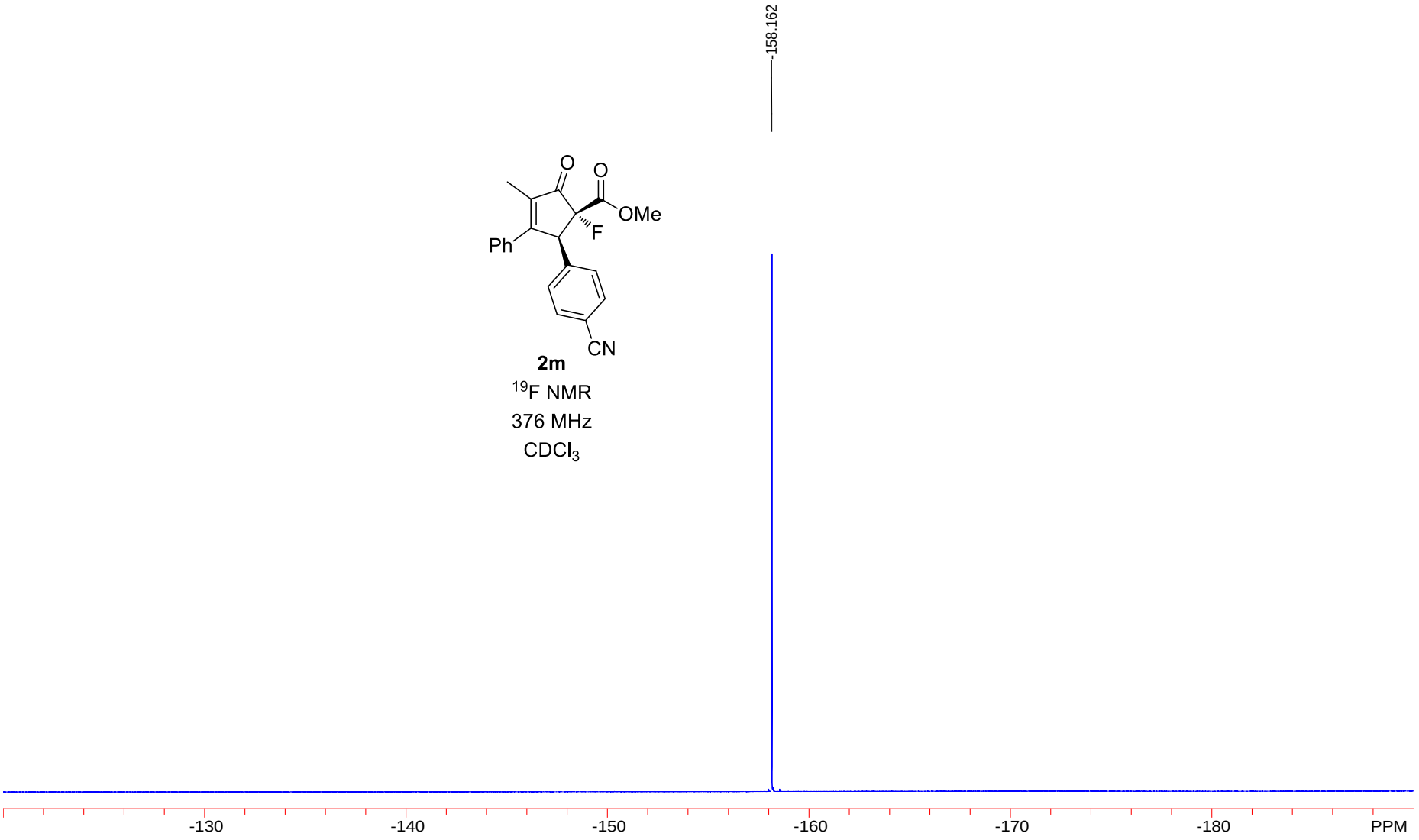

196.829
196.646
165.650
165.358
164.155
164.112
140.115
140.093
137.629
132.962
131.927
130.571
130.374
128.915
128.500
118.102
111.861
97.650
95.615
77.314
77.000
76.679
56.890
56.649
52.318
10.472
O
O
OMe
F
Ph
CN
2m
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

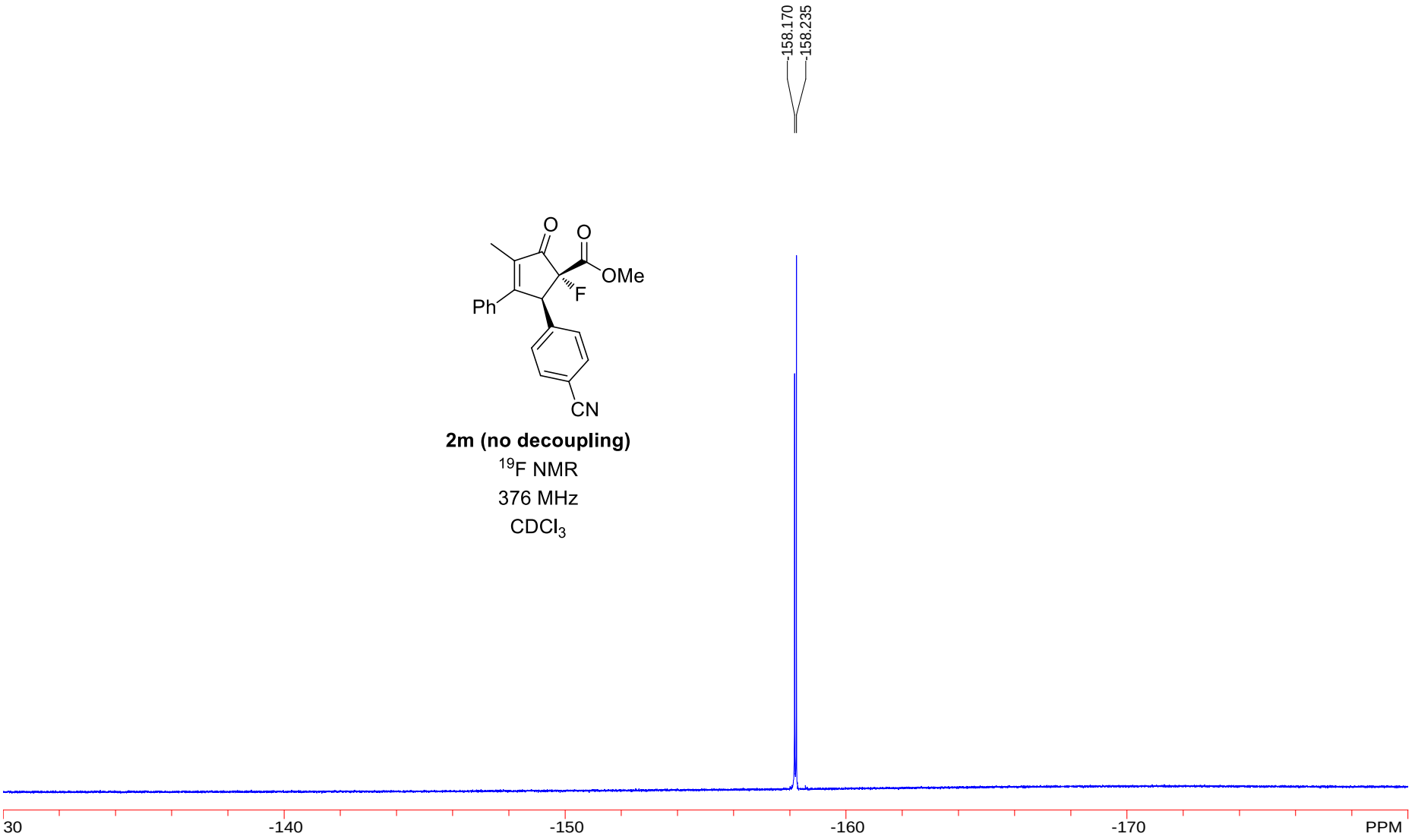
2m

^{19}F NMR

376 MHz

$CDCl_3$



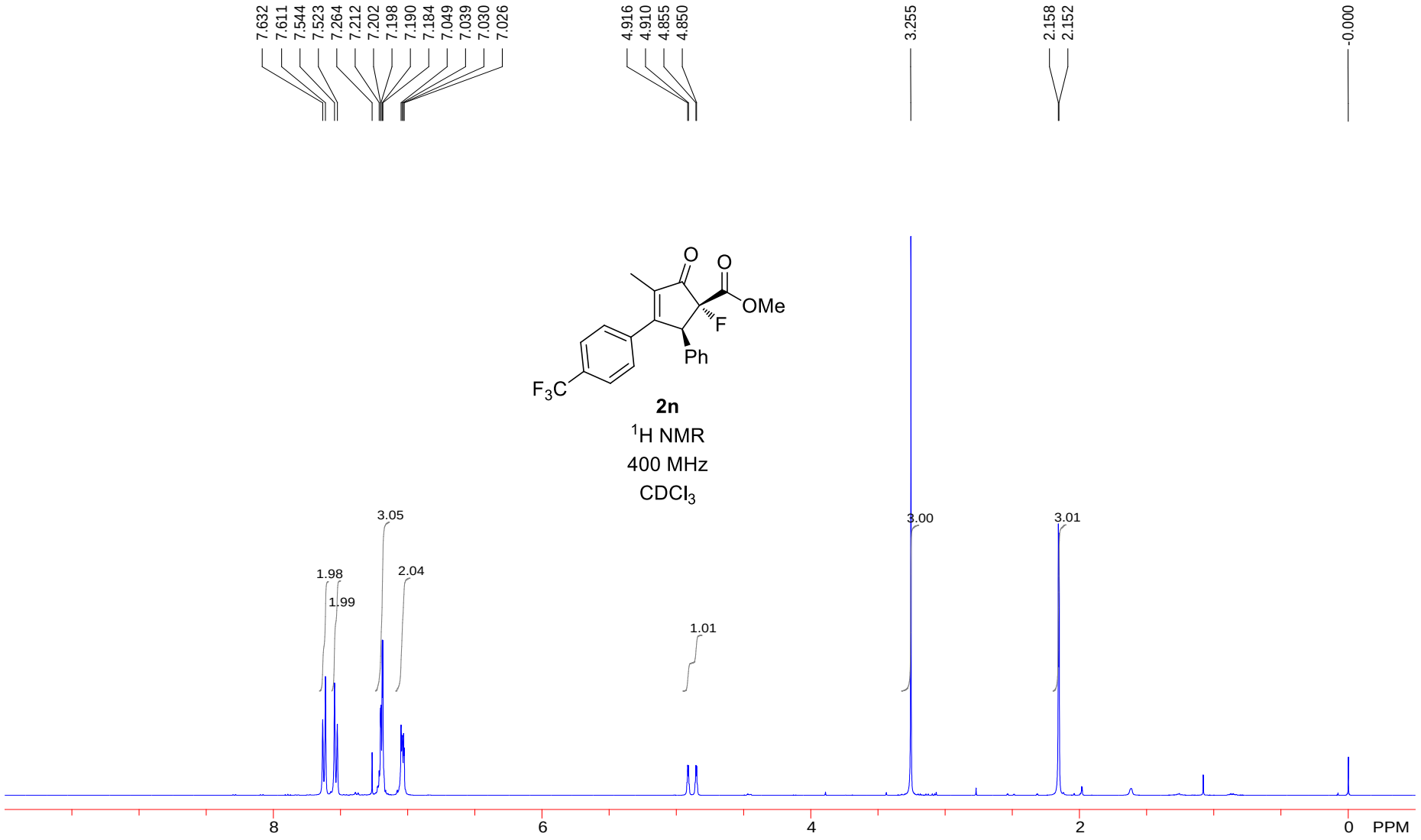


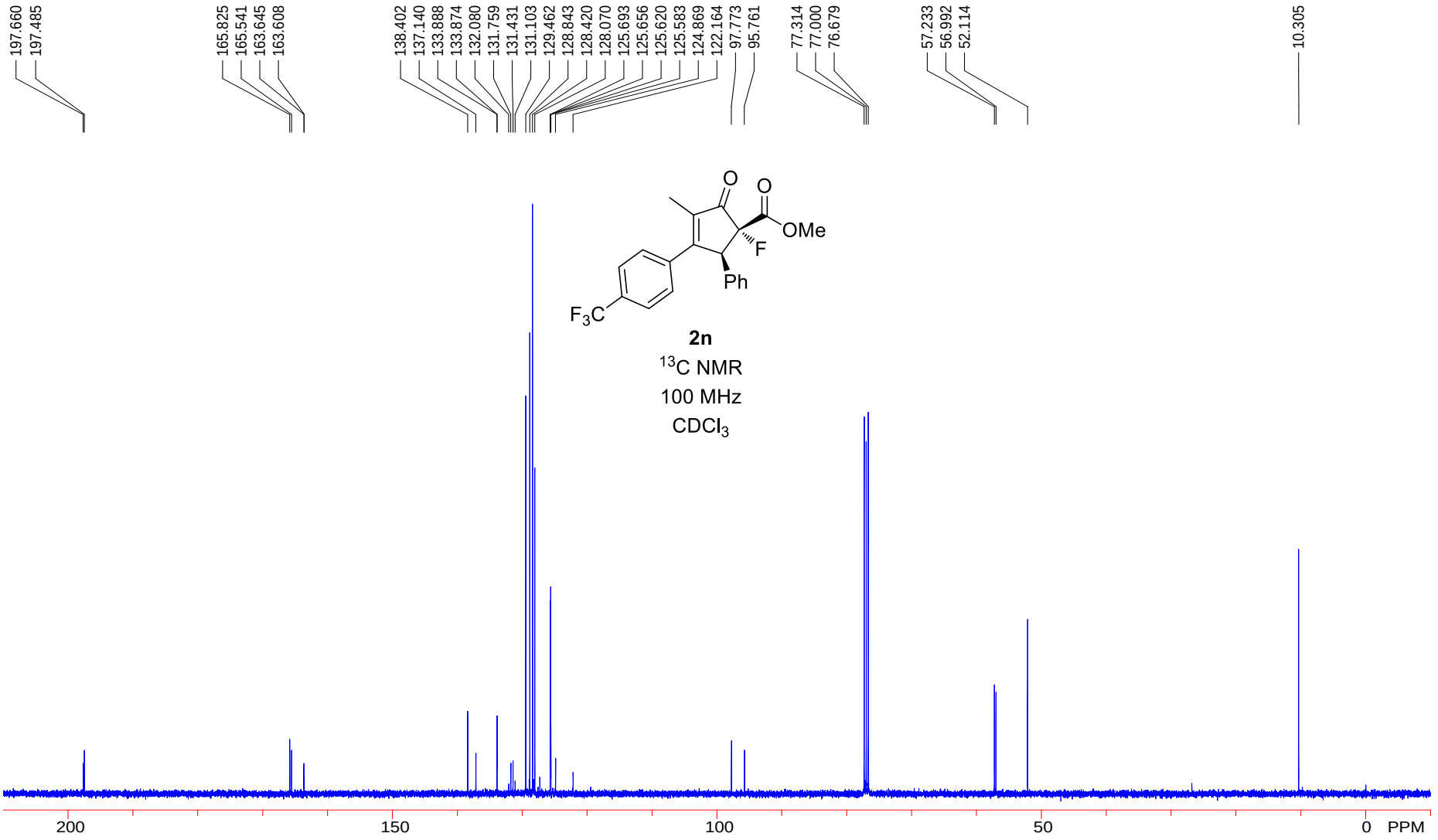
2m (no decoupling)

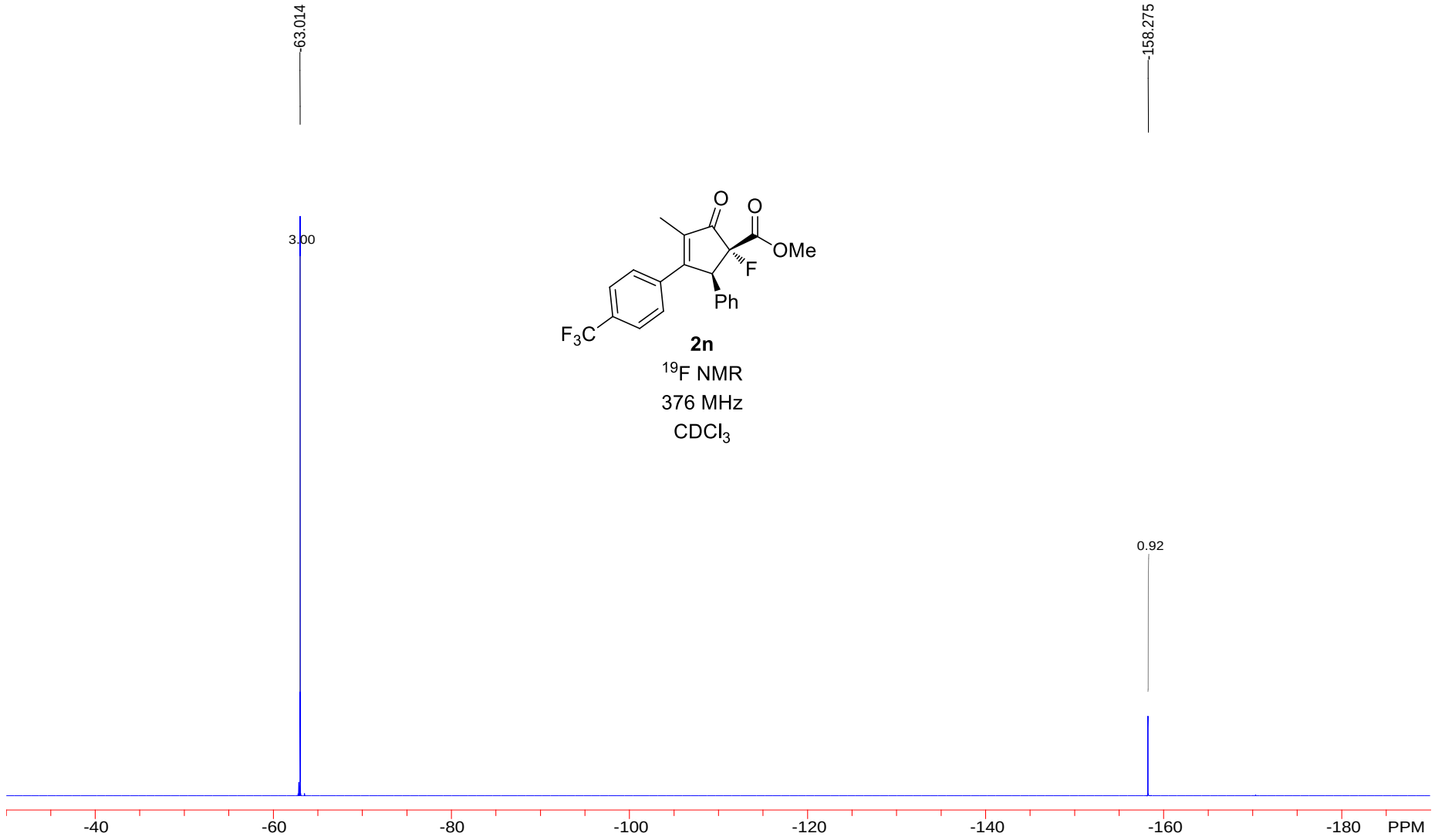
^{19}F NMR

376 MHz

$CDCl_3$


7.632
7.611
7.544
7.523
7.264
7.212
7.202
7.198
7.190
7.184
7.049
7.039
7.030
7.026
4.916
4.910
4.855
4.850
3.255
2.158
2.152
-0.000
O
O
OMe
F
Ph
F3C
2n
1H NMR
400 MHz
CDCl3
3.05
1.98
1.99
2.04
1.01
3.00
3.01
8
6
4
2
0
PPM


197.660
197.485
165.825
165.541
163.645
163.608
138.402
137.140
133.888
133.874
132.080
131.759
131.431
131.103
129.462
128.843
128.420
128.070
125.693
125.656
125.620
125.583
124.869
122.164
97.773
95.761
77.314
77.000
76.679
57.233
56.992
52.114
10.305
O
O
OMe
F
Ph
F3C
2n
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

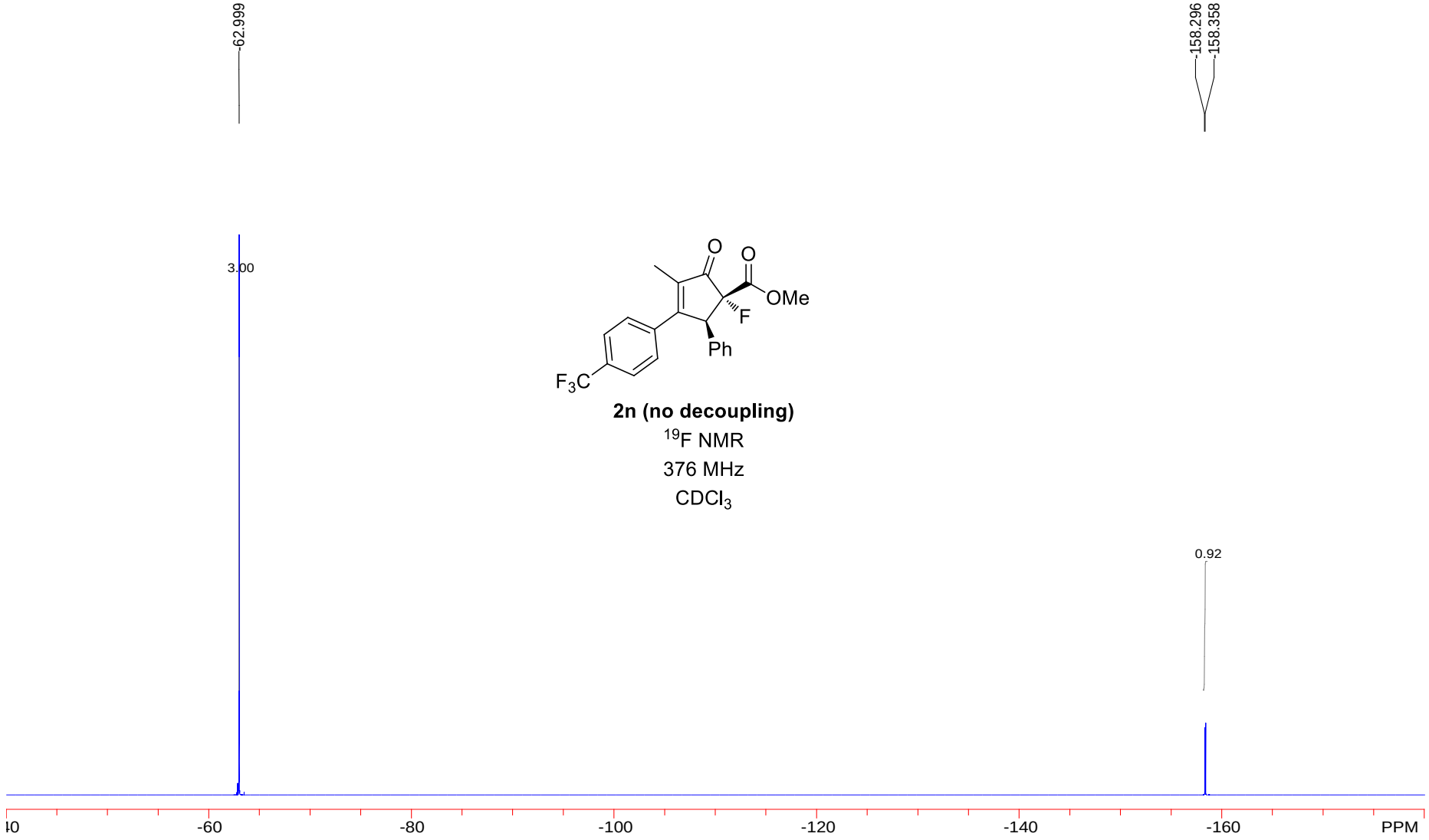


2n

^{19}F NMR

376 MHz

$CDCl_3$

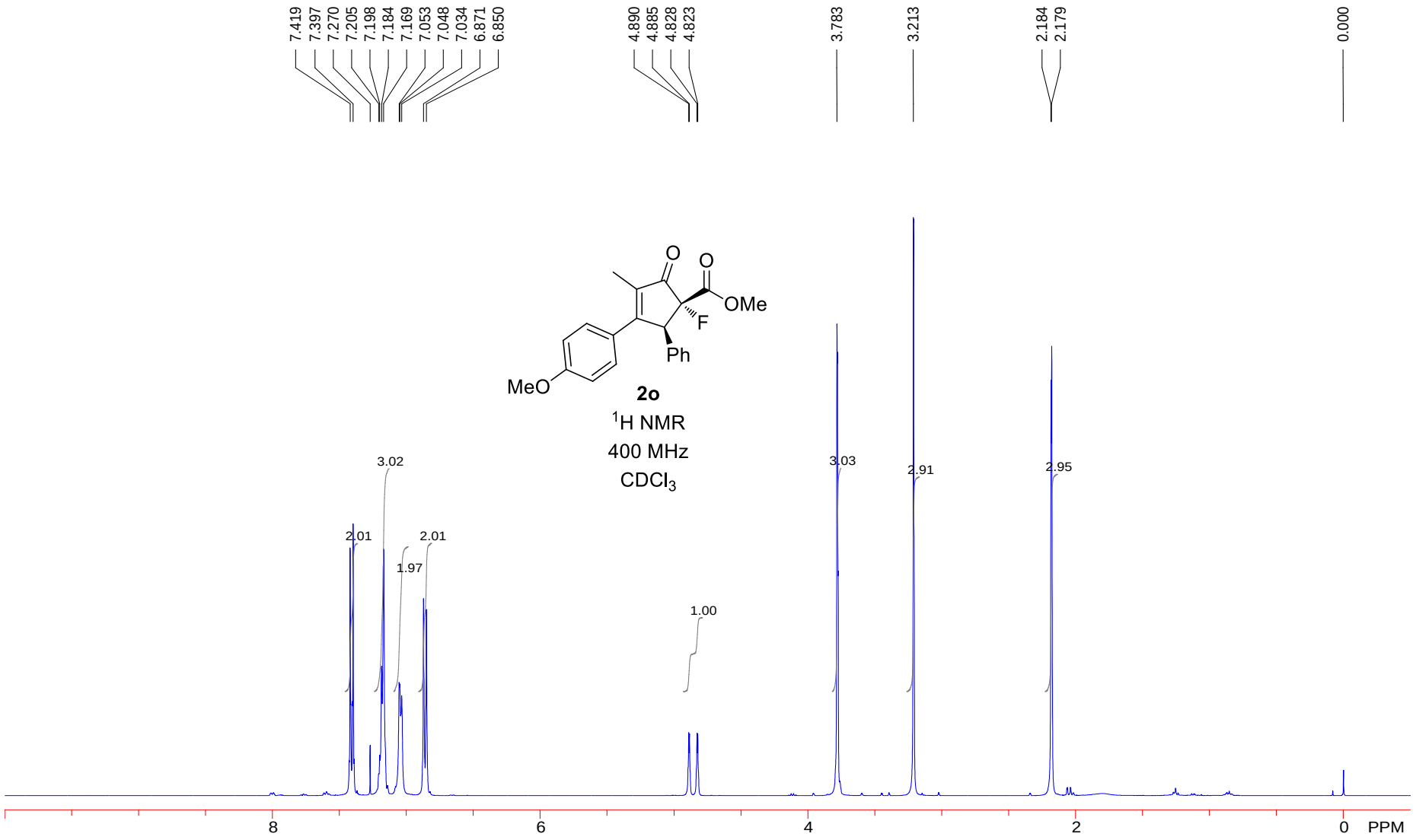


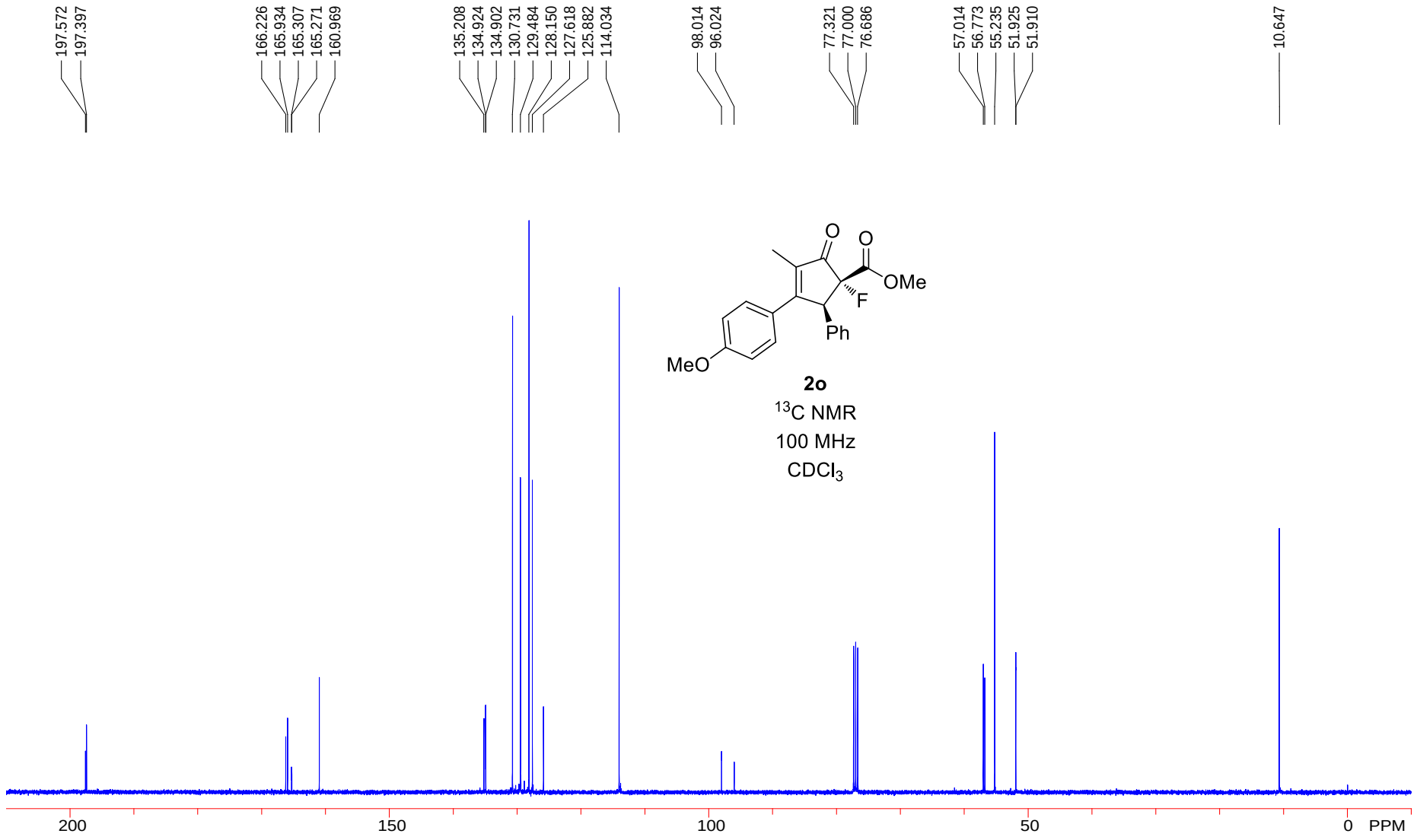
2n (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$


7.419
7.397
7.270
7.205
7.198
7.184
7.169
7.053
7.048
7.034
6.871
6.850
4.890
4.885
4.828
4.823
3.783
3.213
2.184
2.179
0.000
O
O
OMe
F
Ph
MeO
2o
1H NMR
400 MHz
CDCl3
3.02
2.01
2.01
1.97
1.00
3.03
2.91
2.95
8
6
4
2
0
PPM

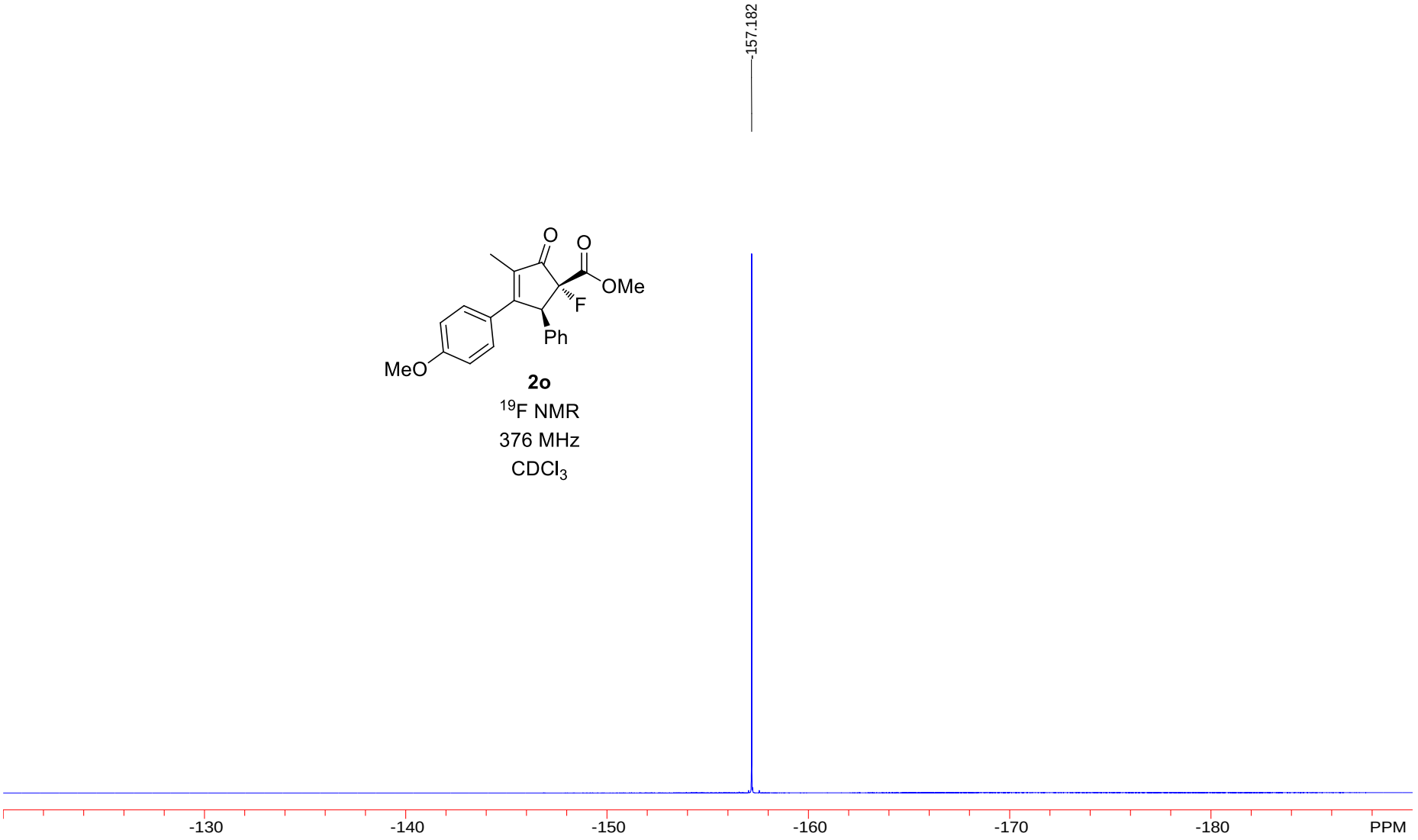

197.572
197.397
166.226
165.934
165.307
165.271
160.969
135.208
134.924
134.902
130.731
129.484
128.150
127.618
125.882
114.034
98.014
96.024
77.321
77.000
76.686
57.014
56.773
55.235
51.925
51.910
10.647
O
O
OMe
F
Ph
MeO
2o
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

2o

^{19}F NMR

376 MHz

$CDCl_3$

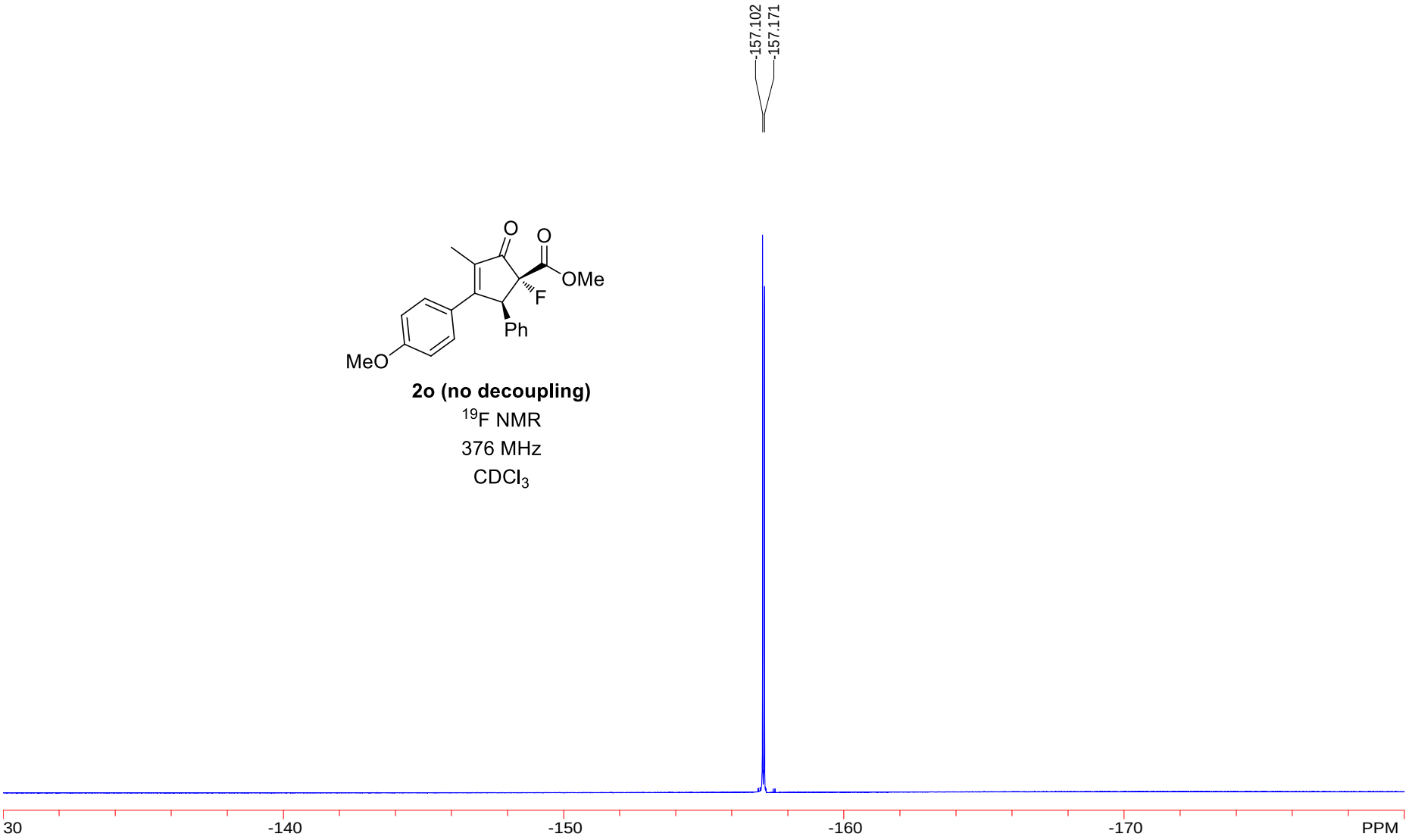


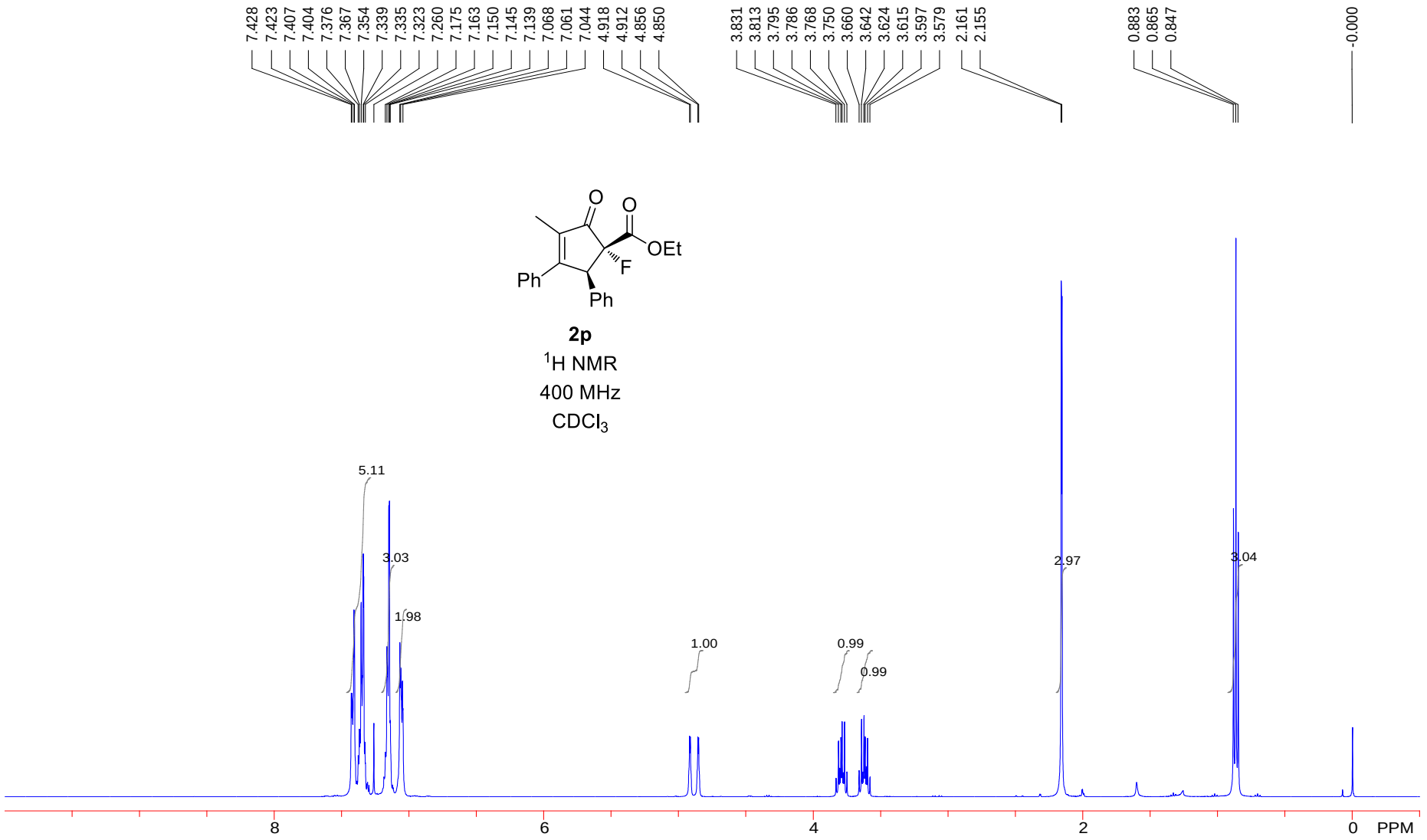
2o (no decoupling)

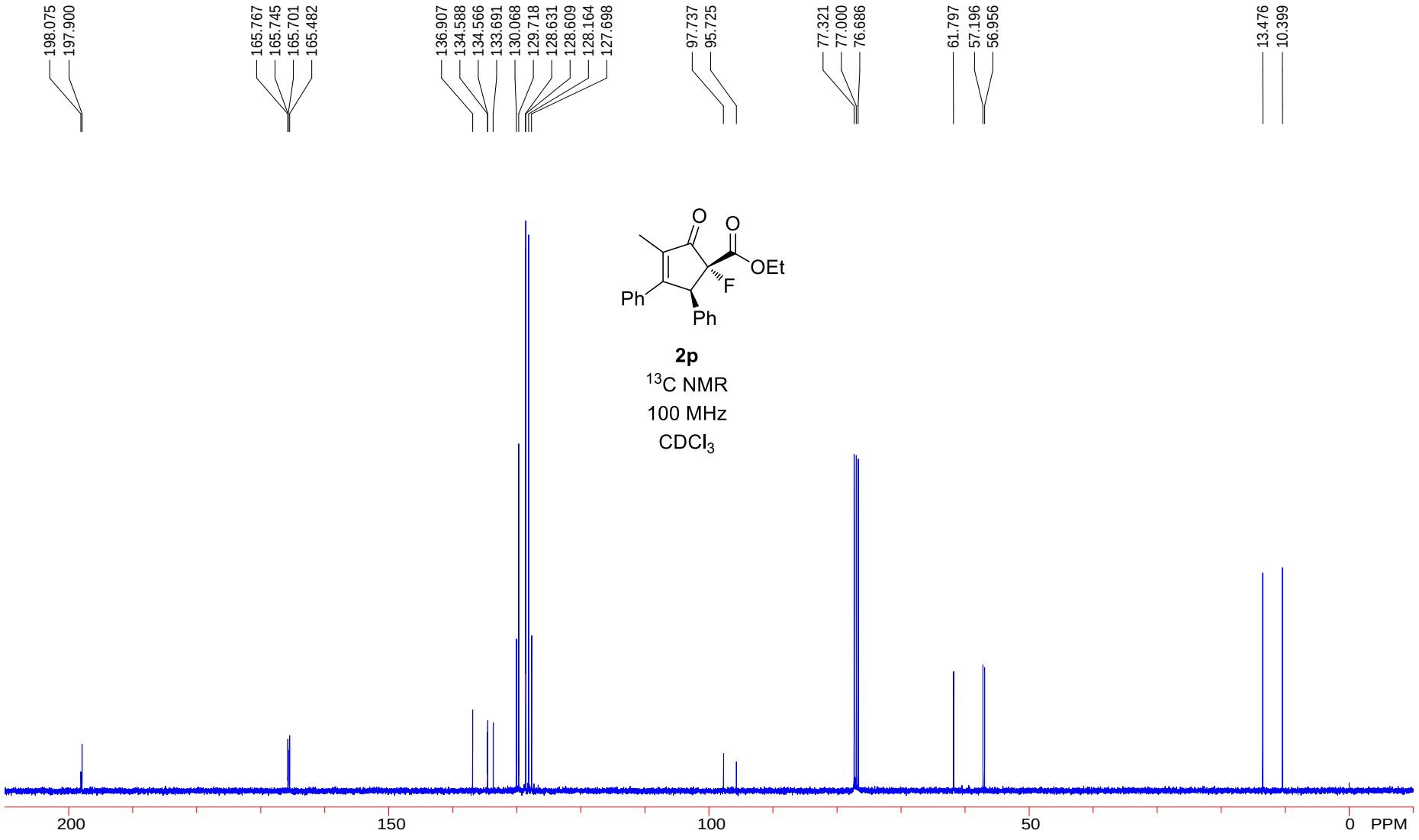
^{19}F NMR

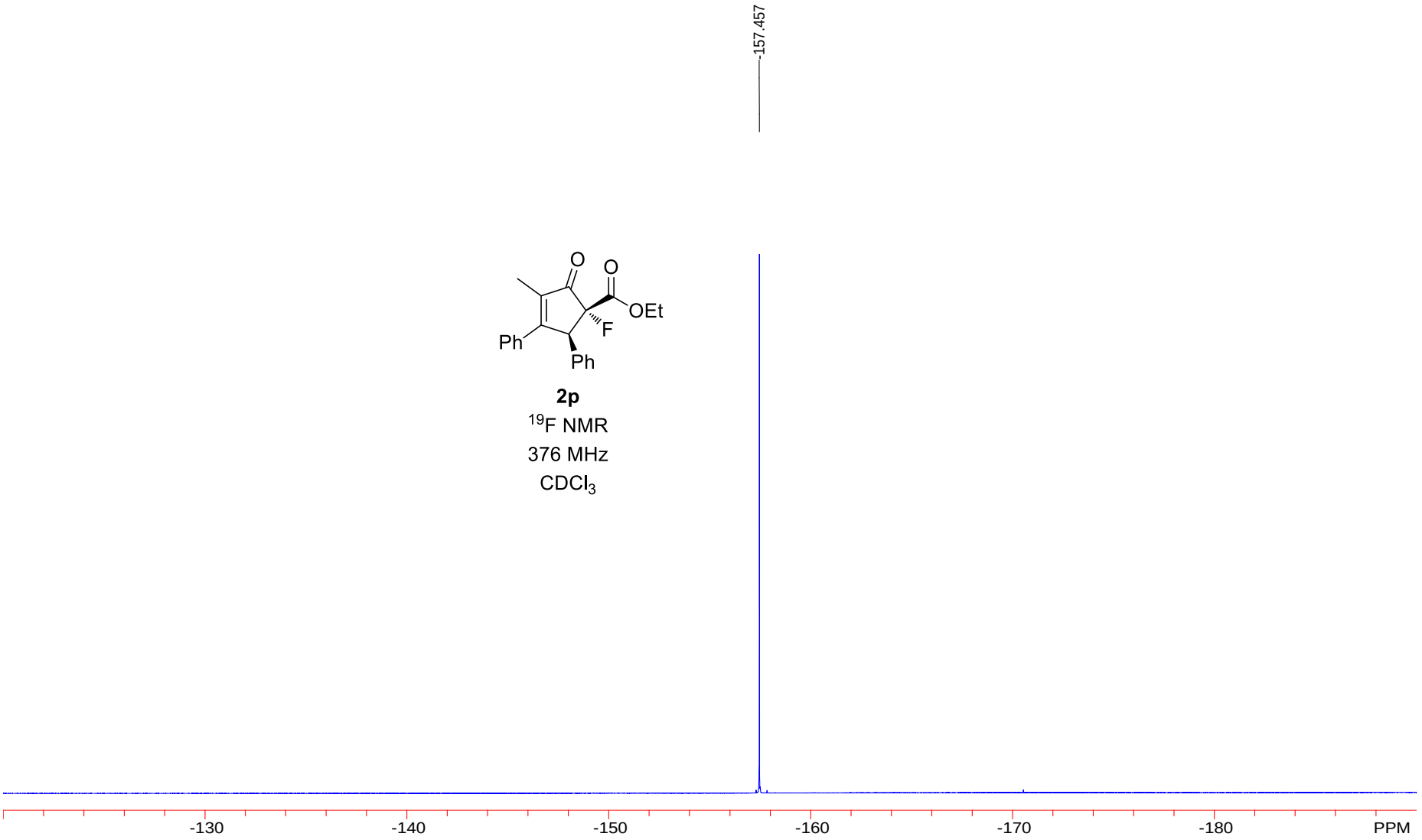
376 MHz

$CDCl_3$




7.428
7.423
7.407
7.404
7.376
7.367
7.354
7.339
7.335
7.323
7.260
7.175
7.163
7.150
7.145
7.139
7.068
7.061
7.044
4.918
4.912
4.856
4.850
3.831
3.813
3.795
3.786
3.768
3.750
3.660
3.642
3.624
3.615
3.597
3.579
2.161
2.155
0.883
0.865
0.847
-0.000
O
O
OEt
F
Ph
Ph
2p
1H NMR
400 MHz
CDCl3
5.11
3.03
1.98
1.00
0.99
0.99
2.97
3.04
8
6
4
2
0
PPM


198.075
197.900
165.767
165.745
165.701
165.482
136.907
134.588
134.566
133.691
130.068
129.718
128.631
128.609
128.164
127.698
97.737
95.725
77.321
77.000
76.686
61.797
57.196
56.956
13.476
10.399
O
O
OEt
F
Ph
Ph
2p
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

