Supporting Information

For

Copper-Catalyzed Regioselective Reaction of Internal Alkynes and Diaryliodonium Salts

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1. General details

All reactions were performed under an atmosphere of dry nitrogen or oxygen, and the workup was carried out in air, unless otherwise noted. Toluene, dichloromethane (CH_2Cl_2) and 1,2-dichloroethane (DCE) were dried and distilled from calcium hydride. Ether (Et_2O) and tetrahydrofuran (THF) were dried and distilled from metal sodium and benzophenone. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. ^{1}H NMR spectra were recorded on Bruker AM-300 or Mercury 300 (300 MHz) spectrometers with TMS as the internal standard. ^{19}F NMR spectra were recorded on Bruker AM-300 or Mercury 300 (282 MHz) spectrometers with $CFCl_3$ as the external standard. ^{13}C NMR spectra were recorded on DPX-400 (101 MHz) or Agilent-400 (101 MHz) spectrometer. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz). IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra were taken on a HP5989A spectrometer. HRMS data were obtained on a high-resolution mass spectrometer.

2. Preparation of diaryliodonium salts

Iododium salts were synthesized according to ref (a) procedures and analytical data can be found in ref (a)-(e)

(a) Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* **2007**, *349*, 2610.

(b) Phipps, R. J.; Gaunt, M. J. *Science* **2009**, *323*, 1593.

(c) Bigot, A.; Williamson, A. E.; Gaunt, M. J.; *J. Am. Chem. Soc.* **2011**, *133*, 13778.
(d) Allen, A.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2011**, *133*, 4260.
(e) Bedford, R. B.; Webster, R. L.; Mitchell, C. J. *Org. Biomol. Chem.*, **2009**, *7*, 4853.

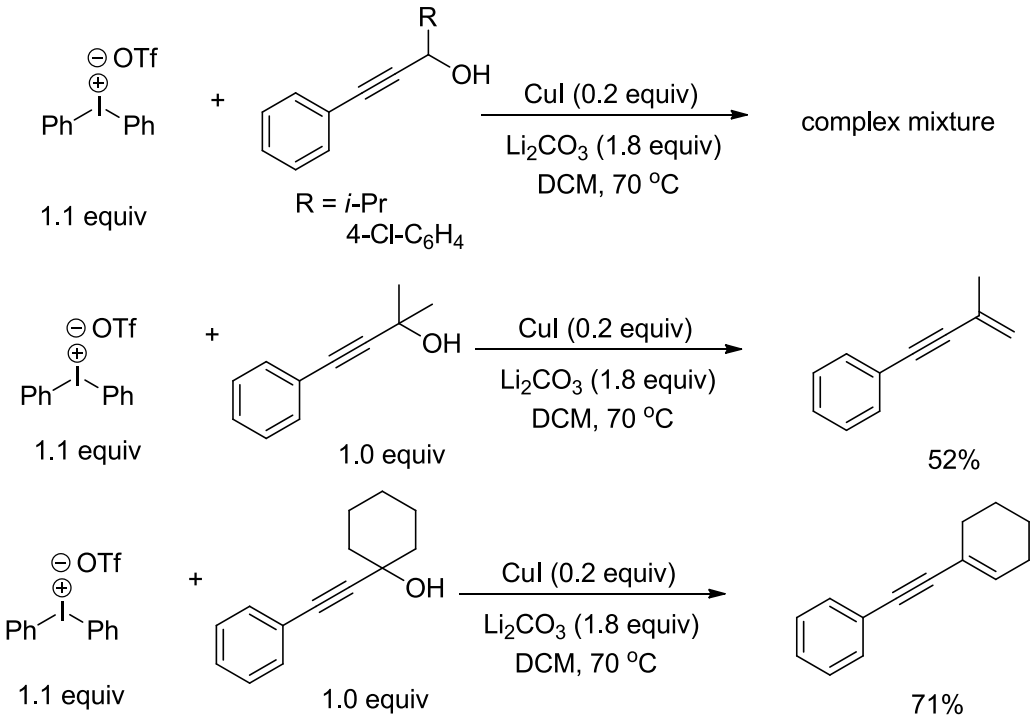
3. Cu-catalyzed synthesis of α-arylketones from propargylic alcohols with diaryliodonium salts

General procedure:

To a reactor charged with iodonium salt (0.25 mmol, 1.1 equiv), CuI (46.5 μmol, 0.20 equiv), Li_2CO_3 (0.41 mmol, 1.8 equiv) under N_2 atmosphere, dichloromethane (5.0 mL) and yn-ol (0.23 mmol, 1.0 equiv) were added. The mixture was heated for the specified time before NH_4Cl (saturated aqueous) was introduced to quench the reaction, and the aqueous phases were then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over sodium sulphate after washing with brine (10 mL×3). The solvent was evaporated in vacuo and the crude residue was purified by flash column chromatography (PE: EA = 5:1) to yield the product.

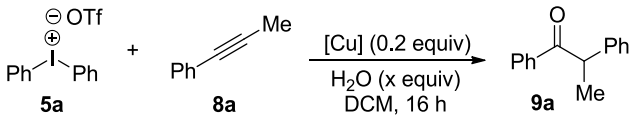
Results of the secondary and tertiary yn-ols:

When R = ^{i}Pr, 4-Cl-C_6H_4, complex mixtures were obtained even after purification by flash column chromatography and preparative TLC. For alcohols with two alkyl substituents at the *α*-carbon, ene-yne was the major product.