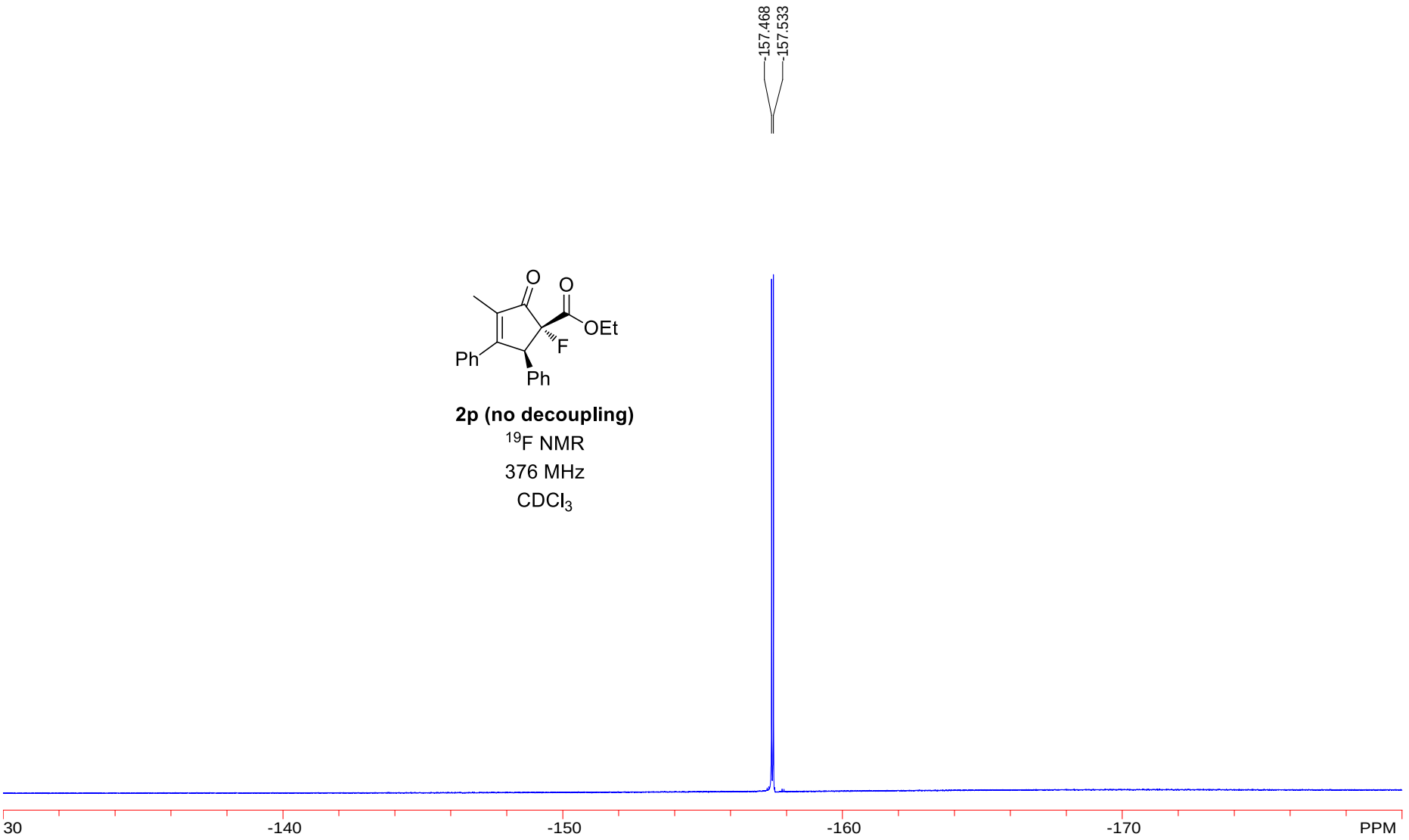


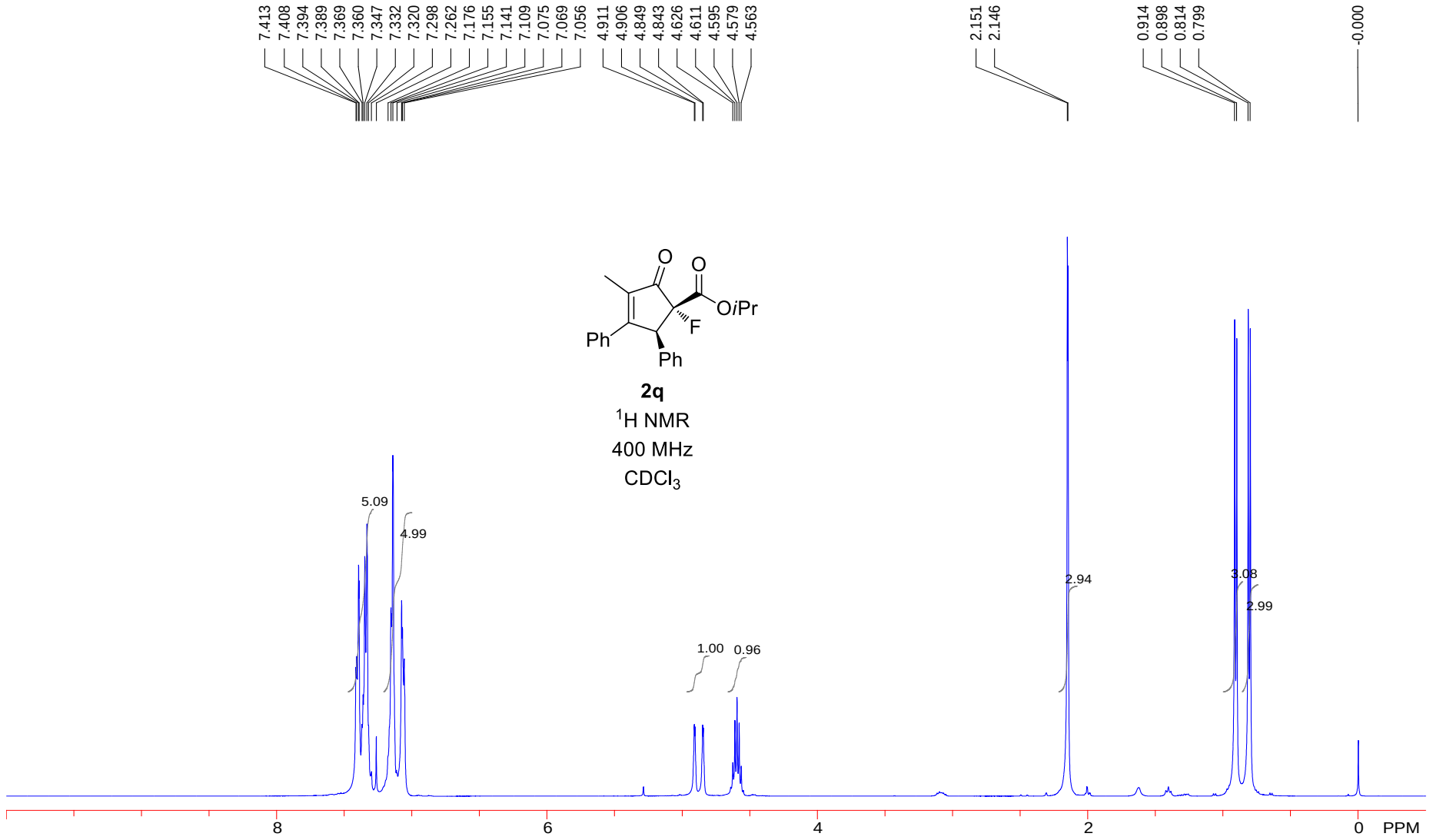
2p

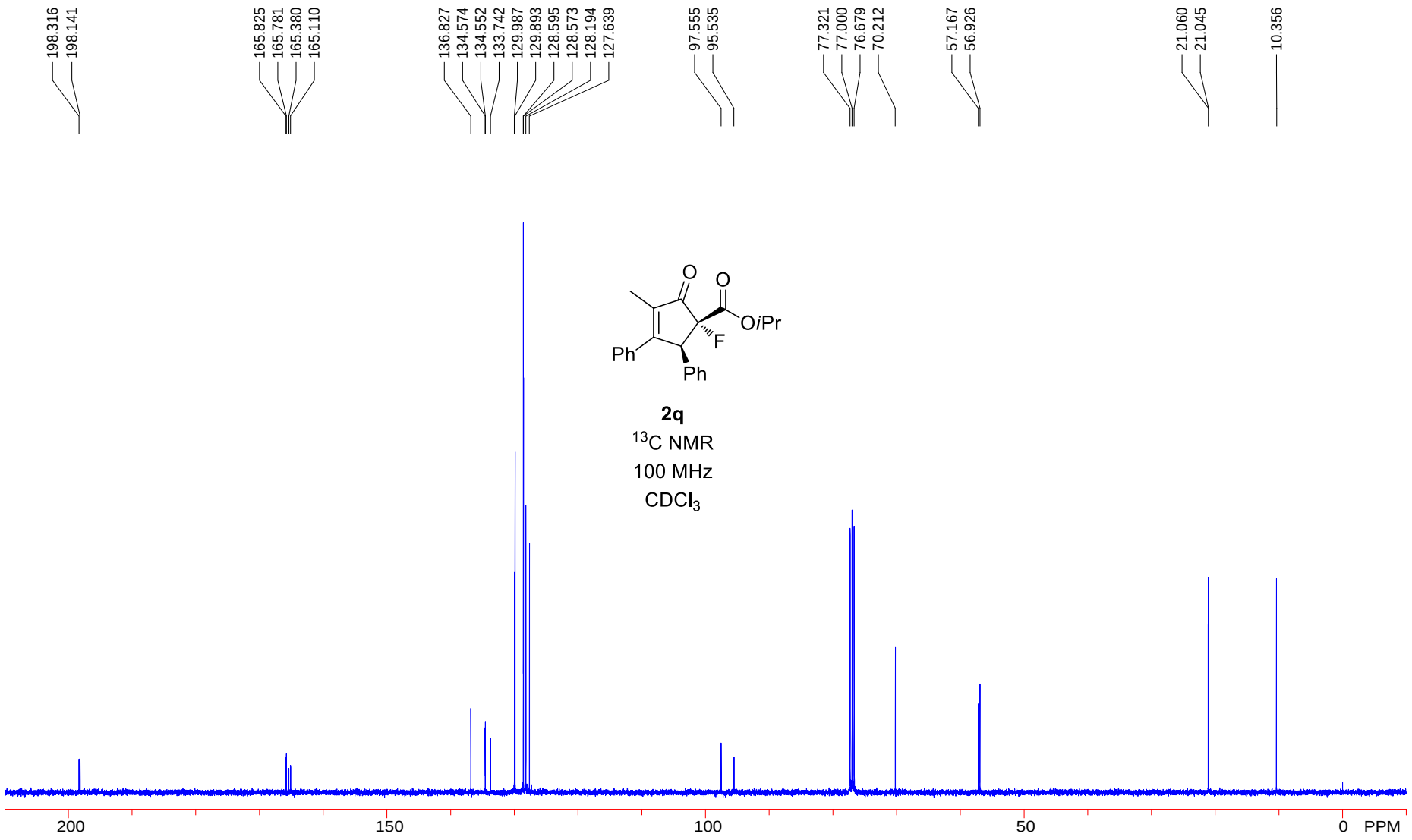
^{19}F NMR

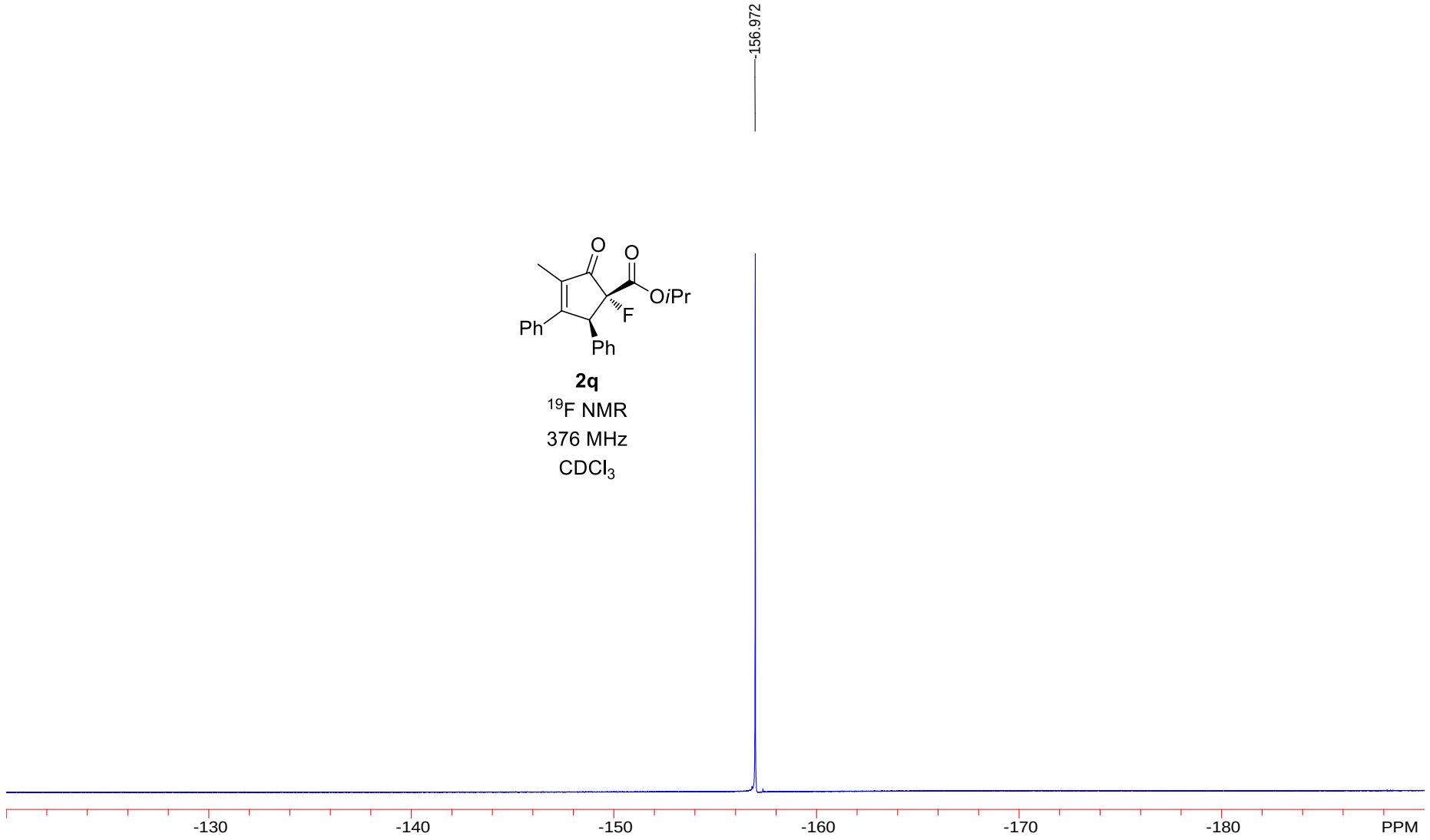
376 MHz

$CDCl_3$


-157.468
-157.533
O
O
OEt
F
Ph
Ph
2p (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.413
7.408
7.394
7.389
7.369
7.360
7.347
7.332
7.320
7.298
7.262
7.176
7.155
7.141
7.109
7.075
7.069
7.056
4.911
4.906
4.849
4.843
4.626
4.611
4.595
4.579
4.563
2.151
2.146
0.914
0.898
0.814
0.799
-0.000
O
O
OiPr
F
Ph
Ph
2q
1H NMR
400 MHz
CDCl3
5.09
4.99
1.00
0.96
2.94
3.08
2.99
8
6
4
2
0
PPM


198.316
198.141
165.825
165.781
165.380
165.110
136.827
134.574
134.552
133.742
129.987
129.893
128.595
128.573
128.194
127.639
97.555
95.535
77.321
77.000
76.679
70.212
57.167
56.926
21.060
21.045
10.356
O
O
OiPr
F
Ph
Ph
2q
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

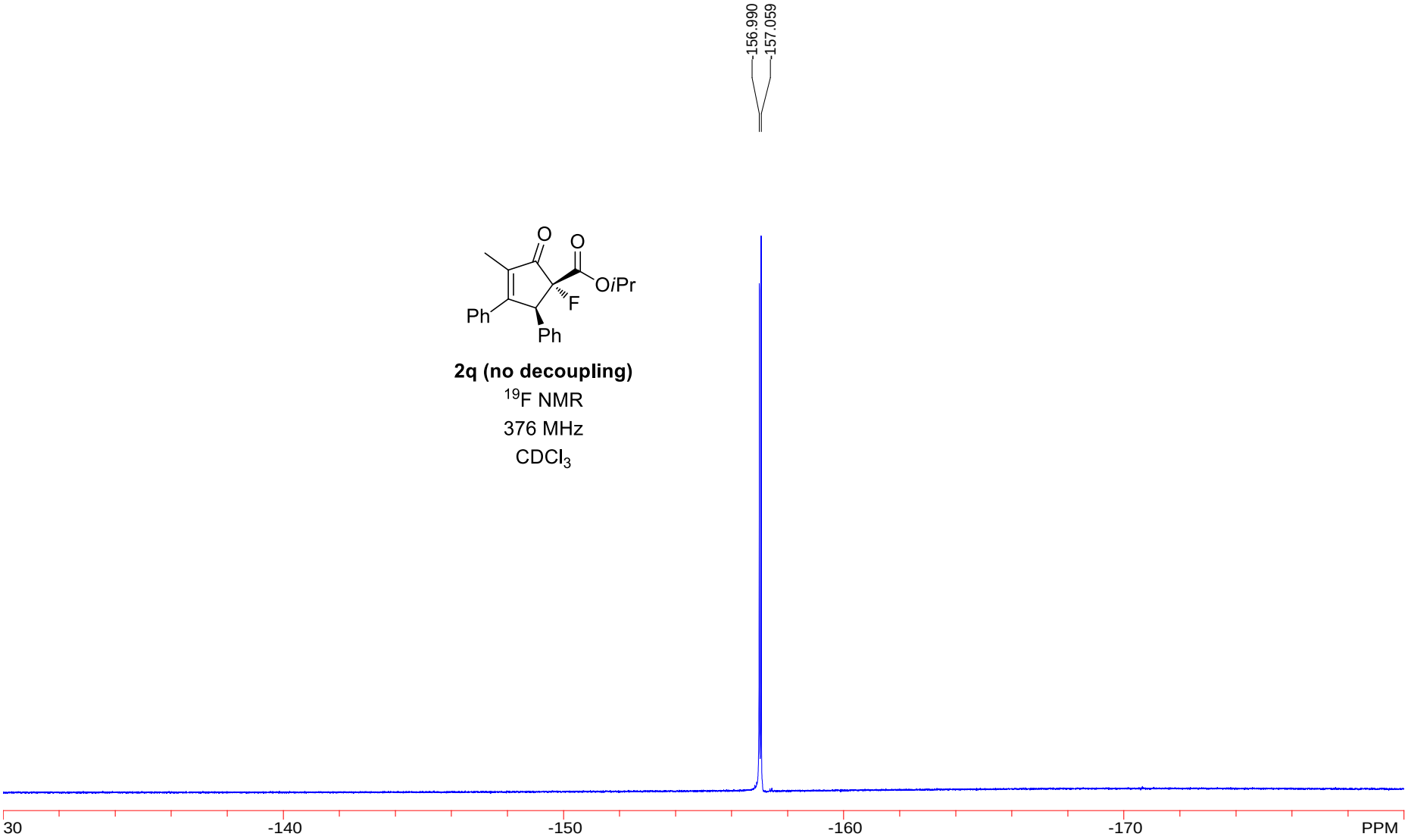


2q

^{19}F NMR

376 MHz

$CDCl_3$

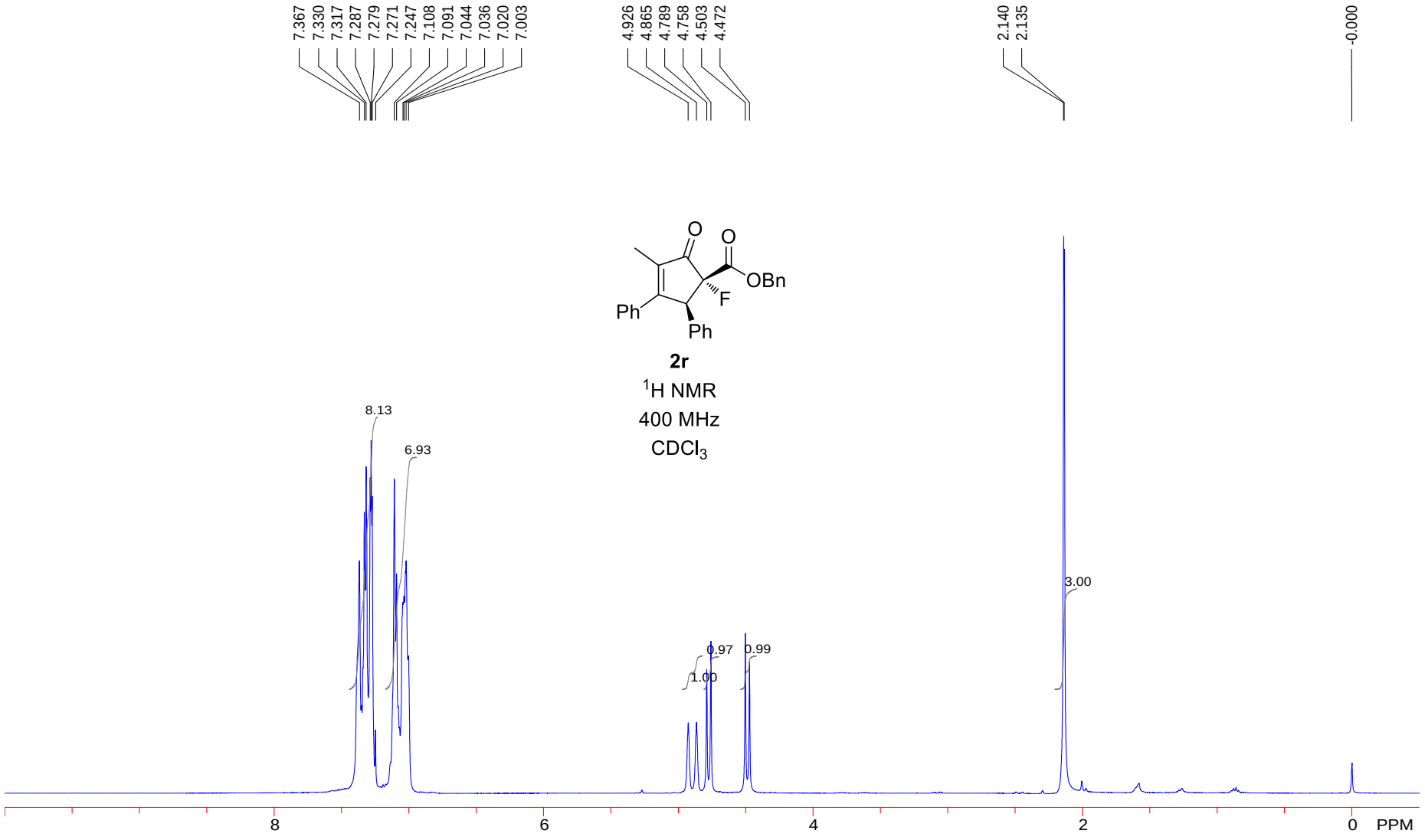


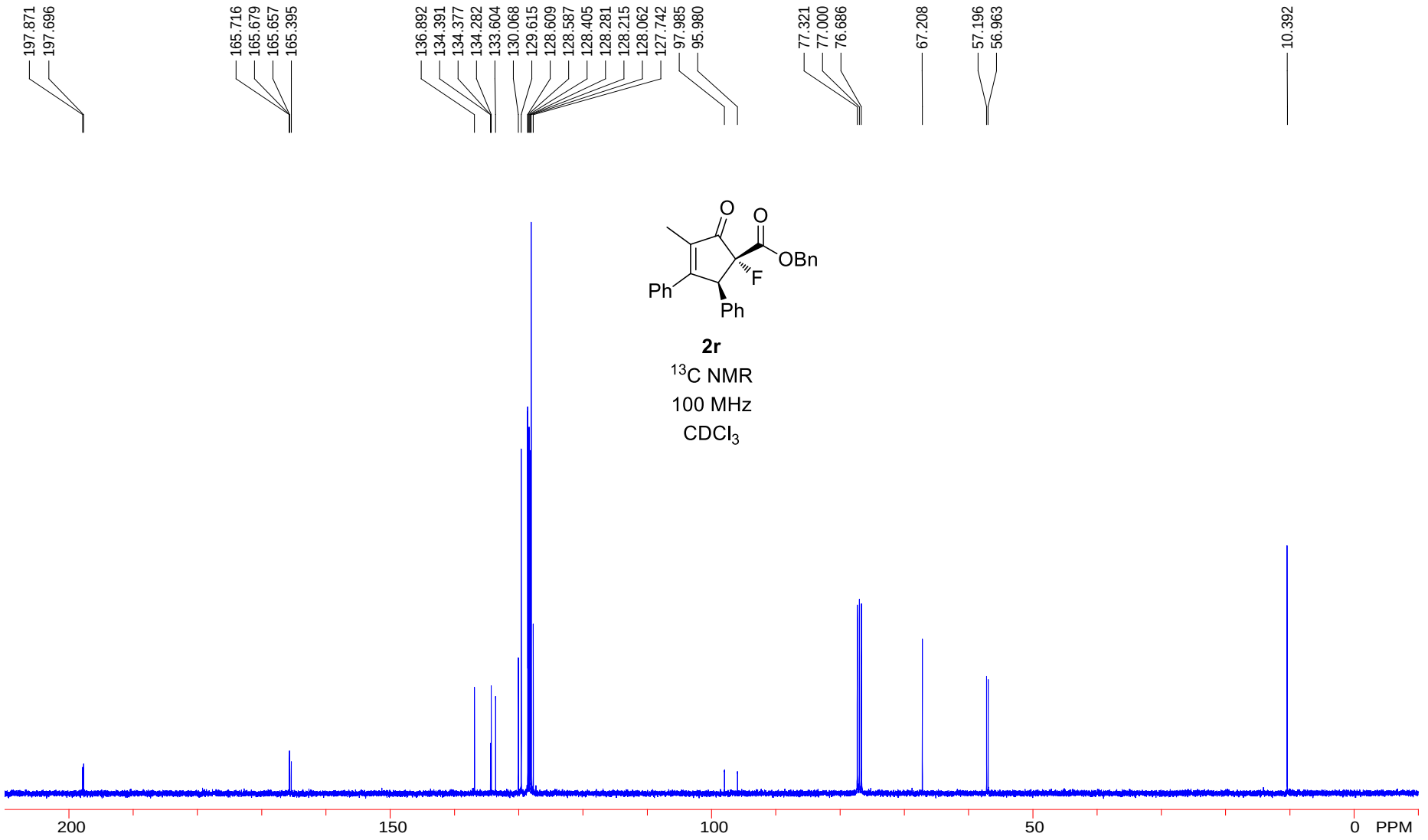
2q (no decoupling)

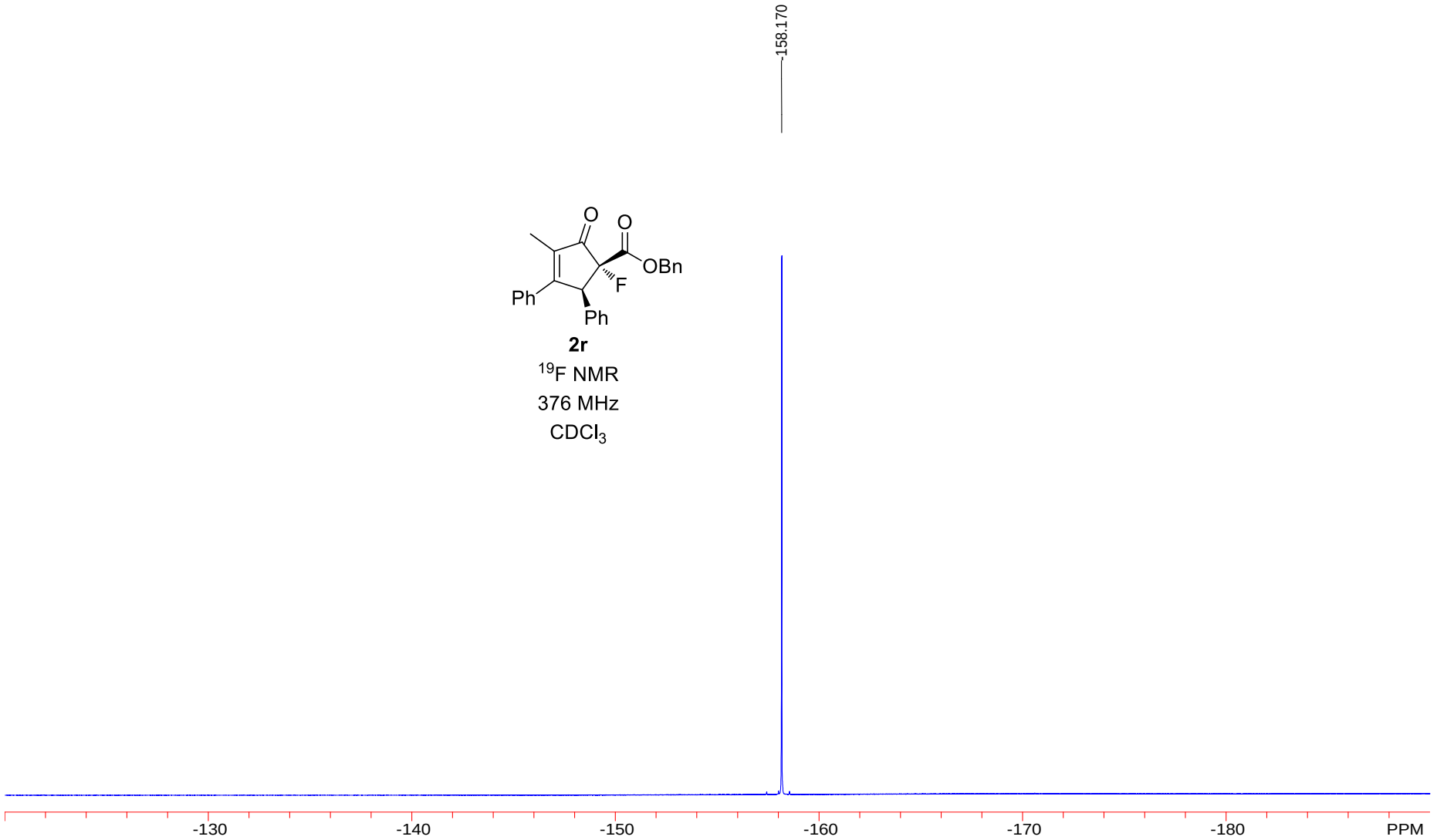
^{19}F NMR

376 MHz

$CDCl_3$


7.367
7.330
7.317
7.287
7.279
7.271
7.247
7.108
7.091
7.044
7.036
7.020
7.003
4.926
4.865
4.789
4.758
4.503
4.472
2.140
2.135
-0.000
O
O
OBn
F
Ph
Ph
2r
1H NMR
400 MHz
CDCl3
8.13
6.93
0.97
0.99
1.00
3.00
8
6
4
2
0
PPM


197.871
197.696
165.716
165.679
165.657
165.395
136.892
134.391
134.377
134.282
133.604
130.068
129.615
128.609
128.587
128.405
128.281
128.215
128.062
127.742
97.985
95.980
77.321
77.000
76.686
67.208
57.196
56.963
10.392
O
O
OBn
F
Ph
Ph
2r
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

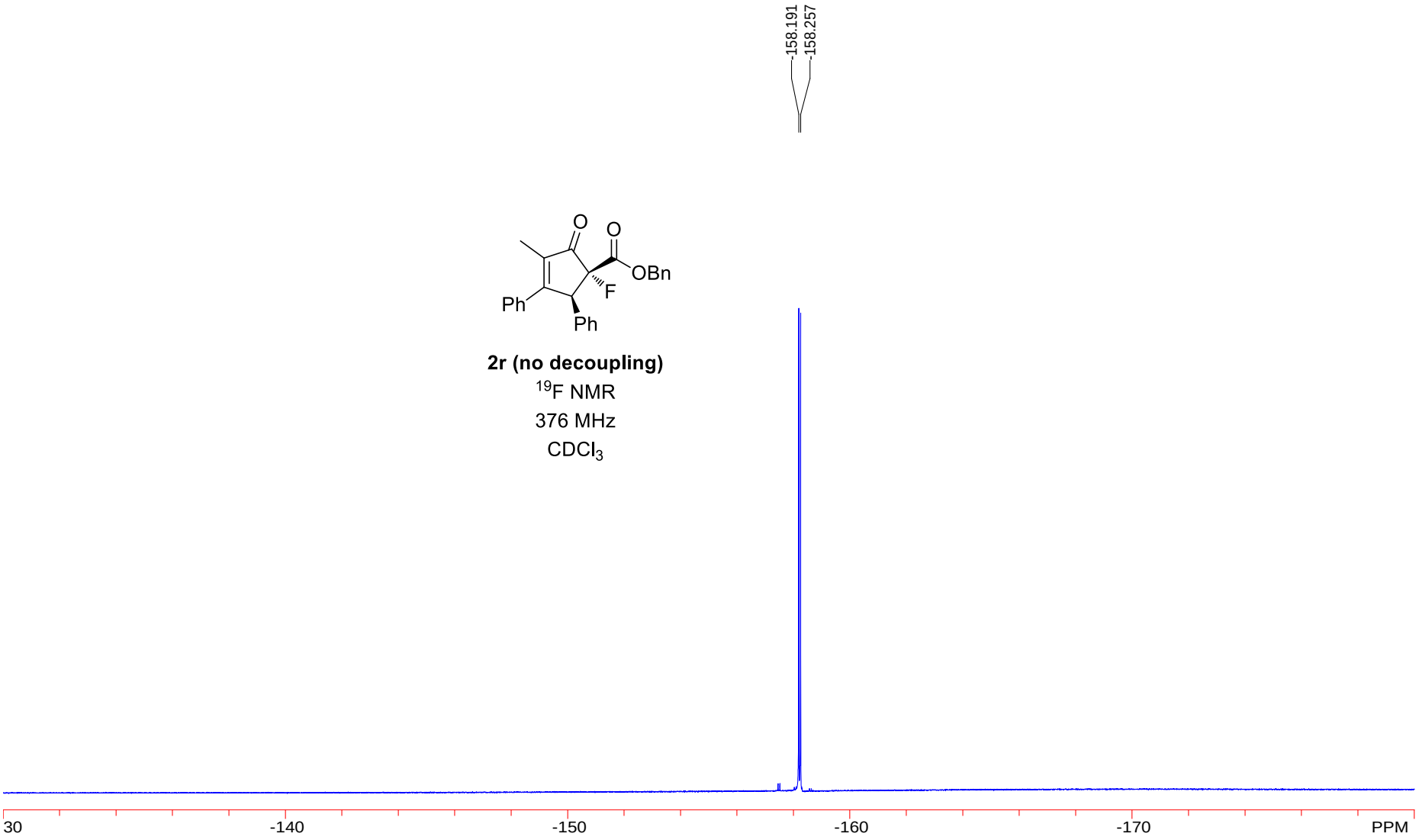


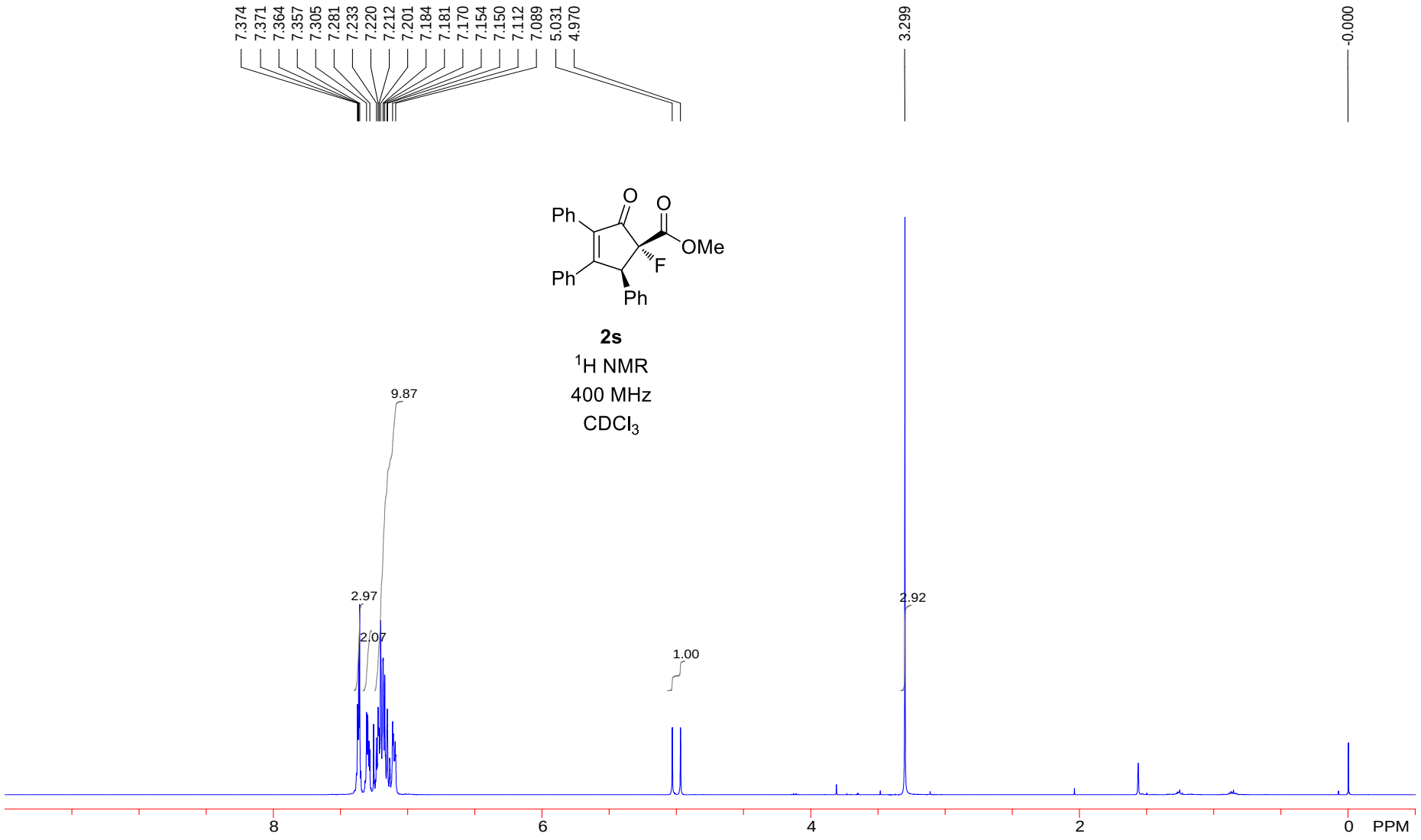
2r

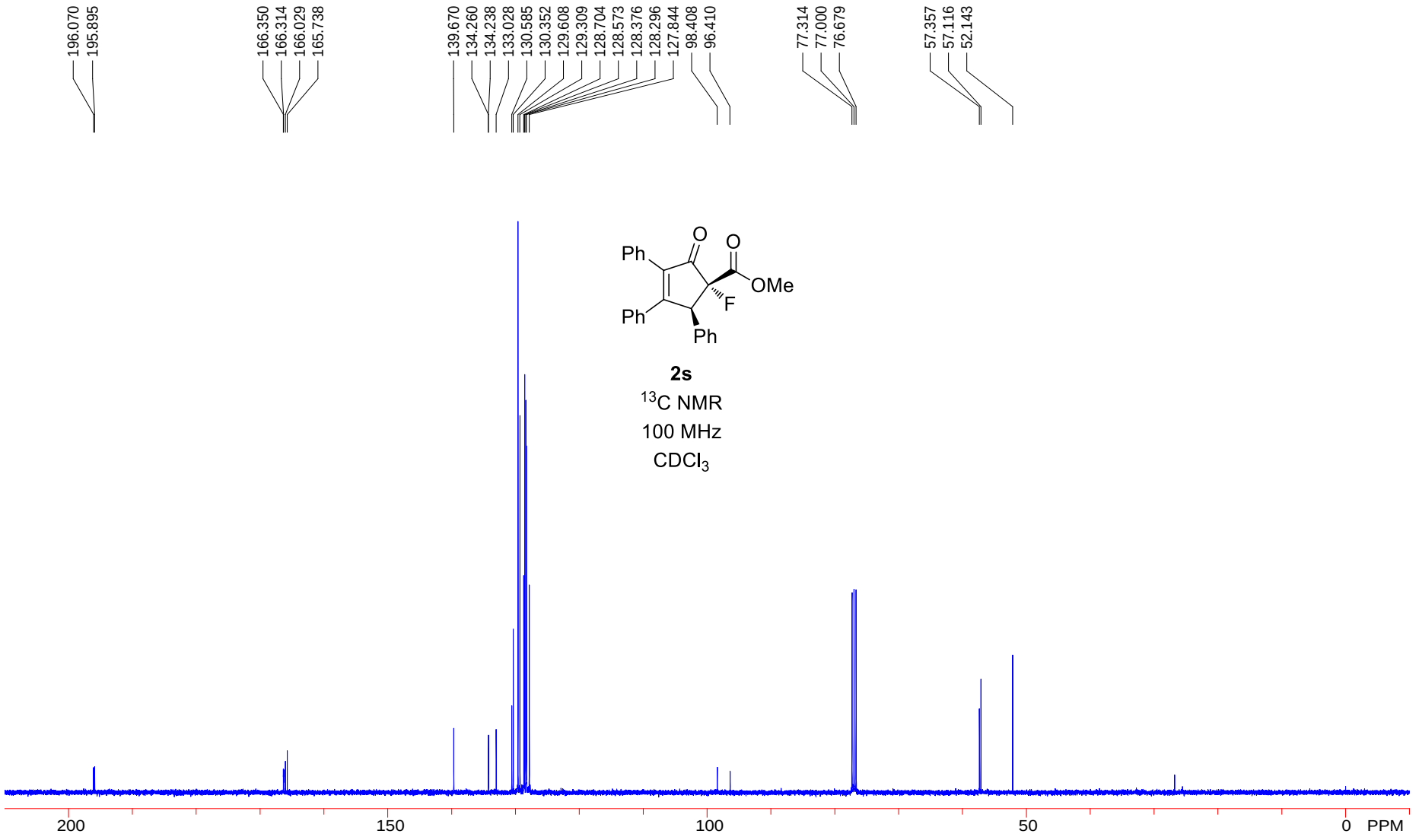
^{19}F NMR

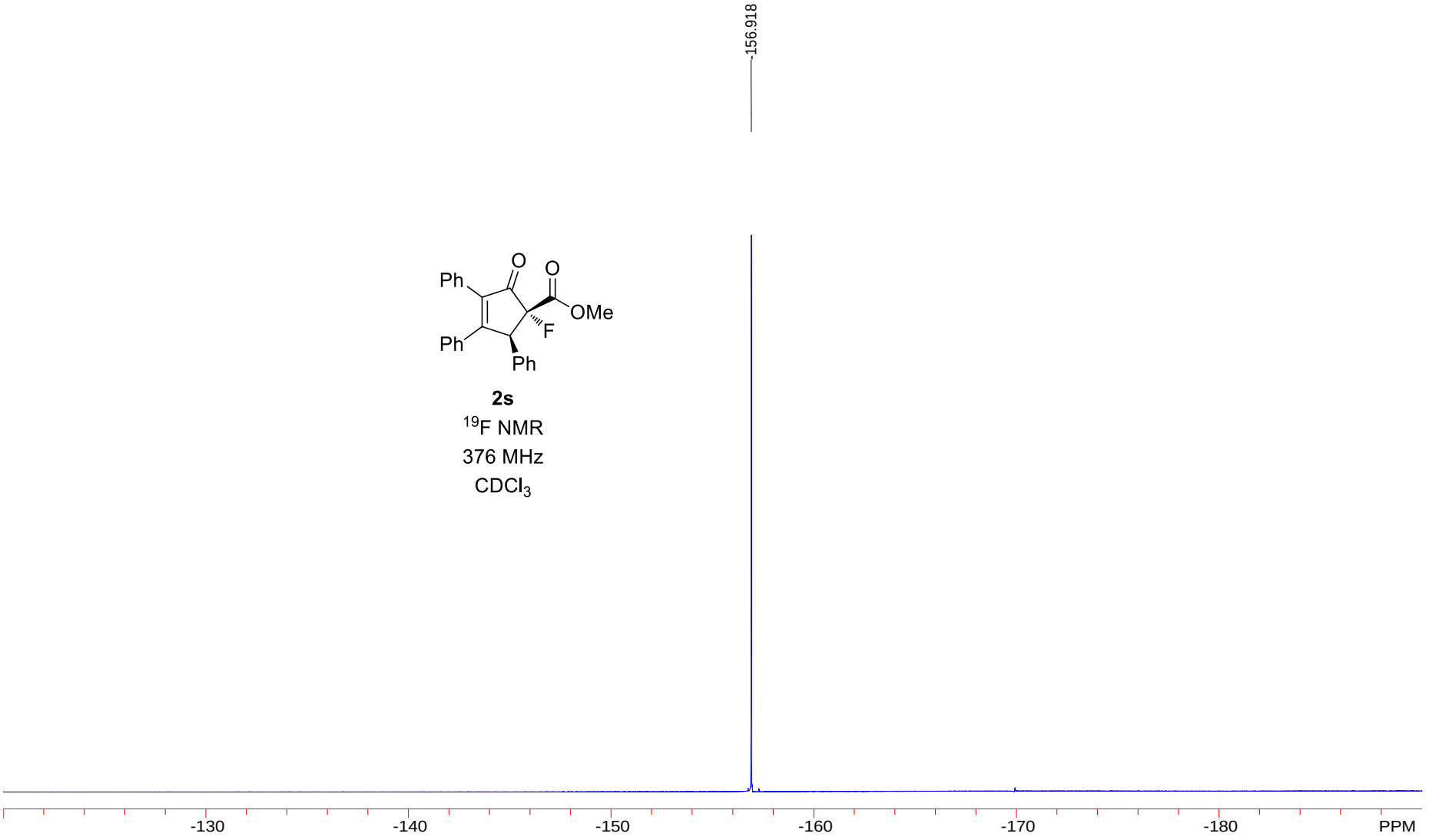
376 MHz

$CDCl_3$


158.191
158.257
O
O
OBn
F
Ph
Ph
2r (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.374
7.371
7.364
7.357
7.305
7.281
7.233
7.220
7.212
7.201
7.184
7.181
7.170
7.154
7.150
7.112
7.089
5.031
4.970
3.299
-0.000
Ph
Ph
Ph
O
O
OMe
F
2s
1H NMR
400 MHz
CDCl3
9.87
2.97
2.07
1.00
2.92
8
6
4
2
0
PPM


196.070
195.895
166.350
166.314
166.029
165.738
139.670
134.260
134.238
133.028
130.585
130.352
129.608
129.309
128.704
128.573
128.376
128.296
127.844
98.408
96.410
77.314
77.000
76.679
57.357
57.116
52.143
O
O
Ph
OMe
F
Ph
Ph
2s
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

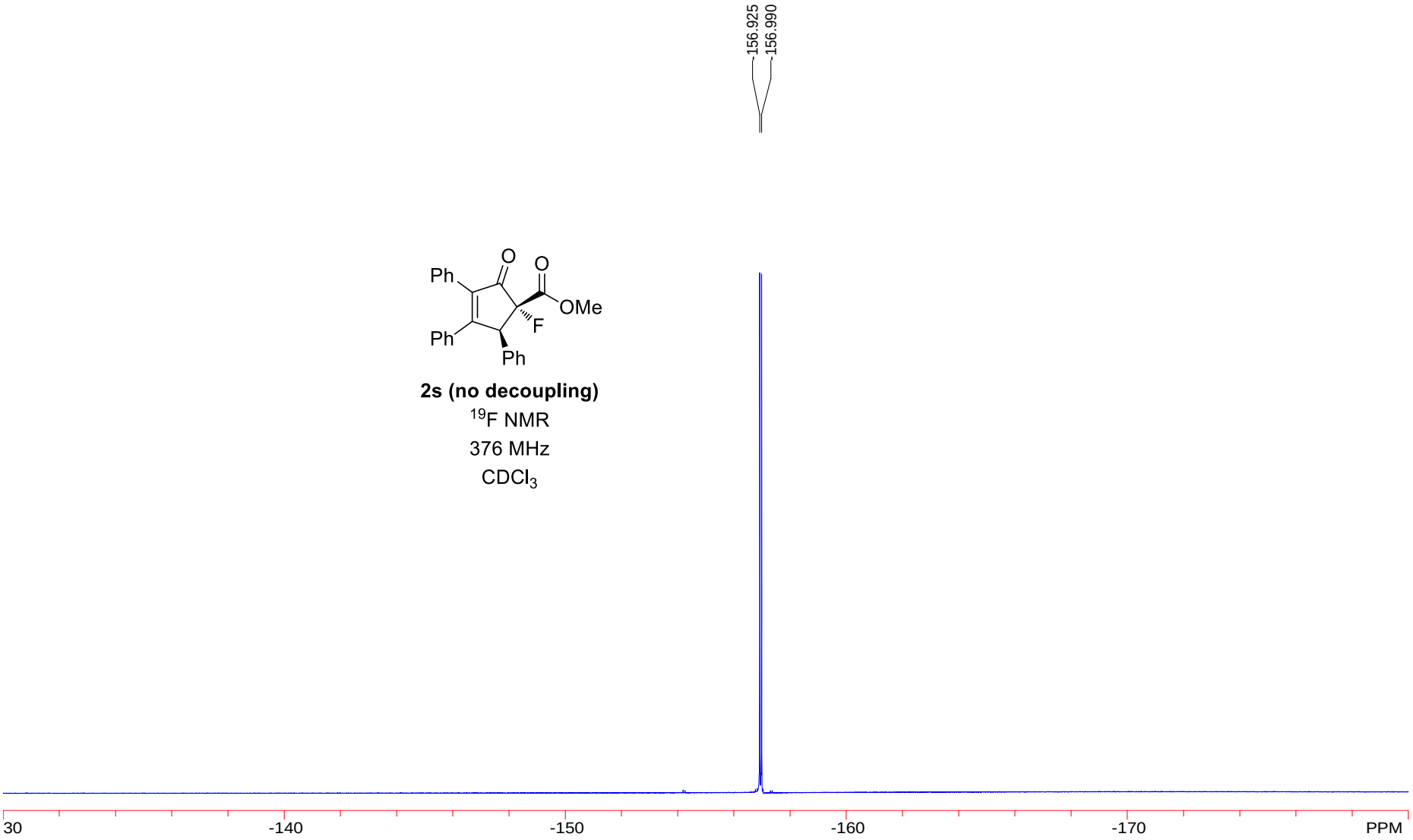


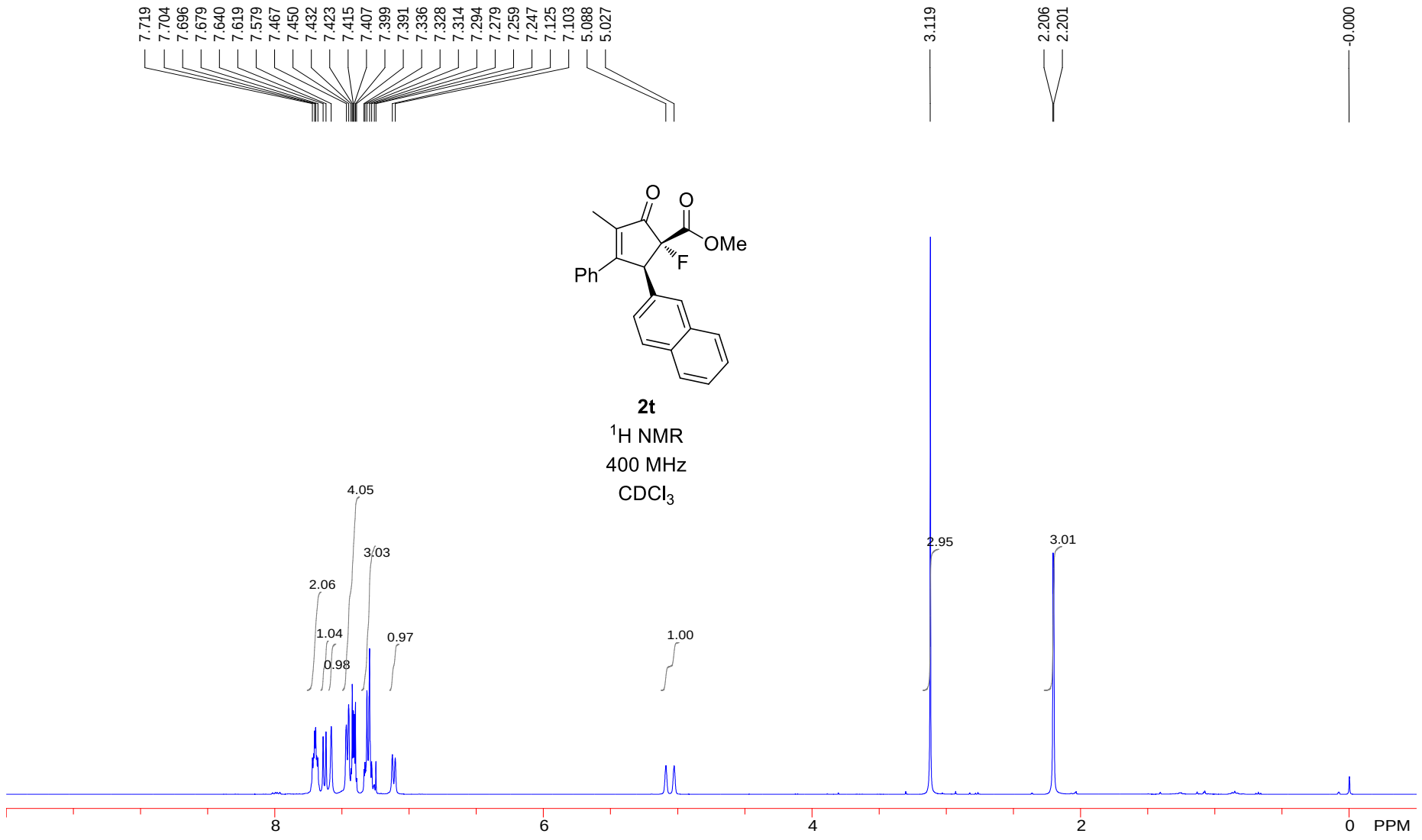
2s

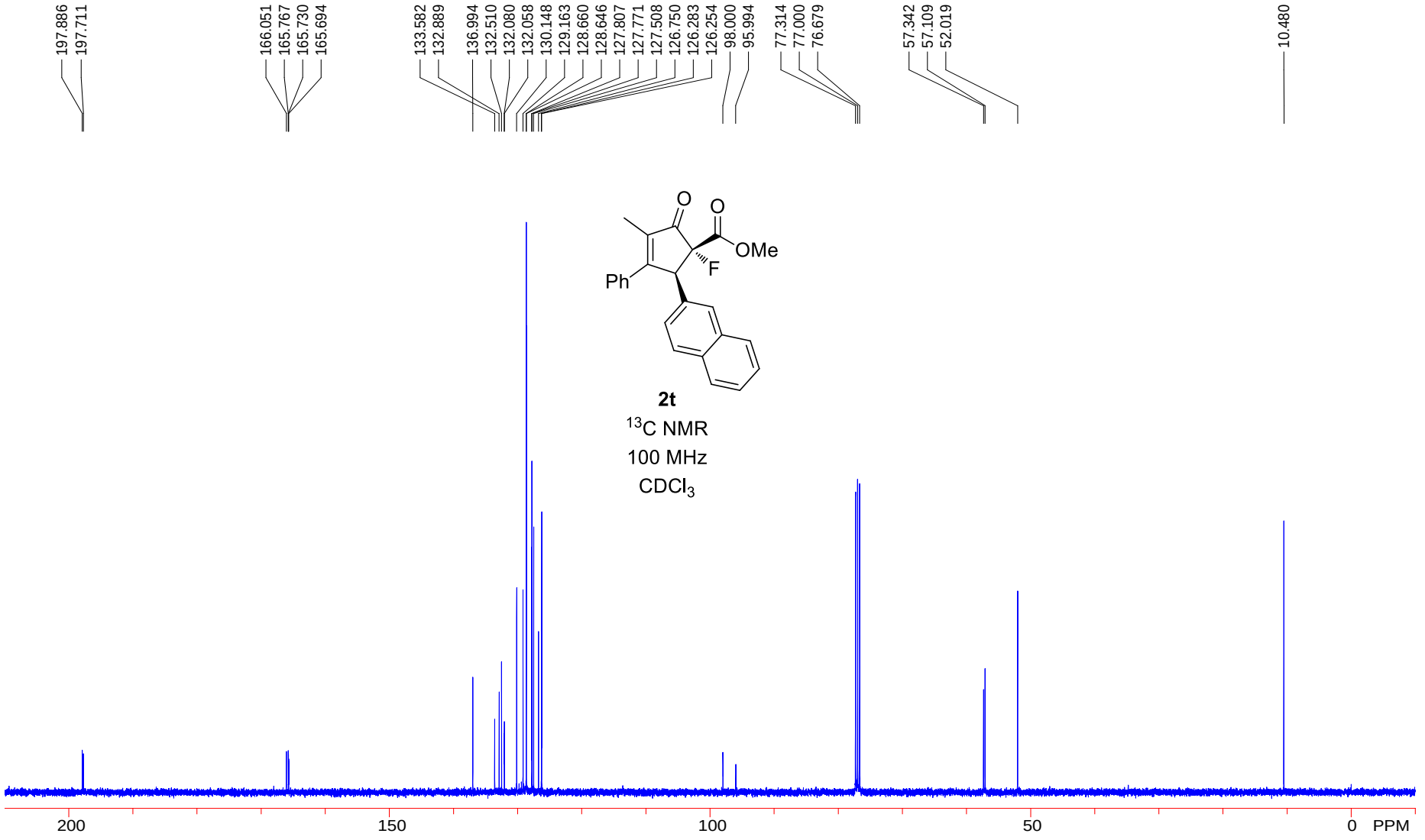
^{19}F NMR

376 MHz

$CDCl_3$


-156.925
-156.990
Ph
O
O
OMe
F
Ph
Ph
2s (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.719
7.704
7.696
7.679
7.640
7.619
7.579
7.467
7.450
7.432
7.423
7.415
7.407
7.399
7.391
7.336
7.328
7.314
7.294
7.279
7.259
7.247
7.125
7.103
5.088
5.027
3.119
2.206
2.201
-0.000
O
O
OMe
F
Ph
2t
1H NMR
400 MHz
CDCl3
4.05
3.03
2.06
1.04
0.98
0.97
1.00
2.95
3.01
8
6
4
2
0
PPM