4. Cu-catalyzed synthesis of α-arylketones from alkynes with diaryliodonium salts

Table S1 Optimization of Reaction Conditions



entry	ratio	[Cu](equiv)	X	temp(°C)	yield(%)[a]	note
1[b]	1:1	CuI	-	70	2	N_2
2	1:1	CuI	-	70	70	N_2
3	1:1	CuI	1.0	70	15	N_2
4	1:1	CuCl	-	70	12	N_2
5	1:1	CuBr	-	70	16	N_2
6	1:1	CuCN	-	70	10	N_2
7	1:1	$CuCl_2$	-	70	22	N_2
8	1:1	$Cu(OTf)_2$	-	70	14	N_2
9	1:1	$Cu(OAc)_2$	-	70	45	N_2
10	1:1	$Cu(OAc)_2$	-	60	12	N_2
11	1:1	$Cu(OAc)_2$	-	80	50	N_2
12	1:1	$Cu(OAc)_2$	-	80	77	O_2
13	1:1	$Cu(OAc)_2$	-	80	42	air
14	1:1	$Cu(OAc)_2$ (0.1)	-	80	75	O_2
15	1:1	$Cu(OAc)_2$ (0.05)	-	80	74	O_2
16	1:1	$Cu(OAc)_2$ (0. 01)	-	80	36	O_2
17	1:1	$Cu(OAc)_2$ (0.05)	1.0	80	84	O_2
18	**1.5:1**	**$Cu(OAc)_2$ (0.05)**	**1.0**	**80**	**91**	**O_2**
19	1:2	$Cu(OAc)_2$ (0.05)	1.0	80	68	O_2
20	2:1	$Cu(OAc)_2$ (0.05)	1.0	80	56	O_2

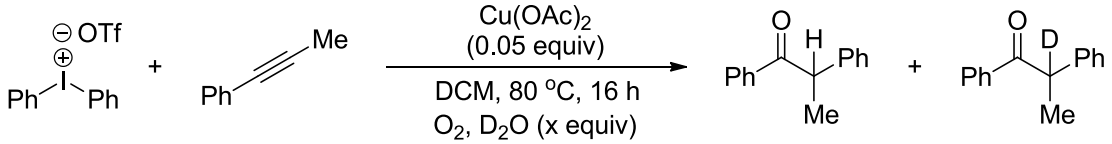
[a] Determined by ^{1}H NMR with MesH as internal standard. [b] Li_2CO_3 (1.8 equiv) was used.

General procedure:

To a reactor charged with iodonium salt (0.35 mmol, 1.5 equiv), $Cu(OAc)_2$ (11.6 μmol, 0.05 equiv) under N_2 atmosphere, dichloromethane (5.0 mL), alkyne (0.23 mmol, 1.0 equiv) and H_2O (0.23 mmol, 1.0 equiv) were added. O_2 was bubbled and the reaction mixture was heated for the specified time, then $NaHCO_3$ (saturated aq.) was introduced to quench the reaction. The aqueous phases were then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over sodium sulphate and evaporated in vacuo after washing with brine (10 mL×3). The crude product was obtained by flash column chromatography (PE: EA = 50:1) and then purified by preparative TLC to yield the product.

5. Mechanism studies

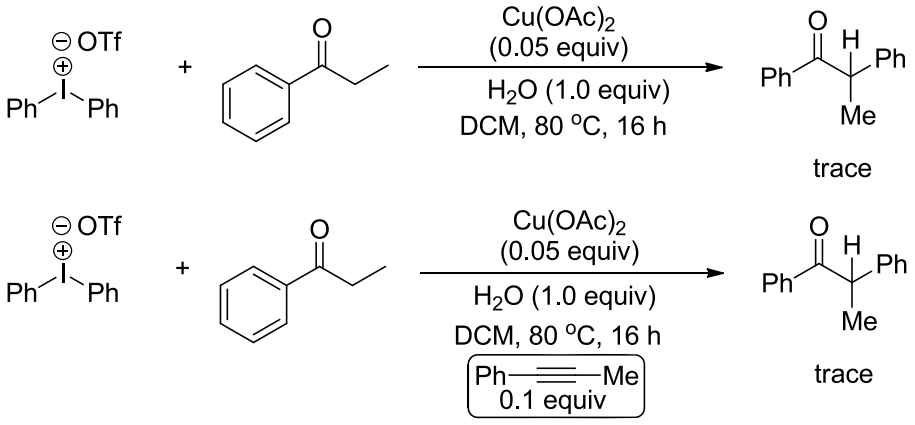
1) Source of the proton: H_2O



X = 1.0	81%	47%	53%
5.0	75%	30%	70%
10.0	56%	11%	89%

Deuterated experiment showed that when D_2O rather than H_2O was added in the reaction, the deuterated product was obtained and the percentage of the deuterated product increased along with the amount of D_2O, indicating that the source of proton in the product was H_2O.