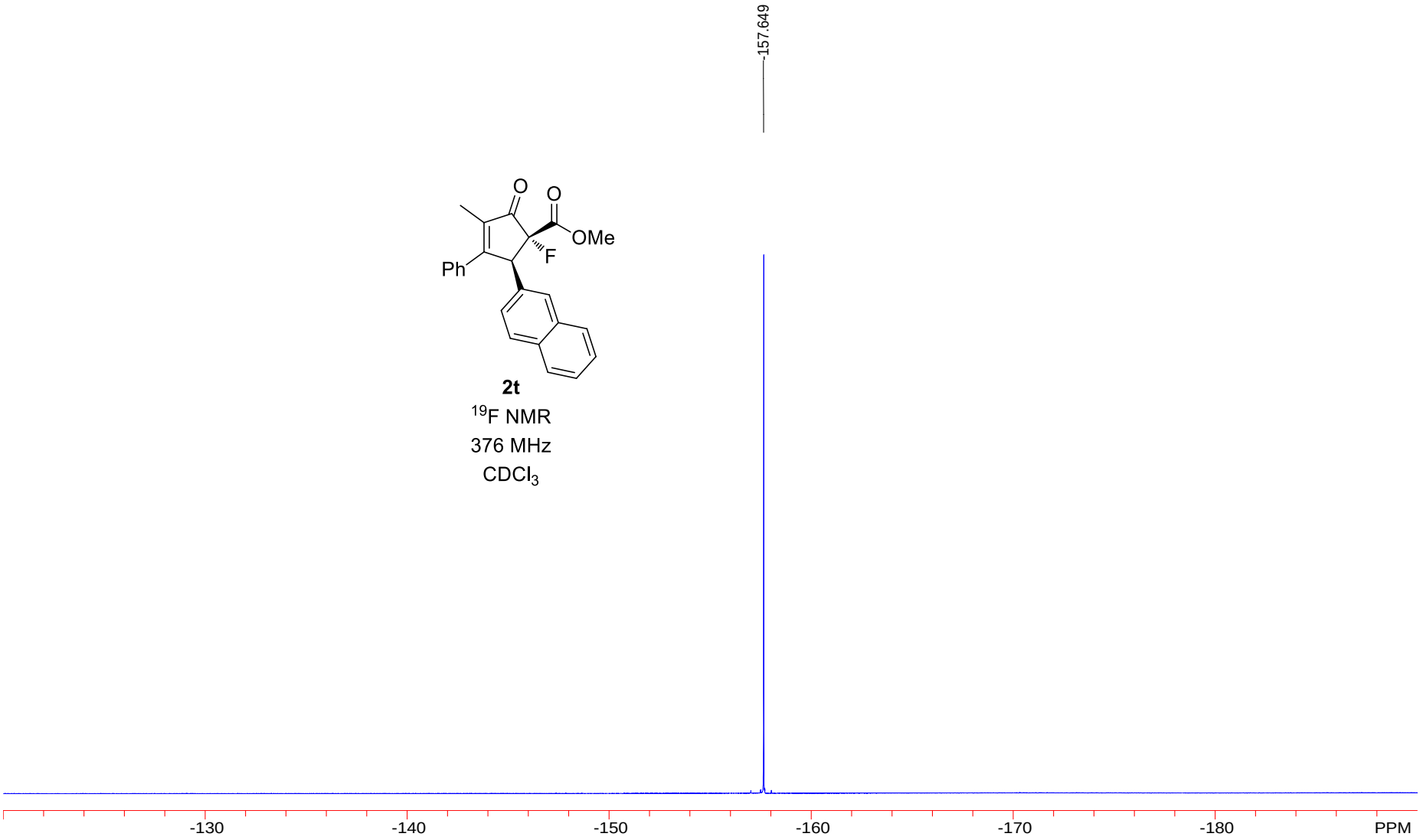

197.886
197.711
166.051
165.767
165.730
165.694
133.582
132.889
136.994
132.510
132.080
132.058
130.148
129.163
128.660
128.646
127.807
127.771
127.508
126.750
126.283
126.254
98.000
95.994
77.314
77.000
76.679
57.342
57.109
52.019
10.480
O
O
OMe
F
Ph
2t
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

2t

^{19}F NMR

376 MHz

$CDCl_3$

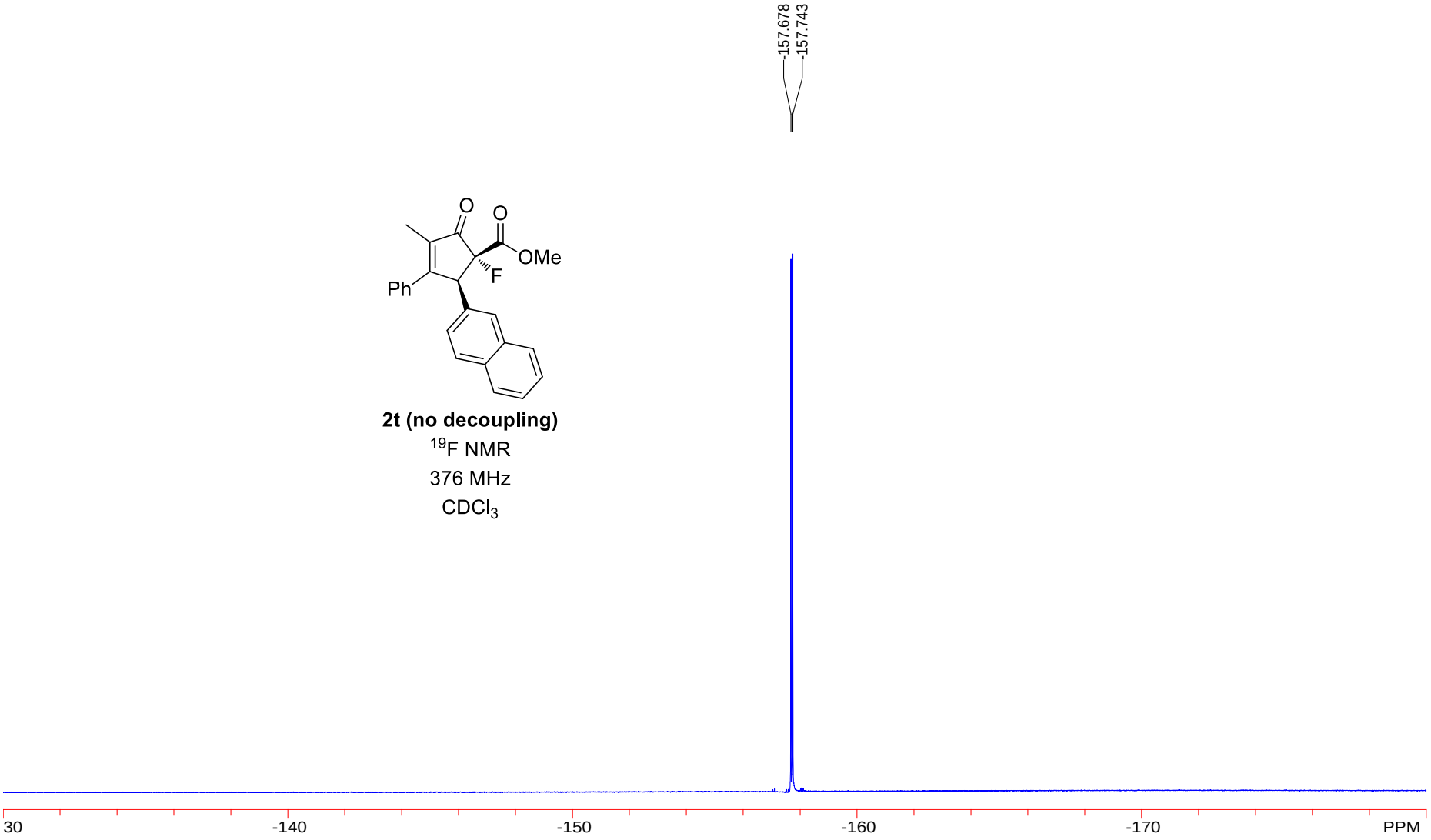


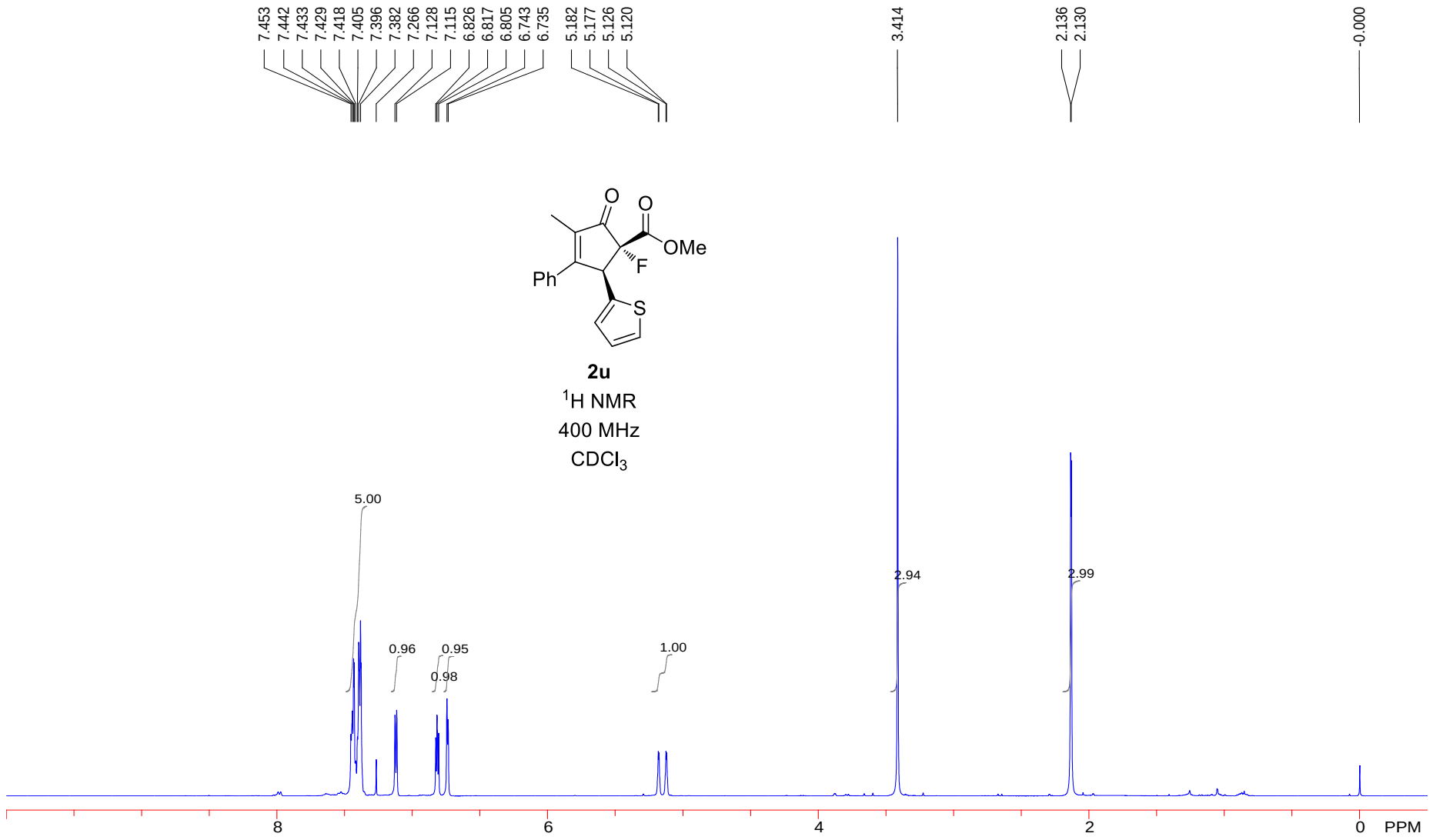
2t (no decoupling)

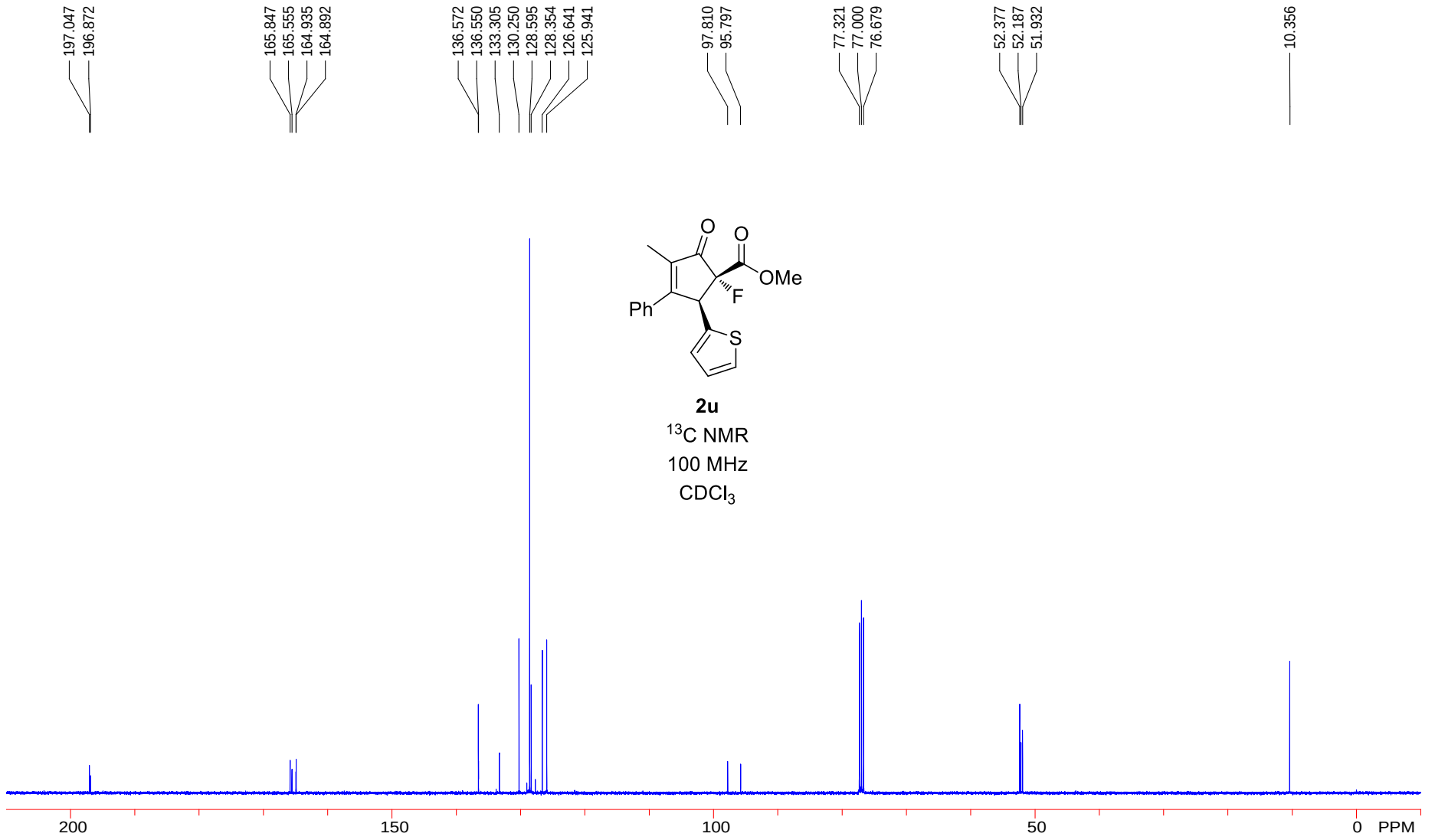
^{19}F NMR

376 MHz

$CDCl_3$




7.453
7.442
7.433
7.429
7.418
7.405
7.396
7.382
7.266
7.128
7.115
6.826
6.817
6.805
6.743
6.735
5.182
5.177
5.126
5.120
3.414
2.136
2.130
-0.000
O
O
OMe
F
Ph
S
2u
1H NMR
400 MHz
CDCl3
5.00
0.96
0.95
0.98
1.00
2.94
2.99
8
6
4
2
0
PPM

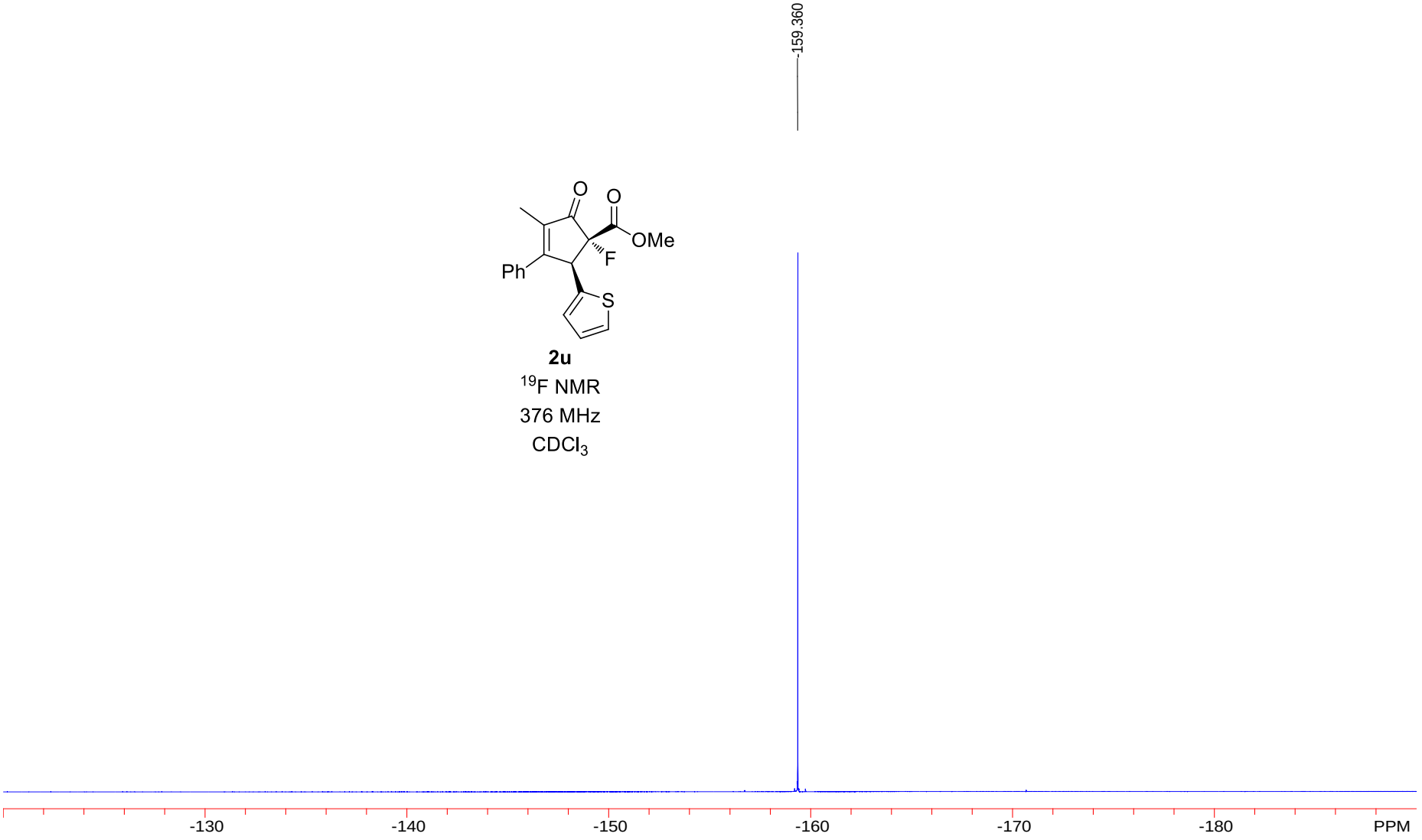

197.047
196.872
165.847
165.555
164.935
164.892
136.572
136.550
133.305
130.250
128.595
128.354
126.641
125.941
97.810
95.797
77.321
77.000
76.679
52.377
52.187
51.932
10.356
O
O
OMe
F
Ph
S
2u
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

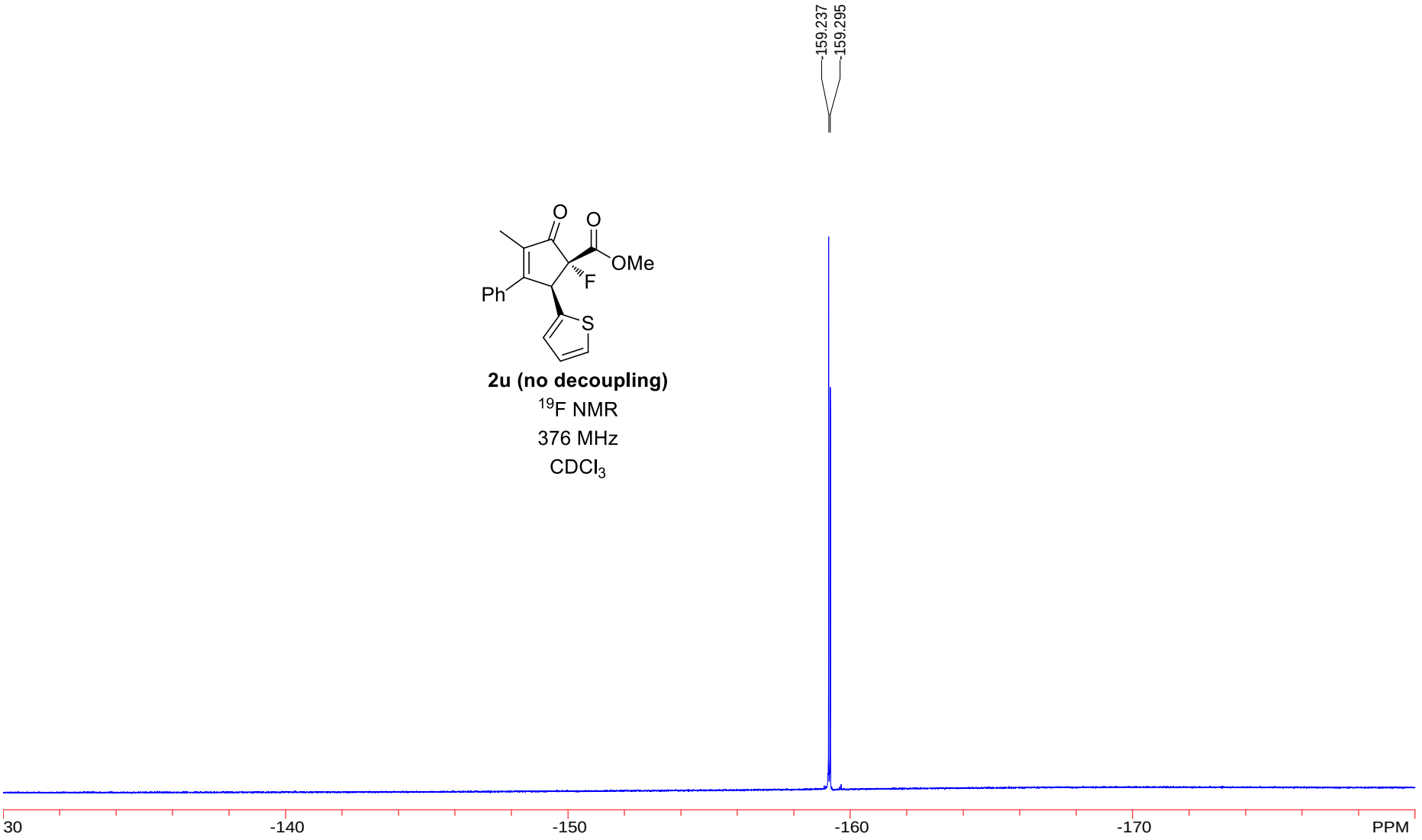
2u

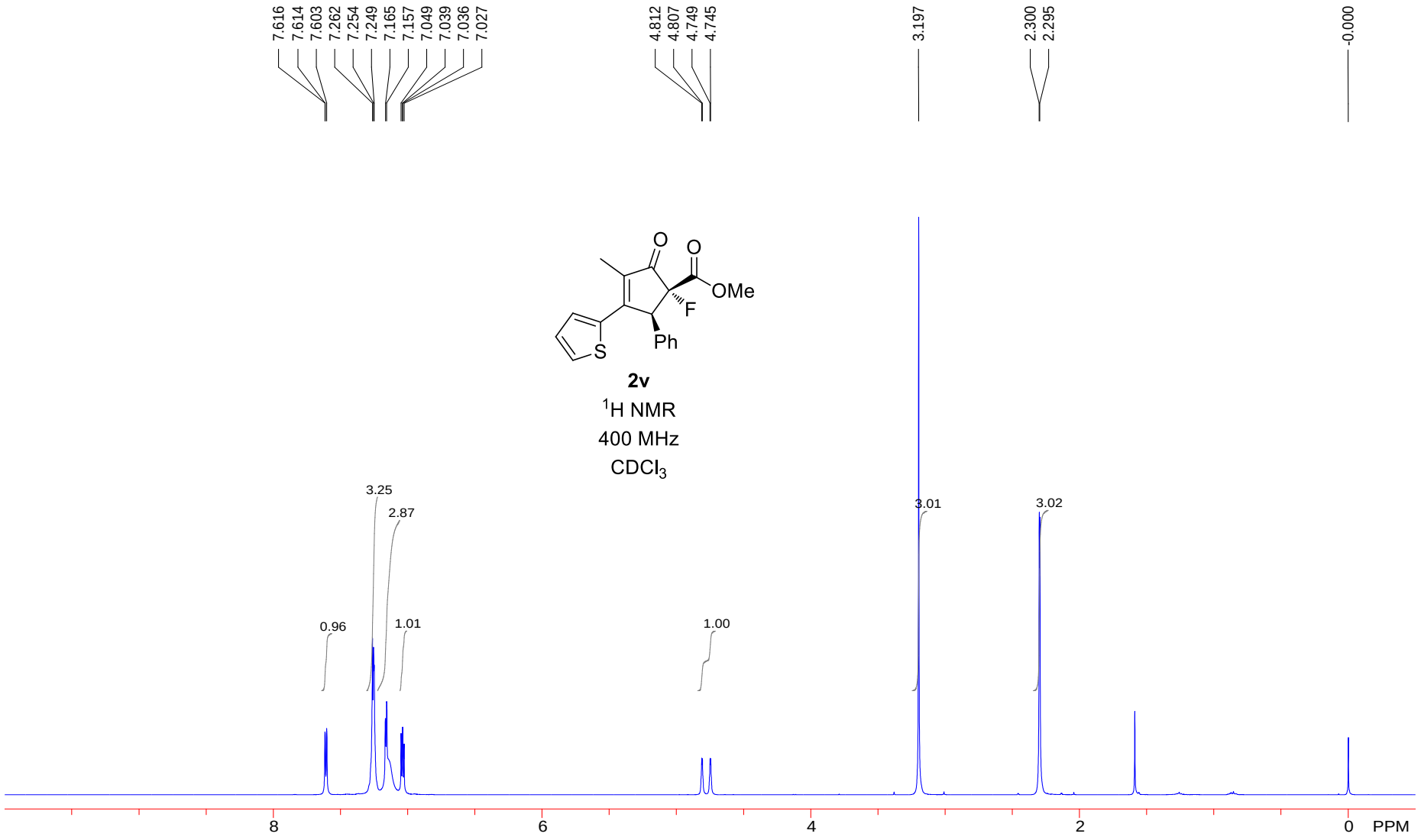
^{19}F NMR

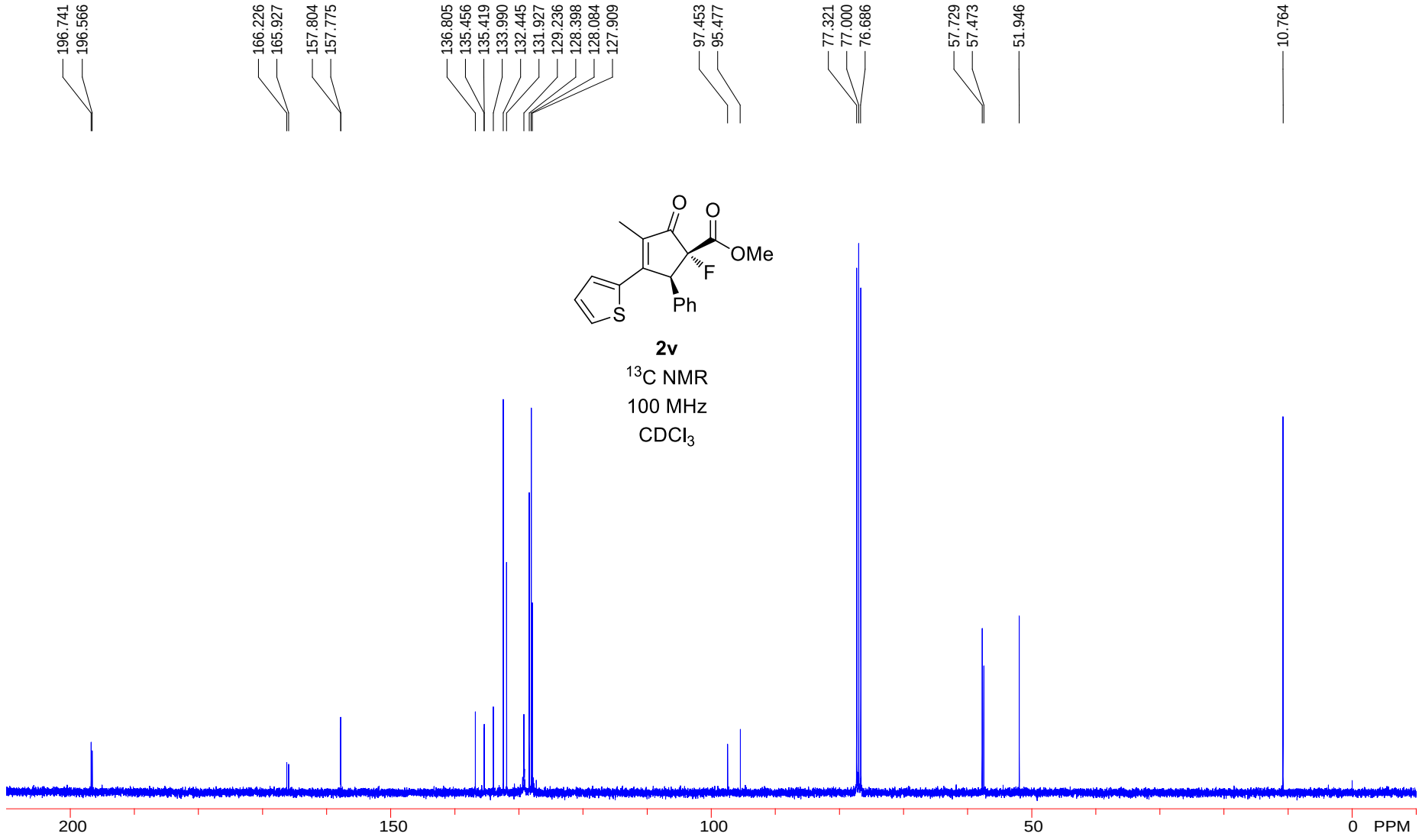
376 MHz

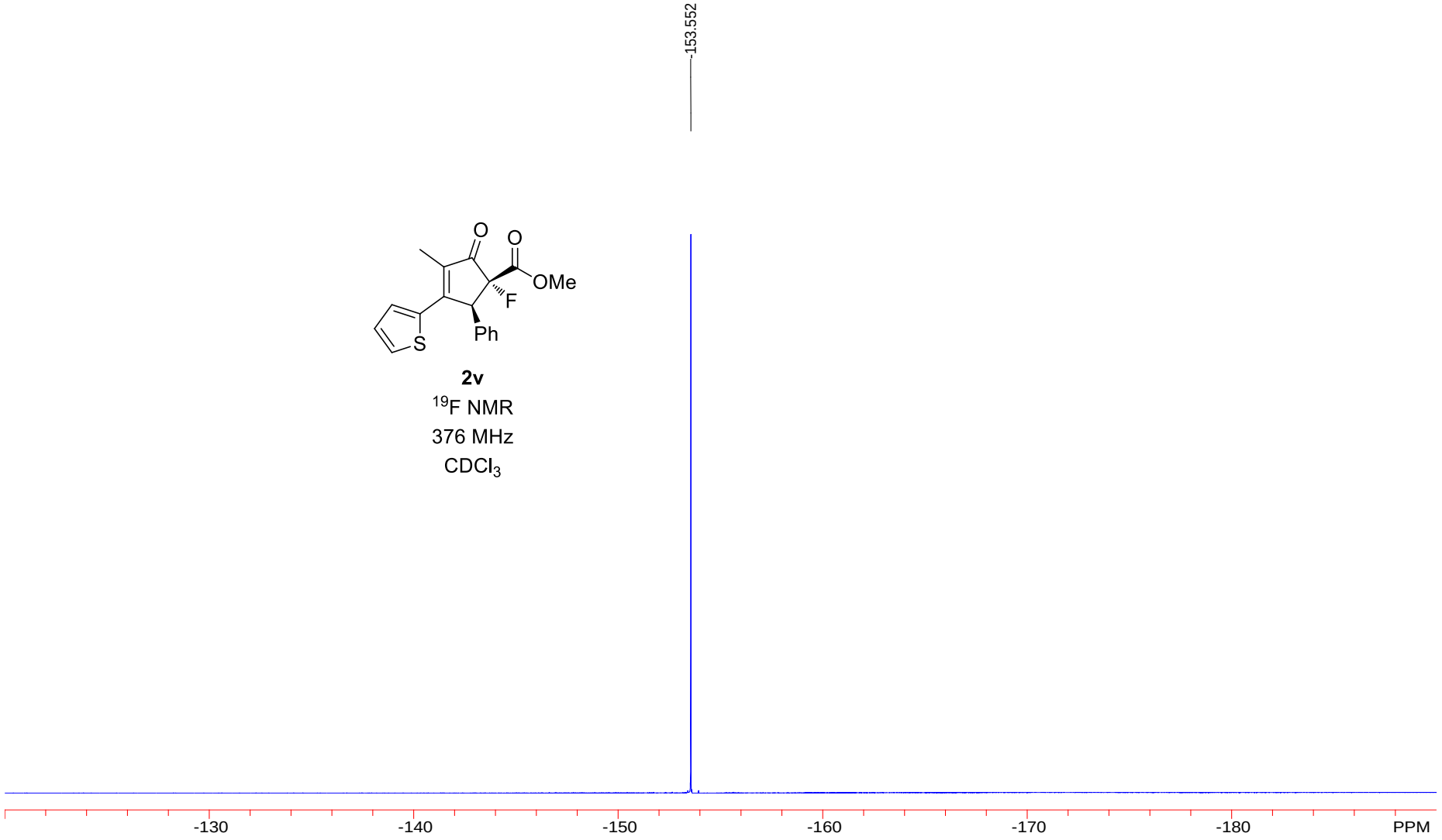
$CDCl_3$




159.237
159.295
O
O
OMe
F
Ph
S
2u (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.616
7.614
7.603
7.262
7.254
7.249
7.165
7.157
7.049
7.039
7.036
7.027
4.812
4.807
4.749
4.745
3.197
2.300
2.295
-0.000
O
O
OMe
F
Ph
S
2v
1H NMR
400 MHz
CDCl3
3.25
2.87
0.96
1.01
1.00
3.01
3.02
8
6
4
2
0
PPM


196.741
196.566
166.226
165.927
157.804
157.775
136.805
135.456
135.419
133.990
132.445
131.927
129.236
128.398
128.084
127.909
97.453
95.477
77.321
77.000
76.686
57.729
57.473
51.946
10.764
O
O
OMe
F
Ph
S
2v
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM



2v

^{19}F NMR

376 MHz

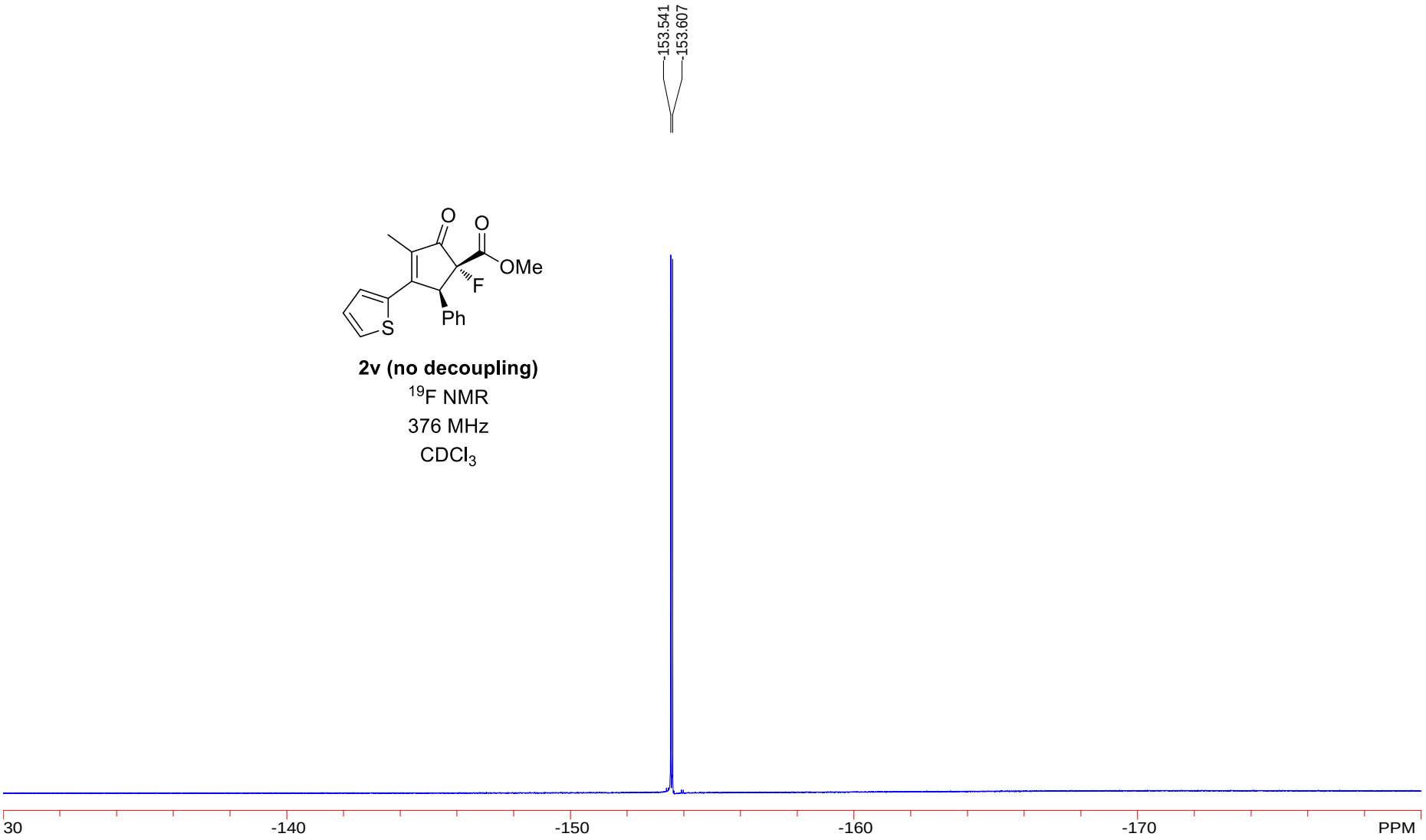
$CDCl_3$

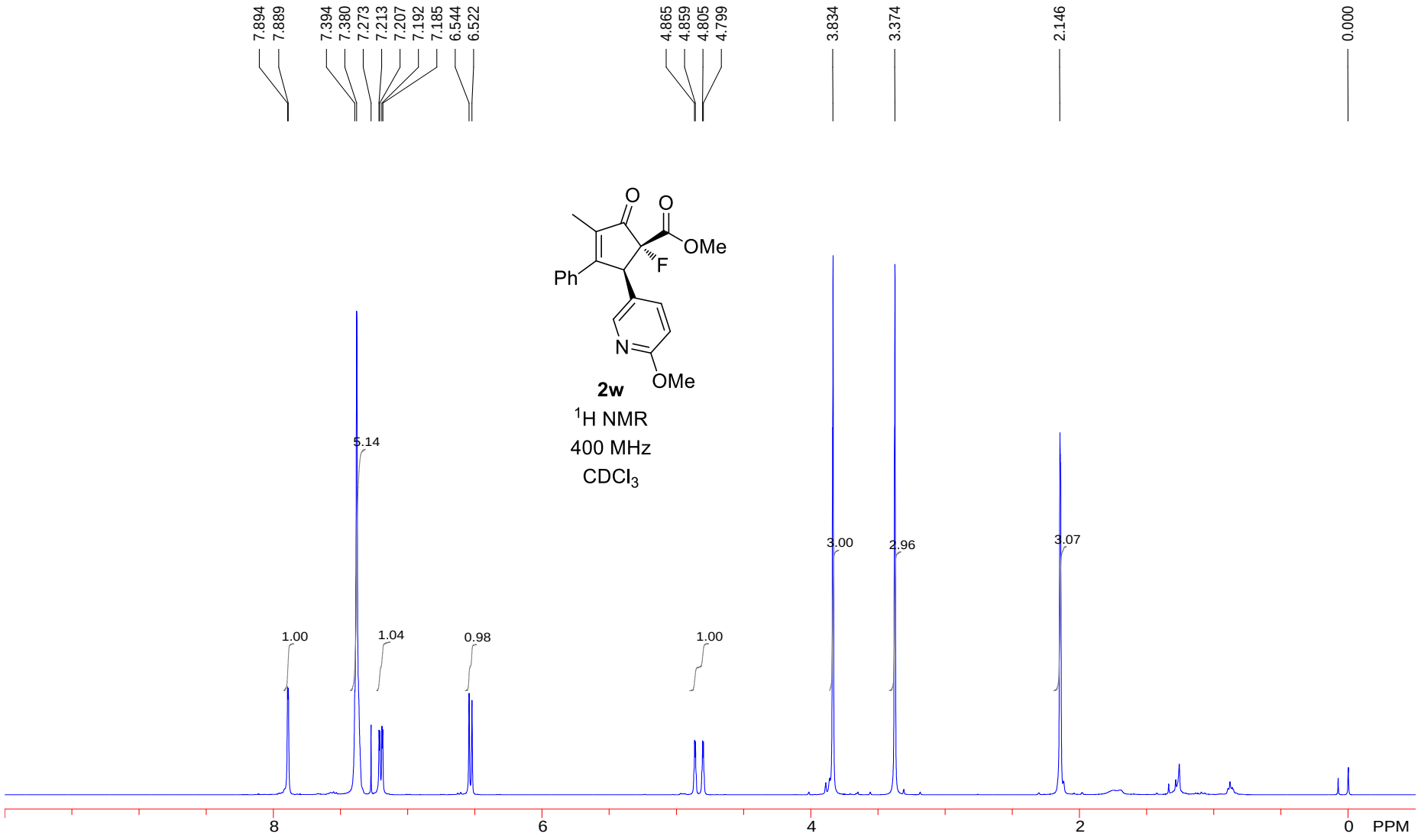
2v (no decoupling)