2) Exclusion of the propiophenone intermediate:

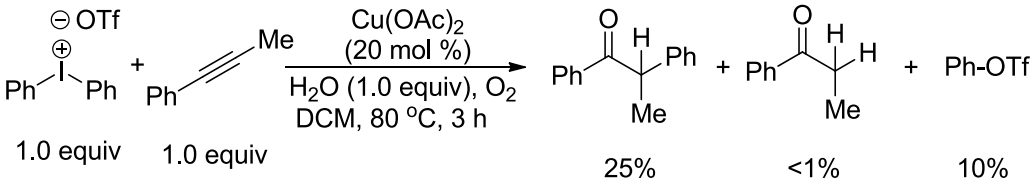


Controlling experiment indicated that the by-product of the reaction, propiophenone, was not arylated under the reaction conditions, indicating that it was not the real intermediate.

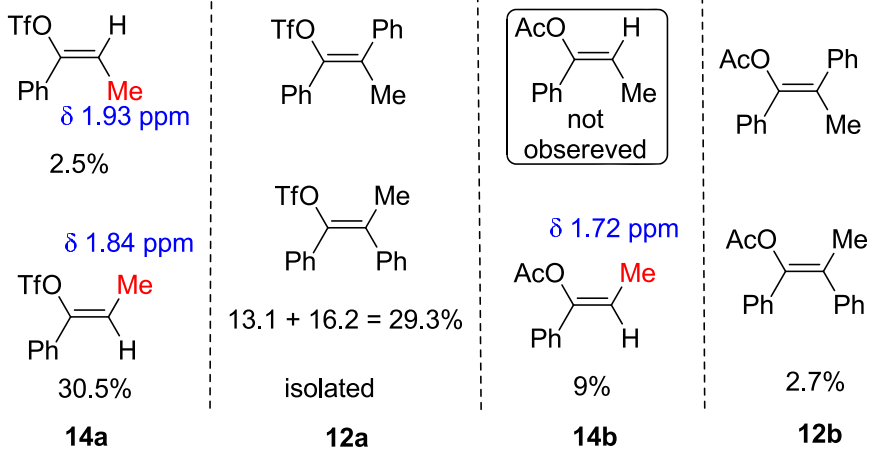
3) The real intermediates:

When the reaction was quenched at the beginning, four groups of intermediates (**12**, **14**) were observed by ^{1}H NMR[1] and GC-MS except for the desired product **9a**, by-product propiophenone**10** and PhOTf. Fortunately, one group (**12a**, L = OTf) was isolated, and all these intermediates disappeared when the reaction was completed.

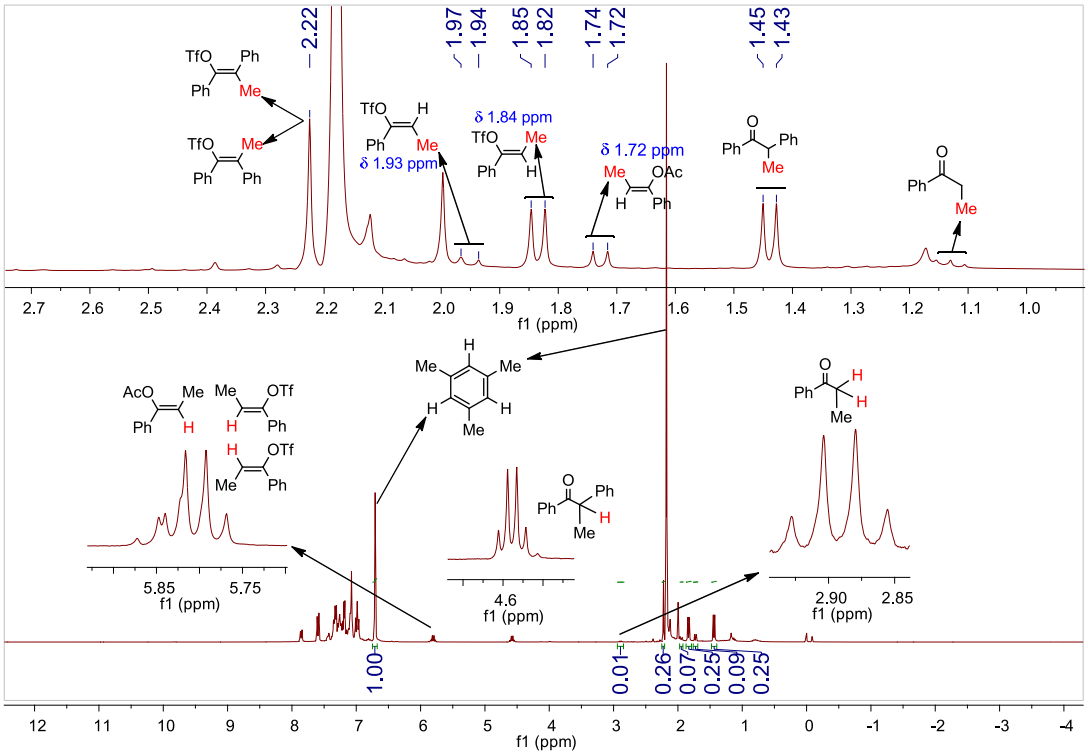
[1] a) Luan, L.; Song, J.; Bullock, R. M. *J. Org. Chem.*, **1995**, 60, 7170. b) Eames, J.; Coumbarides, G. S.; Suggate, M. J.; Weerasooriya, N. *Eur. J. Org. Chem.* **2003**, 634.

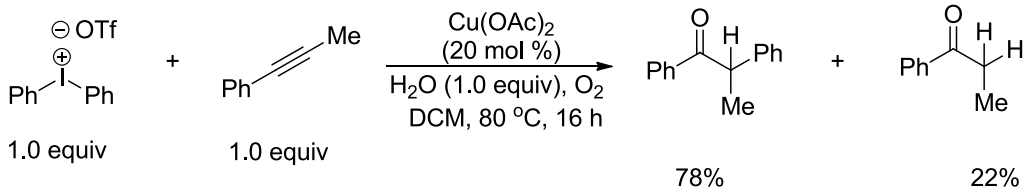


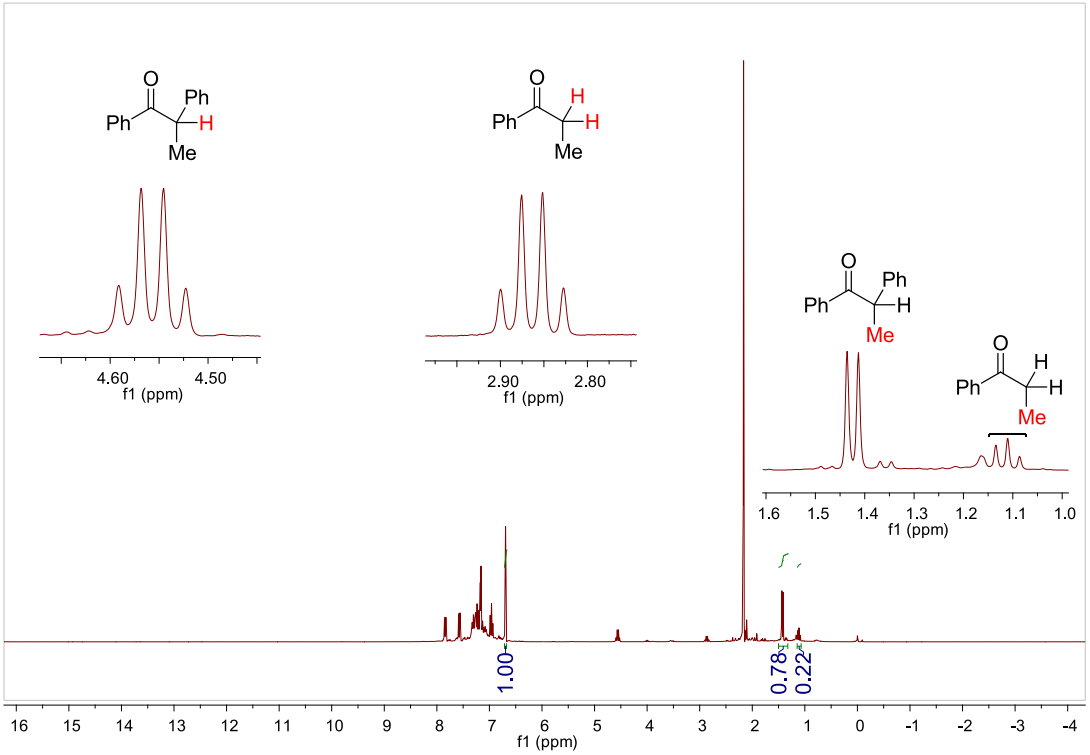
observed in ^{1}H NMR; GC-MS | ^{1}H NMR | GC-MS



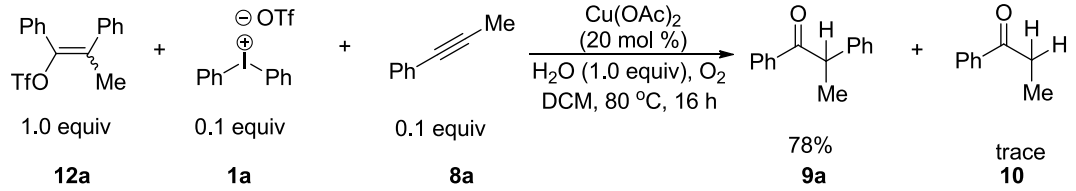
δ in reference







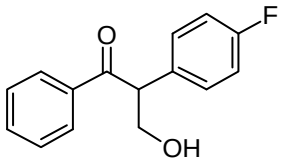
4) Transformation of intermediates:



The isolated inintermediate **12a** can be transferred into the desired final product **9a** in about 70% yield under the standard reaction conditions with 0.1 equiv **1a** and **8a** in the mixture to trigger the reaction.