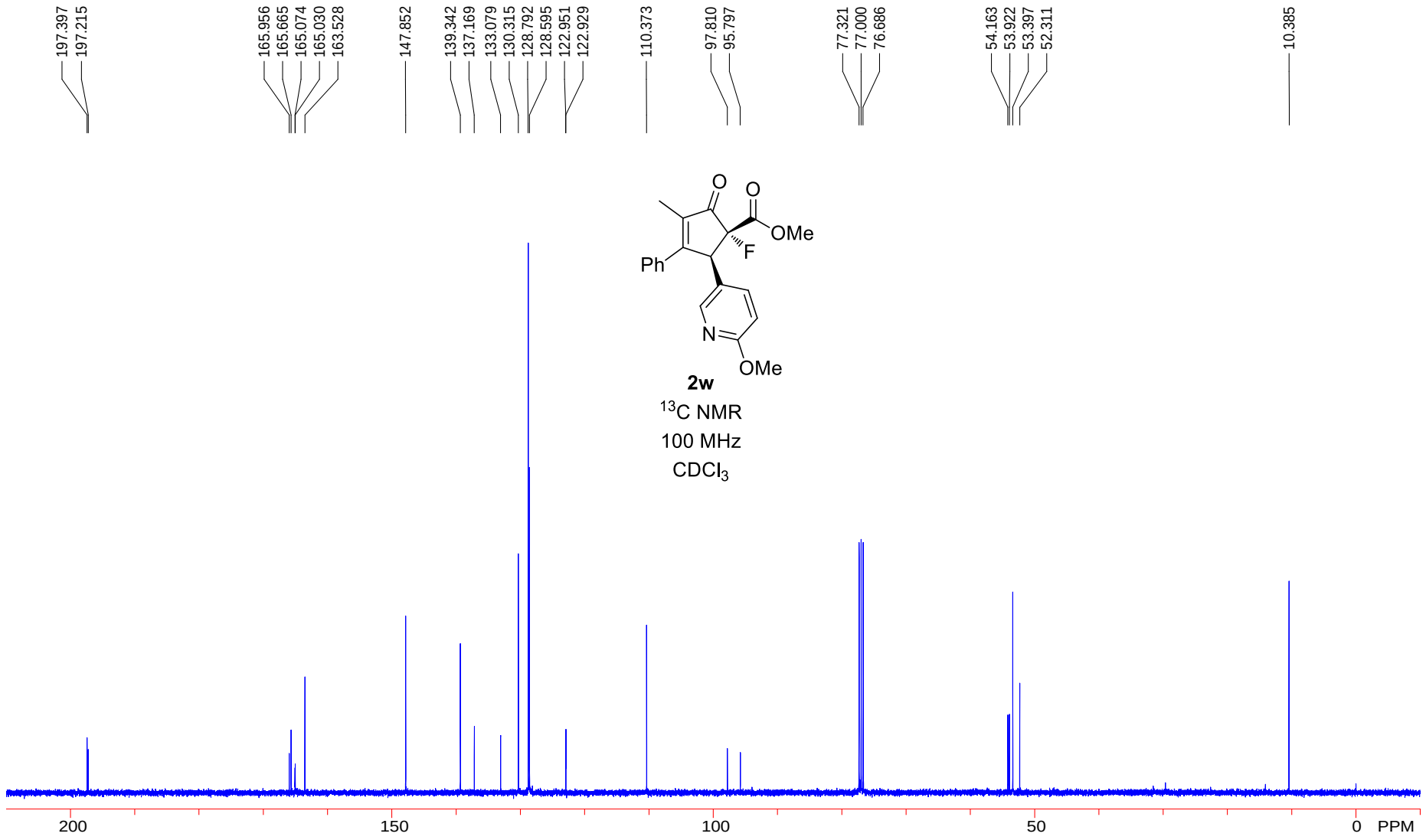
^{19}F NMR

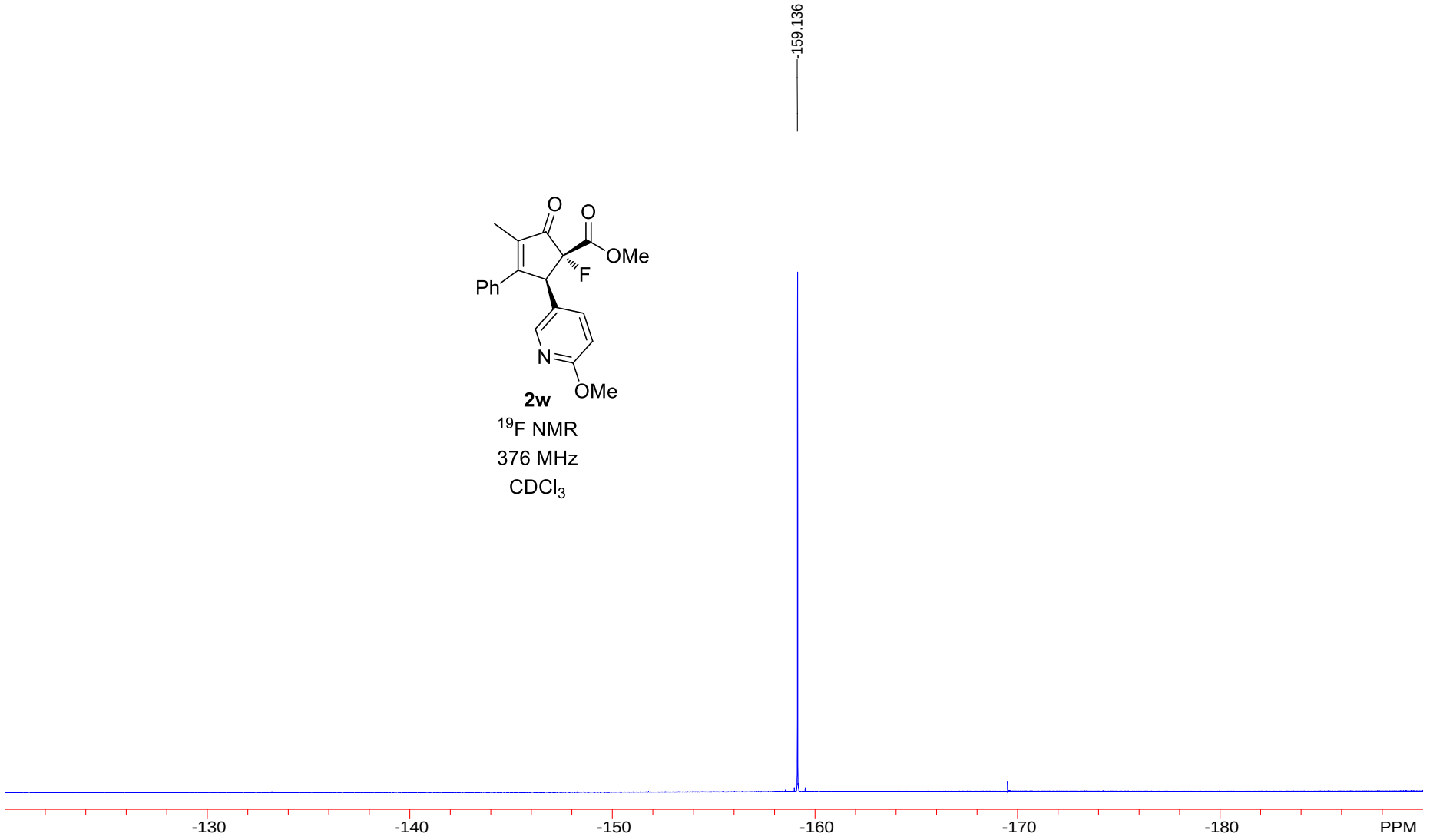
376 MHz

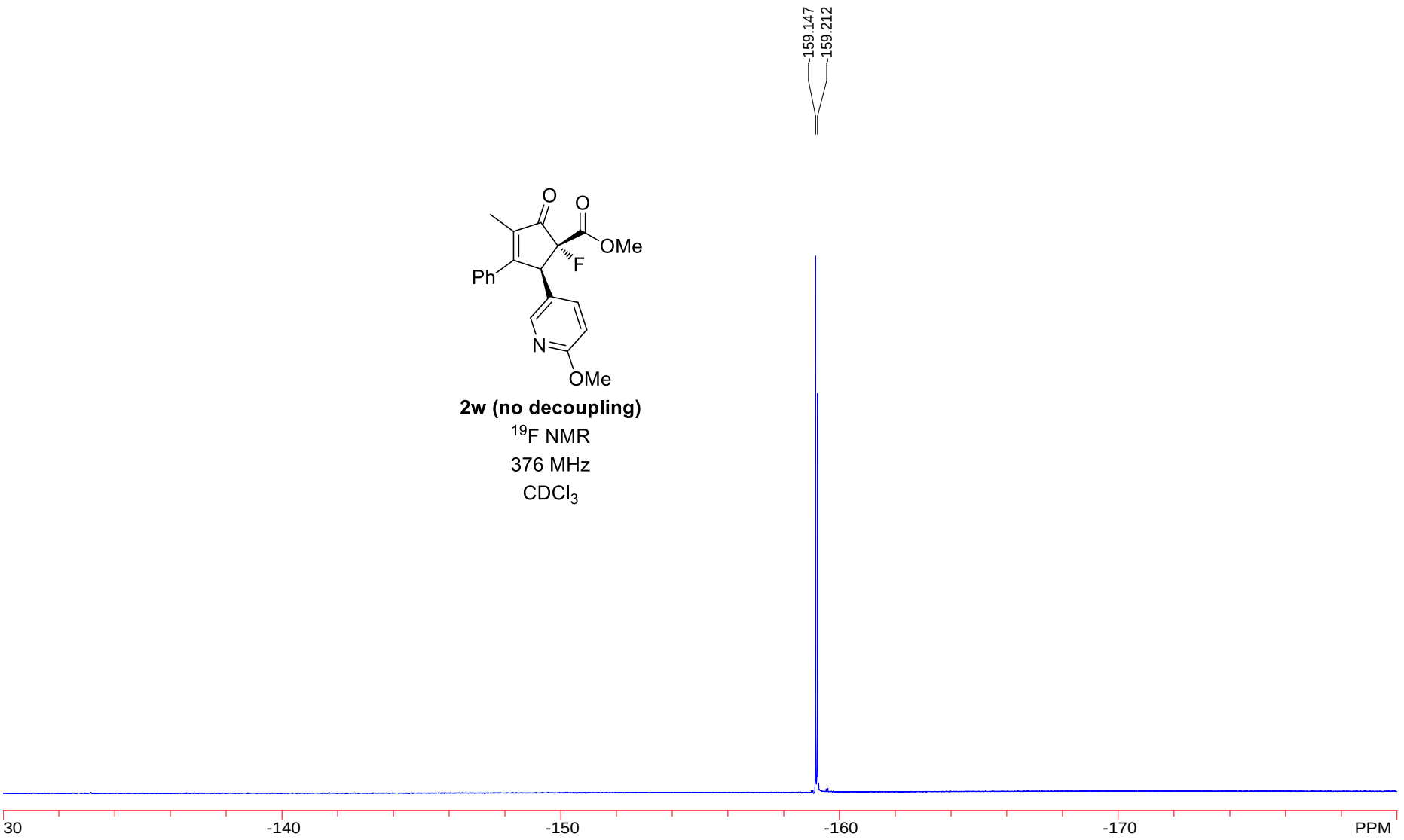
$CDCl_3$

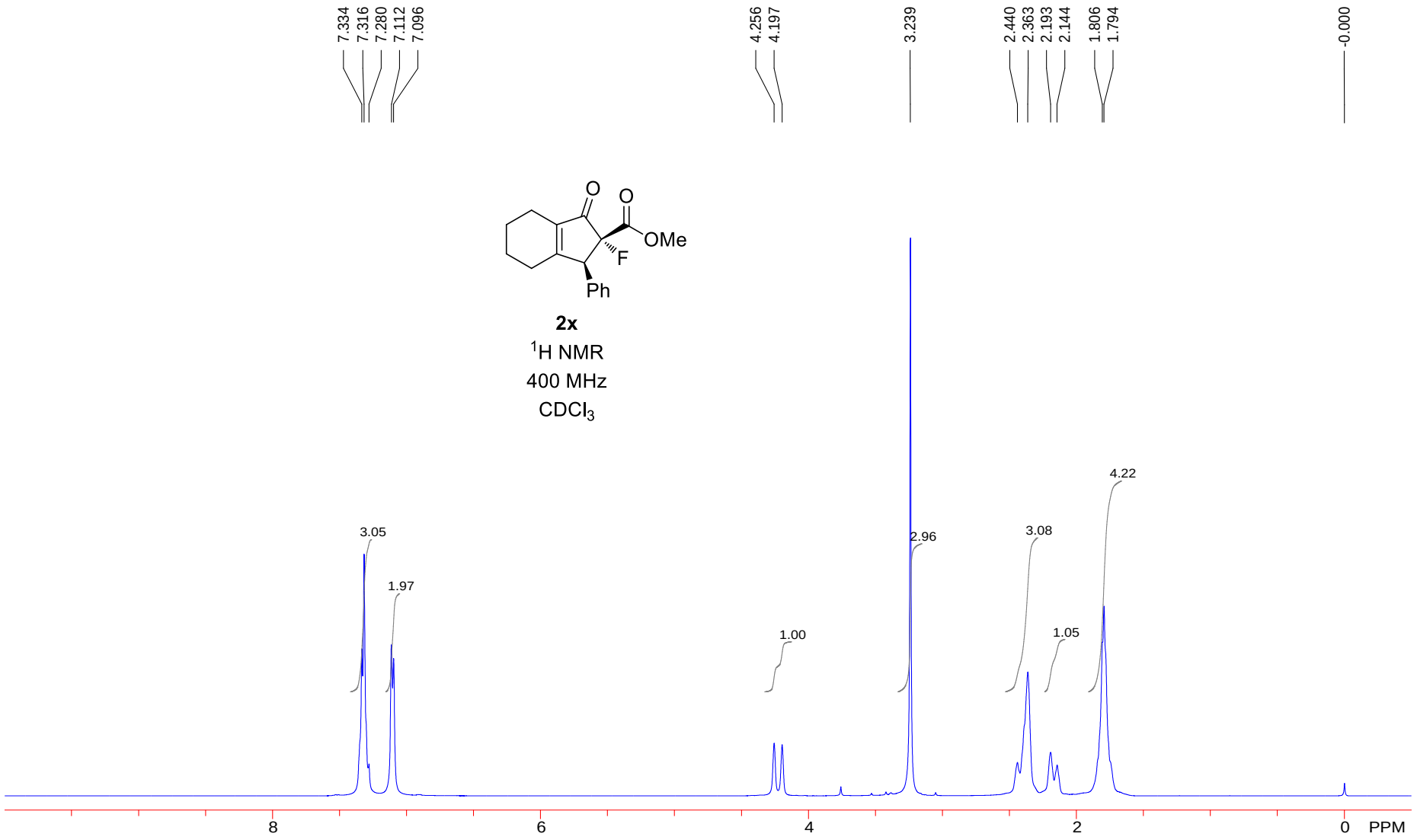


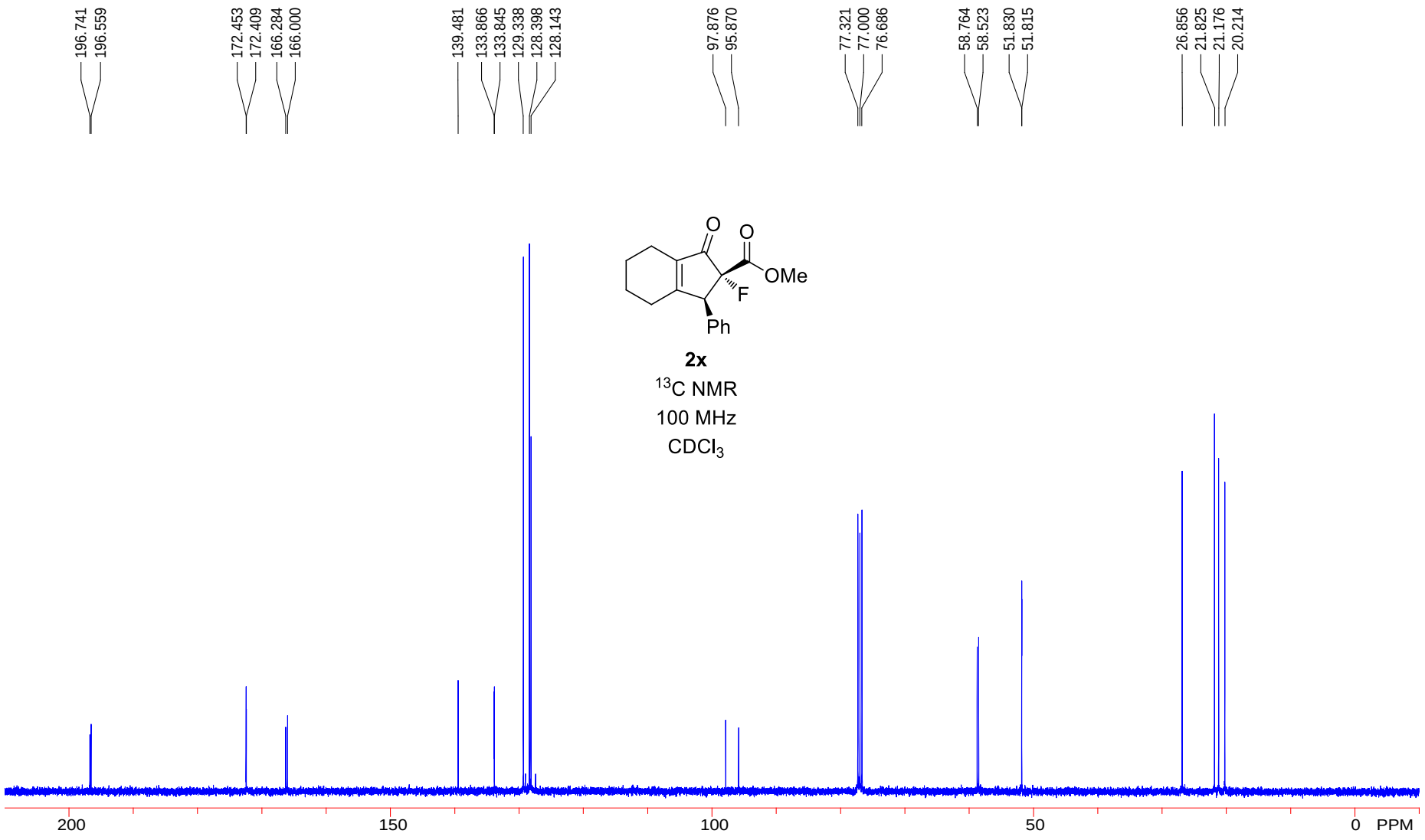

7.894
7.889
7.394
7.380
7.273
7.213
7.207
7.192
7.185
6.544
6.522
4.865
4.859
4.805
4.799
3.834
3.374
2.146
0.000
O
O
OMe
F
Ph
N
OMe
2w
1H NMR
400 MHz
CDCl3
5.14
1.00
1.04
0.98
1.00
3.00
2.96
3.07
8
6
4
2
0
PPM

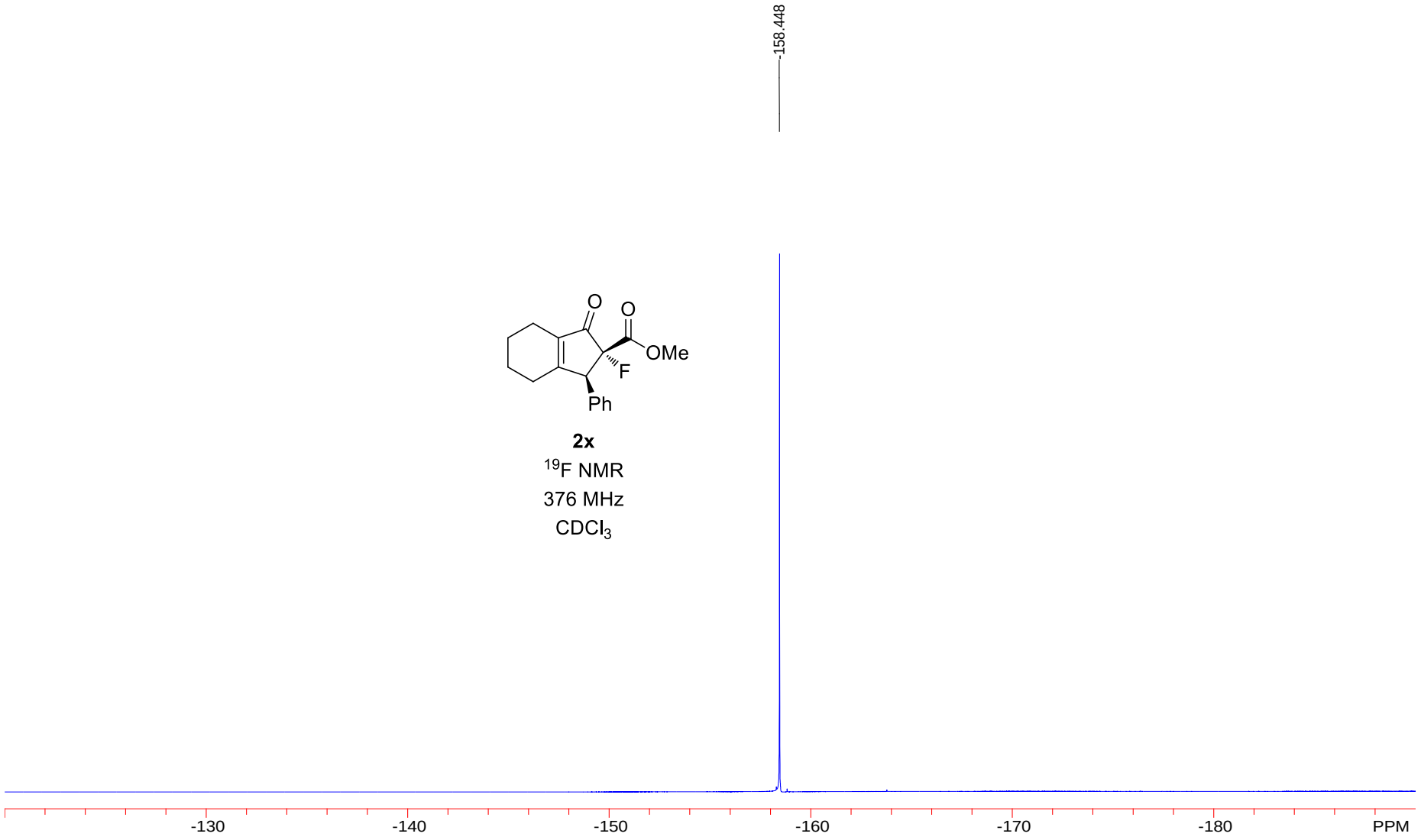

197.397
197.215
165.956
165.665
165.074
165.030
163.528
147.852
139.342
137.169
133.079
130.315
128.792
128.595
122.951
122.929
110.373
97.810
95.797
77.321
77.000
76.686
54.163
53.922
53.397
52.311
10.385
O
O
OMe
F
Ph
N
OMe
2w
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM


-159.136
O
O
OMe
F
Ph
N
OMe
2w
19F NMR
376 MHz
CDCl3
-130
-140
-150
-160
-170
-180
PPM


159.147
159.212
O
O
OMe
F
Ph
N
OMe
2w (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.334
7.316
7.280
7.112
7.096
4.256
4.197
3.239
2.440
2.363
2.193
2.144
1.806
1.794
-0.000
O
O
OMe
F
Ph
2x
1H NMR
400 MHz
CDCl3
3.05
1.97
1.00
2.96
3.08
1.05
4.22
8
6
4
2
0
PPM


196.741
196.559
172.453
172.409
166.284
166.000
139.481
133.866
133.845
129.338
128.398
128.143
97.876
95.870
77.321
77.000
76.686
58.764
58.523
51.830
51.815
26.856
21.825
21.176
20.214
O
O
OMe
F
Ph
2x
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

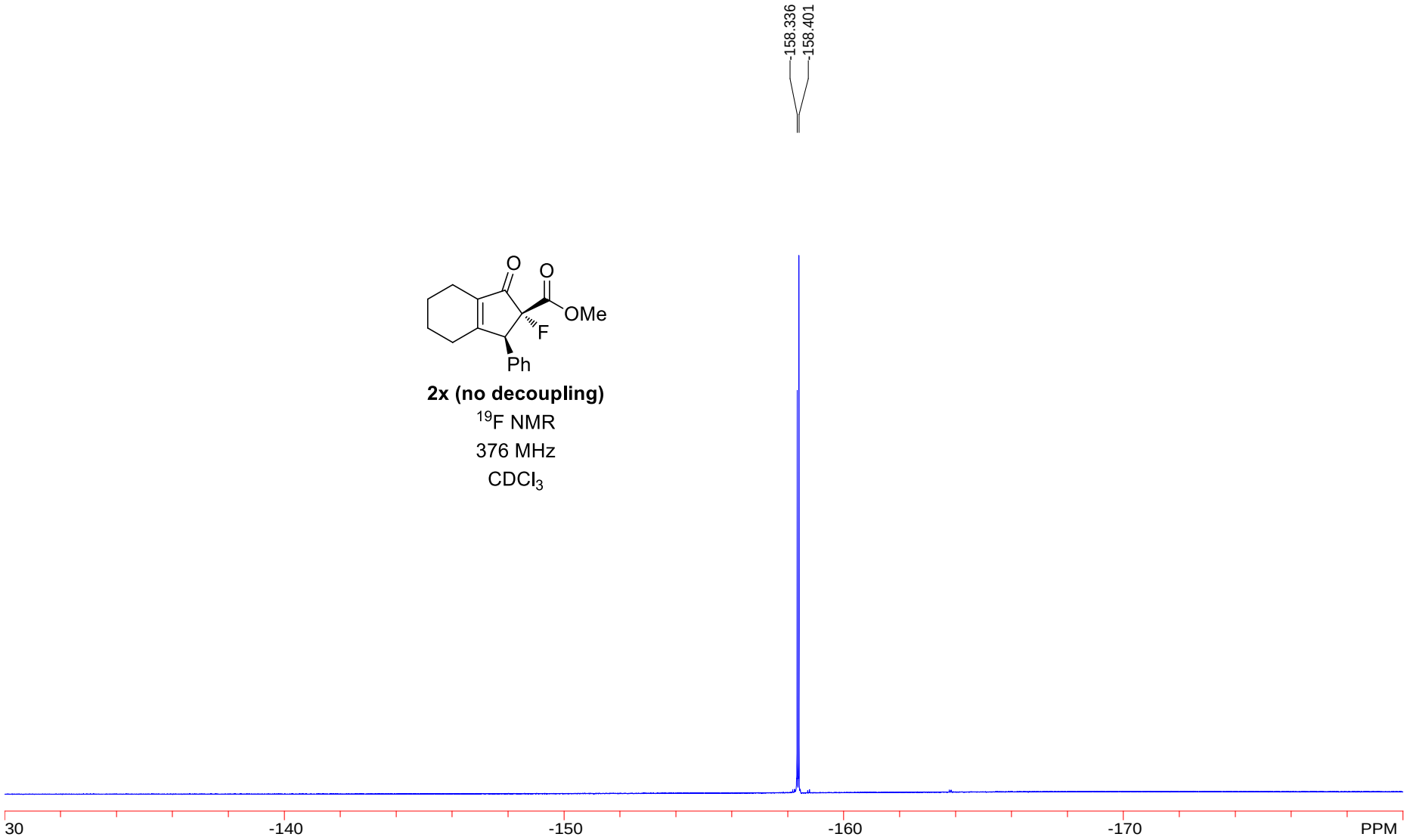


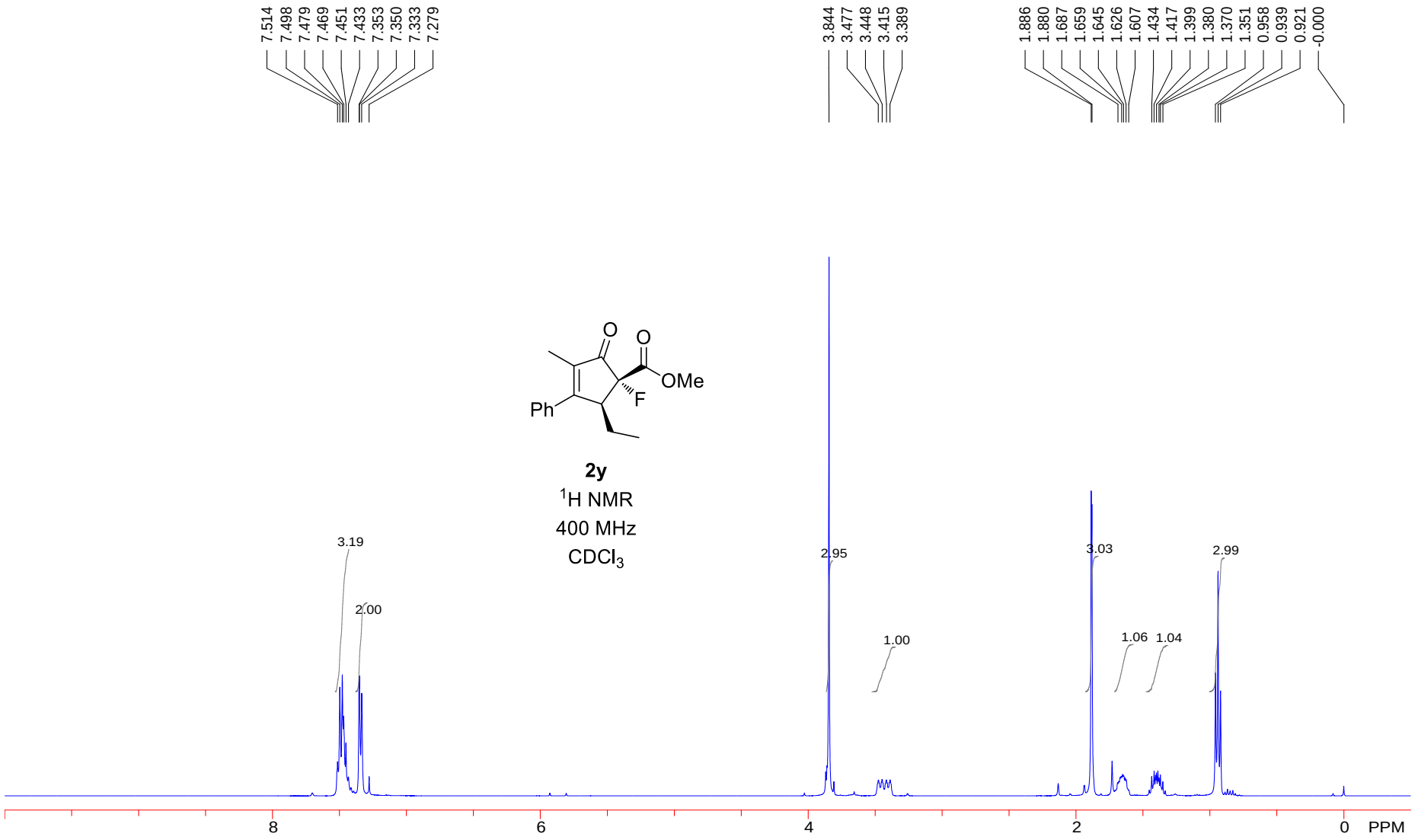
2x

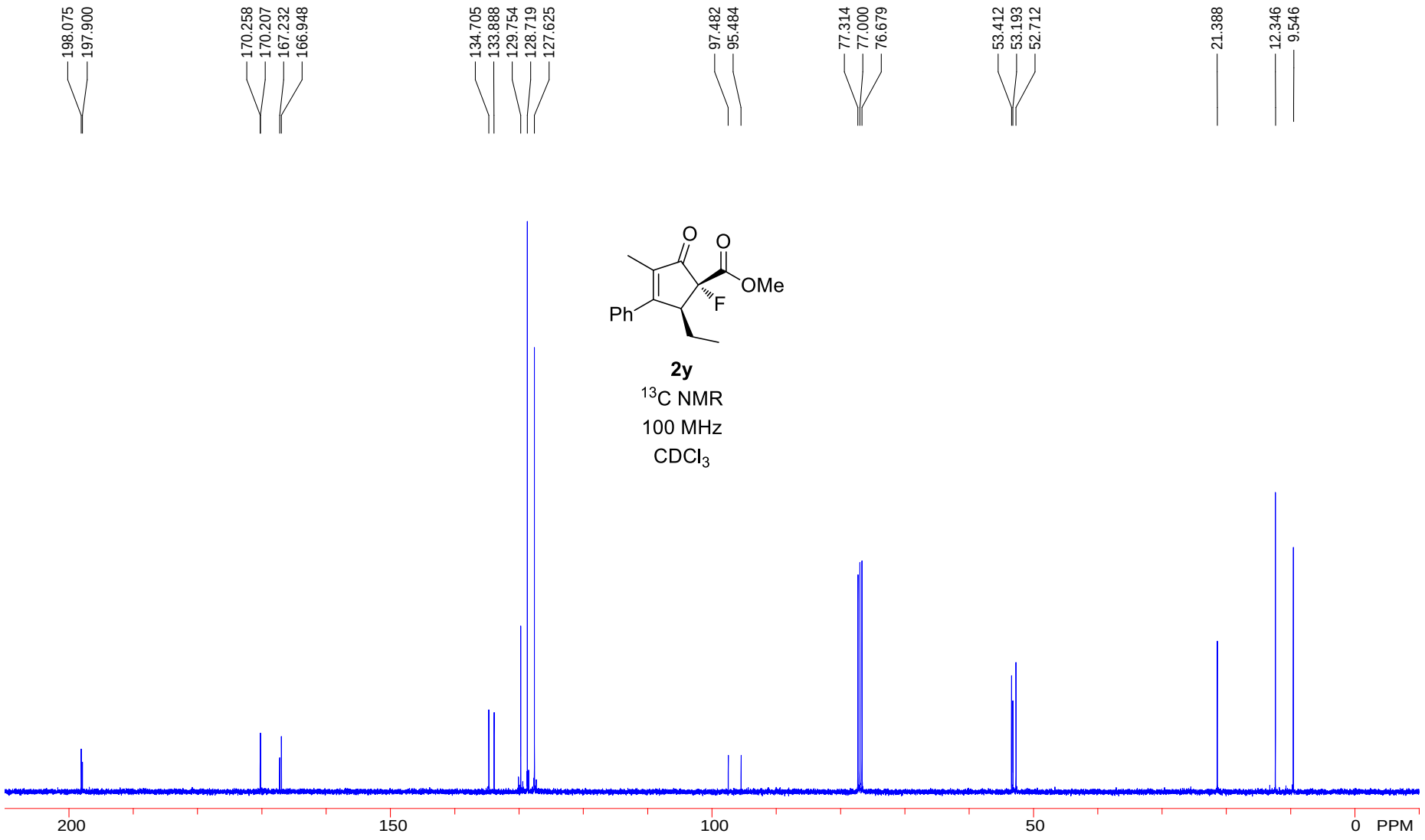
^{19}F NMR

376 MHz

$CDCl_3$


-158.336
-158.401
O
O
OMe
F
Ph
2x (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM


7.514
7.498
7.479
7.469
7.451
7.433
7.353
7.350
7.333
7.279
3.844
3.477
3.448
3.415
3.389
1.886
1.880
1.687
1.659
1.645
1.626
1.607
1.434
1.417
1.399
1.380
1.370
1.351
0.958
0.939
0.921
-0.000
O
O
OMe
F
Ph
2y
1H NMR
400 MHz
CDCl3
3.19
2.00
2.95
1.00
3.03
1.06
1.04
2.99
8
6
4
2
0
PPM

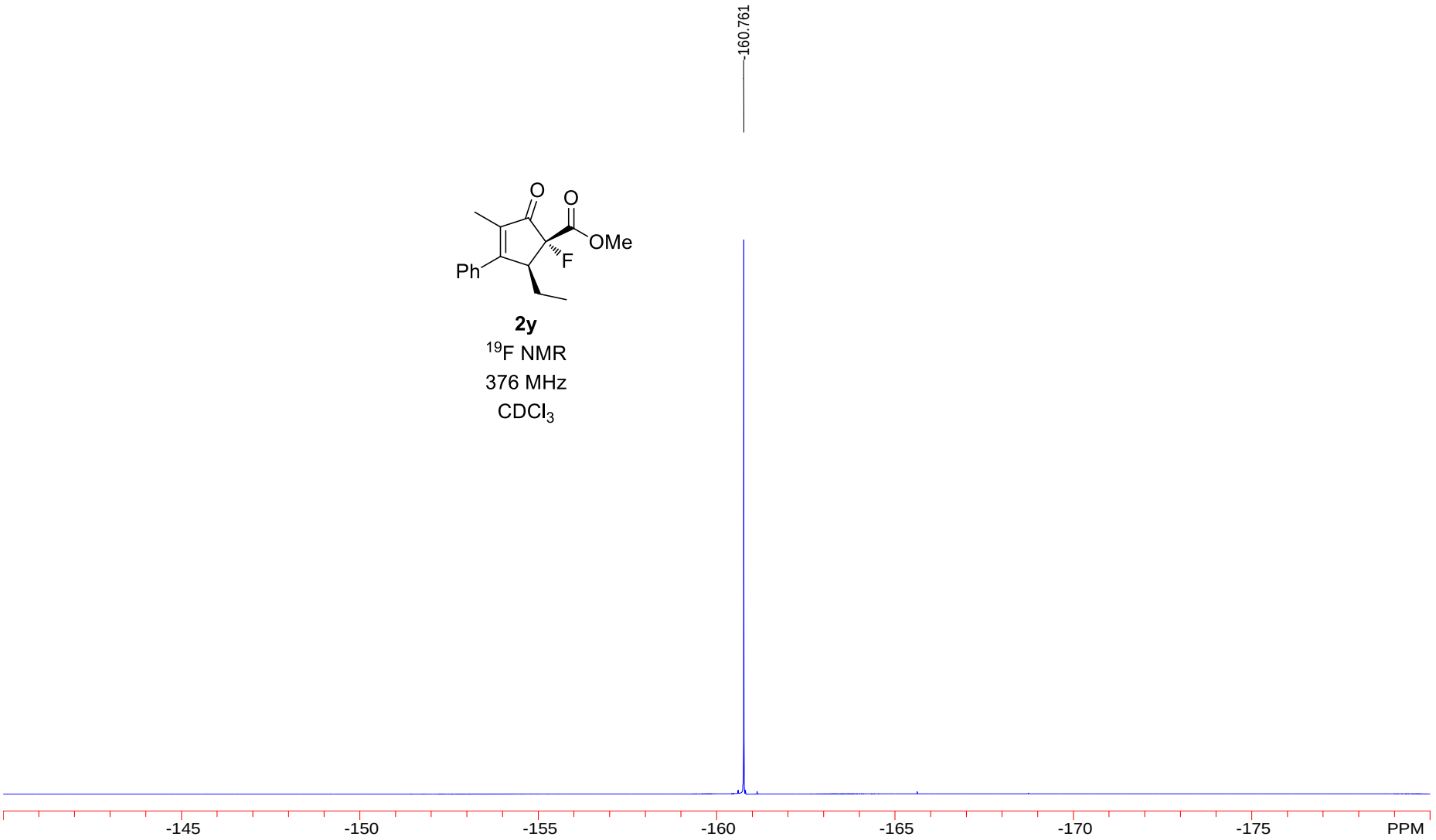

198.075
197.900
170.258
170.207
167.232
166.948
134.705
133.888
129.754
128.719
127.625
97.482
95.484
77.314
77.000
76.679
53.412
53.193
52.712
21.388
12.346
9.546
O
O
OMe
F
Ph
2y
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

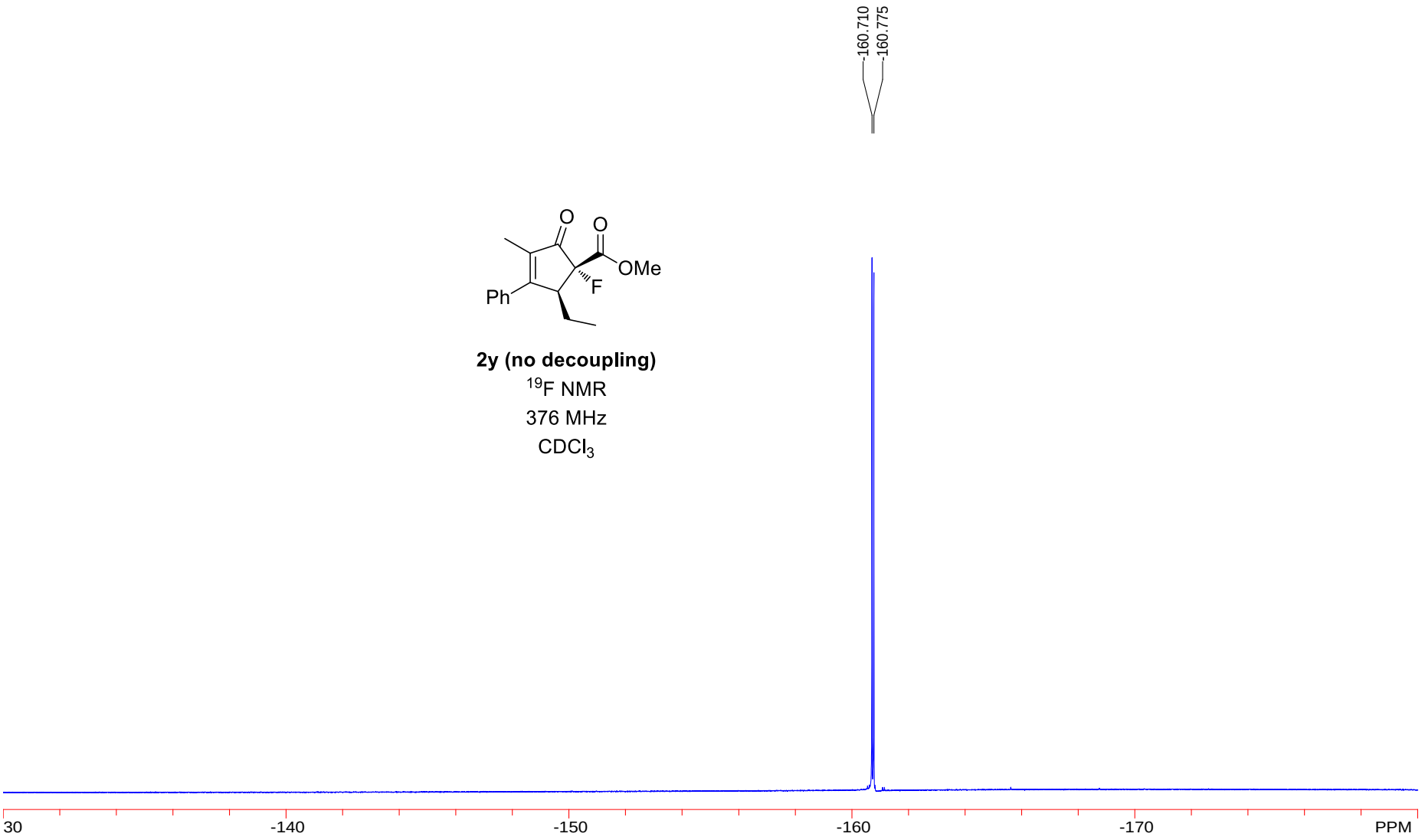
2y

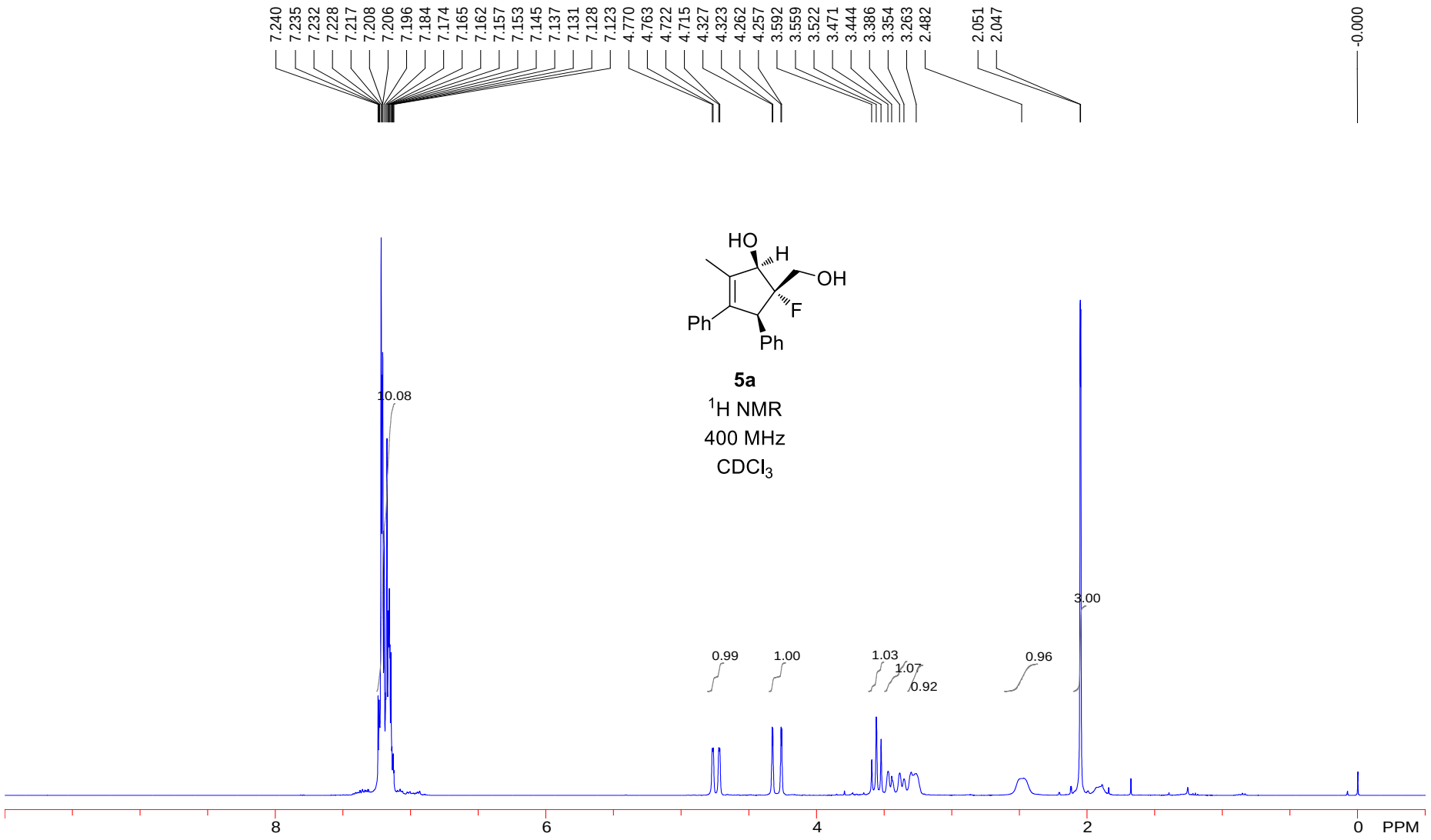
^{19}F NMR

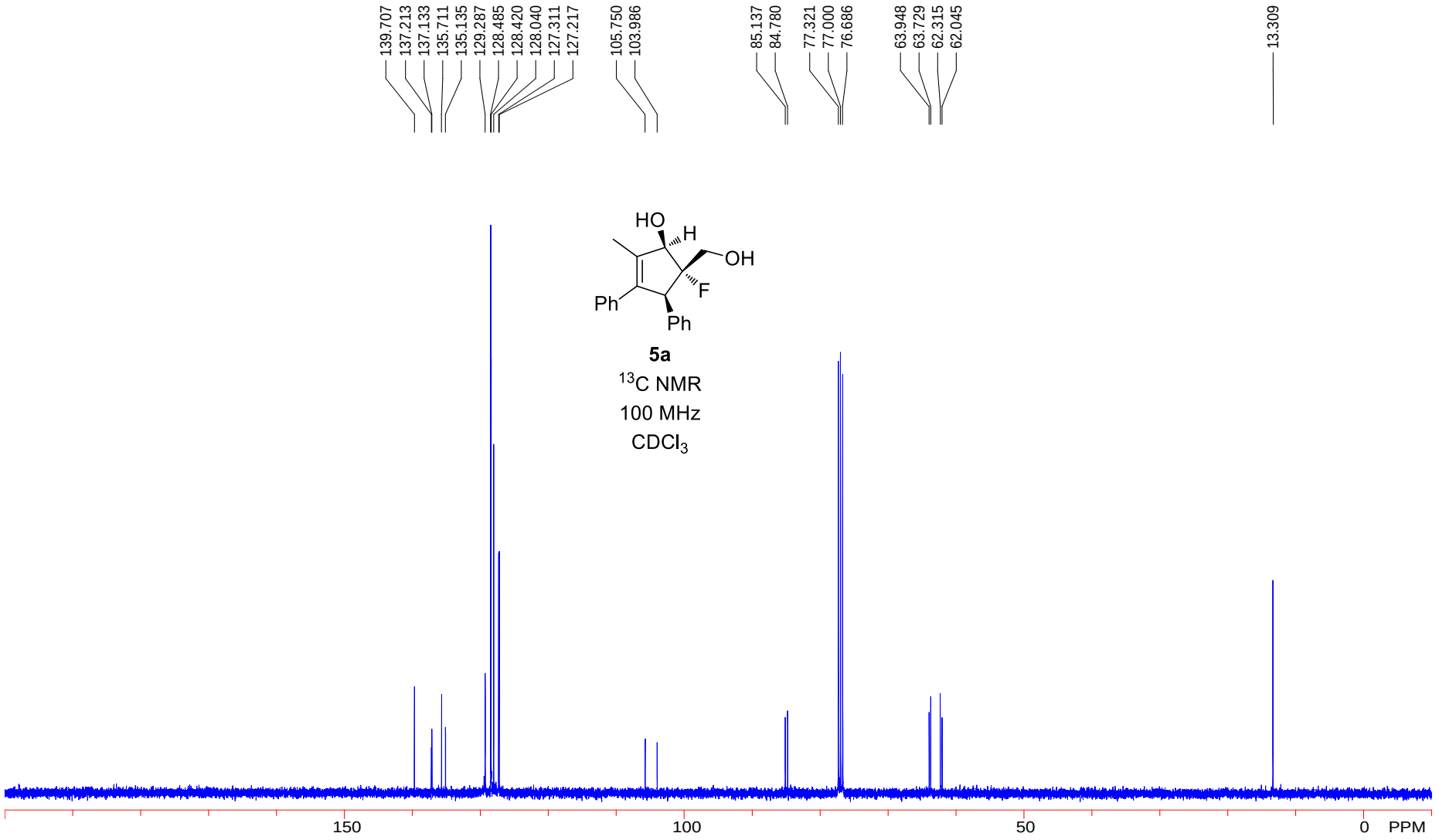
376 MHz

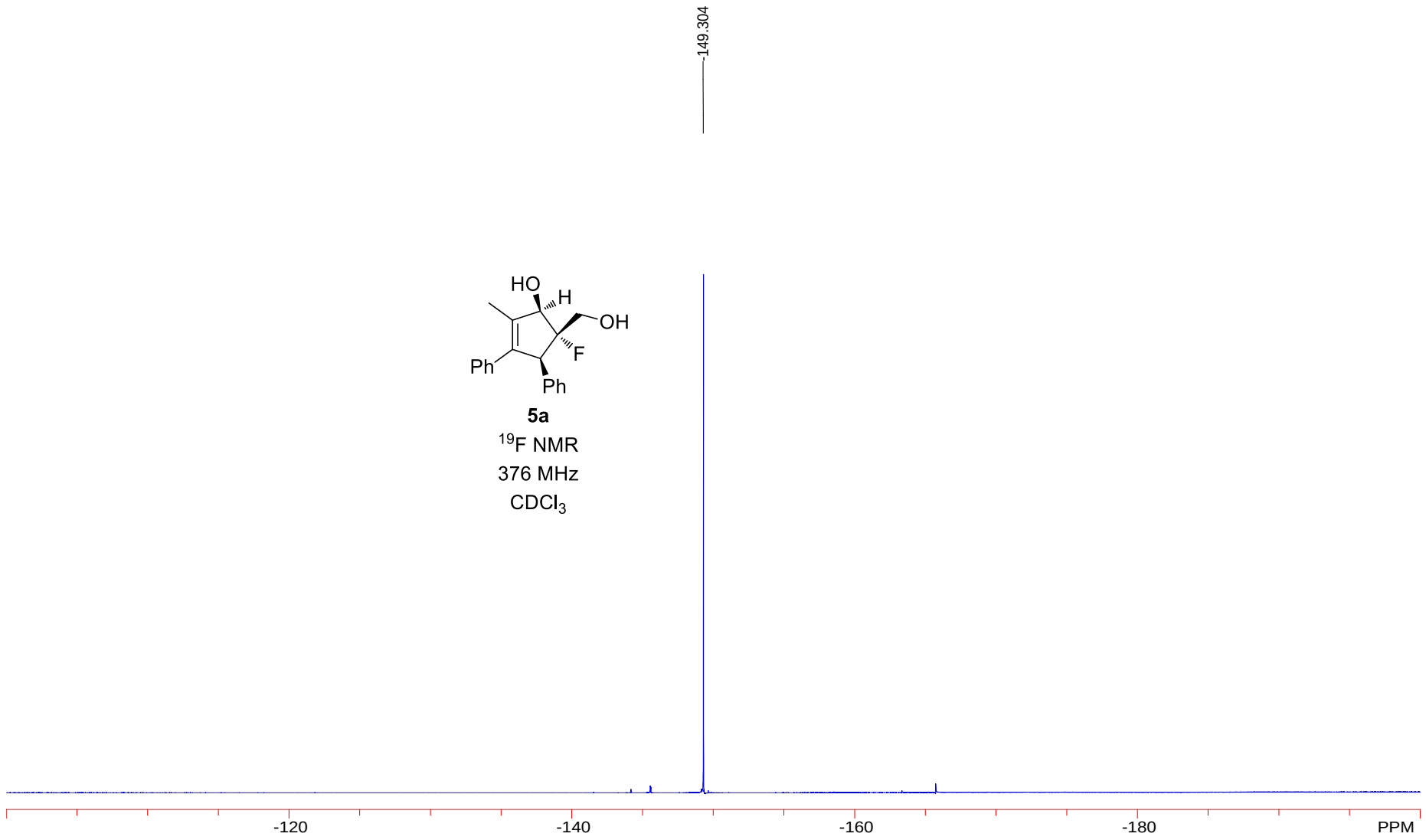
$CDCl_3$

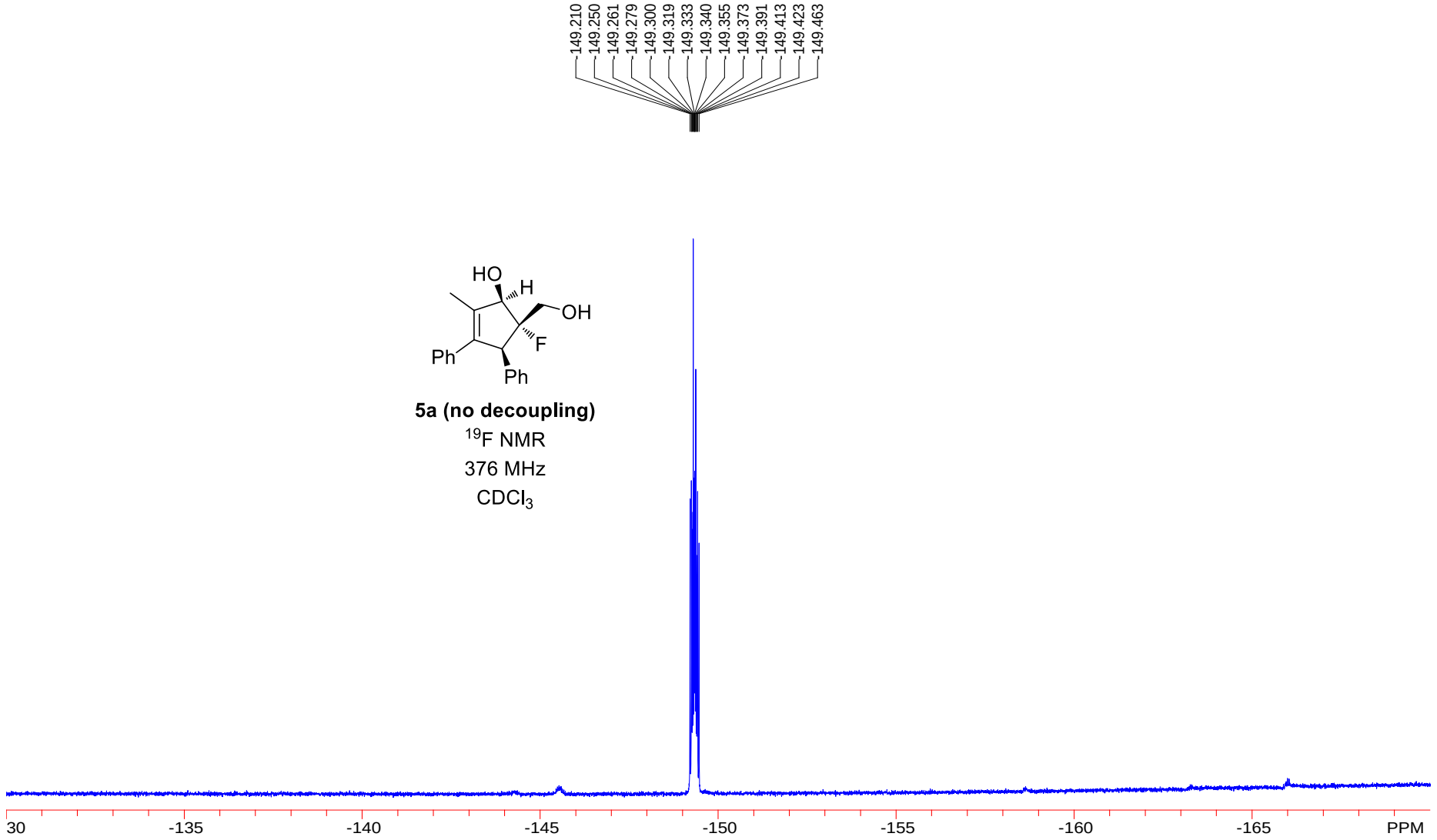


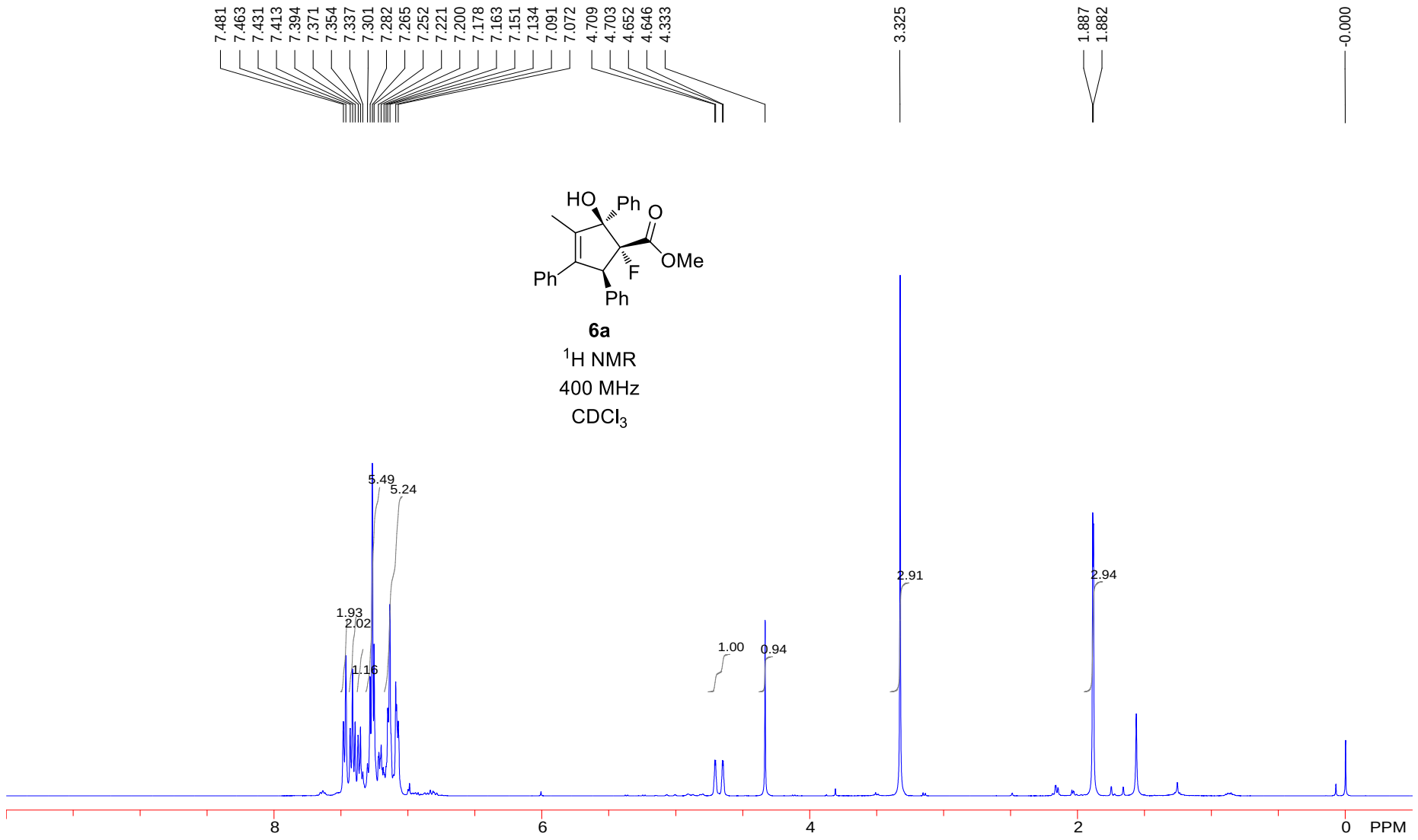

160.710
160.775
O
O
OMe
F
Ph
2y (no decoupling)
19F NMR
376 MHz
CDCl3
30
-140
-150
-160
-170
PPM