6. Characterization data for the new products

2-(4-fluorophenyl)-3-hydroxy-1-phenylpropan-1-one 6b

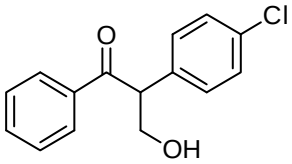


Yellow oil, yield: 72%

FT-IR (film) ν 3398, 3066, 2928, 2880, 1676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28-7.20 (m, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.78 (dd, *J* = 8.3, 4.8 Hz, 1H), 4.24 (dd, *J* = 11.3, 8.3 Hz, 1H), 3.87 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.43 (b, 1H)

ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.49 (m, 1F) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.82, 162.15 (d, *J* = 246.7 Hz), 136.04, 133.38, 131.91 (d, *J* = 3.1 Hz), 129.99 (d, *J* = 8.1 Hz), 128.83, 128.59, 116.14 (d, *J* = 21.5 Hz, 9H), 65.03, 55.34 ppm; EI-MS (TOF) (*m/z*) 226 $[M-H_2O]^+$, 105, 77; HRMS (EI) Calcd for $C_{15}H_{11}FO$ $[M-H_2O]^+$ 226.0794, found 224.0797.

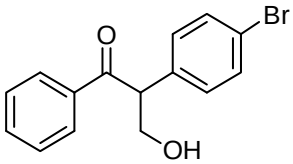
2-(4-chlorophenyl)-3-hydroxy-1-phenylpropan-1-one 6c



Yellow oil, yield: 83%

FT-IR (film) ν 3408, 2925, 1784 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.46, 7.14 (AB, *J* = 8.4 Hz, 4H), 4.75 (dd, *J* = 8.1, 4.8 Hz, 1H), 4.23 (dd, *J* = 11.3, 8.1 Hz, 1H), 3.87 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.48 (b, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.52, 135.95, 135.17, 133.47, 132.32, 130.08, 128.82, 128.64, 121.72, 64.86, 55.55 ppm; EI-MS (TOF) (*m/z*) 242 $[M-H_2O]^+$, 105, 77; HRMS (EI) Calcd for $C_{15}H_{15}ClO$ $[M-H_2O]^+$ 242.0498, found 242.0500.

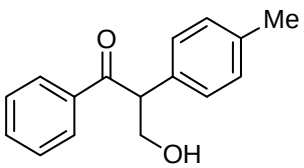
2-(4-bromophenyl)-3-hydroxy-1-phenylpropan-1-one 6d



Yellow oil, yield: 73%

FT-IR (film) ν 3419, 3063, 2927, 2879, 2853, 1680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H),7.28, 7.18 (AB, *J* = 8.5 Hz, 4H), 4.77 (dd, *J* = 8.2, 4.8 Hz, 1H), 4.24 (dd, *J* = 11.3, 8.2 Hz, 1H), 3.87 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.42 (b, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.59, 135.98, 134.65, 133.59, 133.45, 129.74, 129.36, 128.83, 128.63, 64.90, 55.48 ppm; EI-MS (TOF) (*m/z*) 286 $[M-H_2O]^+$, 105, 77; HRMS (EI) Calcd for $C_{15}H_{15}BrO$ $[M-H_2O]^+$ 285.9993, found 285.9992.

2-(4-methylphenyl)-3-hydroxy-1-phenylpropan-1-one 6e

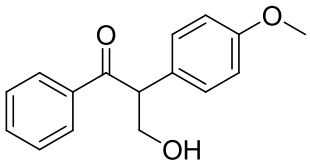


Yellow oil, yield: 83%

FT-IR (film) ν 3400, 3057, 3025, 2923, 2878, 1679 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* =

7.4 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.13 (m, 4H), 4.76 (dd, *J* = 8.4, 4.9 Hz, 1H), 4.26 (dd, *J* = 11.3, 8.4 Hz, 1H), 3.85 (dd, *J* = 11.3, 4.9 Hz, 1H), 2.66 (b, 1H), 2.27 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.07, 137.34, 136.25, 133.19, 133.08, 129.91, 128.90, 128.52, 128.29, 65.12, 56.00, 21.05 ppm; EI-MS (TOF) (*m/z*) 240 $[M]^+$, 222, 181, 105, 77; HRMS (EI) Calcd for $C_{15}H_{16}O_2$ $[M]^+$ 240.1150, found 240.1151.

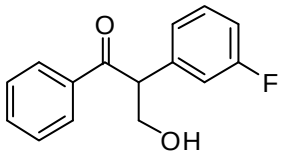
2-(4-methoxyphenyl)-3-hydroxy-1-phenylpropan-1-one 6f



Yellow oil, yield: 83%

FT-IR (film) ν 3478, 3061, 3001, 2931, 2837, 1678, 1511 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.67-7.43 (m, 1H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.18, 6.84 (AB, *J* = 8.0 Hz, 4H), 4.74 (dd, *J* = 7.5, 4.4 Hz, 1H), 4.40- 4.07 (m, 1H), 3.85 (dd, *J* = 11.1, 4.4 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.13, 158.97, 136.21, 133.17, 129.48, 128.86, 128.51, 128.07, 114.62, 65.14, 55.48, 55.20 ppm; EI-MS (TOF) (*m/z*) 238 $[M\text{-}H_2O]^+$, 226, 133, 121, 105, 77; HRMS (EI) Calcd for $C_{16}H_{14}O_2$ $[M\text{-}H_2O]^+$ 238.0994, found 238.0996.