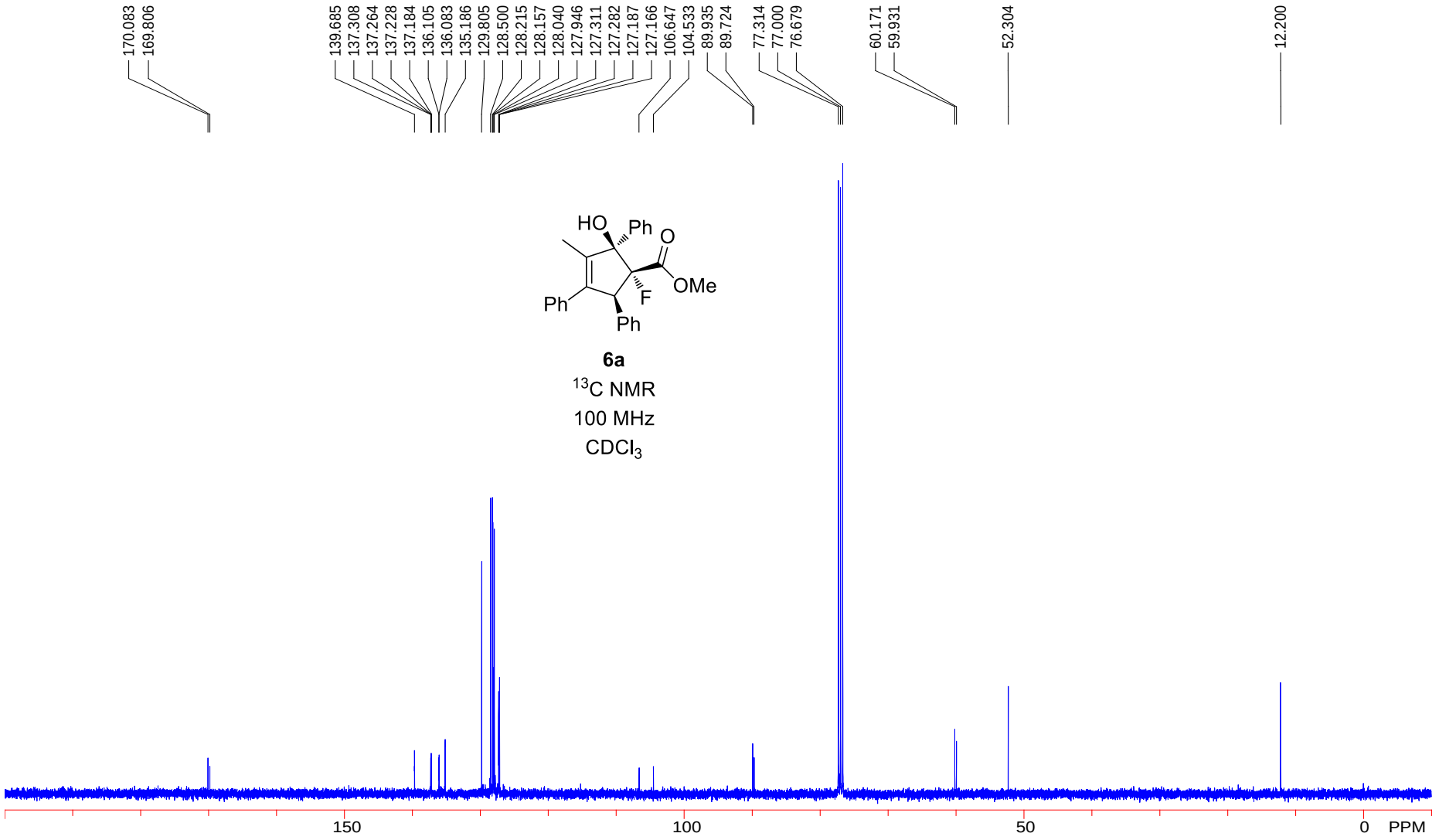

7.240
7.235
7.232
7.228
7.217
7.208
7.206
7.196
7.184
7.174
7.165
7.162
7.157
7.153
7.145
7.137
7.131
7.128
7.123
4.770
4.763
4.722
4.715
4.327
4.323
4.262
4.257
3.592
3.559
3.522
3.471
3.444
3.386
3.354
3.263
2.482
2.051
2.047
-0.000
HO
H
OH
F
Ph
Ph
5a
1H NMR
400 MHz
CDCl3
10.08
0.99
1.00
1.03
1.07
0.92
0.96
3.00
8
6
4
2
0
PPM


139.707
137.213
137.133
135.711
135.135
129.287
128.485
128.420
128.040
127.311
127.217
105.750
103.986
85.137
84.780
77.321
77.000
76.686
63.948
63.729
62.315
62.045
13.309
HO
H
OH
F
Ph
Ph
5a
13C NMR
100 MHz
CDCl3
150
100
50
0
PPM


-149.304
HO
H
OH
F
Ph
Ph
5a
19F NMR
376 MHz
CDCl3
-120
-140
-160
-180
PPM


149.210
149.250
149.261
149.279
149.300
149.319
149.333
149.340
149.355
149.373
149.391
149.413
149.423
149.463
HO
H
OH
F
Ph
Ph
5a (no decoupling)
19F NMR
376 MHz
CDCl3
30
-135
-140
-145
-150
-155
-160
-165
PPM


7.481
7.463
7.431
7.413
7.394
7.371
7.354
7.337
7.301
7.282
7.265
7.252
7.221
7.200
7.178
7.163
7.151
7.134
7.091
7.072
4.709
4.703
4.652
4.646
4.333
3.325
1.887
1.882
-0.000
HO
Ph
O
OMe
F
Ph
Ph
6a
1H NMR
400 MHz
CDCl3
5.49
5.24
1.93
2.02
1.16
1.00
0.94
2.91
2.94
8
6
4
2
0
PPM

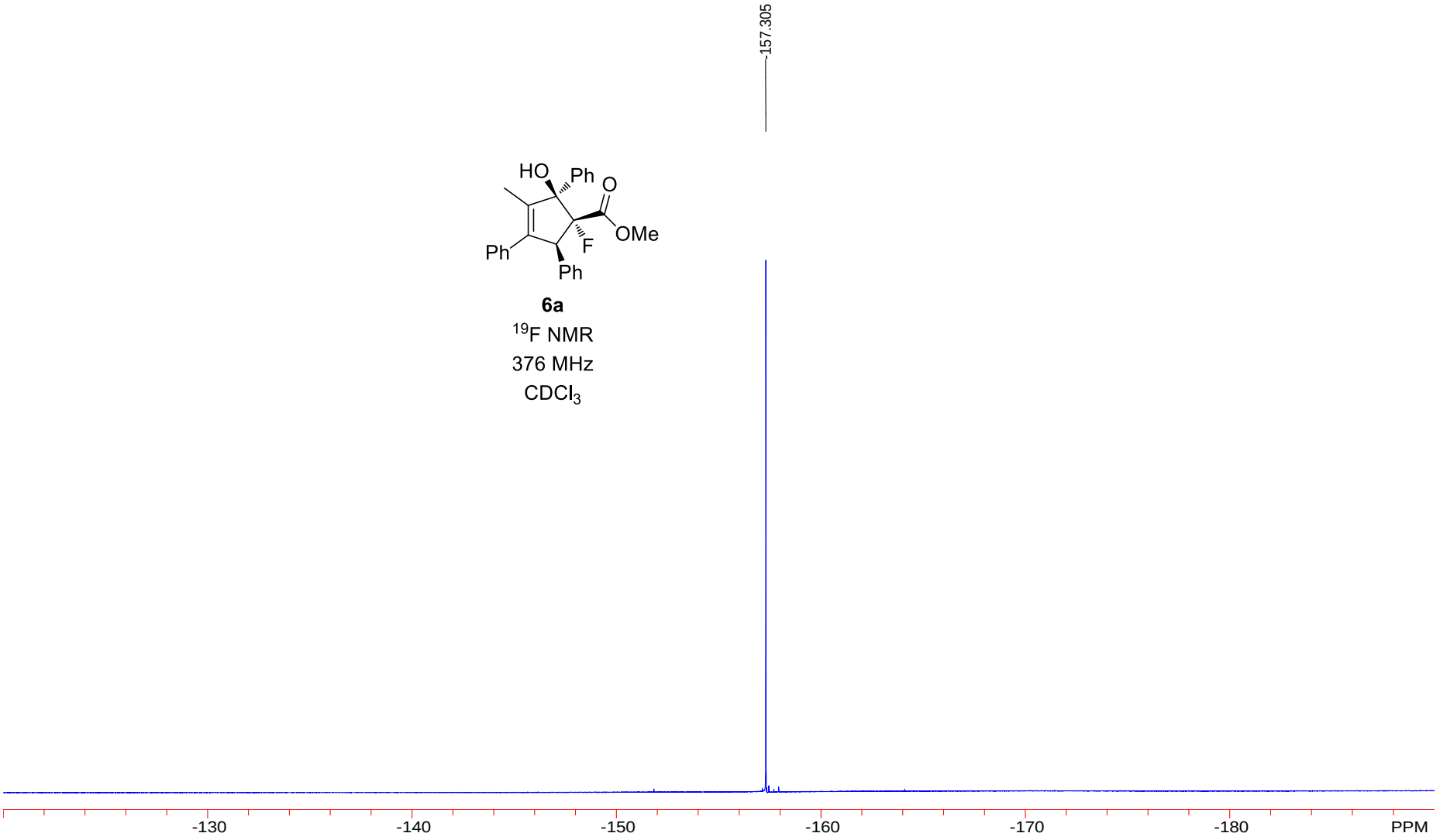

170.083
169.806
139.685
137.308
137.264
137.228
137.184
136.105
136.083
135.186
129.805
128.500
128.215
128.157
128.040
127.946
127.311
127.282
127.187
127.166
106.647
104.533
89.935
89.724
77.314
77.000
76.679
60.171
59.931
52.304
12.200
HO
Ph
O
OMe
F
Ph
Ph
6a
13C NMR
100 MHz
CDCl3
150
100
50
0
PPM

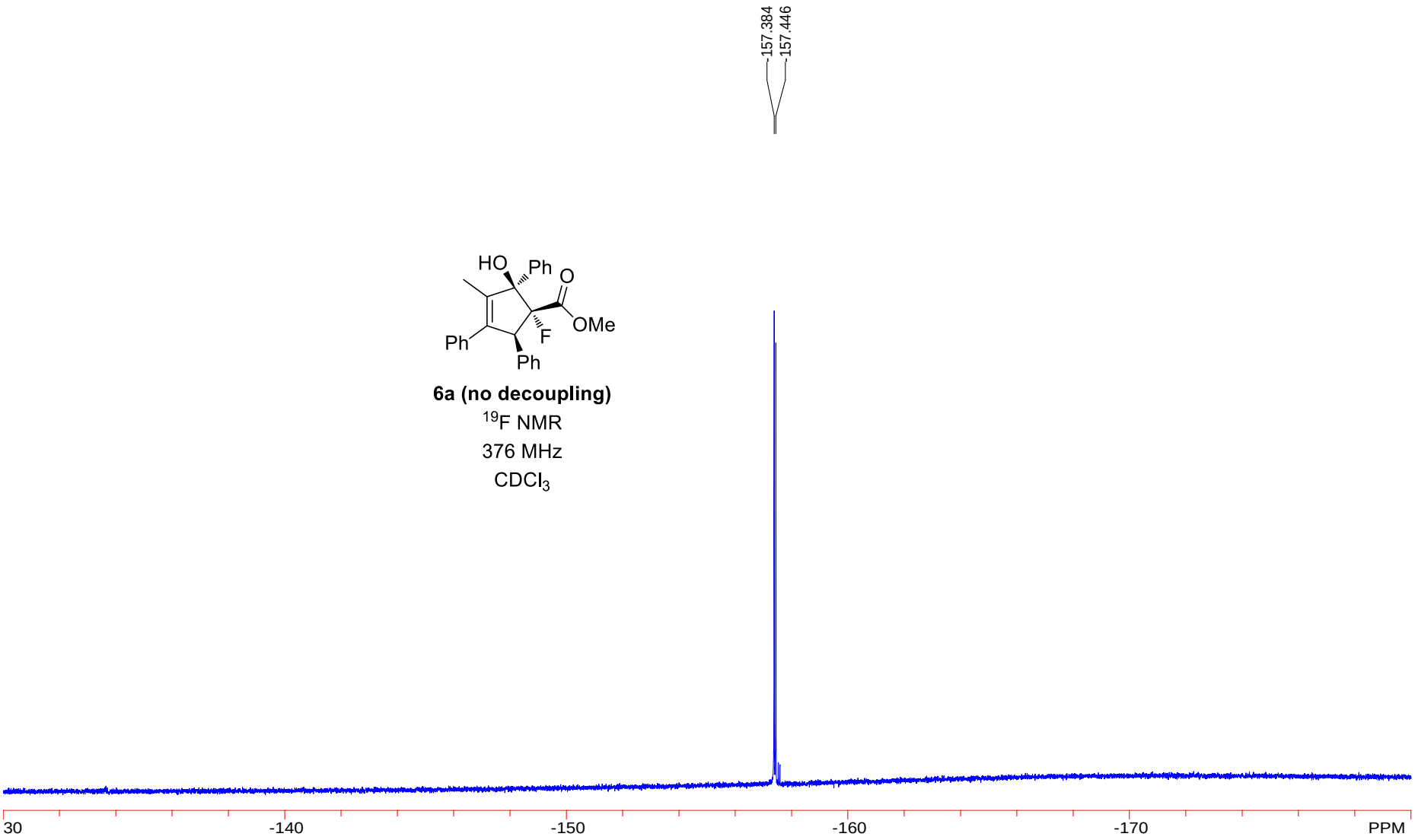
6a

^{19}F NMR

376 MHz

$CDCl_3$



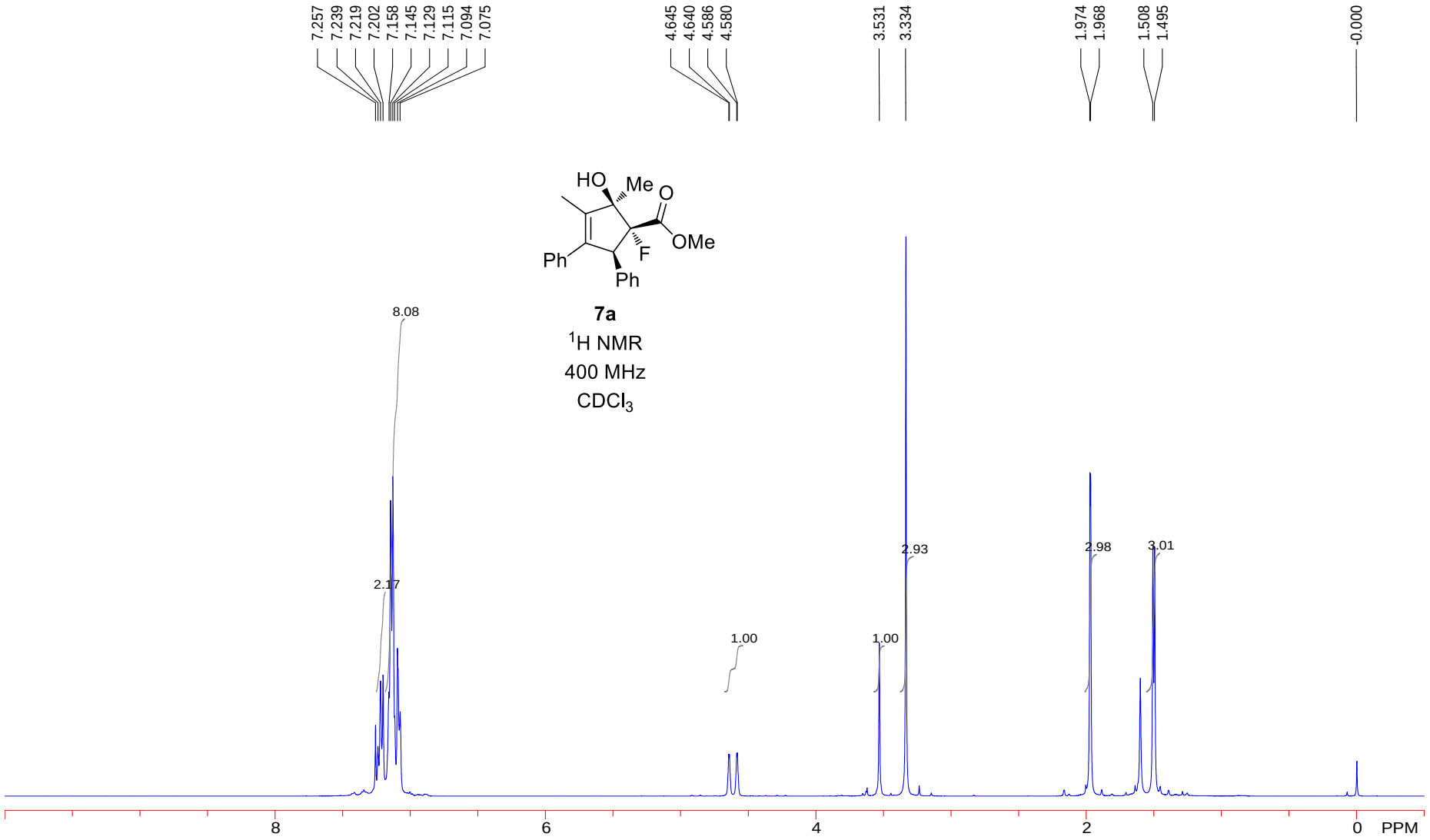


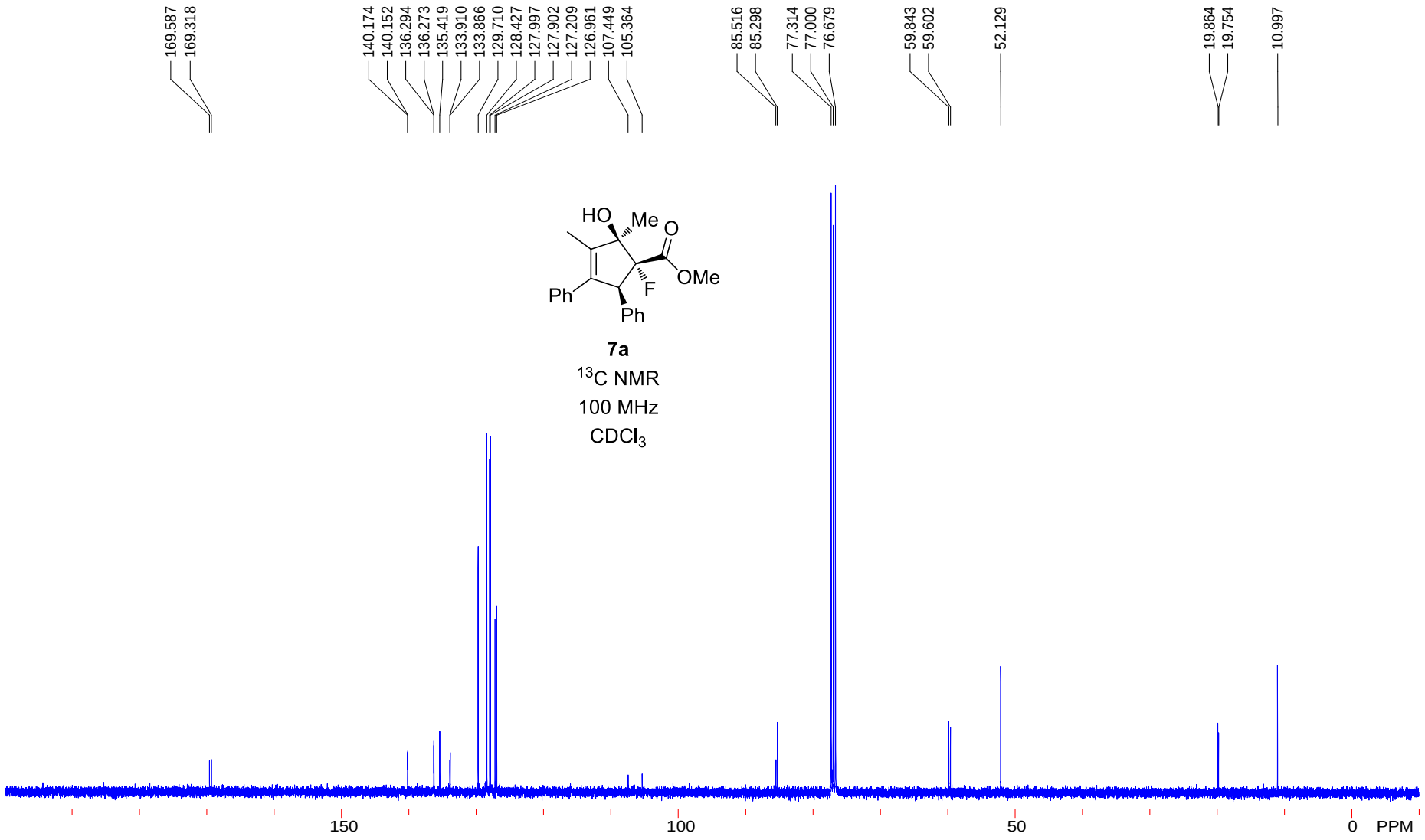
6a (no decoupling)

^{19}F NMR

376 MHz

$CDCl_3$


7.257
7.239
7.219
7.202
7.158
7.145
7.129
7.115
7.094
7.075
4.645
4.640
4.586
4.580
3.531
3.334
1.974
1.968
1.508
1.495
-0.000
HO
Me
O
OMe
F
Ph
Ph
7a
1H NMR
400 MHz
CDCl3
8.08
2.17
1.00
1.00
2.93
2.98
3.01
8
6
4
2
0
PPM

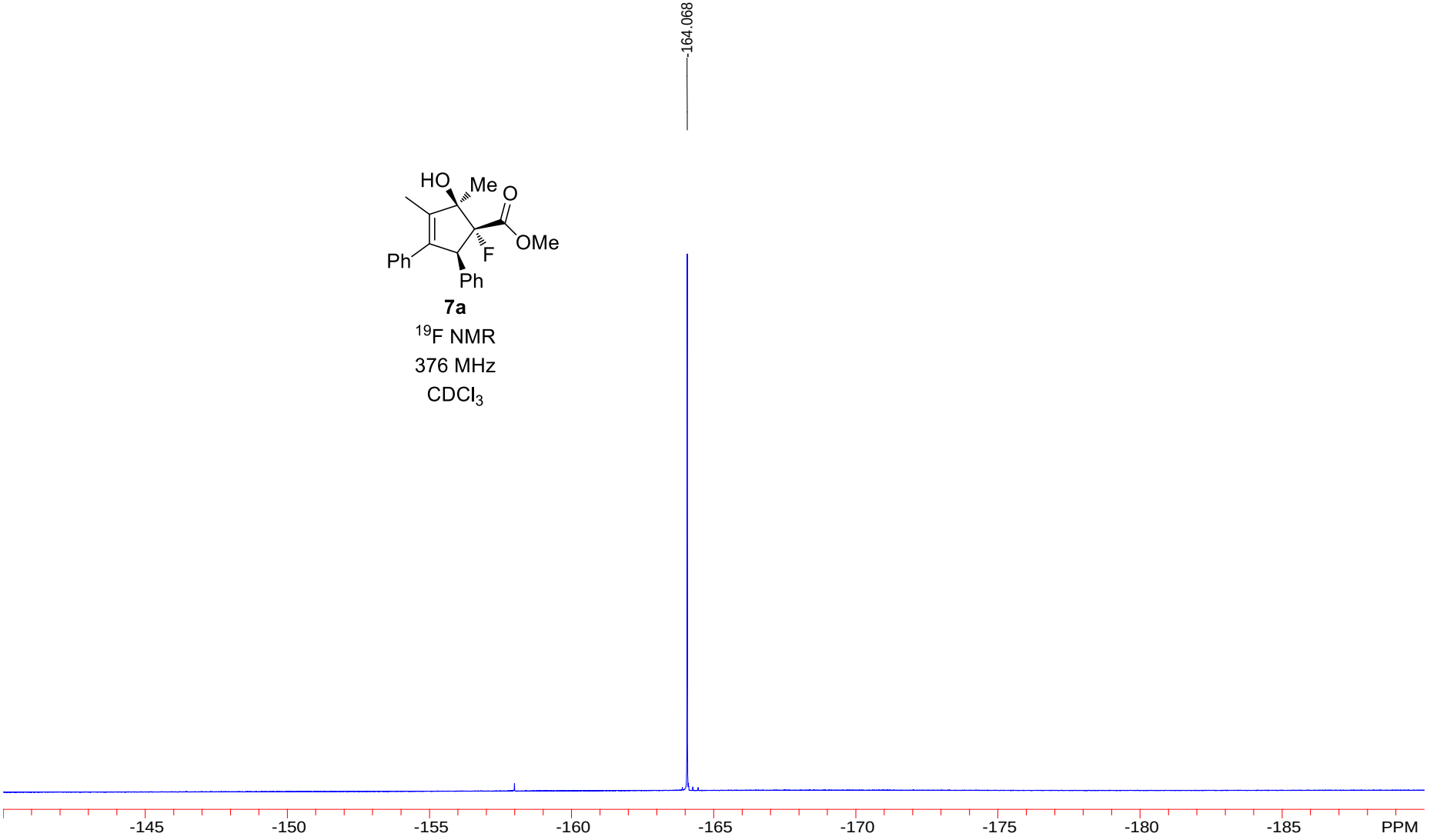

169.587
169.318
140.174
140.152
136.294
136.273
135.419
133.910
133.866
129.710
128.427
127.997
127.902
127.209
126.961
107.449
105.364
85.516
85.298
77.314
77.000
76.679
59.843
59.602
52.129
19.864
19.754
10.997
HO
Me
O
OMe
F
Ph
Ph
7a
13C NMR
100 MHz
CDCl3
150
100
50
0
PPM

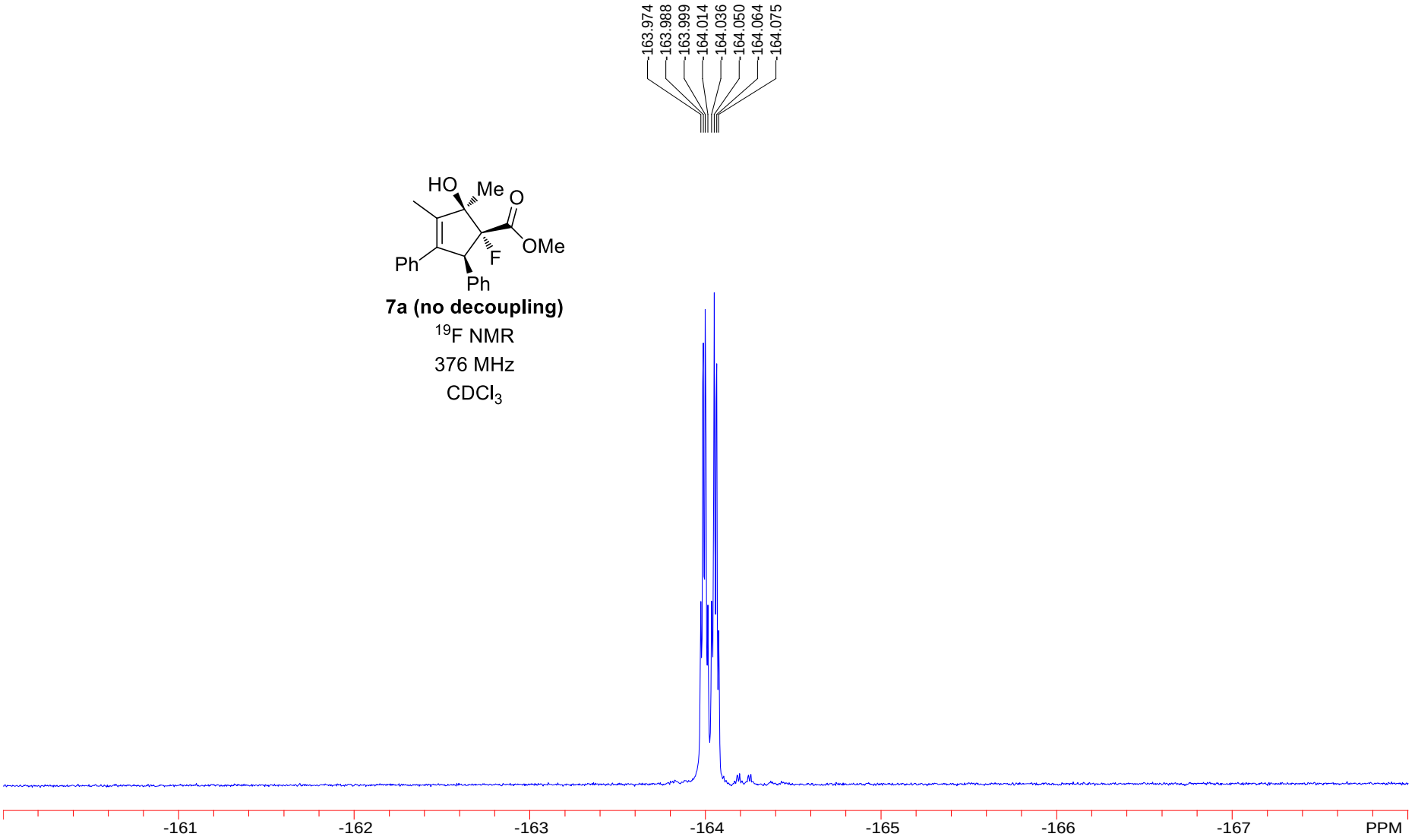
7a

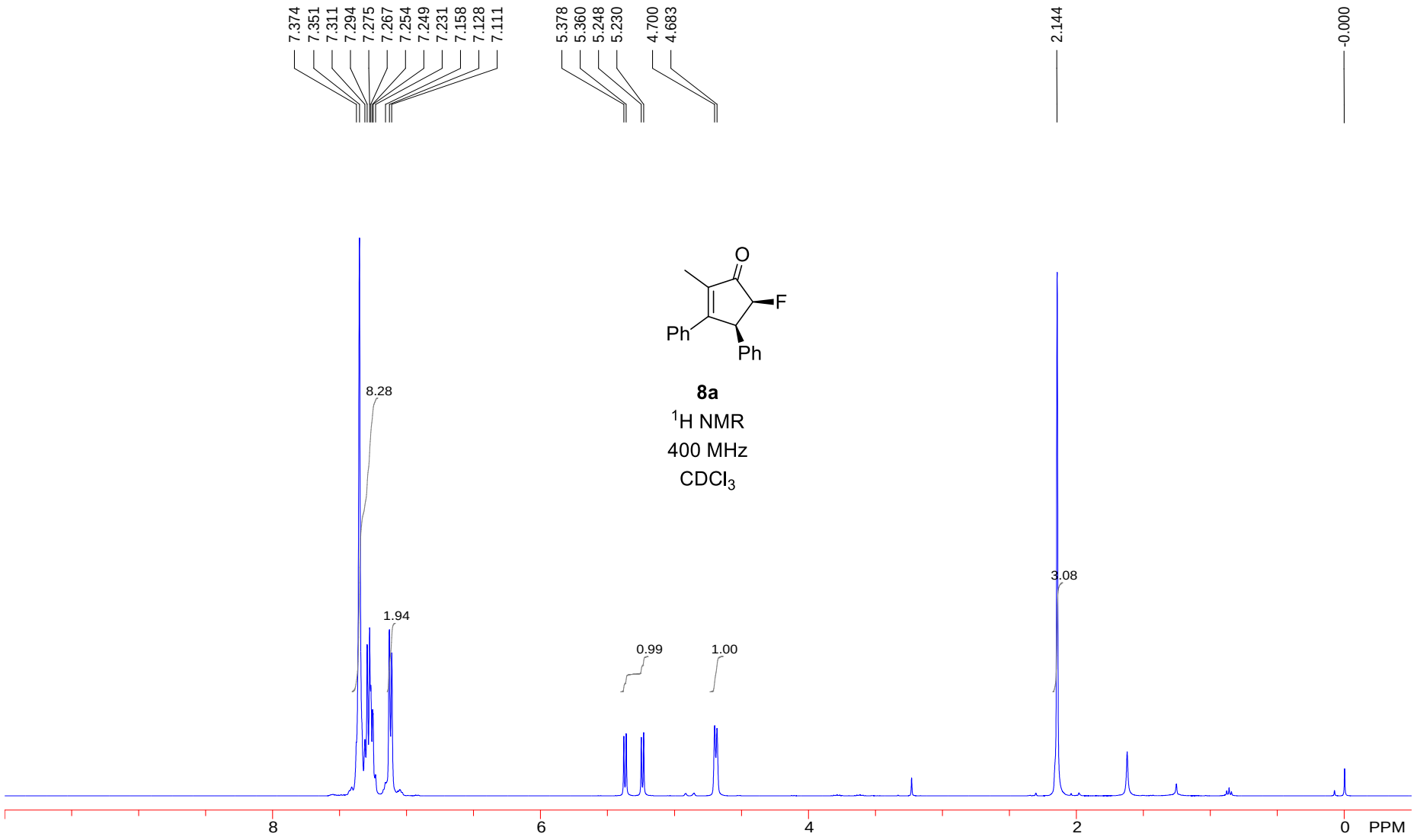
^{19}F NMR

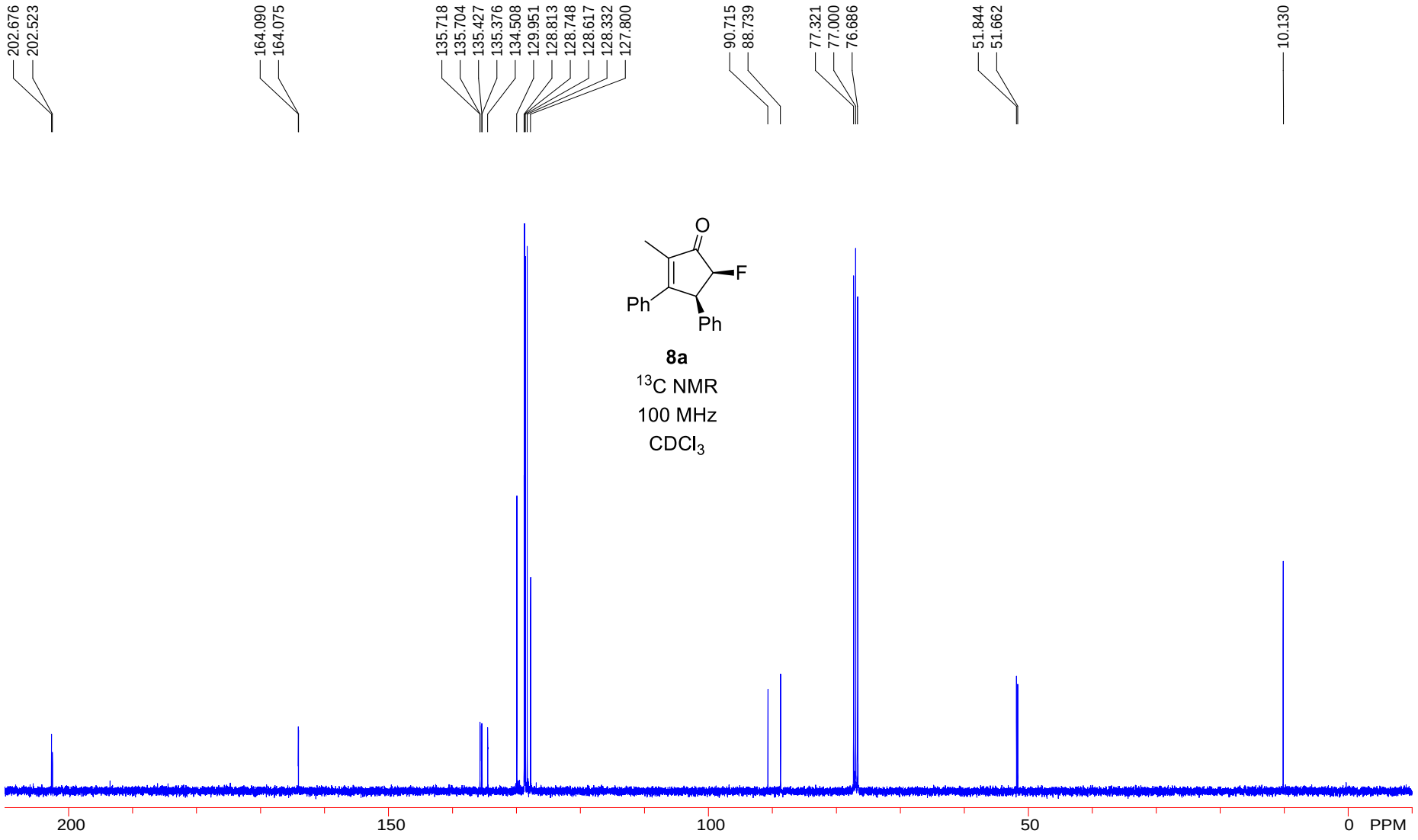
376 MHz

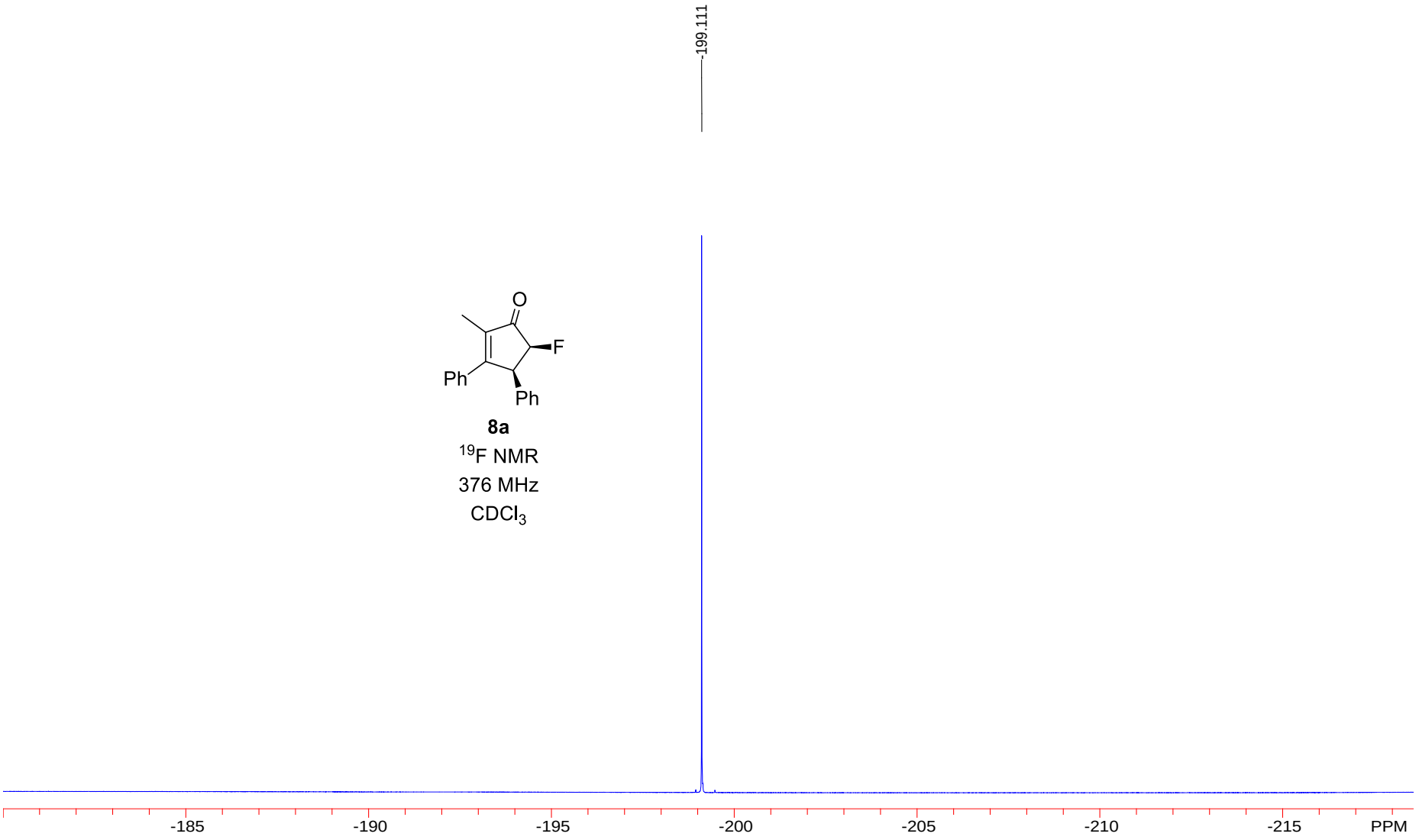
$CDCl_3$




163.974
163.988
163.999
164.014
164.036
164.050
164.064
164.075
HO
Me
O
OMe
F
Ph
Ph
7a (no decoupling)
19F NMR
376 MHz
CDCl3
-161
-162
-163
-164
-165
-166
-167
PPM


7.374
7.351
7.311
7.294
7.275
7.267
7.254
7.249
7.231
7.158
7.128
7.111
5.378
5.360
5.248
5.230
4.700
4.683
2.144
-0.000
O
F
Ph
Ph
8a
1H NMR
400 MHz
CDCl3
8.28
1.94
0.99
1.00
3.08
8
6
4
2
0
PPM


202.676
202.523
164.090
164.075
135.718
135.704
135.427
135.376
134.508
129.951
128.813
128.748
128.617
128.332
127.800
90.715
88.739
77.321
77.000
76.686
51.844
51.662
10.130
O
F
Ph
Ph
8a
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

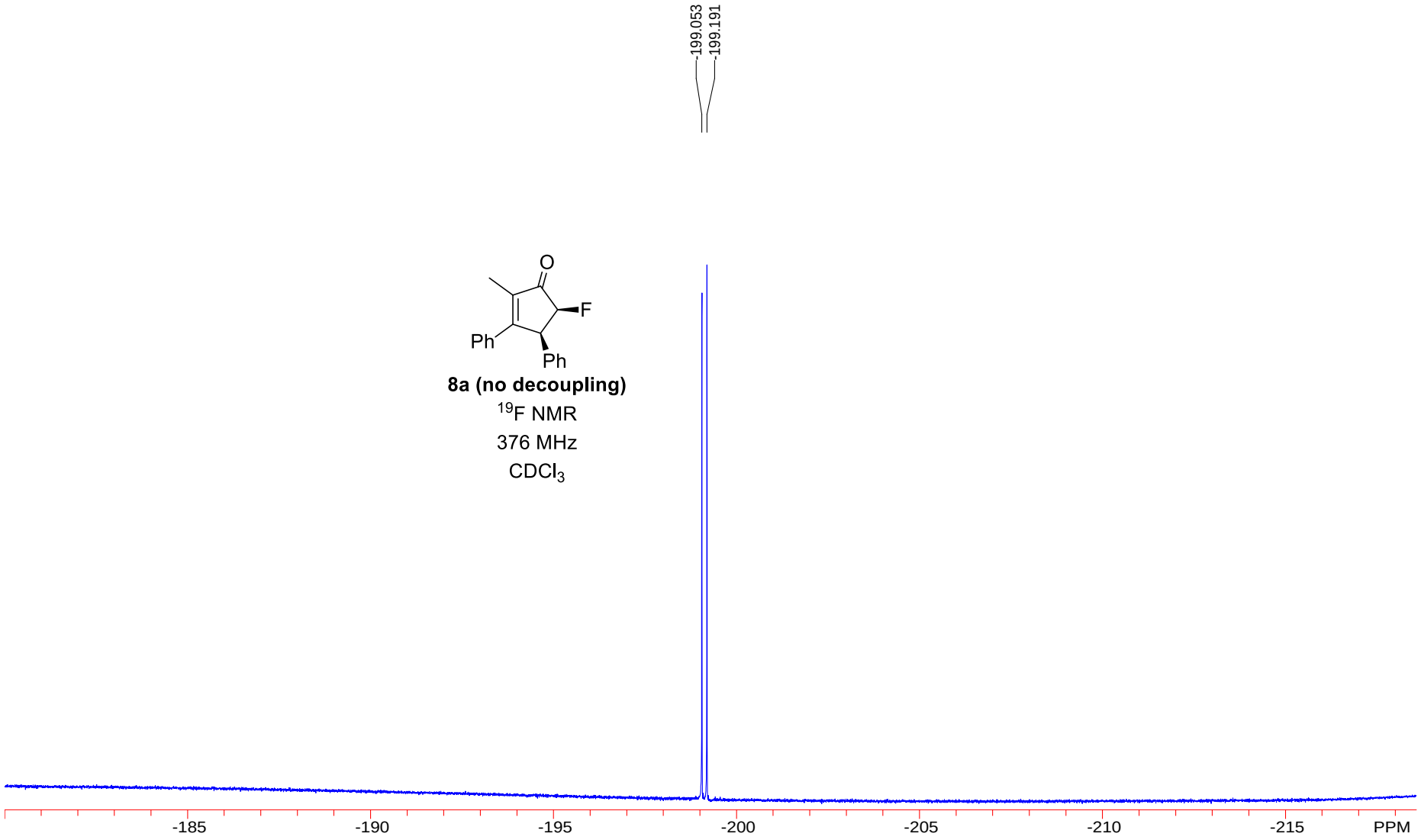


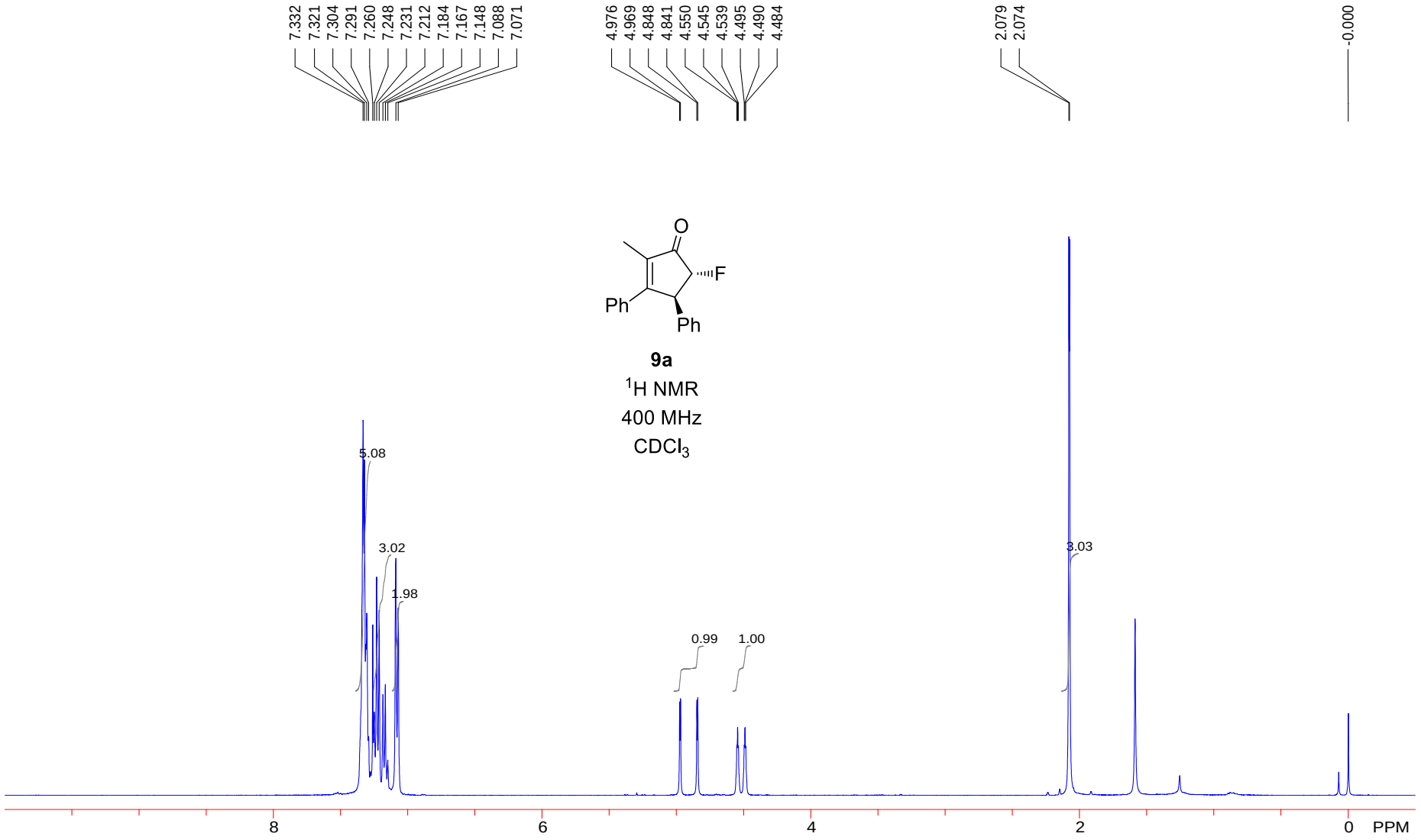
8a

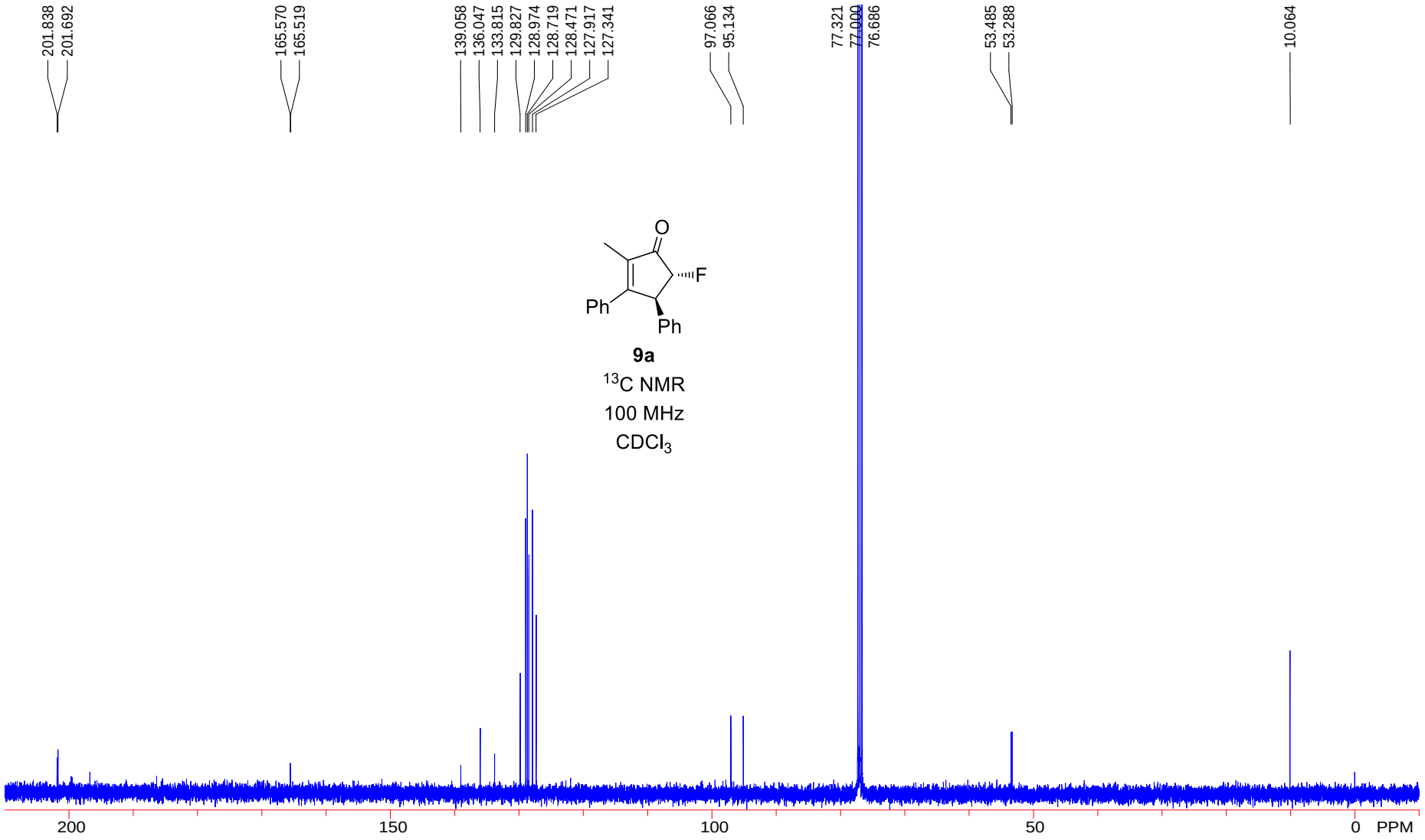
^{19}F NMR

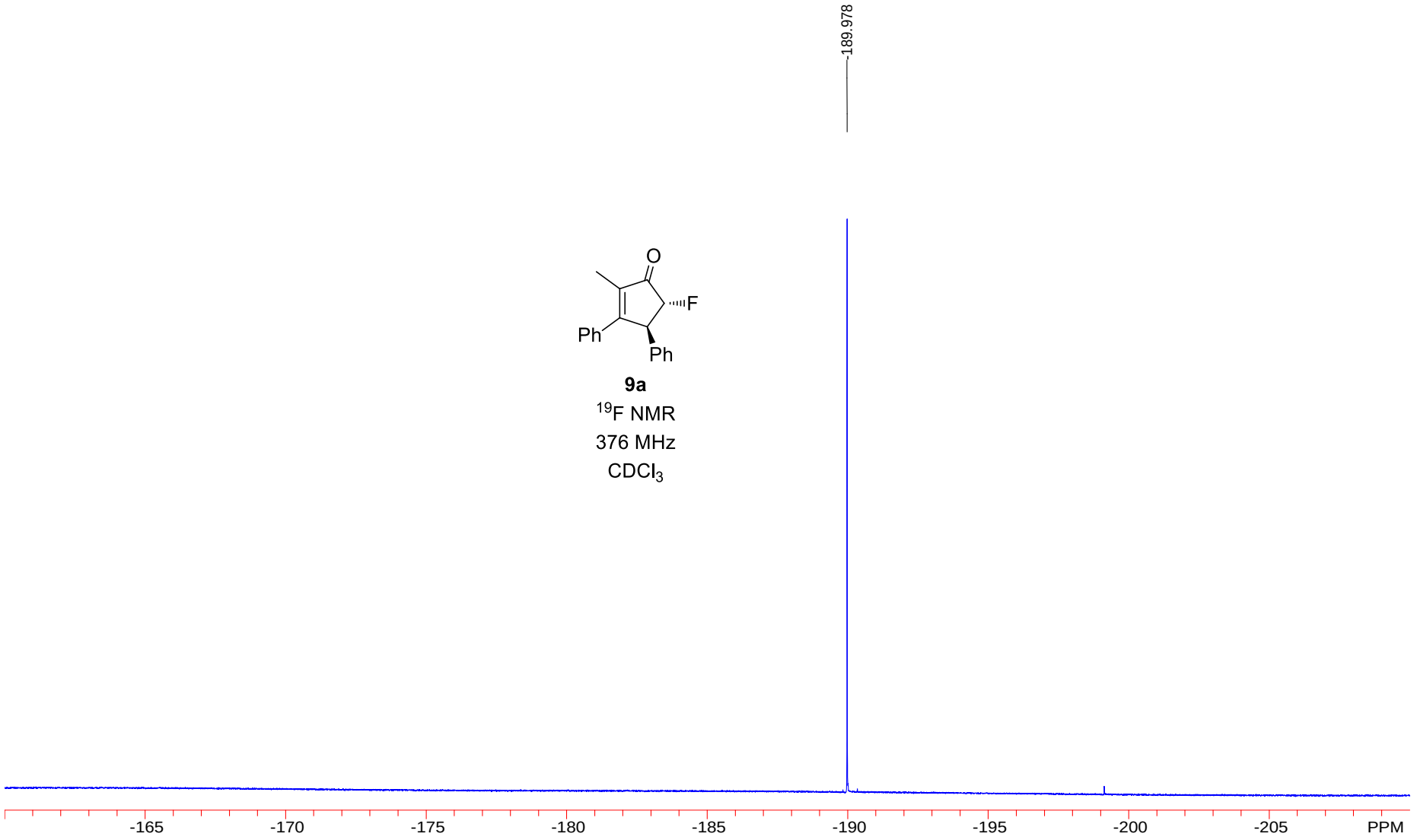
376 MHz

$CDCl_3$


-199.053
-199.191
O
F
Ph
Ph
8a (no decoupling)
19F NMR
376 MHz
CDCl3
-185
-190
-195
-200
-205
-210
-215
PPM


7.332
7.321
7.304
7.291
7.260
7.248
7.231
7.212
7.184
7.167
7.148
7.088
7.071
4.976
4.969
4.848
4.841
4.550
4.545
4.539
4.495
4.490
4.484
2.079
2.074
-0.000
O
F
Ph
Ph
9a
1H NMR
400 MHz
CDCl3
5.08
3.02
1.98
0.99
1.00
3.03
8
6
4
2
0
PPM


201.838
201.692
165.570
165.519
139.058
136.047
133.815
129.827
128.974
128.719
128.471
127.917
127.341
97.066
95.134
77.321
77.000
76.686
53.485
53.288
10.064
O
F
Ph
Ph
9a
13C NMR
100 MHz
CDCl3
200
150
100
50
0
PPM

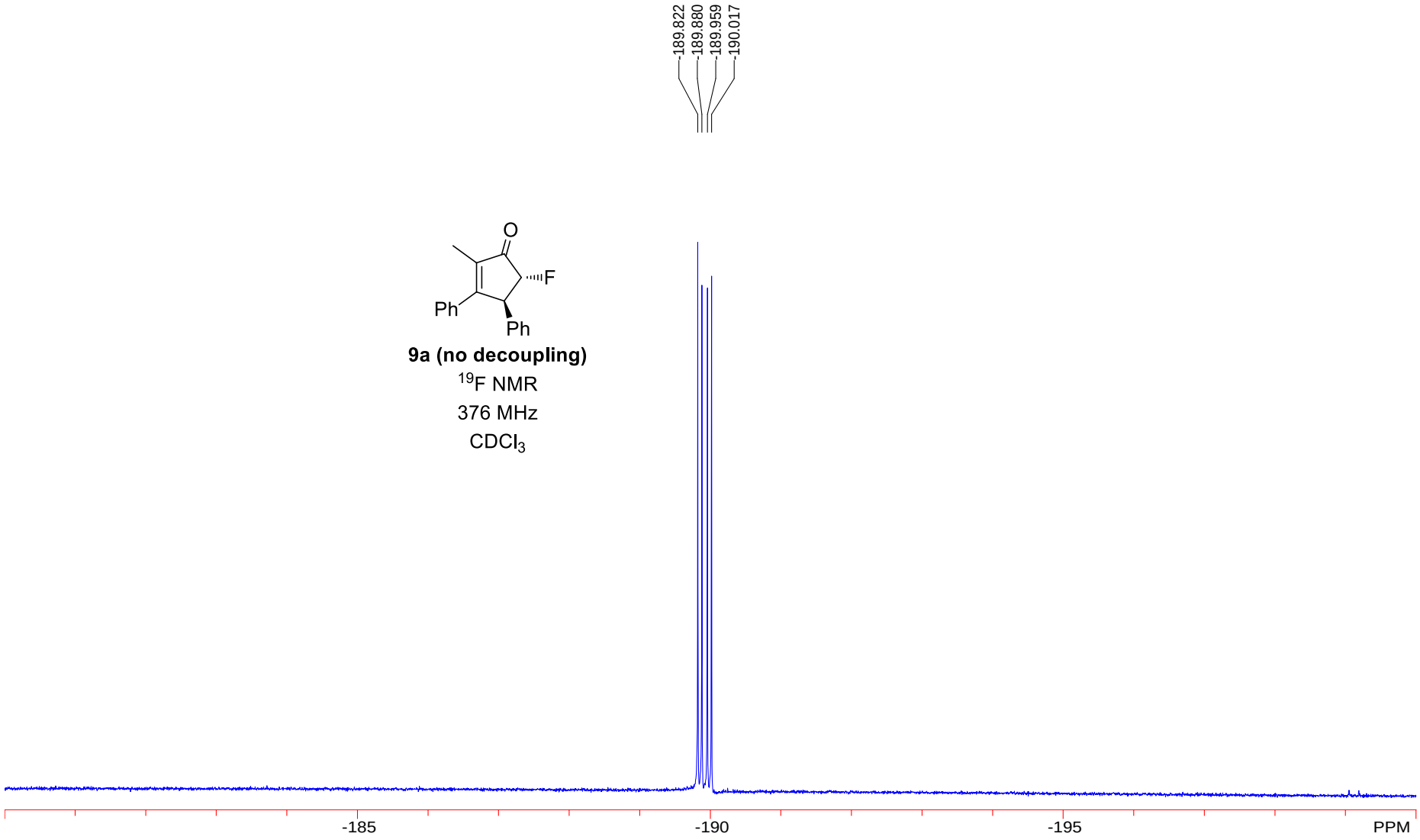


9a

^{19}F NMR

376 MHz

$CDCl_3$


189.822
189.880
189.959
190.017
O
F
Ph
Ph
9a (no decoupling)
19F NMR
376 MHz
CDCl3
-185
-190
-195
PPM

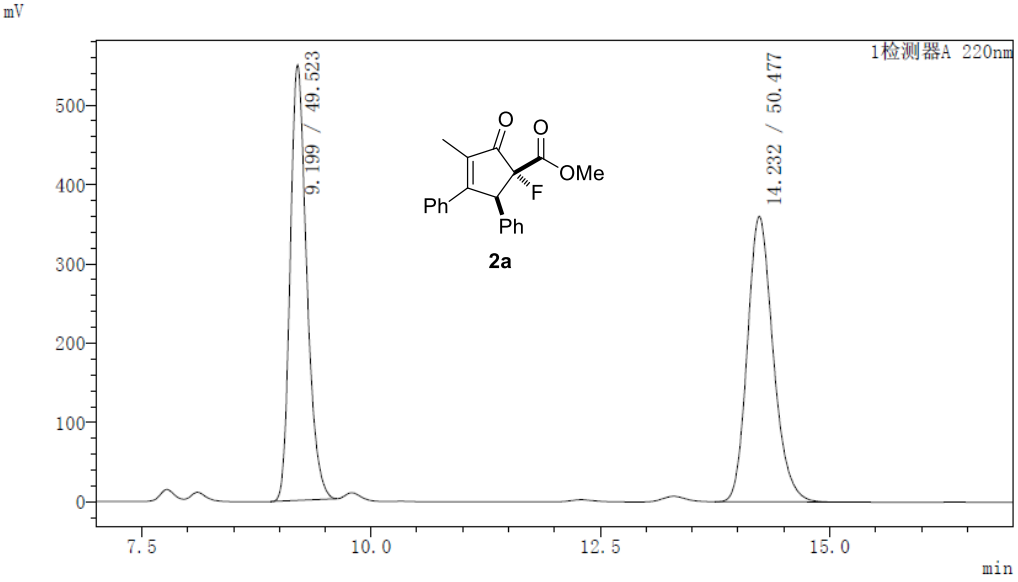
IX. HPLC Spectra

Translation of Chinese characters in HPLC spectra to English.

Chinese Characters	English
分析日期/时间	Analysis Date / Time
处理日期/时间	Processing Date / Time
重复进样计数	Number of Repeat Injection
描述	HPLC Condition
色谱图	HPLC Spectra
检测器	Detector
峰表	Area Percent Report
峰号	Peak Number
保留时间	Remaining Time
面积	Area
高度	Height
标记	Note
总计	Total

分析日期/时间 : 2018/2/5 14:10:55
处理日期/时间 : 2018/2/5 14:31:10
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



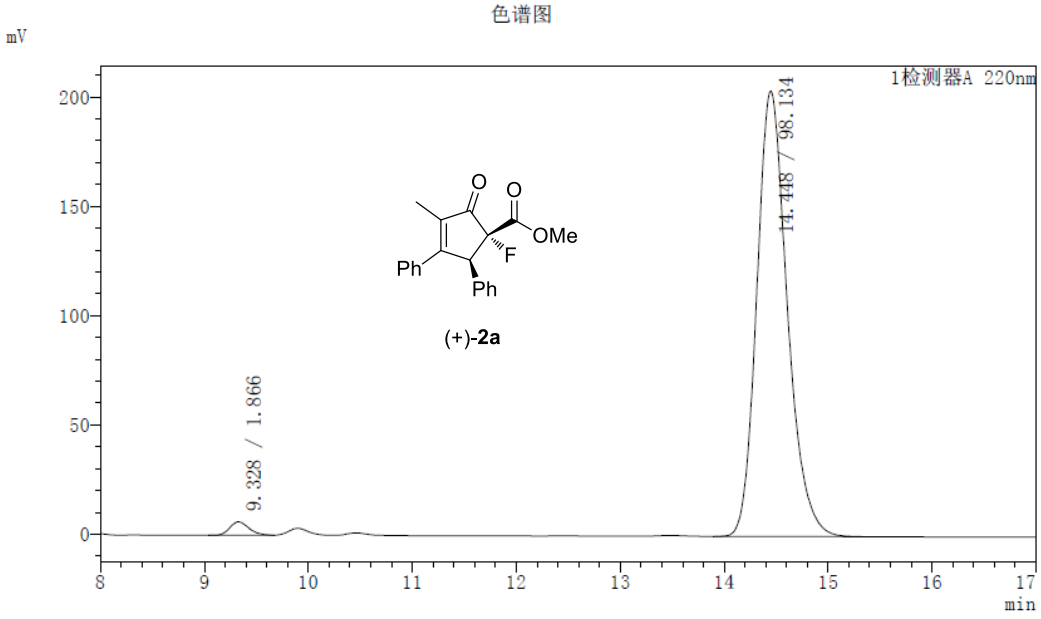
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.199	6902400	548875		49.523
2	14.232	7035266	359840		50.477
总计		13937665	908716		100.000

分析日期/时间 : 2018/2/5 13:50:40
处理日期/时间 : 2018/2/5 14:09:15
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



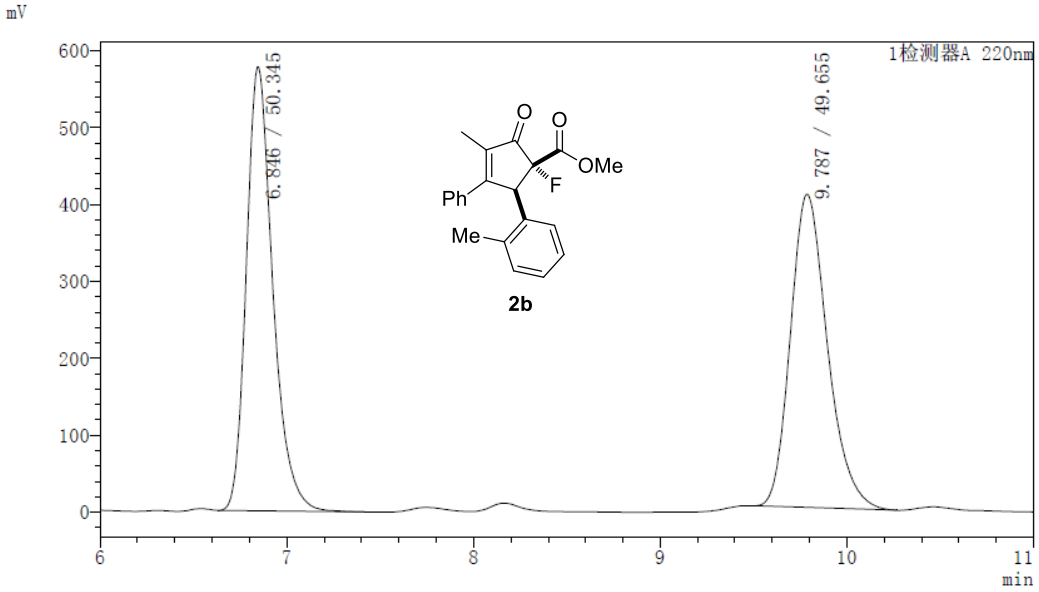
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.328	79066	6169		1.866
2	14.448	4158344	203805		98.134
总计		4237410	209974		100.000

分析日期/时间 : 2018/2/5 15:03:27
处理日期/时间 : 2018/2/5 15:16:25
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



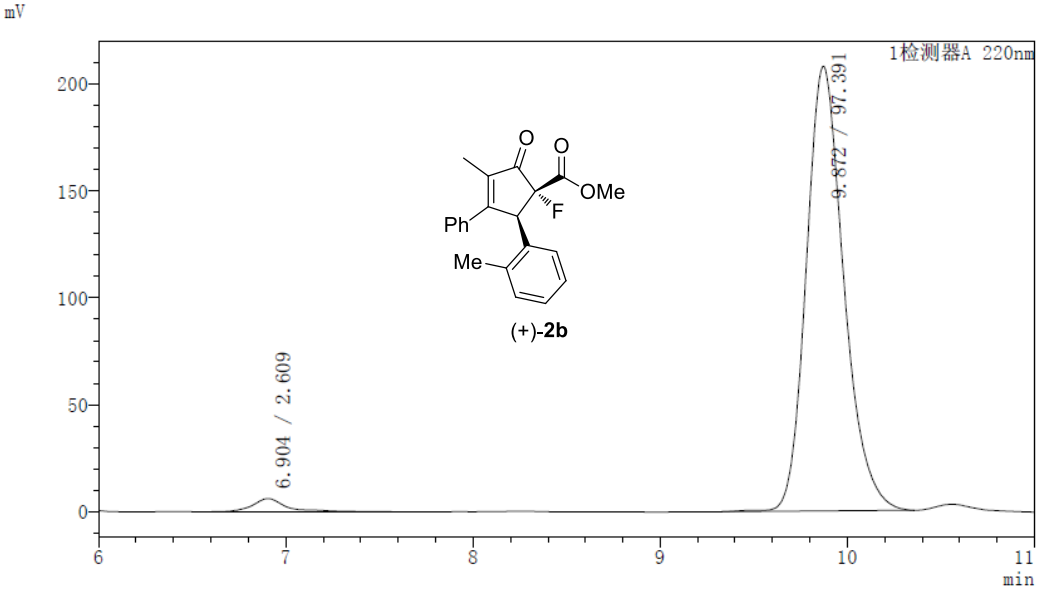
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.846	5688256	577121		50.345
2	9.787	5610193	407192		49.655
总计		11298449	984313		100.000

分析日期/时间 : 2018/2/5 15:17:47
处理日期/时间 : 2018/2/5 15:31:13
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



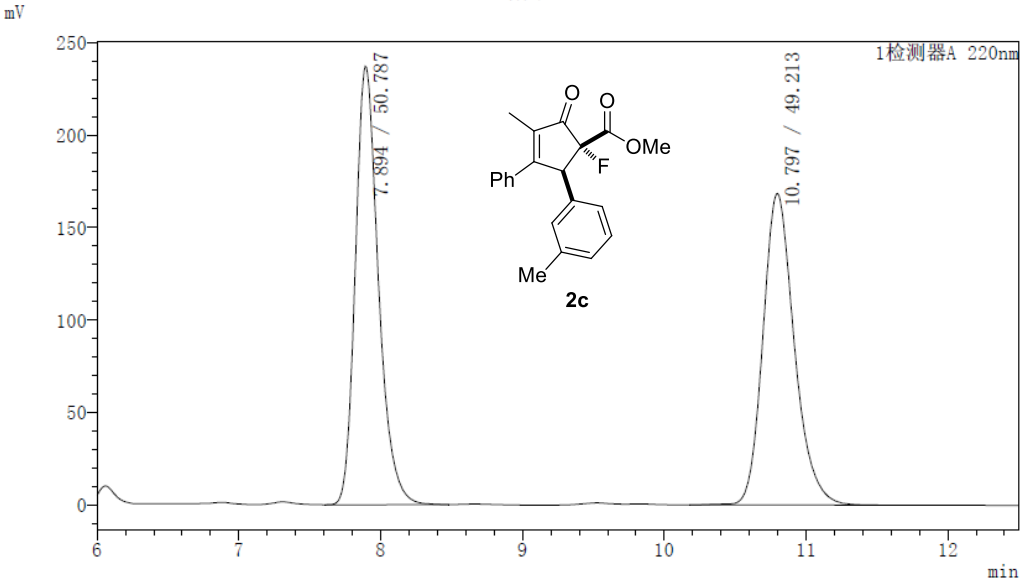
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.904	77752	6145		2.609
2	9.872	2902154	207852		97.391
总计		2979907	213997		100.000

分析日期/时间 : 2018/2/5 15:32:59
处理日期/时间 : 2018/2/5 15:47:34
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



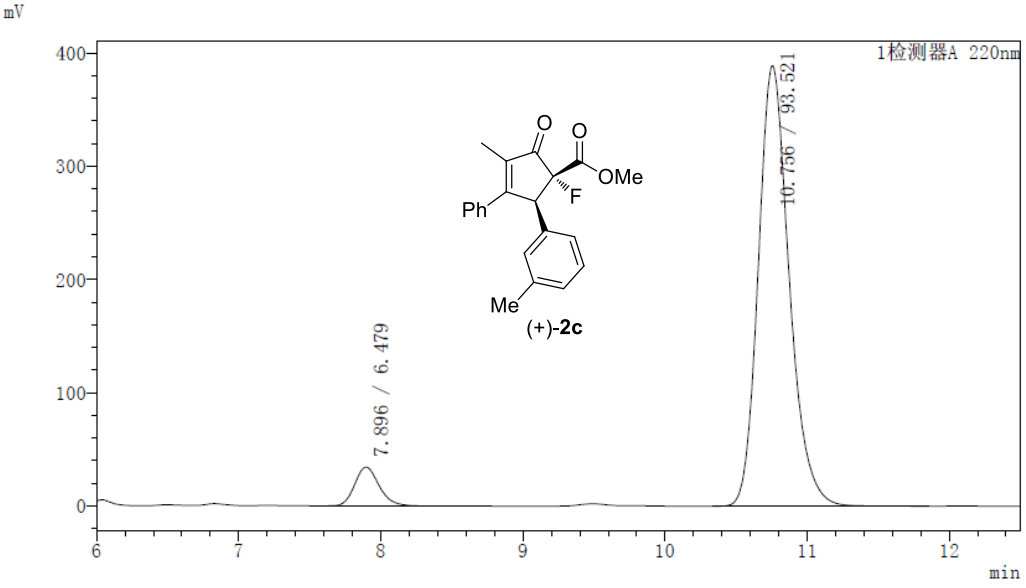
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.894	2677087	237128		50.787
2	10.797	2594094	168440		49.213
总计		5271181	405567		100.000

分析日期/时间 : 2018/2/5 15:49:40
处理日期/时间 : 2018/2/5 16:03:16
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



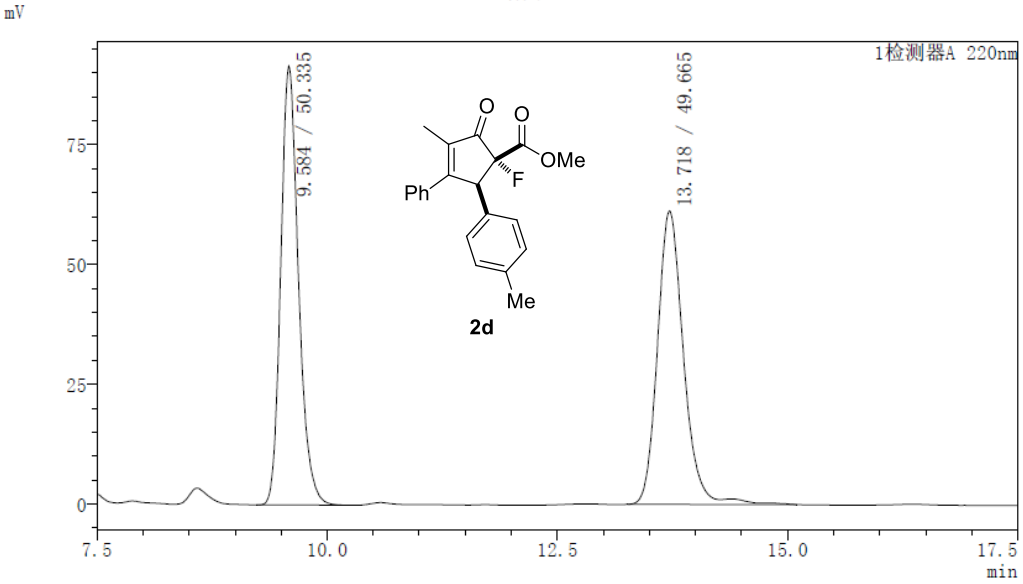
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.896	406894	34224		6.479
2	10.756	5873317	388888		93.521
总计		6280211	423112		100.000

分析日期/时间 : 2018/2/5 16:05:16
处理日期/时间 : 2018/2/5 16:23:16
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



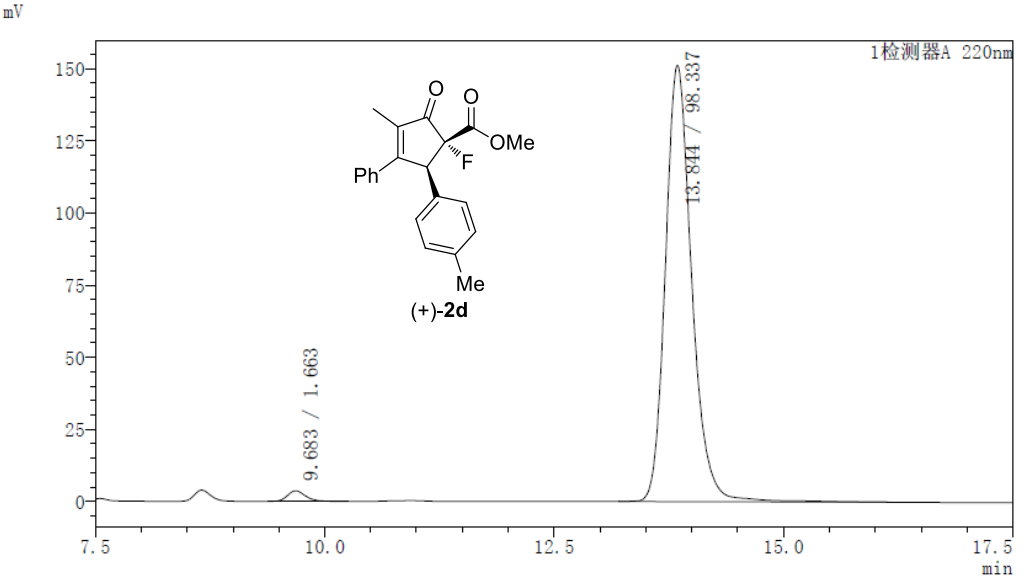
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.584	1224736	91600		50.335
2	13.718	1208434	61257	M	49.665
总计		2433170	152857		100.000

分析日期/时间 : 2018/2/5 16:26:01
处理日期/时间 : 2018/2/5 16:44:41
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



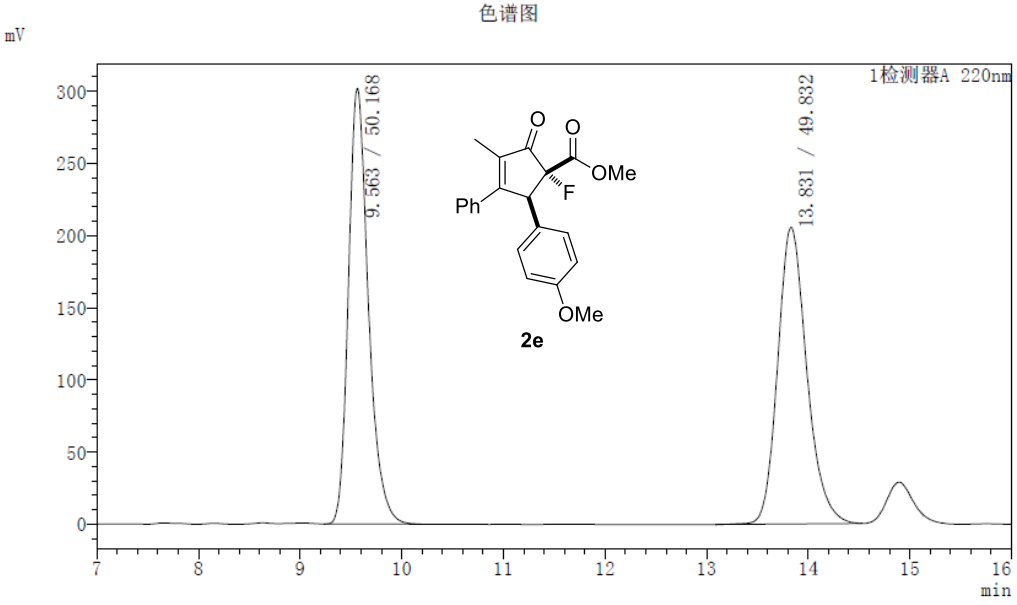
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.683	51051	3689		1.663
2	13.844	3018170	151218		98.337
总计		3069221	154908		100.000

分析日期/时间 : 2018/3/7 21:49:27
处理日期/时间 : 2018/3/7 22:06:44
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



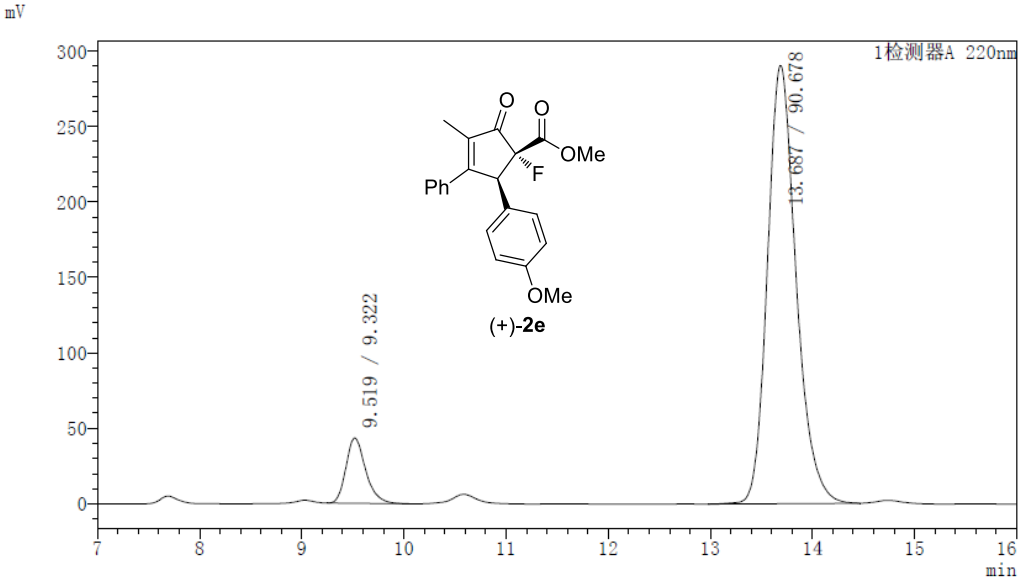
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.563	4120387	301861	S	50.168
2	13.831	4092806	205685		49.832
总计		8213193	507546		100.000

分析日期/时间 : 2018/3/7 22:07:53
处理日期/时间 : 2018/3/7 22:24:33
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



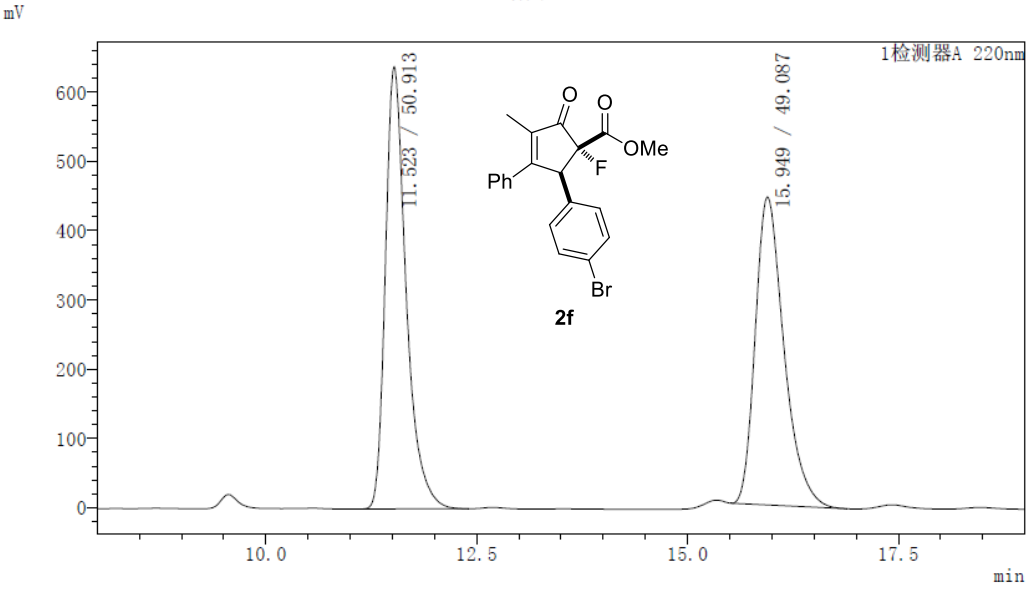
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.519	581560	43346		9.322
2	13.687	5657188	290214		90.678
总计		6238748	333560		100.000

分析日期/时间 : 2018/3/5 14:29:05
处理日期/时间 : 2018/3/5 14:48:48
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



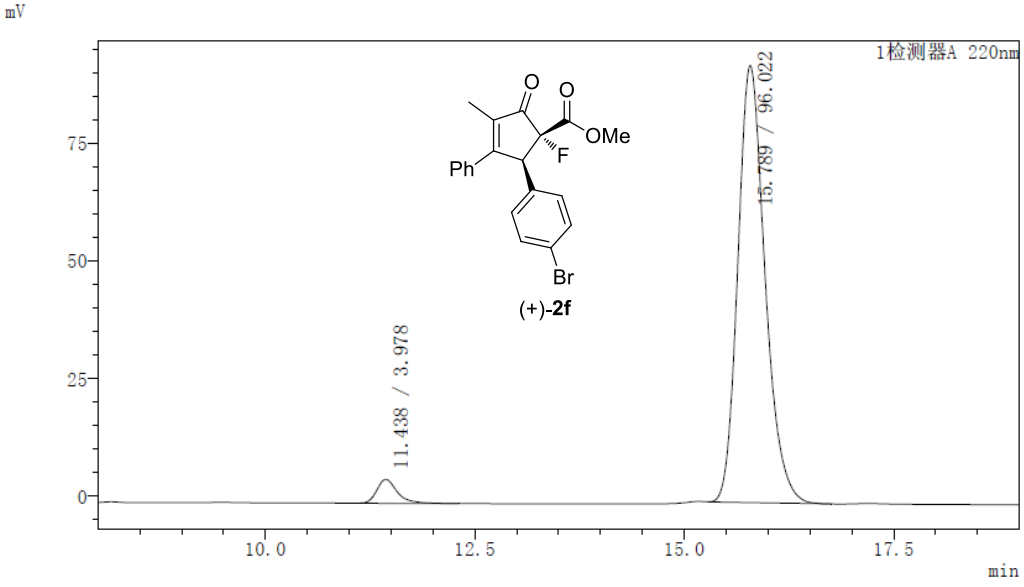
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.523	10920983	638144		50.913
2	15.949	10529160	444788		49.087
总计		21450143	1082931		100.000

分析日期/时间 : 2018/3/5 14:49:52
处理日期/时间 : 2018/3/5 15:09:35
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



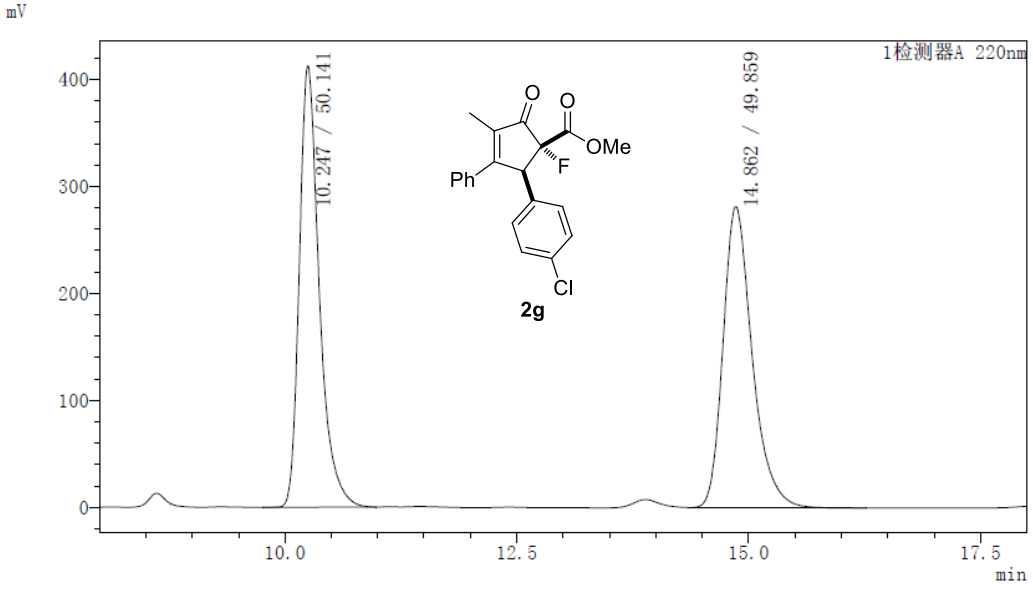
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.438	86833	5108		3.978
2	15.789	2095771	92933		96.022
总计		2182604	98040		100.000

分析日期/时间 : 2018/3/5 15:10:54
处理日期/时间 : 2018/3/5 15:29:07
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



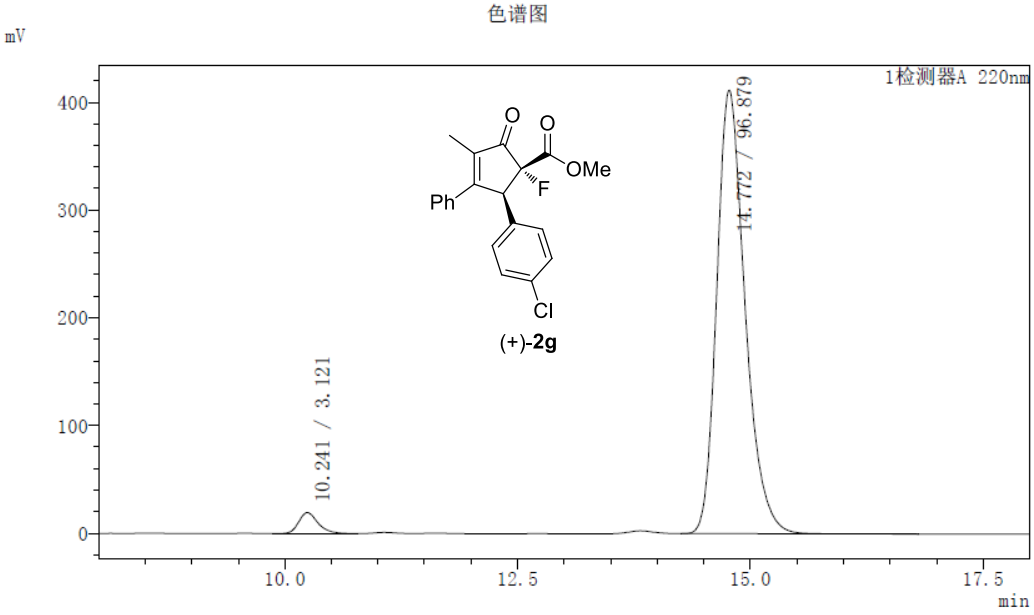
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.247	6173042	412692		50.141
2	14.862	6138356	281232		49.859
总计		12311398	693925		100.000

分析日期/时间 : 2018/3/5 15:30:43
处理日期/时间 : 2018/3/5 15:49:12
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



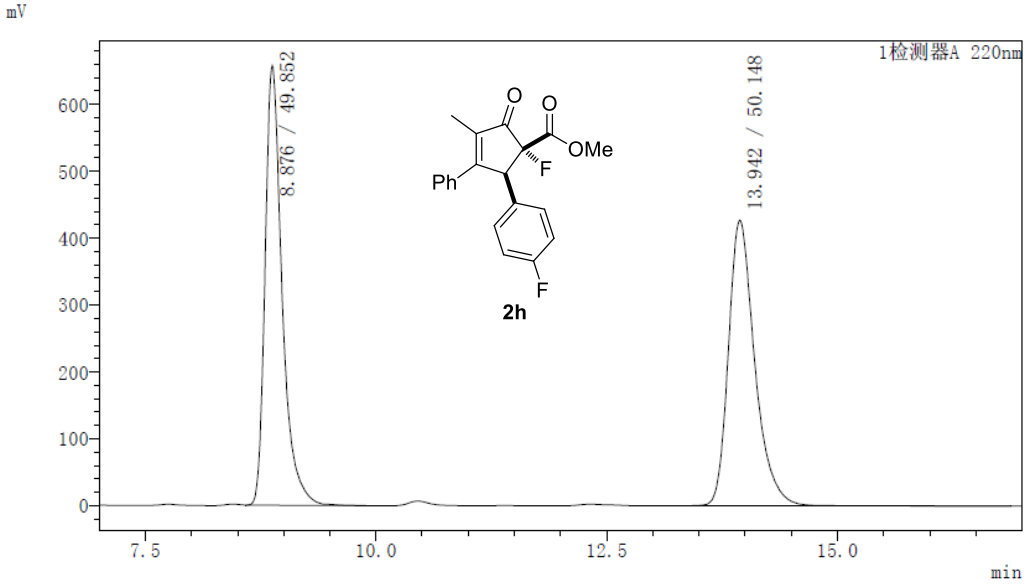
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.241	280434	19535		3.121
2	14.772	8705173	411640		96.879
总计		8985607	431175		100.000

分析日期/时间 : 2018/3/5 15:50:58
处理日期/时间 : 2018/3/5 16:08:28
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



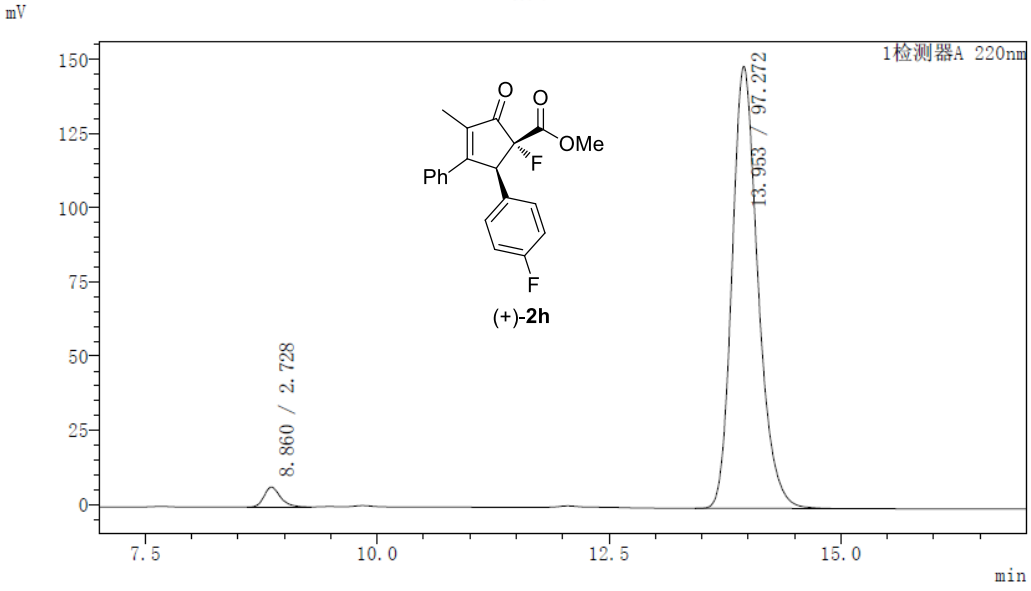
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.876	8417648	657077		49.852
2	13.942	8467706	426824	S	50.148
总计		16885355	1083900		100.000

分析日期/时间 : 2018/3/5 16:09:42
处理日期/时间 : 2018/3/5 16:26:55
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



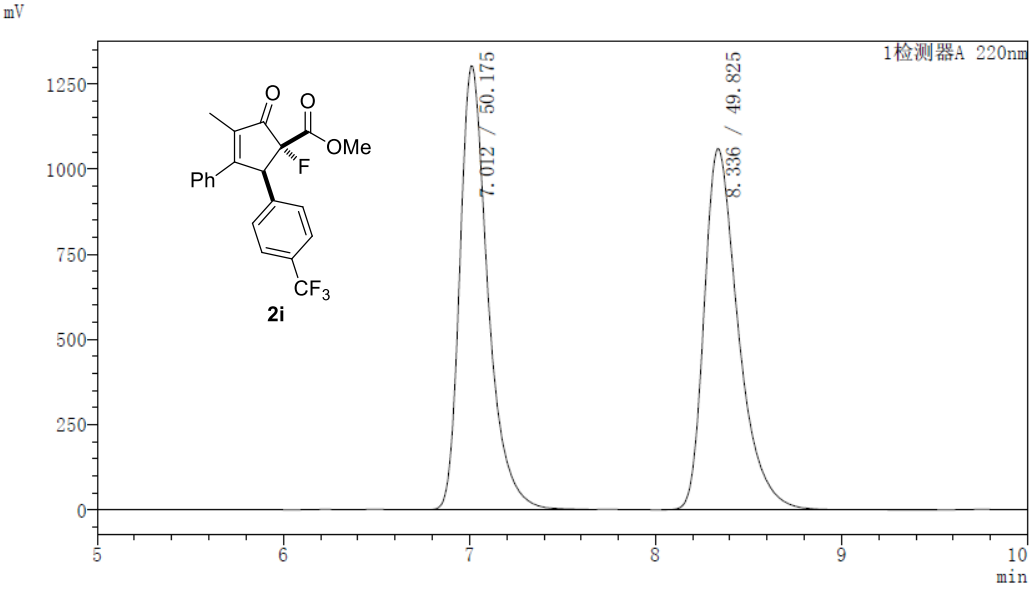
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.860	81213	6689		2.728
2	13.953	2895267	148934		97.272
总计		2976480	155623		100.000

分析日期/时间 : 2018/3/7 20:41:15
处理日期/时间 : 2018/3/7 20:52:29
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