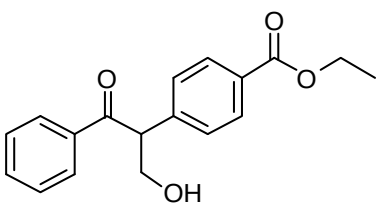
2-(3-fluorophenyl)-3-hydroxy-1-phenylpropan-1-one 6g



Yellow oil, yield: 63%

FT-IR (film) ν 3431, 3137, 2930, 1682, 1400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33-7.22 (m, 1H), 7.11-6.86 (m, 3H), 4.79 (dd, *J* = 8.2, 4.8 Hz, 1H), 4.26 (dd, *J* = 11.3, 8.2 Hz, 1H), 3.89 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.53 (b, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.71 (m, 1F) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.38, 163.06 (d, *J* = 247.3 Hz), 138.50 (d, *J* = 7.3 Hz), 136.03, 133.45, 130.69 (d, *J* = 8.3 Hz), 128.83, 128.63, 124.16 (d, *J* = 2.9 Hz), 115.40 (d, *J* = 21.9 Hz), 114.64 (d, *J* = 21.0 Hz), 64.93, 55.83 (d, *J* = 1.5 Hz) ppm; EI-MS (TOF) (*m/z*) 226 $[M\text{-}H_2O]^+$, 122, 105, 77; HRMS (EI) Calcd for $C_{15}H_{11}FO$ $[M\text{-}H_2O]^+$ 226.0794, found 224.0798.

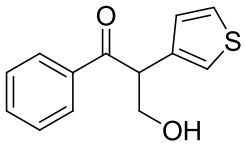
ethyl 4-(3-hydroxy-1-oxo-1-phenylpropan-2-yl)benzoate 6h



Yellow oil, yield: 78%

FT-IR (film) ν 3365, 2975, 2927, 1716, 1682, 1278 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42-7.30 (m, 4H), 4.85 (dd, *J* = 8.1, 4.7 Hz, 1H), 4.39-4.22 (m, 3H), 3.91 (dd, *J* = 11.4, 4.7 Hz, 1H), 2.51 (b, 1H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.40, 166.09, 141.15, 139.54, 133.50, 130.39, 129.83, 128.84, 128.63, 128.44, 64.88, 61.02, 56.24, 14.28 ppm; EI-MS (TOF) (*m/z*) 280 $[M-H_2O]^+$, 105, 77; HRMS (EI) Calcd for $C_{18}H_{16}O_3$ $[M-H_2O]^+$ 280.1099, found 280.1192.

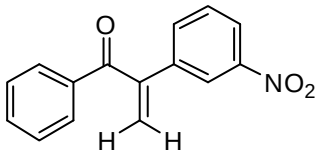
3-hydroxy-1-phenyl-2-(thiophen-3-yl)propan-1-one 6j



Yellow oil, yield: 65%

FT-IR (film) ν 3080, 3431, 3103, 2925, 2903, 1678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03-7.94 (m, 1H), 7.74-7.22 (m, 5H), 7.14-7.03 (m, 1H), 5.18-4.78 (m, 1H), 4.45- 4.11 (m, 1H), 4.11-3.65 (m, 1H), 2.35 (b, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.63, 136.14, 136.00, 133.36, 128.78, 128.59, 127.25, 126.62, 123.03, 64.53, 51.23 ppm; EI-MS (TOF) (*m/z*) 214 $[M-H_2O]^+$, 105, 77; HRMS (EI) Calcd for $C_{13}H_{10}OS$ $[M-H_2O]^+$ 214.0452, found 214.0455.

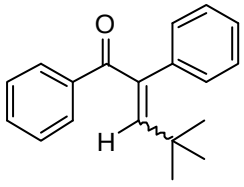
2-(3-nitrophenyl)-1-phenylprop-2-en-1-one 4i



Yellow oil, yield: 46%

FT-IR (film) ν 3429, 3136, 2924, 2852, 1655, 1399 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.20 (d, *J* = 10.1 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.69-7.40 (m, 4H), 6.28 (s, 1H), 5.87 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.27, 148.40, 145.83, 138.67, 136.73, 133.46, 133.44, 129.93, 129.52, 128.60, 125.00, 123.15, 122.26 ppm; EI-MS (TOF) (*m/z*) 253 $[M]^+$, 149, 105, 77; HRMS (EI) Calcd for $C_{15}H_{11}NO_3$ $[M]^+$ 253.0739, found 253.0737.

(E/Z)-4,4-dimethyl-1,2-diphenylpent-2-en-1-one 4k

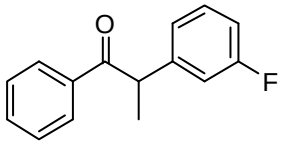


Yellow oil, yield: 48%

FT-IR (film) ν 3080, 3057, 3025, 2962, 2903, 2867, 1684, 1655 cm^{-1}; For the major: ^1H NMR (300 MHz, $CDCl_3$) δ 7.84-7.81 (m, 1H), 7.46-7.41 (m, 2H), 7.34-7.24 (m, 6H), 7.17-7.13 (m, 1H), 6.36 (s,

1H), 0.97 (s, 9H) ppm; For the minor: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84-7.81 (m, 1H), 7.54-7.50 (m, 2H), 7.34-7.24 (m, 6H), 7.17-7.13 (m, 1H), 6.36 (s, 1H) ppm; 1.20 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.40, 197.93, 154.56, 153.30, 141.79, 139.44, 139.08, 138.27, 136.49, 131.95, 129.98, 129.80, 129.46, 129.19, 129.07, 128.64, 128.37, 128.18, 127.98, 127.69, 127.35, 121.58, 44.12, 34.78, 30.64, 26.62; EI-MS (TOF) (*m/z*) 264 $[M]^+$, 249, 207; HRMS (EI) Calcd for $C_{19}H_{20}O$ $[M]^+$ 264.1514, found 264.1512.