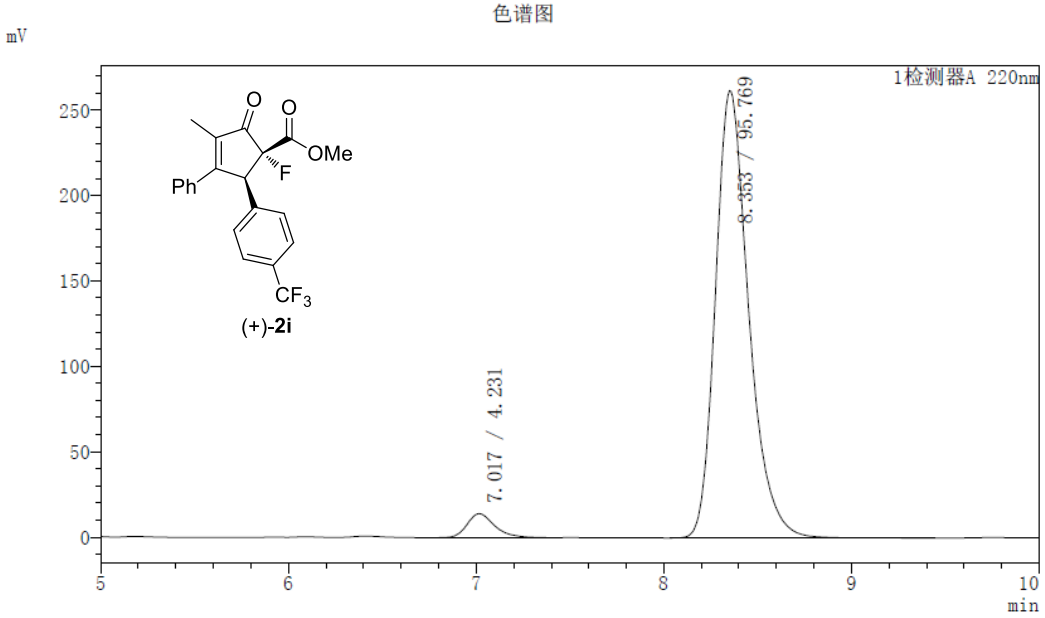
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.012	13611311	1301938		50.175
2	8.336	13516514	1060186		49.825
总计		27127825	2362124		100.000

分析日期/时间 : 2018/3/7 20:53:42
处理日期/时间 : 2018/3/7 21:04:41
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



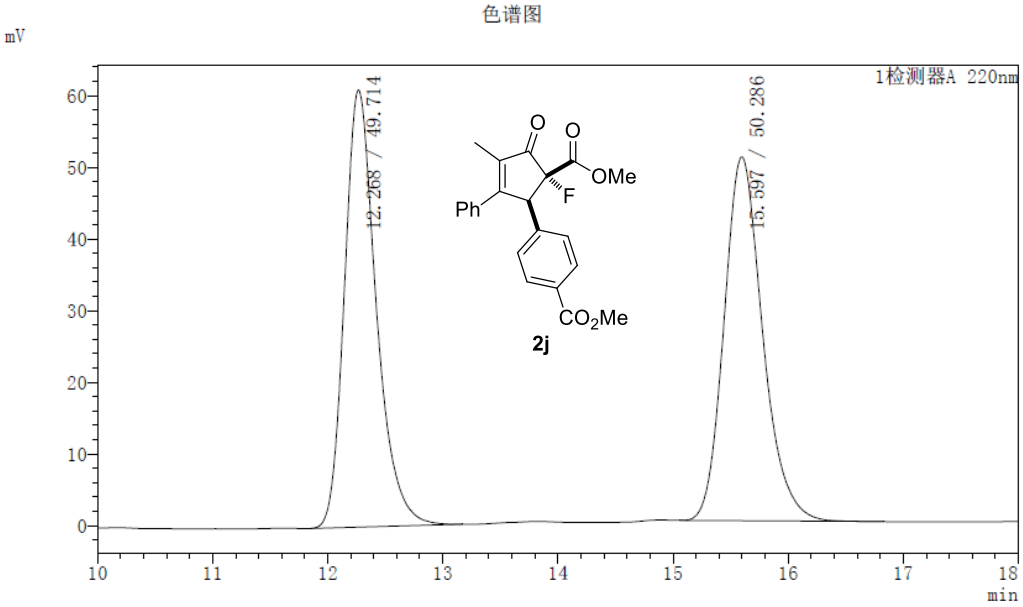
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.017	142307	13992		4.231
2	8.353	3221051	261792	S	95.769
总计		3363358	275784		100.000

分析日期/时间 : 2018/3/7 21:06:15
处理日期/时间 : 2018/3/7 21:27:16
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



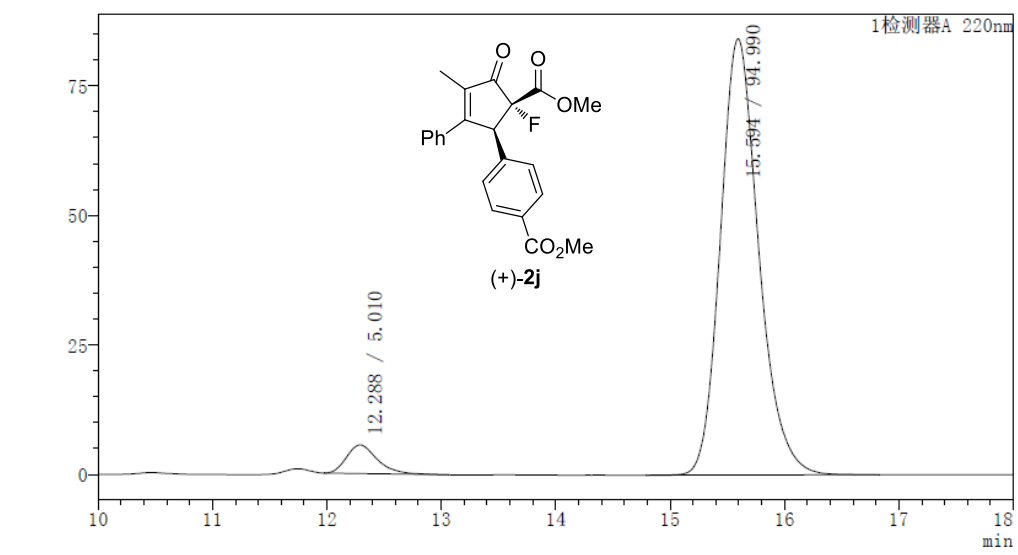
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	12.268	1170546	61020		49.714
2	15.597	1184013	50795		50.286
总计		2354559	111815		100.000

分析日期/时间 : 2018/3/7 21:28:34
处理日期/时间 : 2018/3/7 21:47:47
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



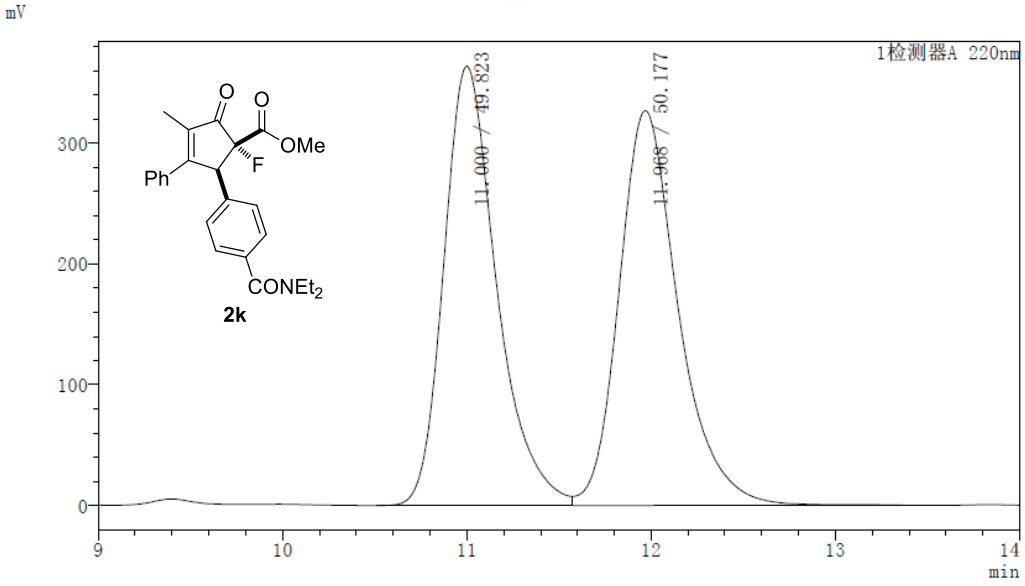
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	12.288	103494	5521		5.010
2	15.594	1962210	84218		94.990
总计		2065704	89739		100.000

分析日期/时间 : 2018/3/30 18:41:10
处理日期/时间 : 2018/3/30 18:56:46
描述 : AD-H, n-hexane/iPrOH = 80/20, 1.0 mL/min, 220 nm

色谱图



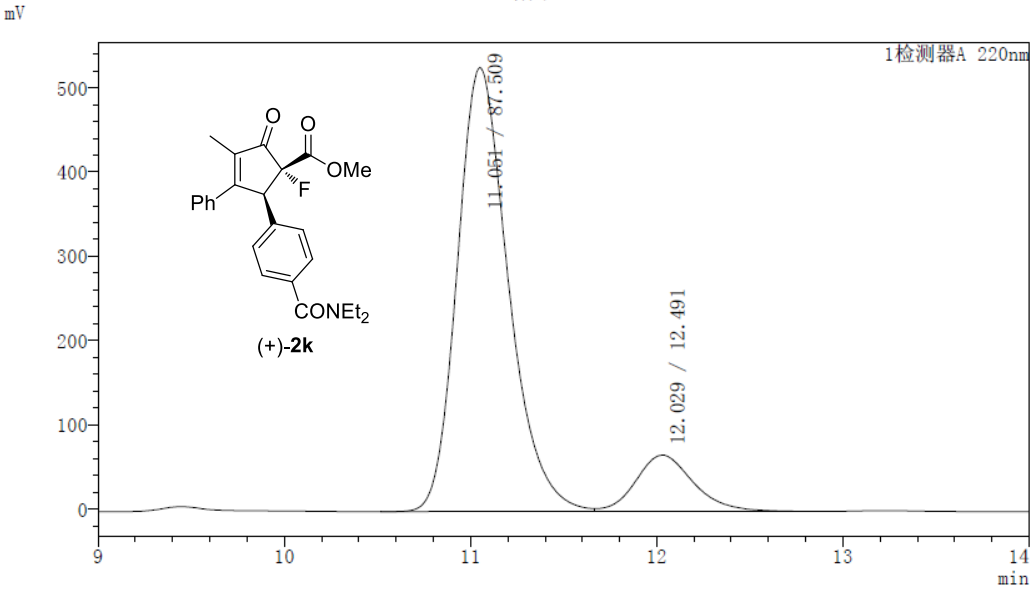
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.000	7242901	363667		49.823
2	11.968	7294305	326836	V	50.177
总计		14537206	690503		100.000

分析日期/时间 : 2018/3/30 18:58:12
处理日期/时间 : 2018/3/30 19:13:24
描述 : AD-H, n-hexane/iPrOH = 80/20, 1.0 mL/min, 220 nm

色谱图



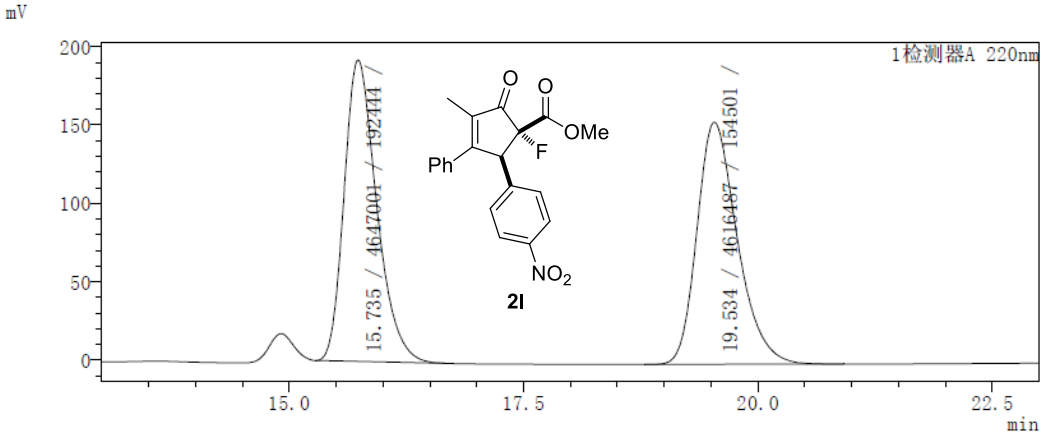
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.051	10043152	526613		87.509
2	12.029	1433521	66754	V	12.491
总计		11476673	593367		100.000

分析日期/时间 : 2018-3-8 17:50:01
处理日期/时间 : 2018-3-8 18:13:57
重复进样计数 : 1
描述 : AD-H, n-hexane:iPrOH = 85/15, 1.0 ml/min, 220 nm

色谱图
ZHY11014-P



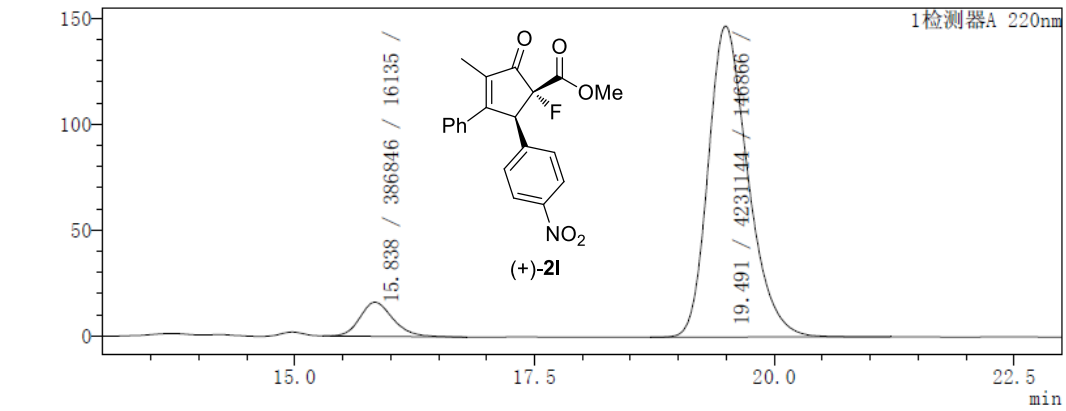
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	15.735	4647001	192444		50.165
2	19.534	4616487	154501		49.835
总计		9263488	346945		100.000

分析日期/时间 : 2018-3-8 18:18:11
处理日期/时间 : 2018-3-8 18:51:32
重复进样计数 : 1
描述 : AD-H, n-hexane:iPrOH = 85/15, 1.0 ml/min, 220 nm

色谱图
ZHY11003-P



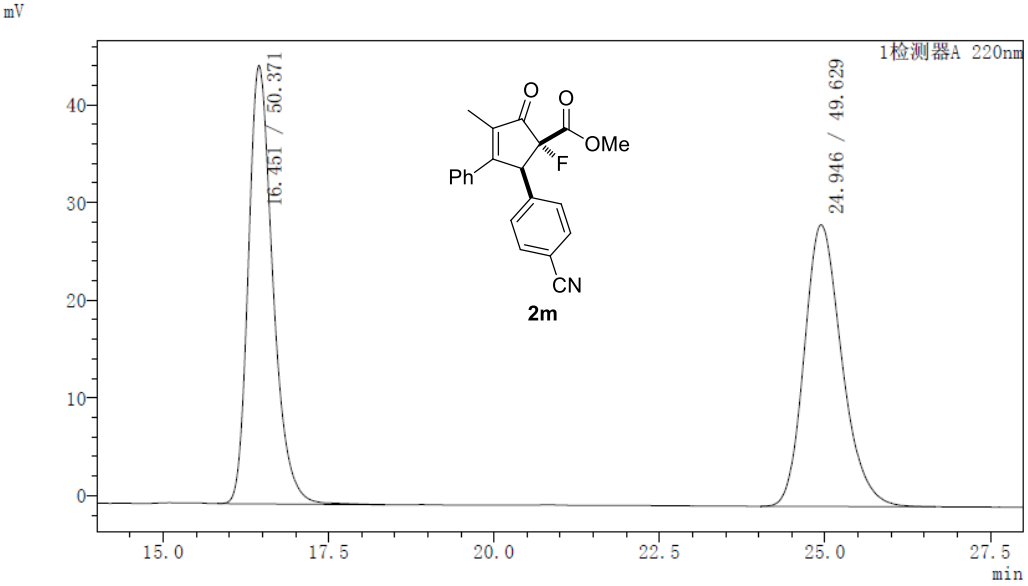
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	15.838	386846	16135		8.377
2	19.491	4231144	146866		91.623
总计		4617990	163001		100.000

分析日期/时间 : 2018/3/30 15:30:54
处理日期/时间 : 2018/3/30 16:00:29
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



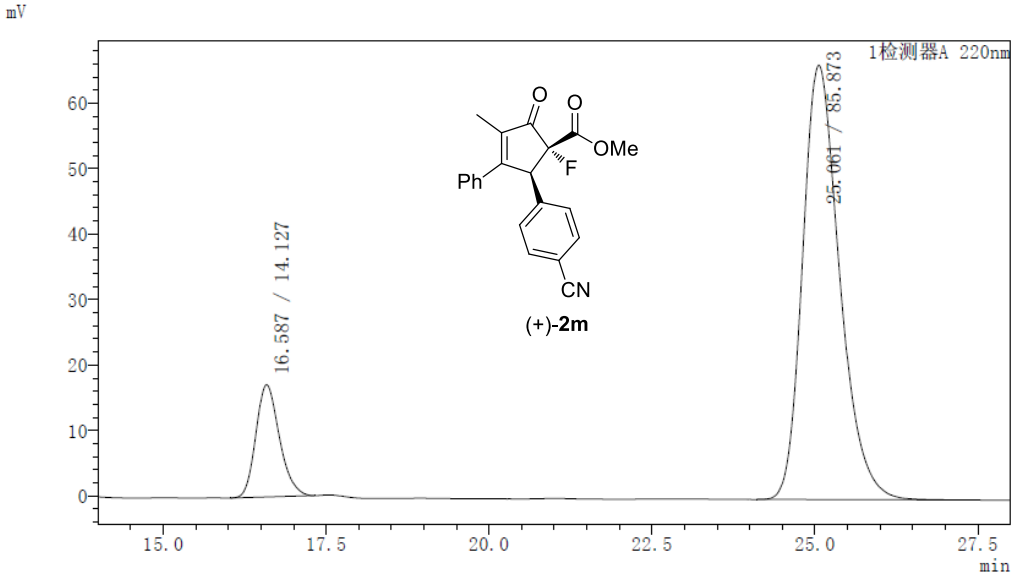
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	16.451	1156536	44911		50.371
2	24.946	1139491	28849		49.629
总计		2296026	73761		100.000

分析日期/时间 : 2018/3/30 16:02:58
处理日期/时间 : 2018/3/30 16:31:47
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



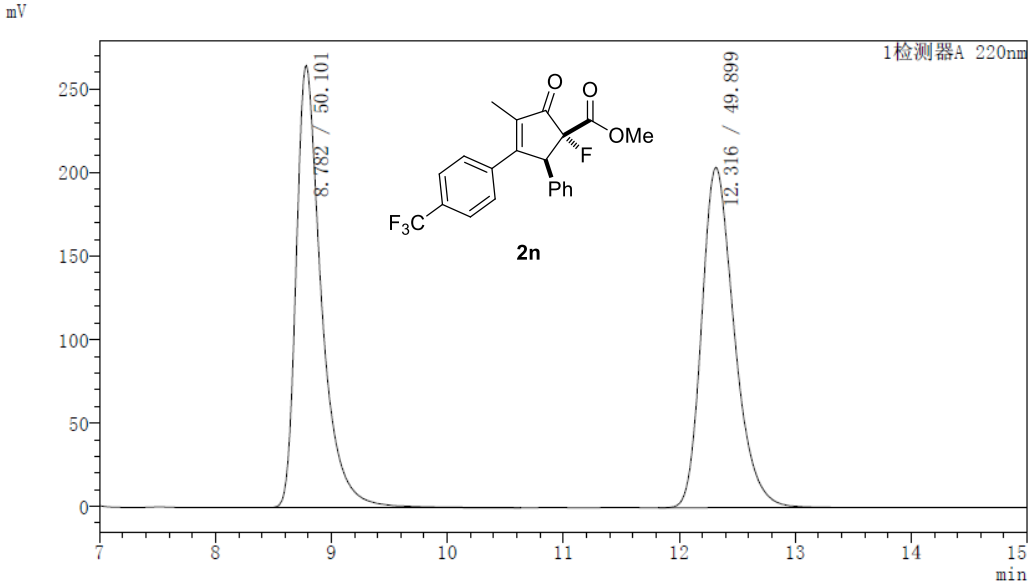
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	16.587	431608	17153		14.127
2	25.061	2623521	66359		85.873
总计		3055129	83513		100.000

分析日期/时间 : 2018/3/31 9:07:01
处理日期/时间 : 2018/3/31 9:22:42
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



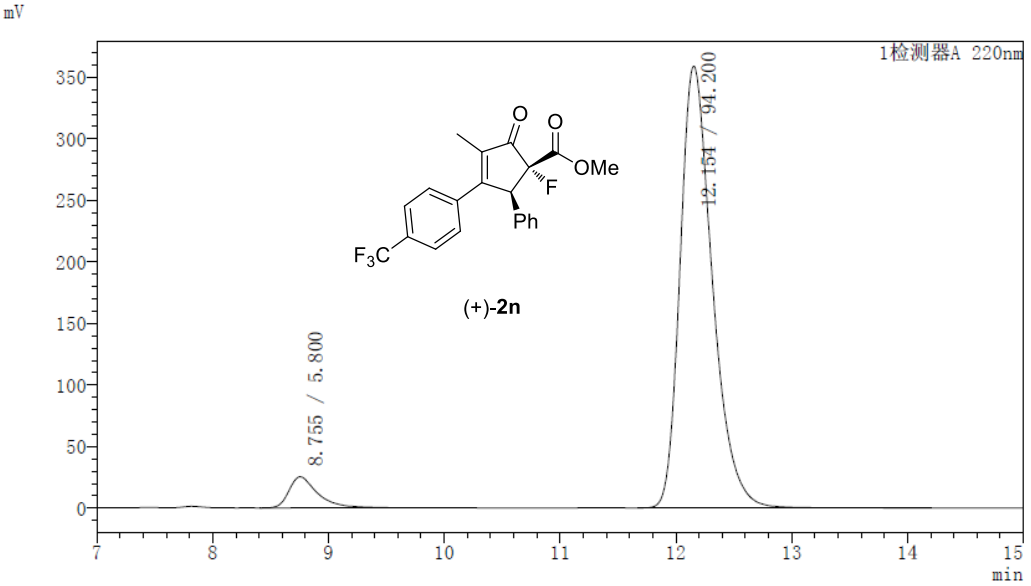
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.782	3997141	264661		50.101
2	12.316	3981048	203744		49.899
总计		7978189	468404		100.000

分析日期/时间 : 2018/3/31 9:23:53
处理日期/时间 : 2018/3/31 9:39:05
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



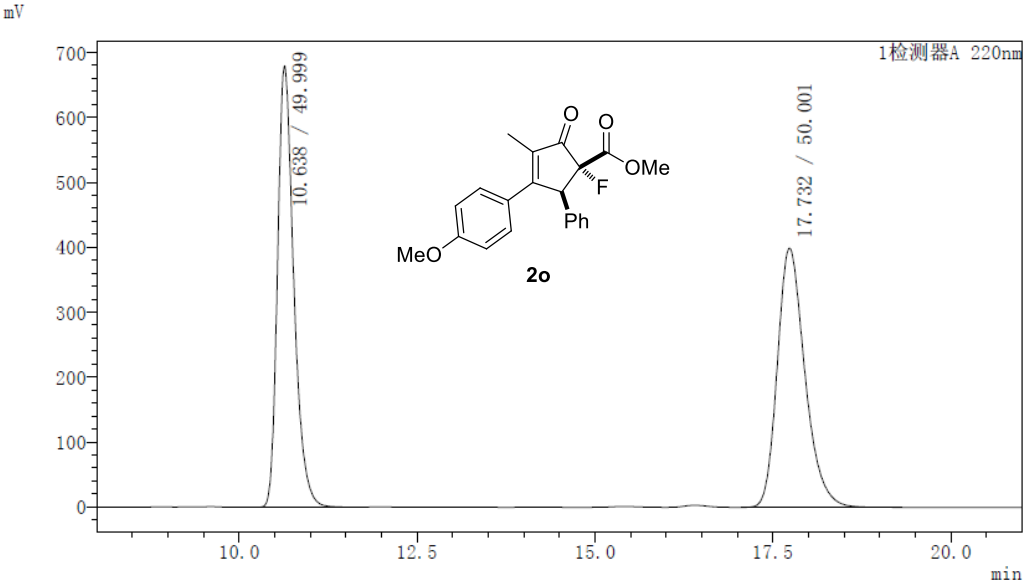
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.755	427491	25191	M	5.800
2	12.154	6943616	358852		94.200
总计		7371107	384043		100.000

分析日期/时间 : 2018/3/31 10:18:24
处理日期/时间 : 2018/3/31 10:39:53
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



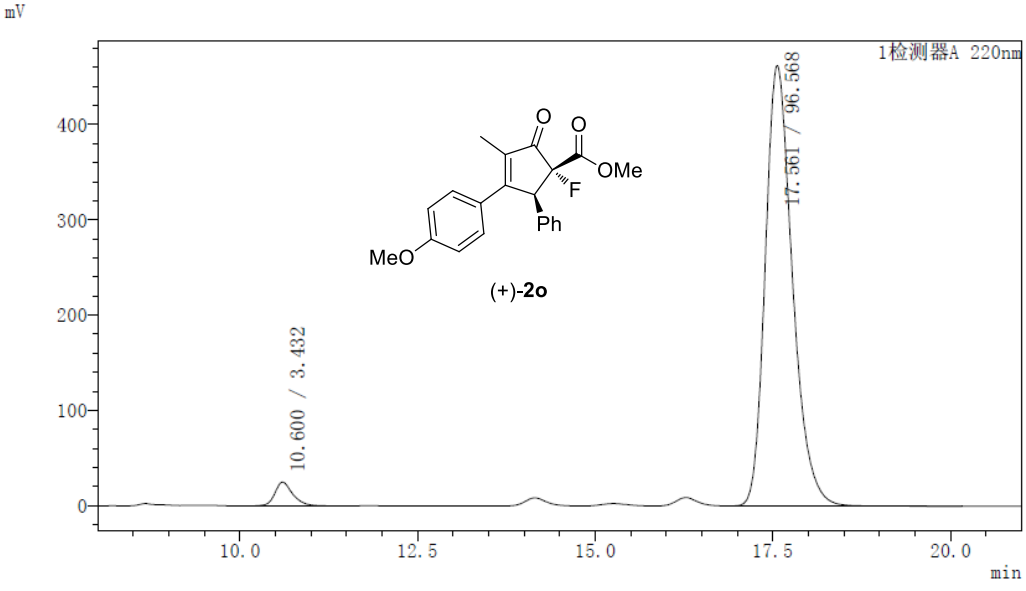
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.638	10753230	679365		49.999
2	17.732	10753784	399083		50.001
总计		21507014	1078448		100.000

分析日期/时间 : 2018/3/31 10:41:07
处理日期/时间 : 2018/3/31 11:02:47
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



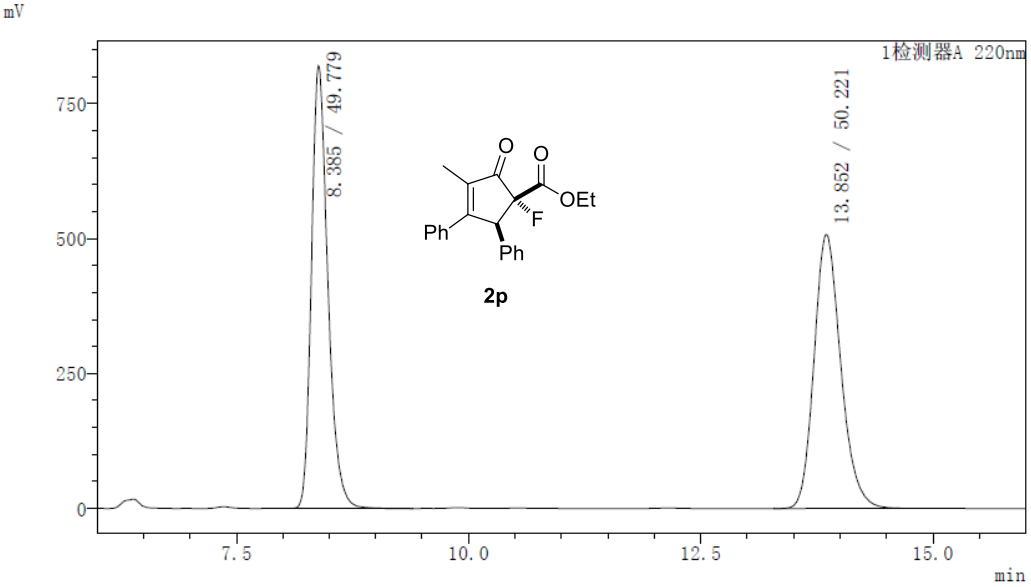
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.600	437285	25036		3.432
2	17.561	12304739	462202		96.568
总计		12742024	487237		100.000

分析日期/时间 : 2018/3/15 8:57:03
处理日期/时间 : 2018/3/15 9:14:09
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



2p

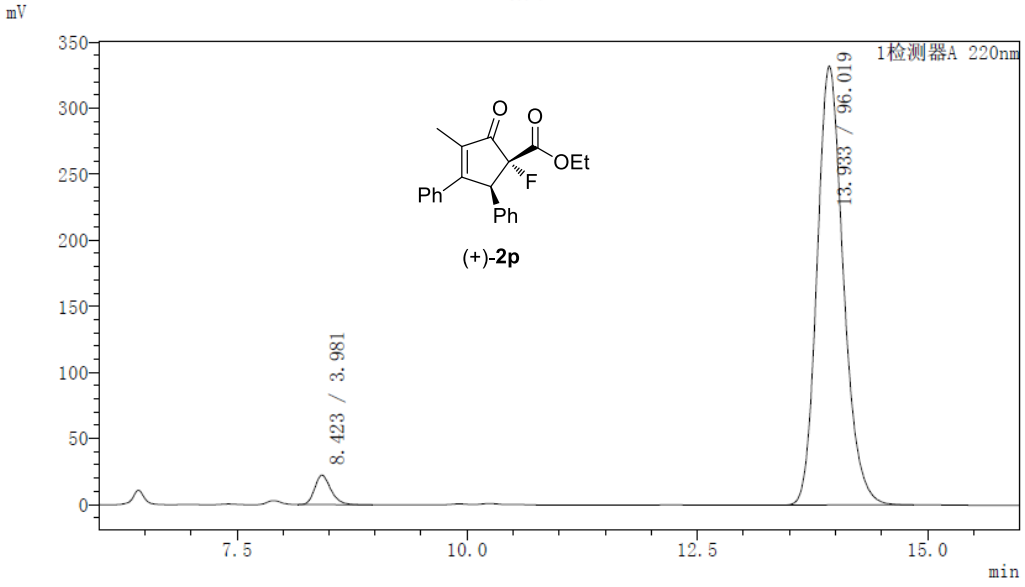
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.385	10074930	820460		49.779
2	13.852	10164430	507651		50.221
总计		20239360	1328111		100.000

分析日期/时间 : 2018/3/15 9:15:47
处理日期/时间 : 2018/3/15 9:32:59
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



(+)-2p

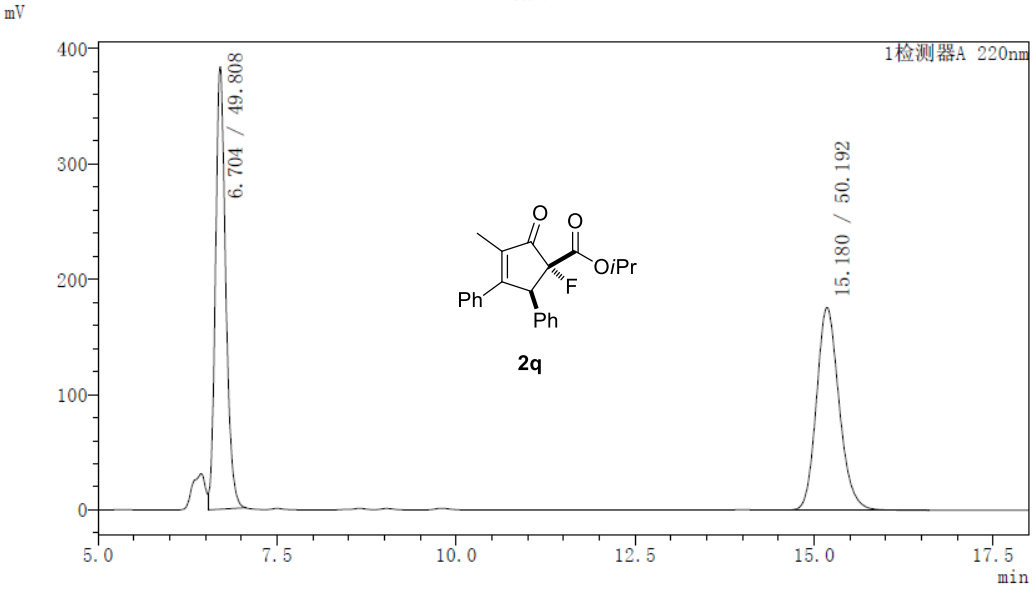
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.423	273371	22360		3.981
2	13.933	6594311	332420		96.019
总计		6867682	354779		100.000

分析日期/时间 : 2018/3/15 9:34:48
处理日期/时间 : 2018/3/15 9:53:27
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



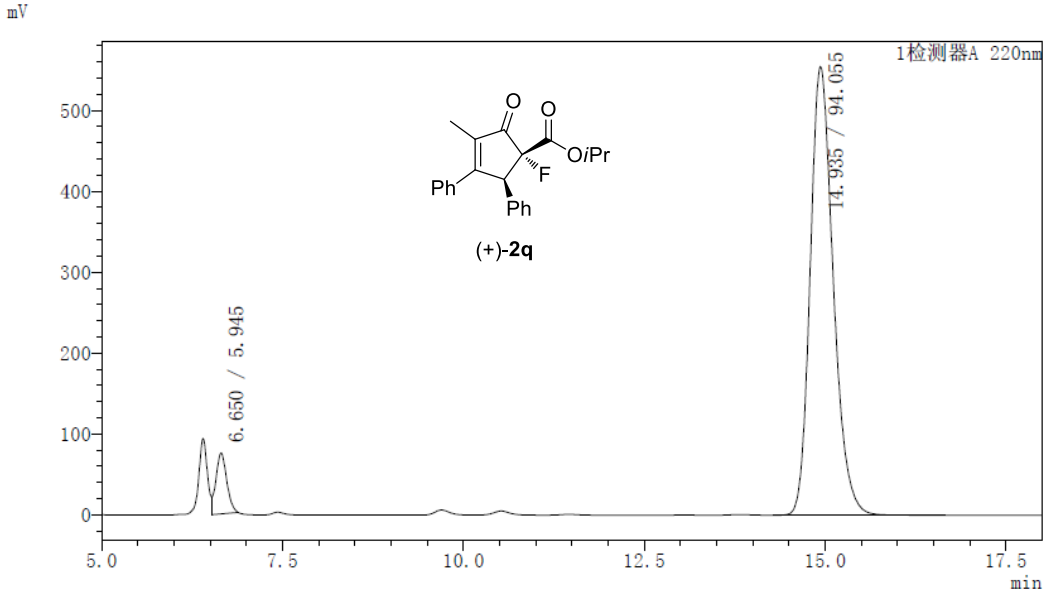
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.704	3828743	383417	M	49.808
2	15.180	3858281	175582		50.192
总计		7687023	558999		100.000

分析日期/时间 : 2018/3/15 11:06:06
处理日期/时间 : 2018/3/15 11:25:41
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



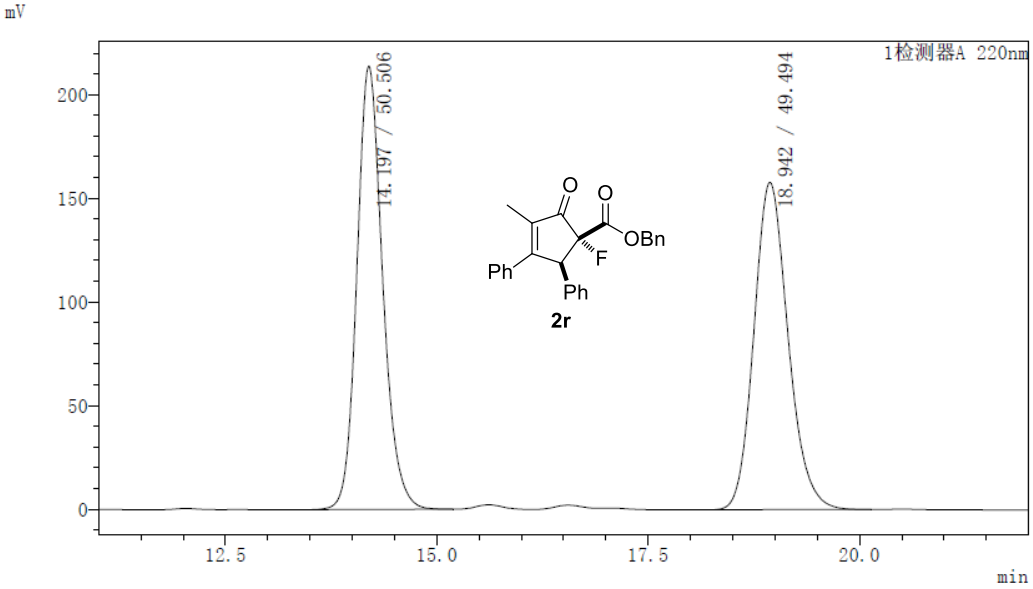
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.650	776814	75272	M	5.945
2	14.935	12289688	554398		94.055
总计		13066502	629670		100.000

分析日期/时间 : 2018/3/15 10:16:39
处理日期/时间 : 2018/3/15 10:39:52
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



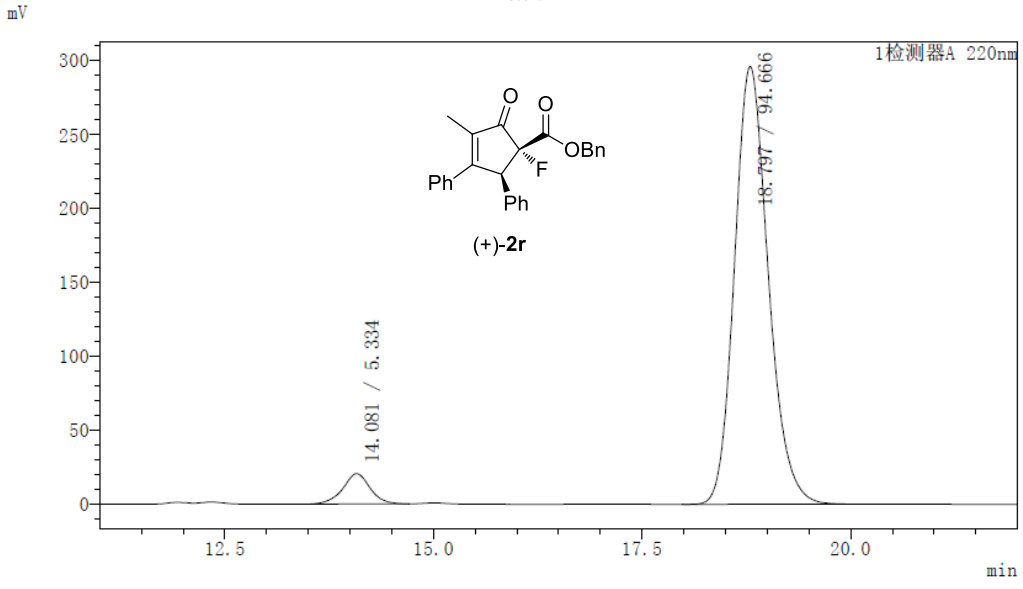
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	14.197	4536619	213978		50.506
2	18.942	4445667	158024		49.494
总计		8982286	372002		100.000

分析日期/时间 : 2018/3/15 10:41:06
处理日期/时间 : 2018/3/15 11:04:18
描述 : AD-H, n-Hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



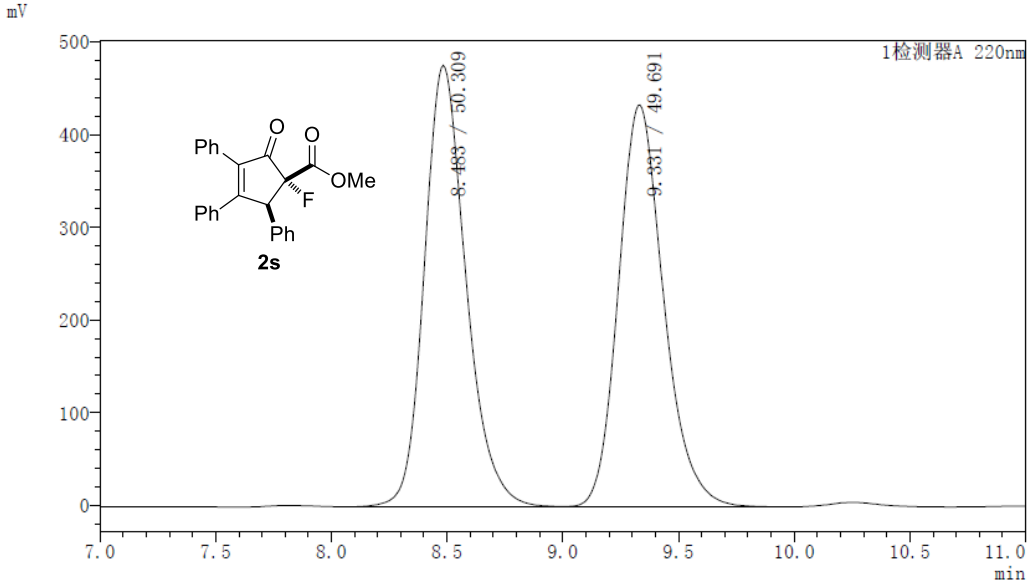
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	14.081	469556	20530		5.334
2	18.797	8334072	296306		94.666
总计		8803629	316836		100.000

分析日期/时间 : 2018/3/30 14:48:48
处理日期/时间 : 2018/3/30 15:01:09
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



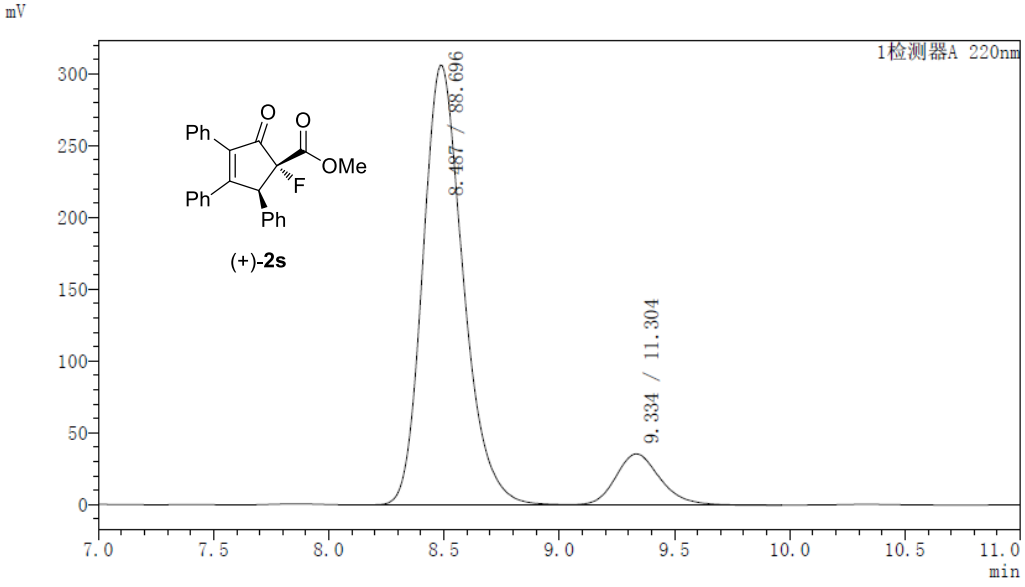
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.483	5957004	476169		50.309
2	9.331	5883742	433517	V	49.691
总计		11840746	909686		100.000

分析日期/时间 : 2018/3/30 15:15:28
处理日期/时间 : 2018/3/30 15:26:46
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



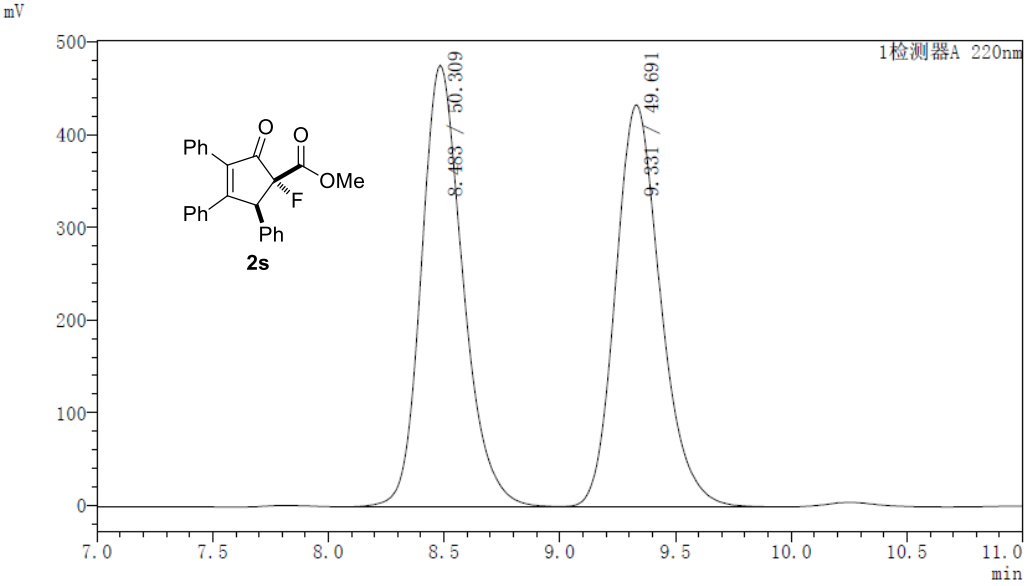
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.487	3733684	306321		88.696
2	9.334	475826	35557	V	11.304
总计		4209510	341877		100.000

分析日期/时间 : 2018/3/30 14:48:48
处理日期/时间 : 2018/3/30 15:01:09
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



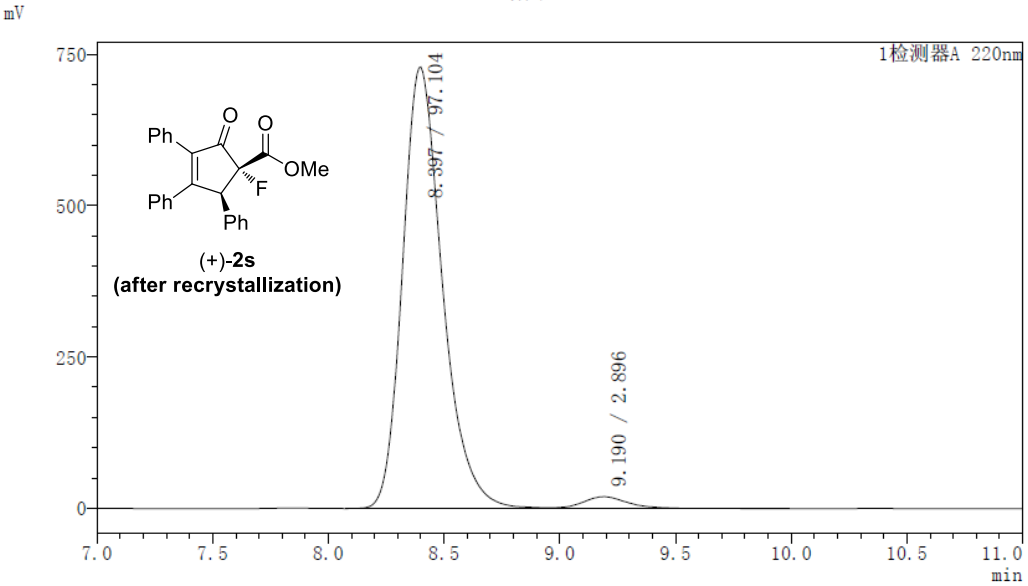
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.483	5957004	476169		50.309
2	9.331	5883742	433517	V	49.691
总计		11840746	909686		100.000

分析日期/时间 : 2018/5/2 11:28:35
处理日期/时间 : 2018/5/2 11:43:28
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



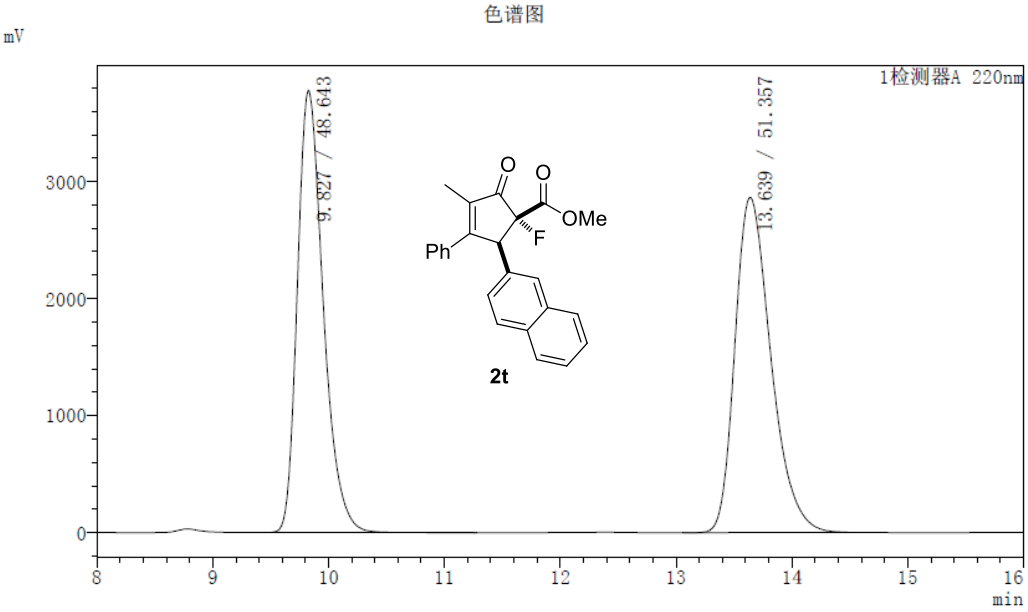
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.397	8729514	728713		97.104
2	9.190	260320	19451	V	2.896
总计		8989834	748164		100.000

分析日期/时间 : 2018/3/7 20:04:28
处理日期/时间 : 2018/3/7 20:20:58
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



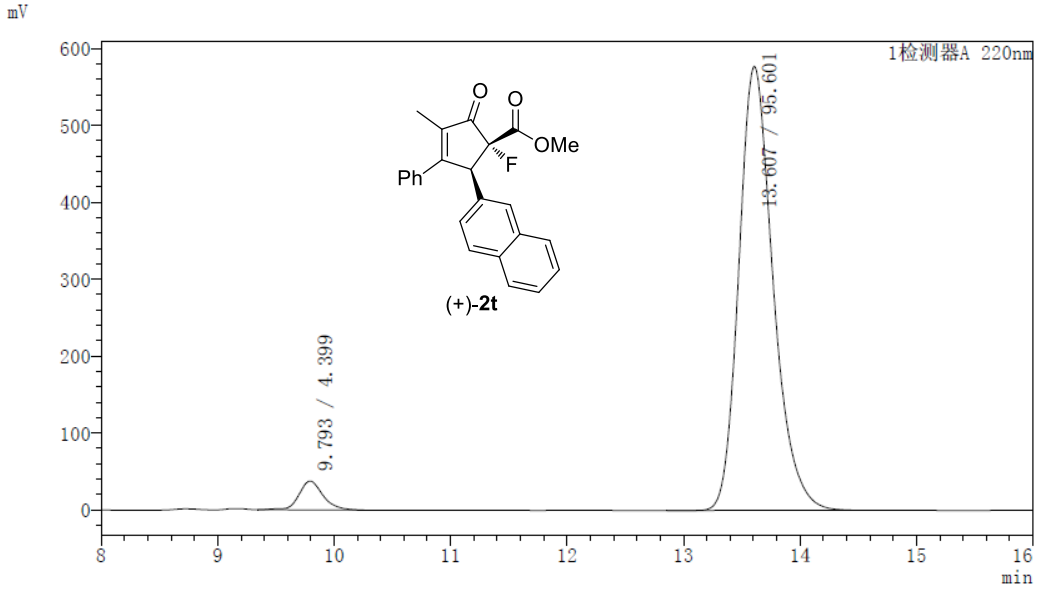
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.827	58630148	3779158	M	48.643
2	13.639	61902426	2865874	M	51.357
总计		120532574	6645032		100.000