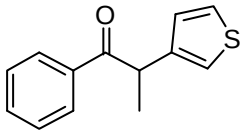
2-(3-fluorophenyl)-1-phenylpropan-1-one 9h



Yellow oil, yield: 69%

FT-IR (film) 2977, 2932, 1683 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.26-7.22 (m, 1H), 7.03 (dd, *J* = 17.6, 8.7 Hz, 2H), 6.89 (t, *J* = 8.7 Hz, 1H), 4.69 (q, *J* = 6.9 Hz, 1H), 1.53 (d, *J* = 6.9 Hz, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.32 (m, 1F) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.72, 163.05 (d, *J* = 246.3 Hz), 143.79 (d, *J* = 7.2 Hz), 136.24, 132.96, 130.37 (d, *J* = 8.3 Hz), 128.68, 128.55, 123.44 (d, *J* = 2.9 Hz), 114.72 (d, *J* = 21.7 Hz), 113.86 (d, *J* = 21.0 Hz), 47.40, 19.33 ppm; EI-MS (TOF) (*m/z*) 228 $[M]^+$, 249,105, 77; HRMS (EI) Calcd for $C_{15}H_{23}FO$ $[M]^+$ 228.0950, found 228.0952.

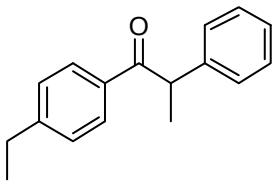
1-phenyl-2-(thiophen-3-yl)propan-1-one 9j



Yellow oil, yield: 48%

FT-IR (film) 3102, 3063, 2975, 2931, 2872, 1684 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.26-7.24 (m, 1H), 7.09 (s, 1H), 7.02 (d, *J* = 4.5 Hz, 1H), 4.84 (q, *J* = 6.9 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.10, 141.39, 136.39, 132.86, 128.63, 128.51, 127.07, 126.02, 121.39, 42.85, 18.87 ppm; EI-MS (TOF) (*m/z*) 216 $[M]^+$, 111,105, 77; HRMS (EI) Calcd for $C_{13}H_{12}OS$ $[M]^+$ 216.0609, found 216.0604.

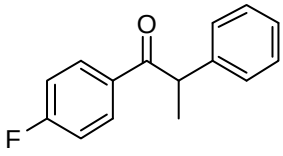
1-(4-ethylphenyl)-2-phenylpropan-1-one 9k



Yellow oil, yield: 42%

FT-IR (film) 3060, 3028, 2968, 2931, 2872, 1679, 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.29-7.26 (m, 4H), 7.21-7.19 (m, 3H), 4.67 (q, *J* = 6.8 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.52 (d, *J* = 6.8 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.89, 149.64, 141.68, 134.15, 128.96, 128.88, 127.95, 127.72, 126.76 , 47.70, 28.83, 19.49, 15.03 ppm; EI-MS (TOF) (*m/z*) 238 $[M]^+$, 223, 209, 133, 105; HRMS (EI) Calcd for $C_{17}H_{18}O$ $[M]^+$ 238.1358, found 238.1356.

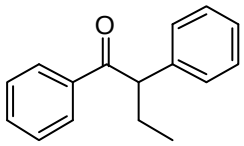
1-(4-fluorophenyl)-2-phenylpropan-1-one 9l



Yellow oil, yield: 61%

FT-IR (film) 3064, 3028, 2977, 2931, 1683, 1598, 1226 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.11-7.82 (m, 2H), 7.42 -7.13 (m, 5H), 7.14- 6.90 (m, 2H), 4.63 (q, *J* = 6.3 Hz, 1H), 1.53 (d, *J* = 6.3 Hz, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.58 (m, 1F) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.64, 165.40 (d, *J* = 254.5 Hz), 141.32, 132.80, 131.35 (d, *J* = 9.3 Hz), 129.03, 127.63, 126.96, 115.52 (d, *J* = 21.8 Hz), 47.97, 19.44 ppm; EI-MS (TOF) (*m/z*) 228 $[M]^+$, 123, 105, 95, 77; HRMS (EI) Calcd for $C_{15}H_{13}FO$ $[M]^+$ 228.0950, found 228.0953.