分析日期/时间 : 2018/3/7 20:22:05
处理日期/时间 : 2018/3/7 20:39:24
描述 : AD-H, n-Hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



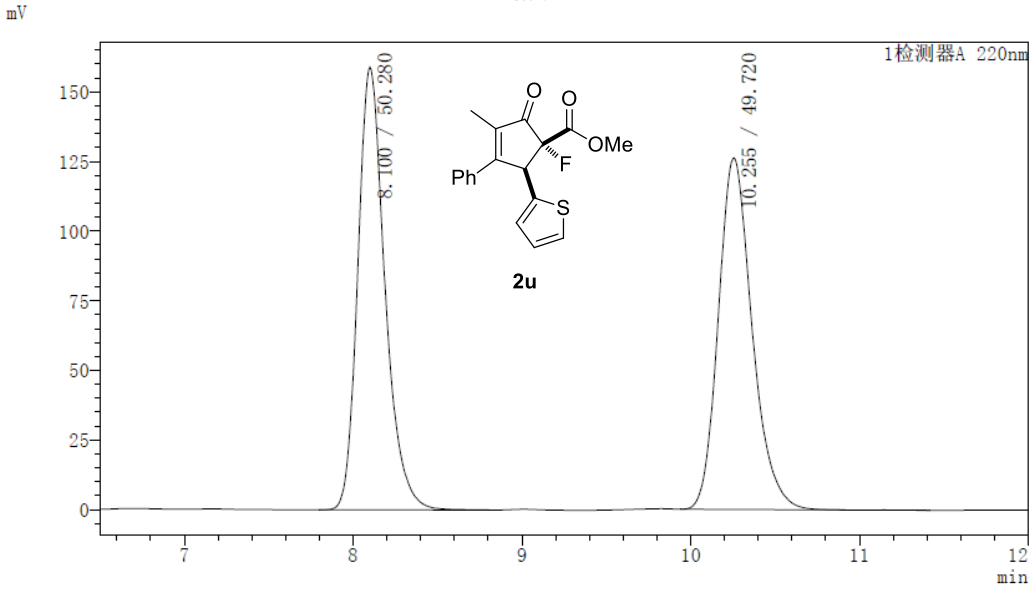
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.793	543055	37674		4.399
2	13.607	11800640	577558		95.601
总计		12343695	615232		100.000

分析日期/时间 : 2018/3/21 14:19:21
处理日期/时间 : 2018/3/21 14:32:09
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



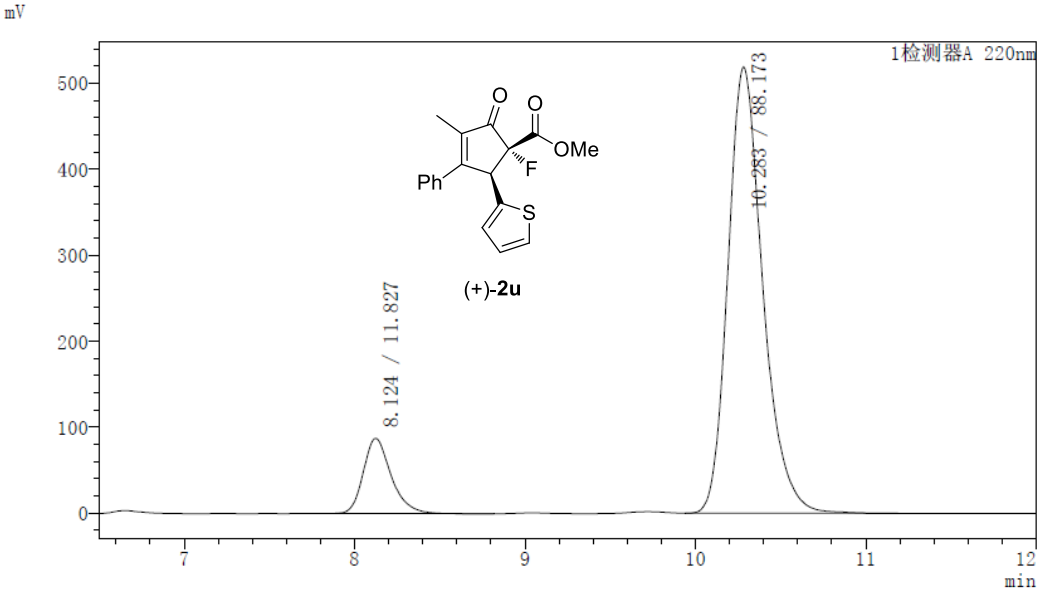
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.100	1775400	159010		50.280
2	10.255	1755619	126244	S	49.720
总计		3531019	285254		100.000

分析日期/时间 : 2018/3/21 14:33:37
处理日期/时间 : 2018/3/21 14:46:20
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



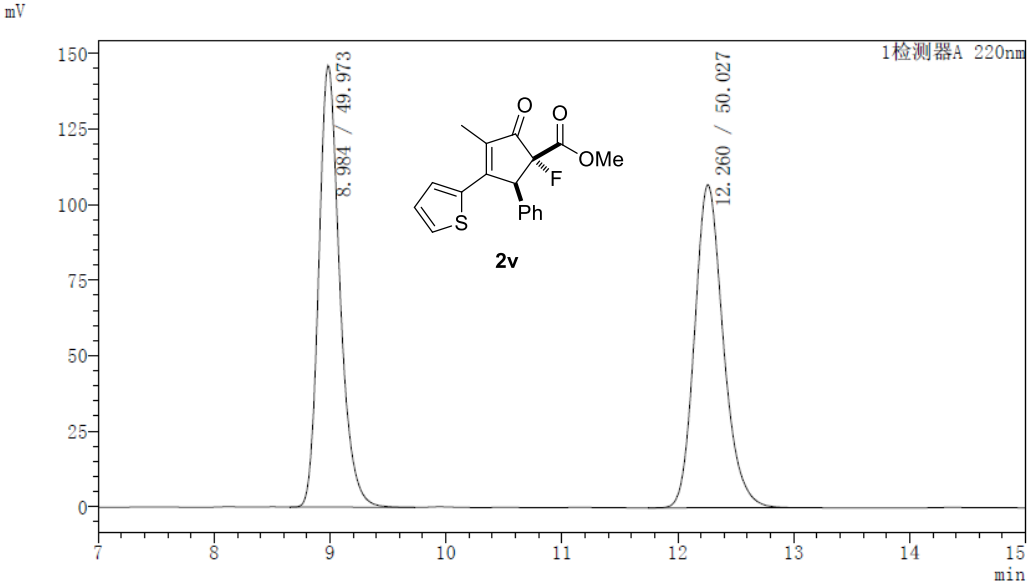
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.124	991507	87295		11.827
2	10.283	7391877	519200		88.173
总计		8383384	606495		100.000

分析日期/时间 : 2018/3/31 9:40:56
处理日期/时间 : 2018/3/31 9:56:09
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



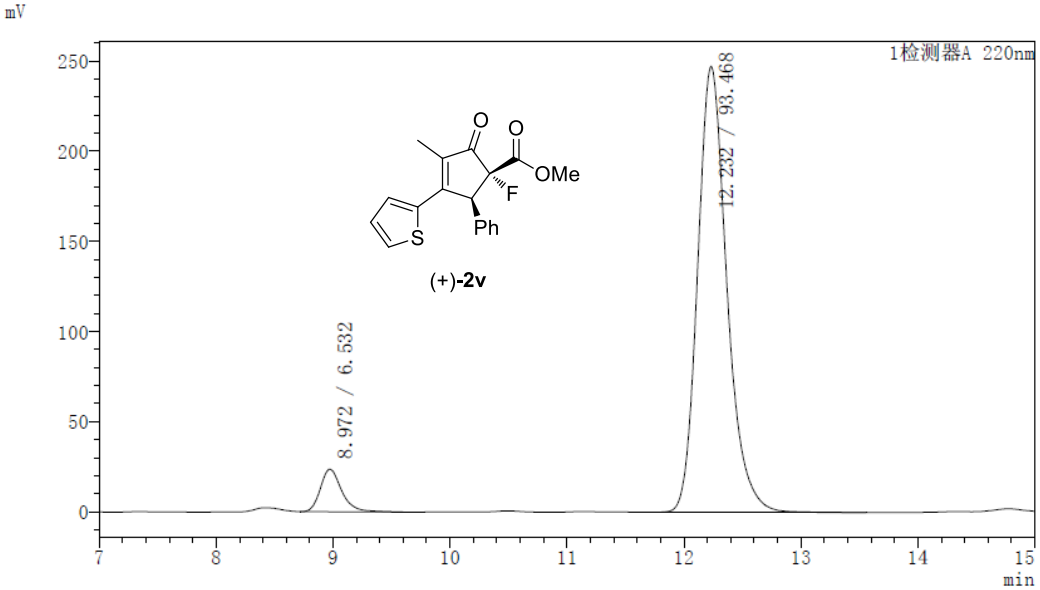
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.984	1838295	146218		49.973
2	12.260	1840280	106931		50.027
总计		3678575	253149		100.000

分析日期/时间 : 2018/3/31 9:58:09
处理日期/时间 : 2018/3/31 10:13:31
描述 : AD-H, n-hexane/iPrOH = 85/15, 1.0 mL/min, 220 nm

色谱图



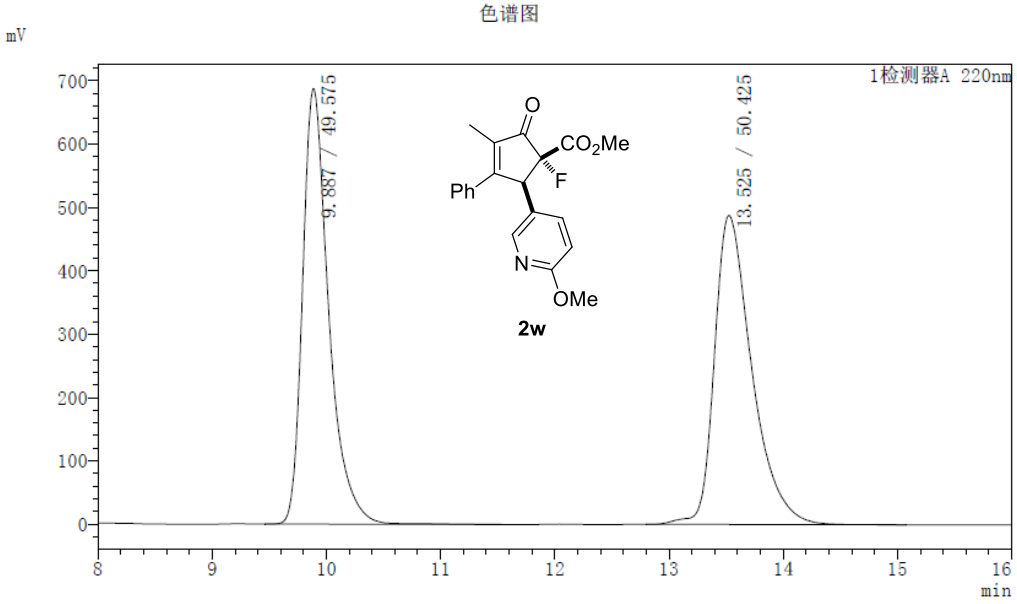
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.972	299899	23655		6.532
2	12.232	4291422	247241		93.468
总计		4591320	270896		100.000

分析日期/时间 : 2018/3/30 18:00:21
处理日期/时间 : 2018/3/30 18:17:21
描述 : AD-H, n-hexane/iPrOH = 80/20, 1.0 mL/min, 220 nm

色谱图



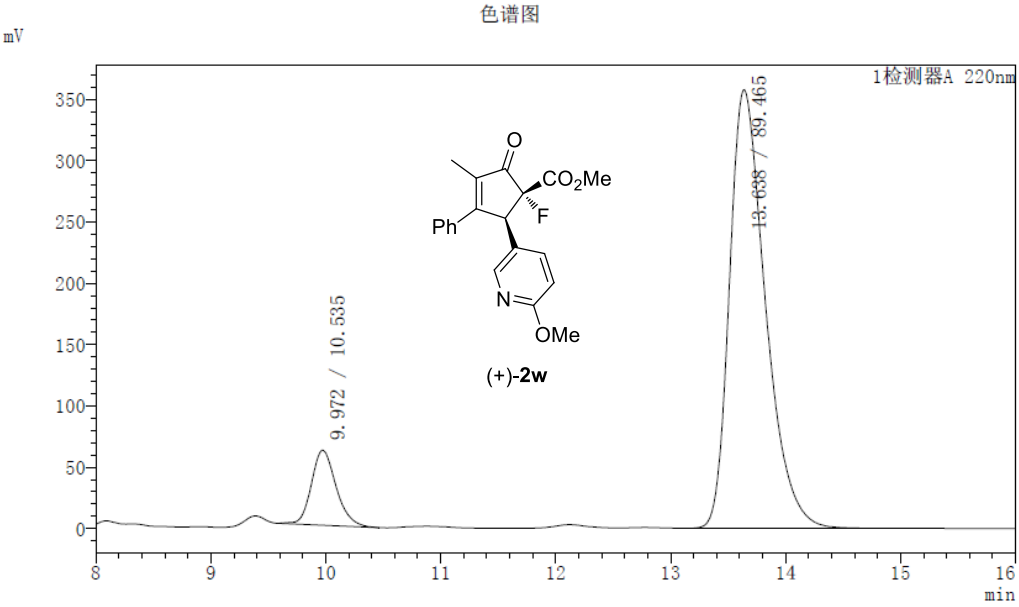
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.887	10914442	687148	S	49.575
2	13.525	11101391	487809		50.425
总计		22015834	1174957		100.000

分析日期/时间 : 2018/3/30 18:18:53
处理日期/时间 : 2018/3/30 18:35:43
描述 : AD-H, n-hexane/iPrOH = 80/20, 1.0 mL/min, 220 nm

色谱图



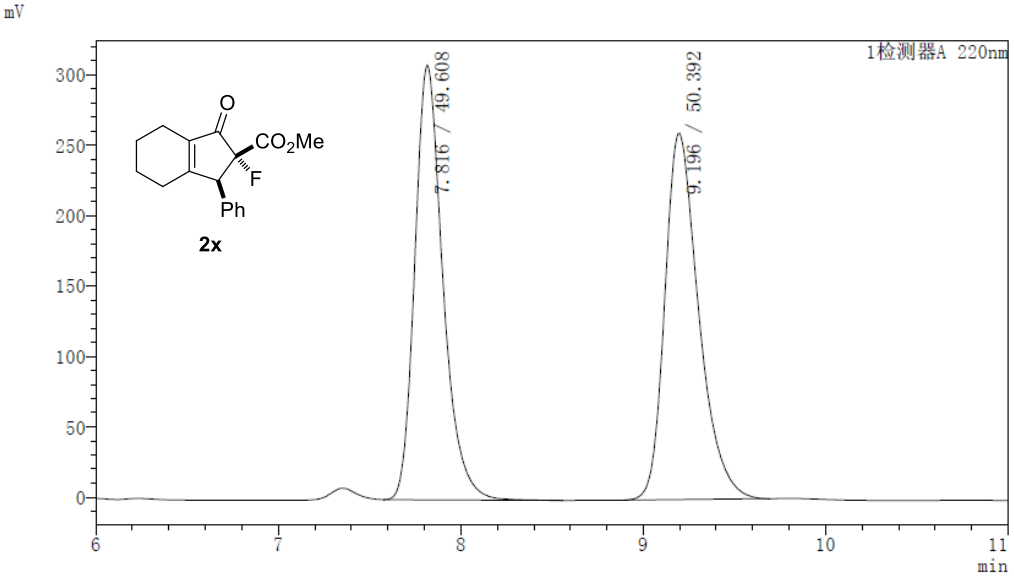
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.972	913607	61163		10.535
2	13.638	7758500	357548		89.465
总计		8672107	418712		100.000

分析日期/时间 : 2018/4/13 14:38:45
处理日期/时间 : 2018/4/13 14:51:00
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



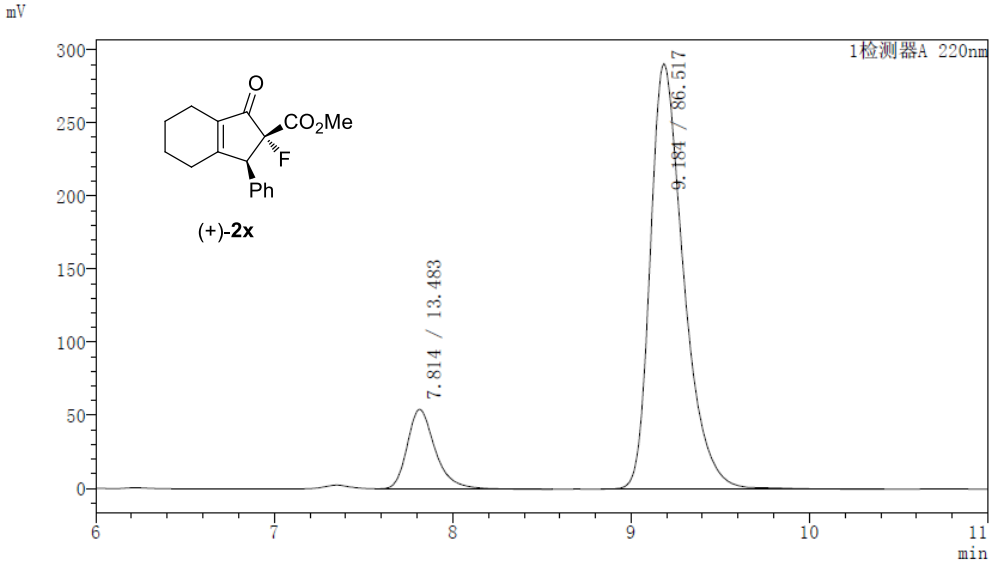
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.816	3306521	308781		49.608
2	9.196	3358826	260133		50.392
总计		6665347	568914		100.000

分析日期/时间 : 2018/4/13 14:52:17
处理日期/时间 : 2018/4/13 15:04:35
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



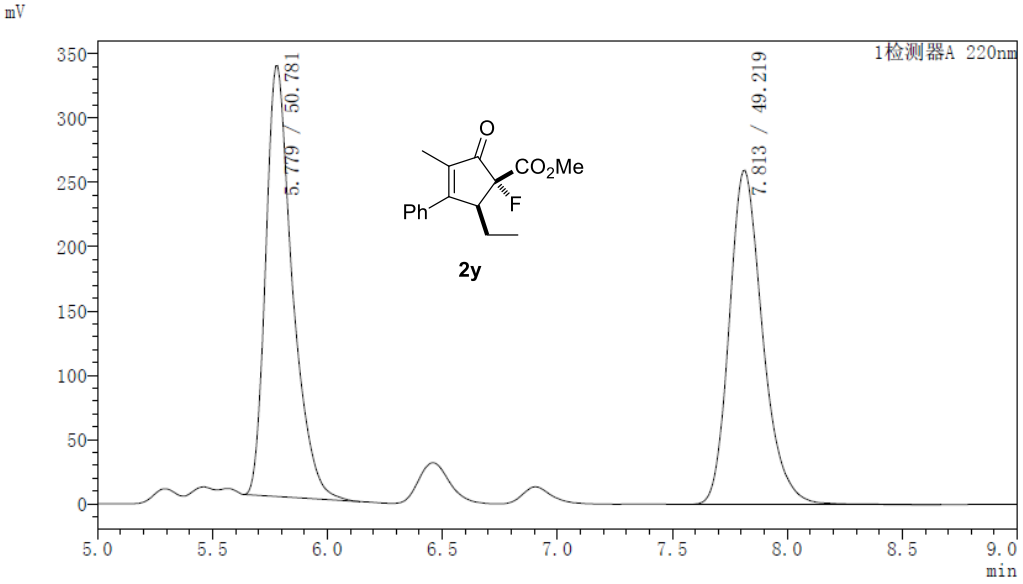
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.814	589311	54426		13.483
2	9.184	3781378	291048	V	86.517
总计		4370689	345474		100.000

分析日期/时间 : 2018/4/10 16:18:02
处理日期/时间 : 2018/4/10 16:28:18
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



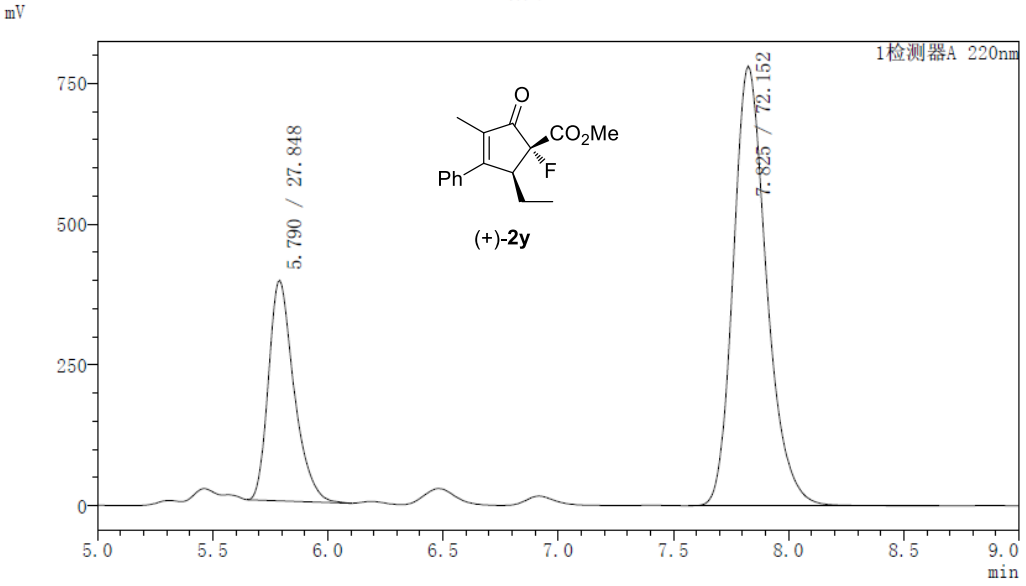
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.779	2708664	334797		50.781
2	7.813	2625390	259704		49.219
总计		5334054	594502		100.000

分析日期/时间 : 2018/4/10 16:29:28
处理日期/时间 : 2018/4/10 16:39:59
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



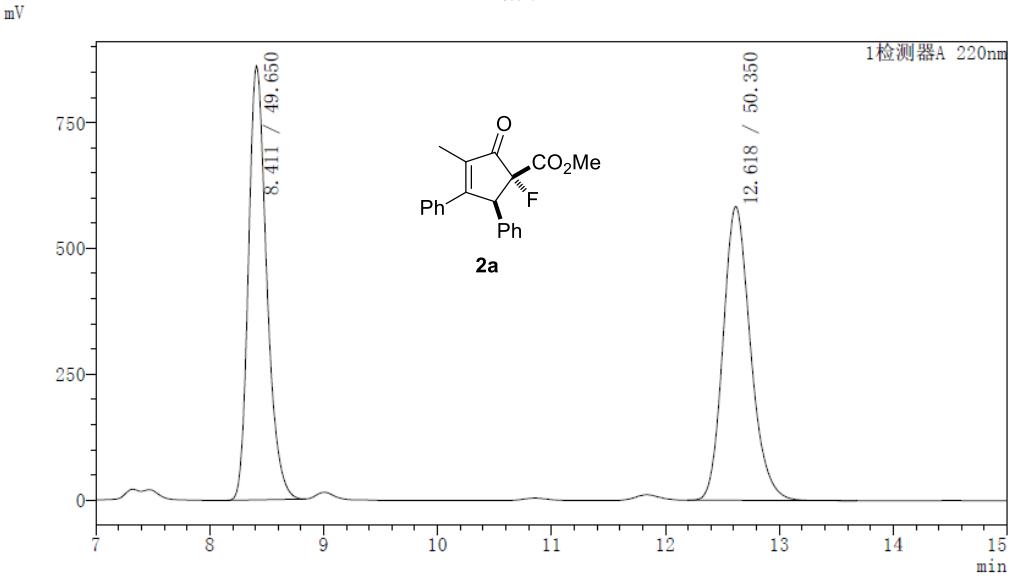
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.790	3024066	391675		27.848
2	7.825	7835086	780820		72.152
总计		10859153	1172495		100.000

分析日期/时间 : 2018/4/10 15:32:41
处理日期/时间 : 2018/4/10 15:48:00
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



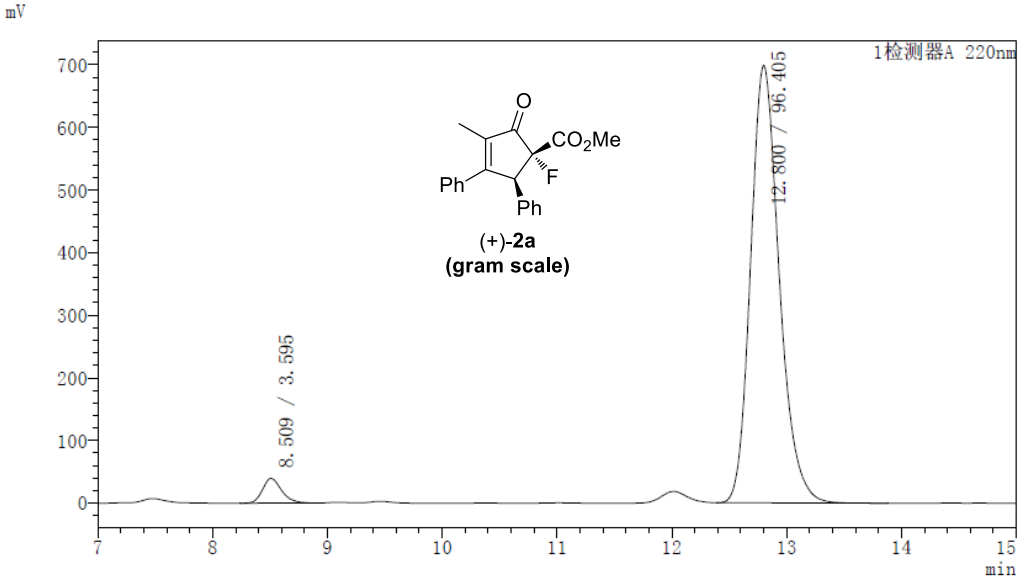
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.411	9624400	861528		49.650
2	12.618	9759899	583762		50.350
总计		19384299	1445289		100.000

分析日期/时间 : 2018/4/3 18:30:23
处理日期/时间 : 2018/4/3 18:45:50
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



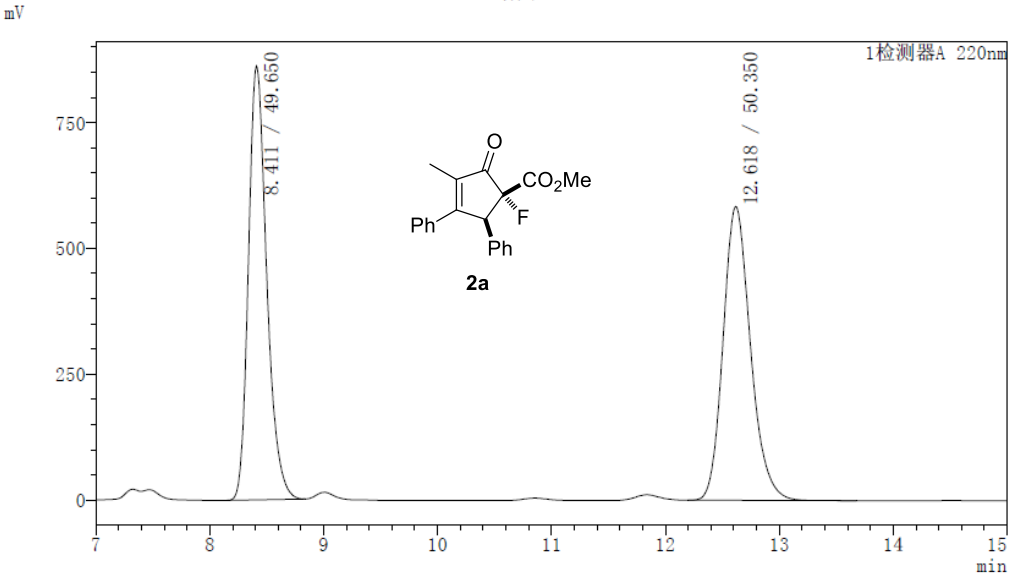
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.509	451489	39415		3.595
2	12.800	12106992	698662		96.405
总计		12558481	738077		100.000

分析日期/时间 : 2018/4/10 15:32:41
处理日期/时间 : 2018/4/10 15:48:00
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



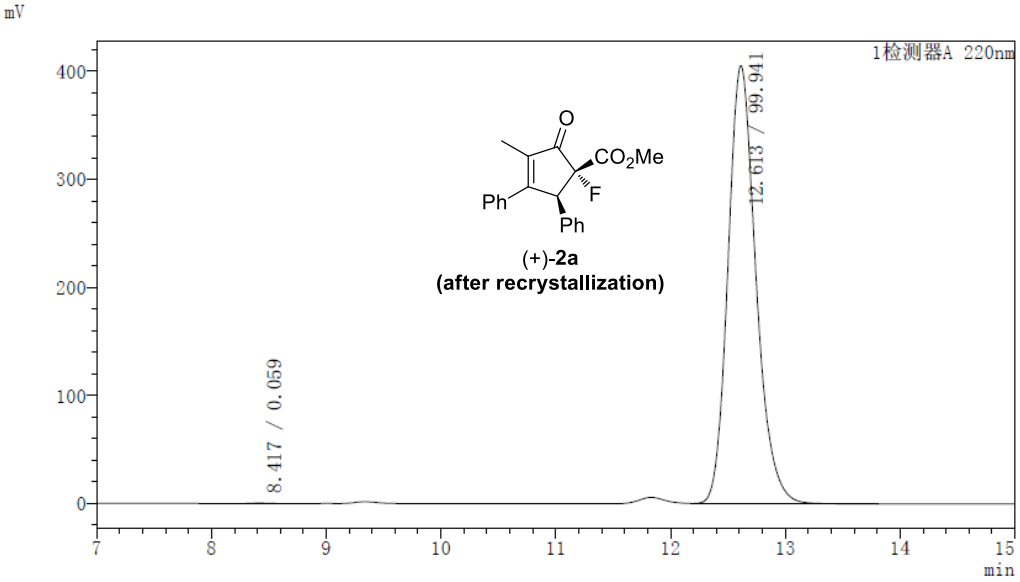
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.411	9624400	861528		49.650
2	12.618	9759899	583762		50.350
总计		19384299	1445289		100.000

分析日期/时间 : 2018/4/10 15:49:57
处理日期/时间 : 2018/4/10 16:05:28
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



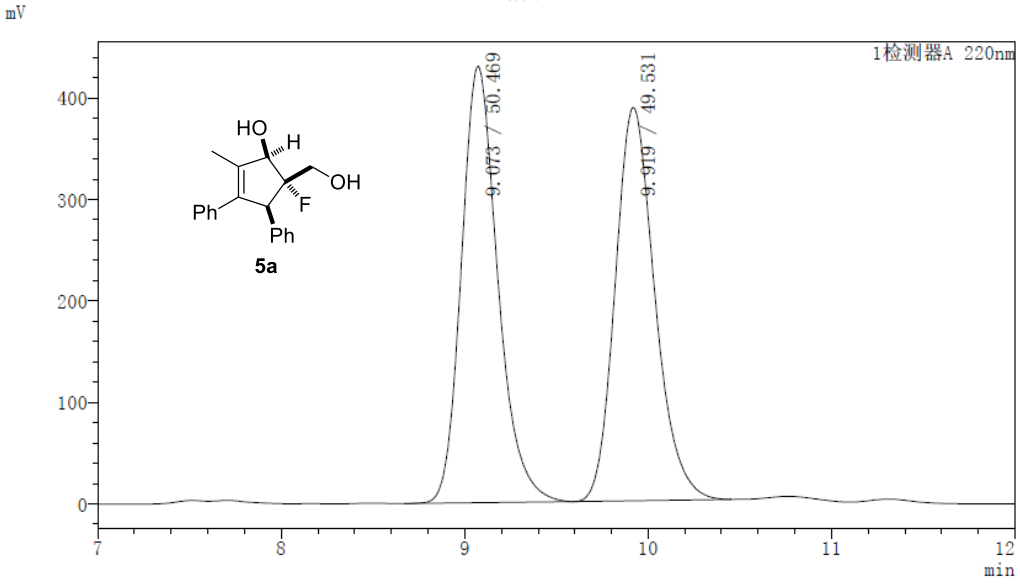
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.417	4022	370		0.059
2	12.613	6858801	405564		99.941
总计		6862823	405934		100.000

分析日期/时间 : 2018/4/17 20:35:24
处理日期/时间 : 2018/4/17 20:48:26
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



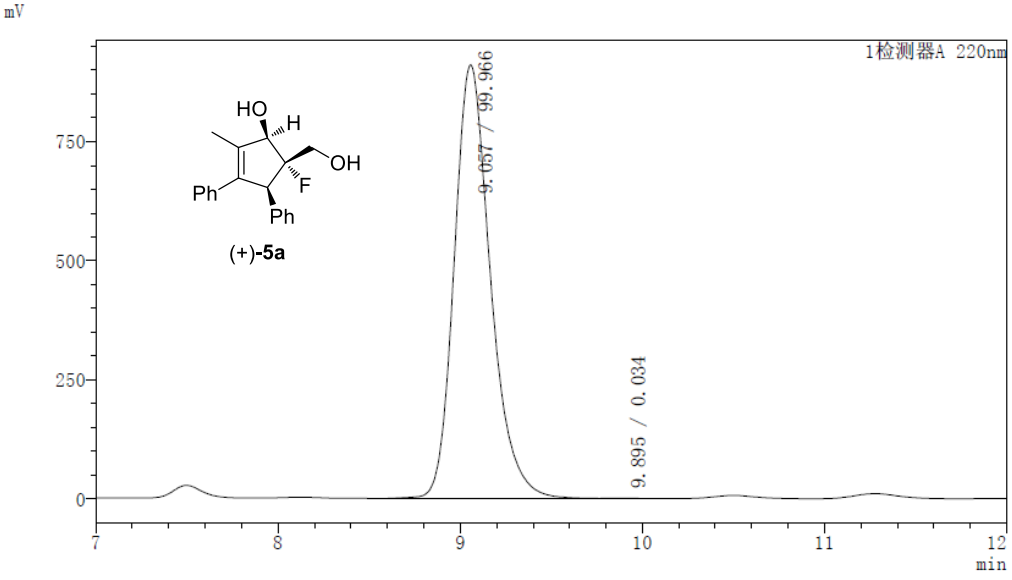
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.073	5932074	430025		50.469
2	9.919	5821871	387694		49.531
总计		11753945	817719		100.000

分析日期/时间 : 2018/4/17 20:49:58
处理日期/时间 : 2018/4/17 21:02:20
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



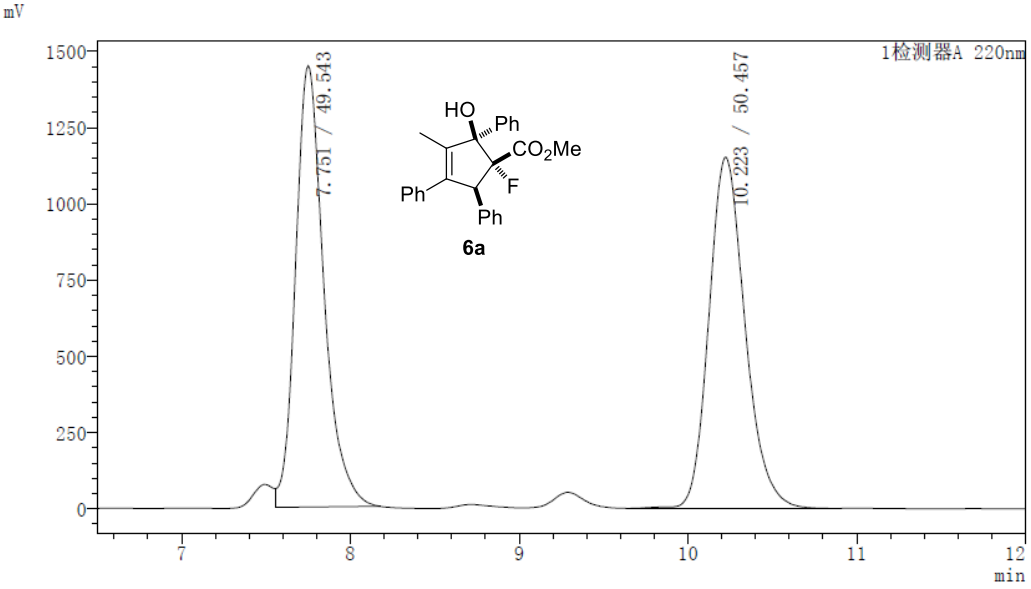
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.057	12610173	911331	S M	99.966
2	9.895	4297	414	T	0.034
总计		12614470	911745		100.000

分析日期/时间 : 2018/4/21 19:59:08
处理日期/时间 : 2018/4/21 20:12:03
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



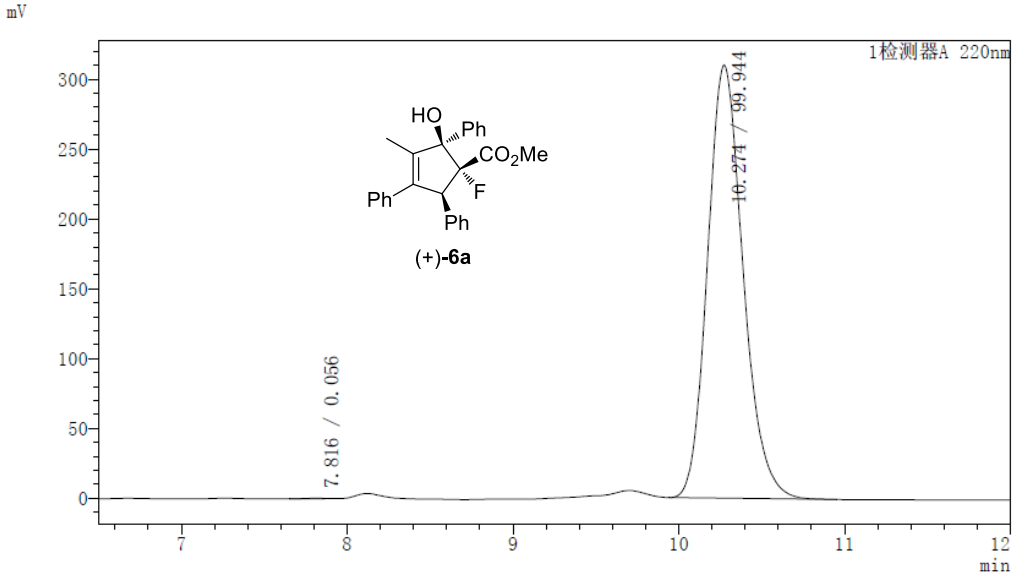
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.751	16844674	1447668	M	49.543
2	10.223	17155581	1152094		50.457
总计		34000255	2599762		100.000

分析日期/时间 : 2018/4/30 13:42:54
处理日期/时间 : 2018/4/30 13:55:21
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



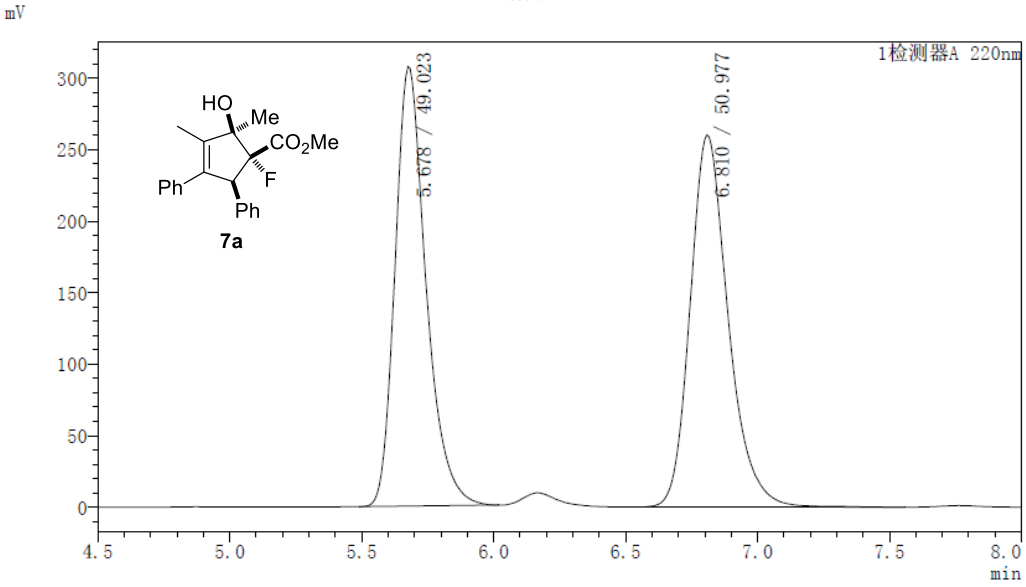
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.816	2592	310		0.056
2	10.274	4623649	310298		99.944
总计		4626242	310608		100.000

分析日期/时间 : 2018/4/26 12:27:11
处理日期/时间 : 2018/4/26 12:37:42
描述 : AD-H, n-hexane/iPrOH = 90/10,1.0 mL/min, 220 nm

色谱图



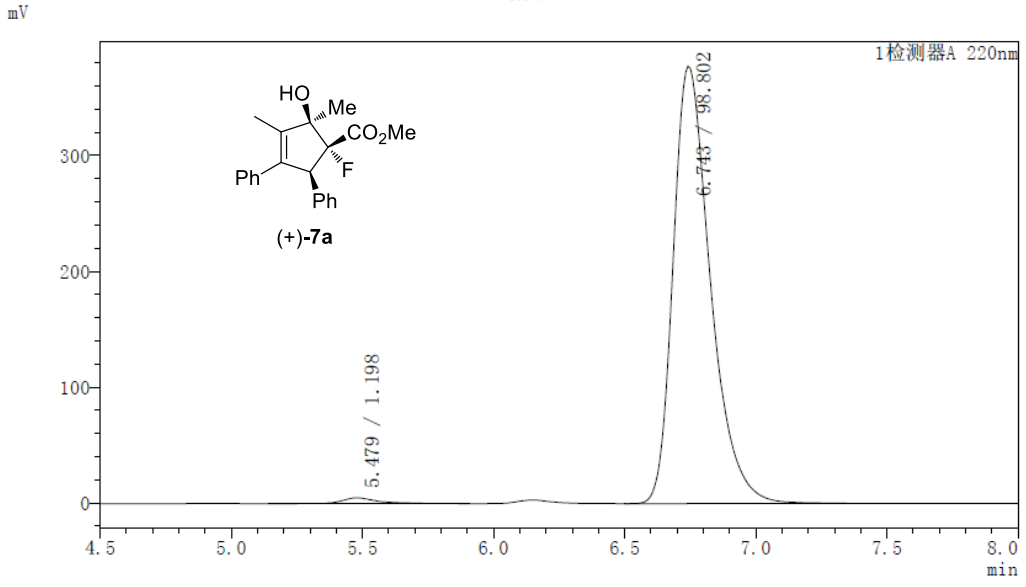
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.678	2510120	307387		49.023
2	6.810	2610206	260408		50.977
总计		5120326	567796		100.000

分析日期/时间 : 2018/4/30 13:56:24
处理日期/时间 : 2018/4/30 14:06:19
描述 : AD-H, n-hexane/iPrOH = 90/10,1.0 mL/min, 220 nm

色谱图



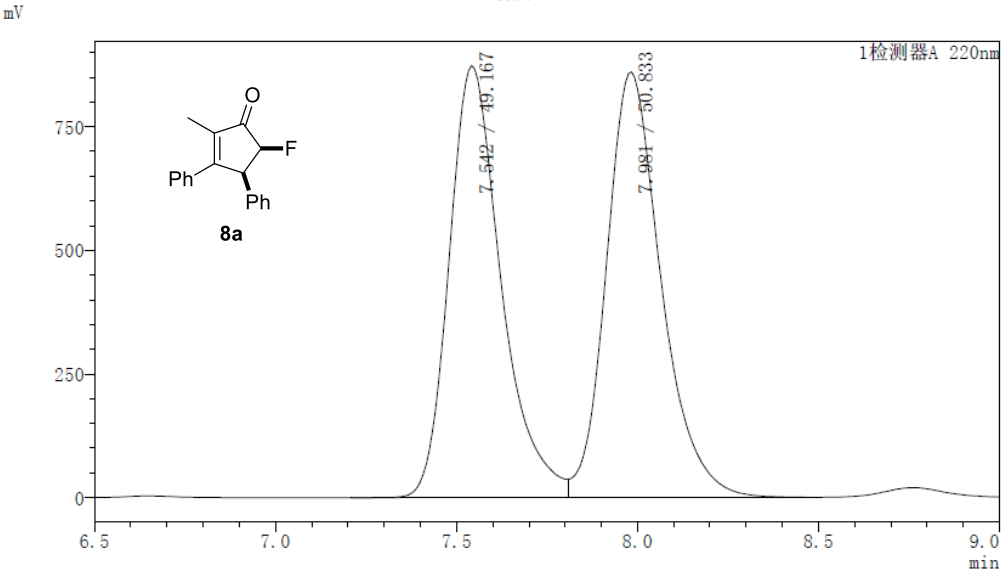
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.479	45216	4841		1.198
2	6.743	3729750	377583		98.802
总计		3774966	382424		100.000

分析日期/时间 : 2018/4/30 14:29:38
处理日期/时间 : 2018/4/30 14:40:28
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



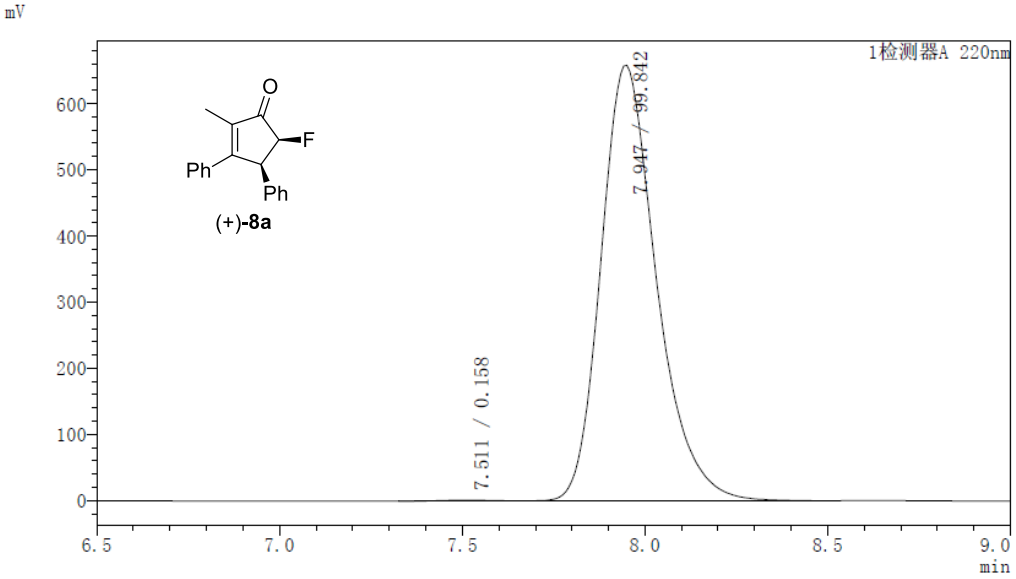
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.542	8731754	873573		49.167
2	7.981	9027559	860263	V	50.833
总计		17759314	1733835		100.000

分析日期/时间 : 2018/4/30 14:41:43
处理日期/时间 : 2018/4/30 14:53:07
描述 : AD-H, n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm

色谱图



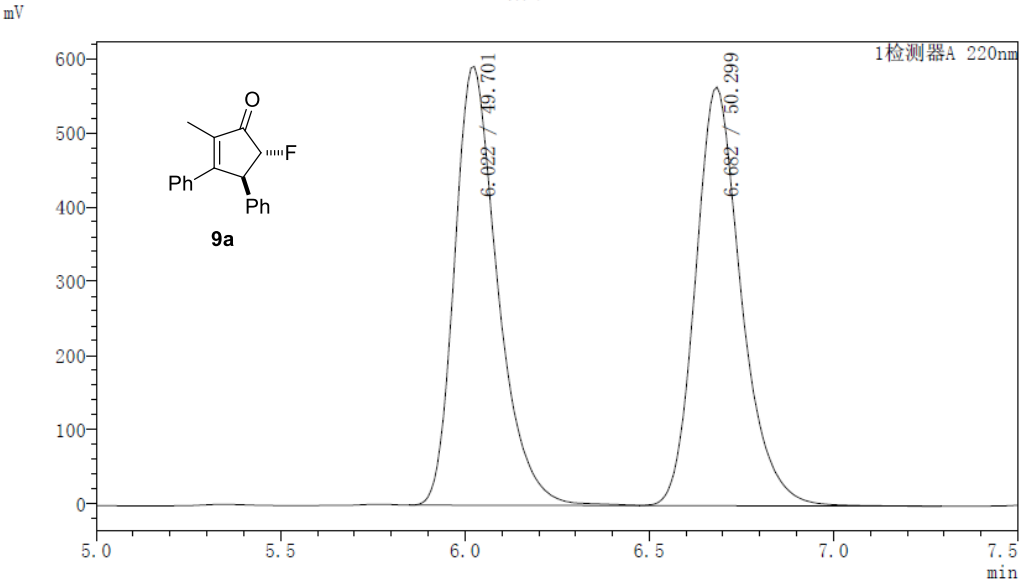
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.511	10991	1164		0.158
2	7.947	6948057	658155	V	99.842
总计		6959048	659319		100.000

分析日期/时间 : 2018/4/30 14:10:11
处理日期/时间 : 2018/4/30 14:18:51
描述 : AD-H, n-hexane/iPrOH = 90/10,1.0 mL/min, 220 nm

色谱图



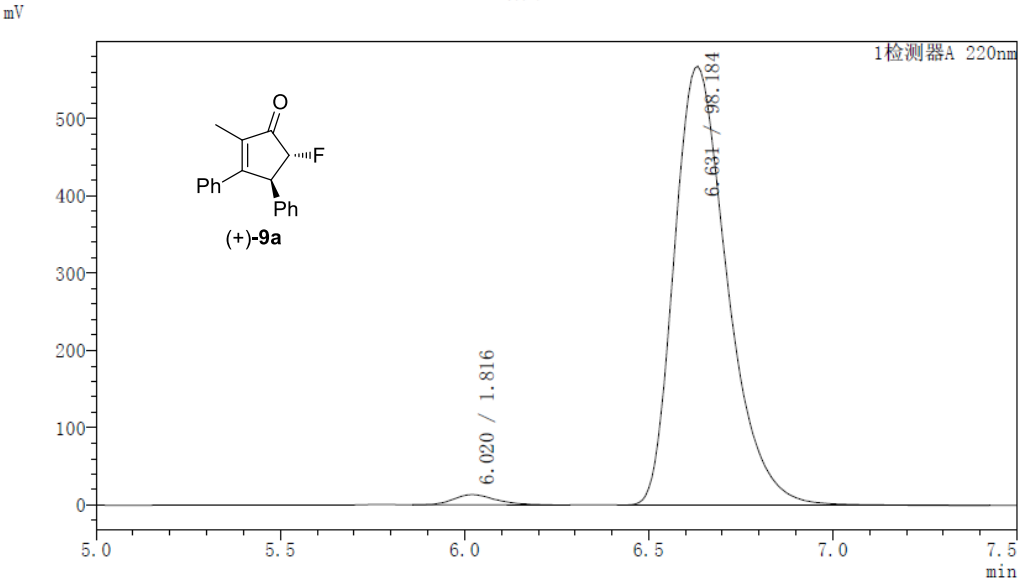
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.022	4823905	591846		49.701
2	6.682	4882037	564645	V	50.299
总计		9705942	1156490		100.000

分析日期/时间 : 2018/4/30 14:19:53
处理日期/时间 : 2018/4/30 14:28:32
描述 : AD-H, n-hexane/iPrOH = 90/10,1.0 mL/min, 220 nm

色谱图



峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.020	105072	13229		1.816
2	6.631	5679303	567667		98.184
总计		5784375	580895		100.000