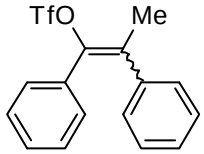
1,2-diphenylbutan-1-one 9m



Yellow oil, yield: 45%

FT-IR (film) 3061, 3027, 2965, 2931, 2874, 1681 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.34-7.23 (m, 4H), 7.23- 7.12 (m, 1H), 4.44 (t, *J* = 7.2 Hz, 1H), 2.28-2.13 (m, 1H), 1.98-1.72 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.06, 139.62, 137.04, 132.72, 128.80, 128.60, 128.44, 128.24, 126.92, 55.46, 27.12, 12.28 ppm; EI-MS (TOF) (*m/z*) 224 $[M]^+$, 118,105, 91, 77; HRMS (EI) Calcd for $C_{16}H_{16}O$ $[M]^+$ 224.1201, found 224.1202.

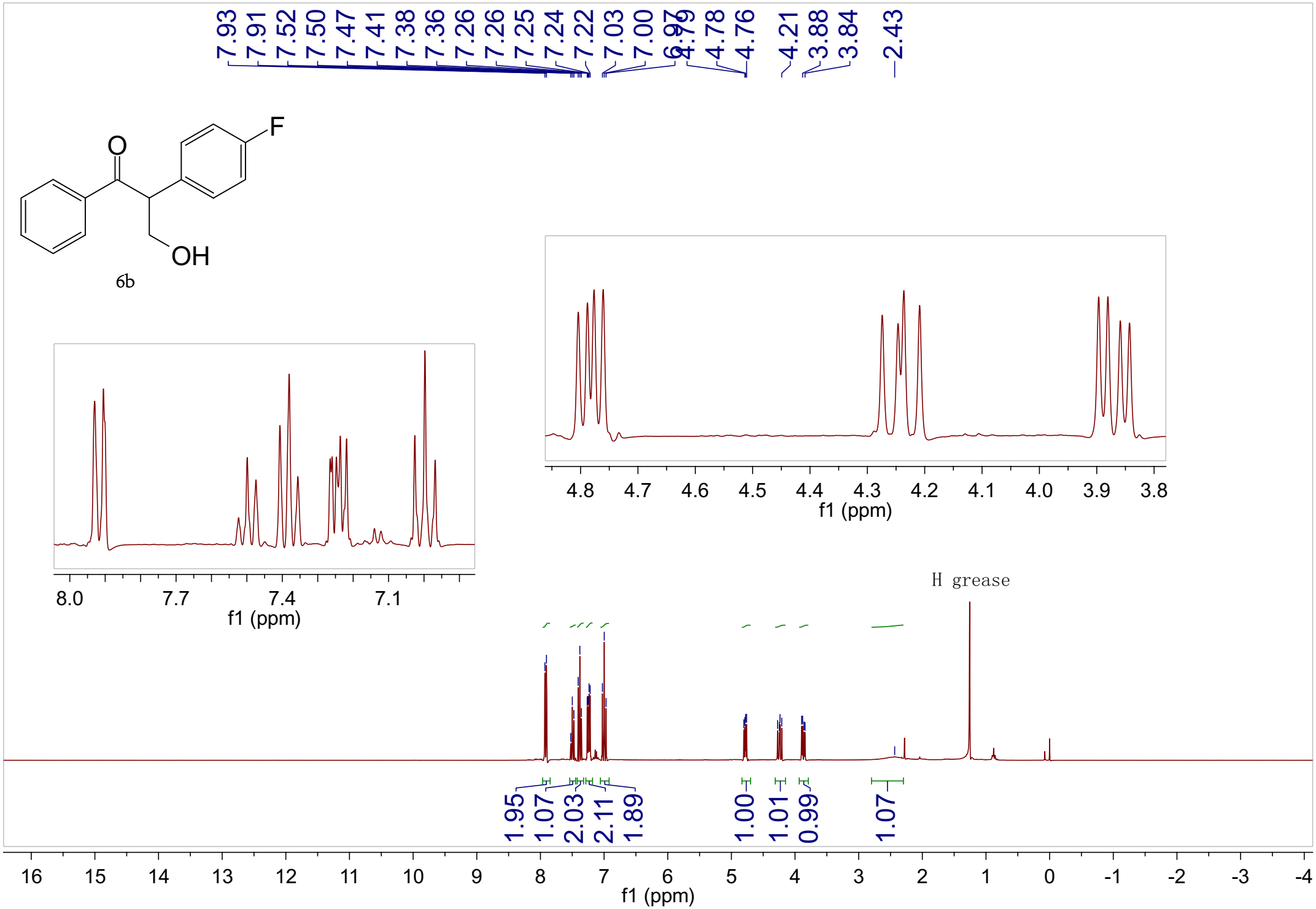
(E/Z)-1,2-diphenylprop-1-en-1-yl trifluoromethanesulfonate 12a



FT-IR (film) 3083, 3059, 2927, 1659, 1600, 1494, 1417 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-1.29 (m, 6H), 7.26-7.16 (m, 4H), 2.23 (s, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.11 (s, 3F) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 138.32, 137.01, 135.55, 129.66, 129.59, 128.48, 128.17, 128.09,

118.13 (q, J = 320.1 Hz), 19.00 ppm; EI-MS (*m/z*, %) 342 (M^+), 165 (100.00), 209 (83.50), 181 (62.19), 103 (55.07), 166 (50.75), 77 (21.93), 194 (10.90); HRMS (EI) Calcd for $C_{16}H_{13}F_3O_3S$ [M^+] 342.0538, found 342.0537.

7. Spectra of New Products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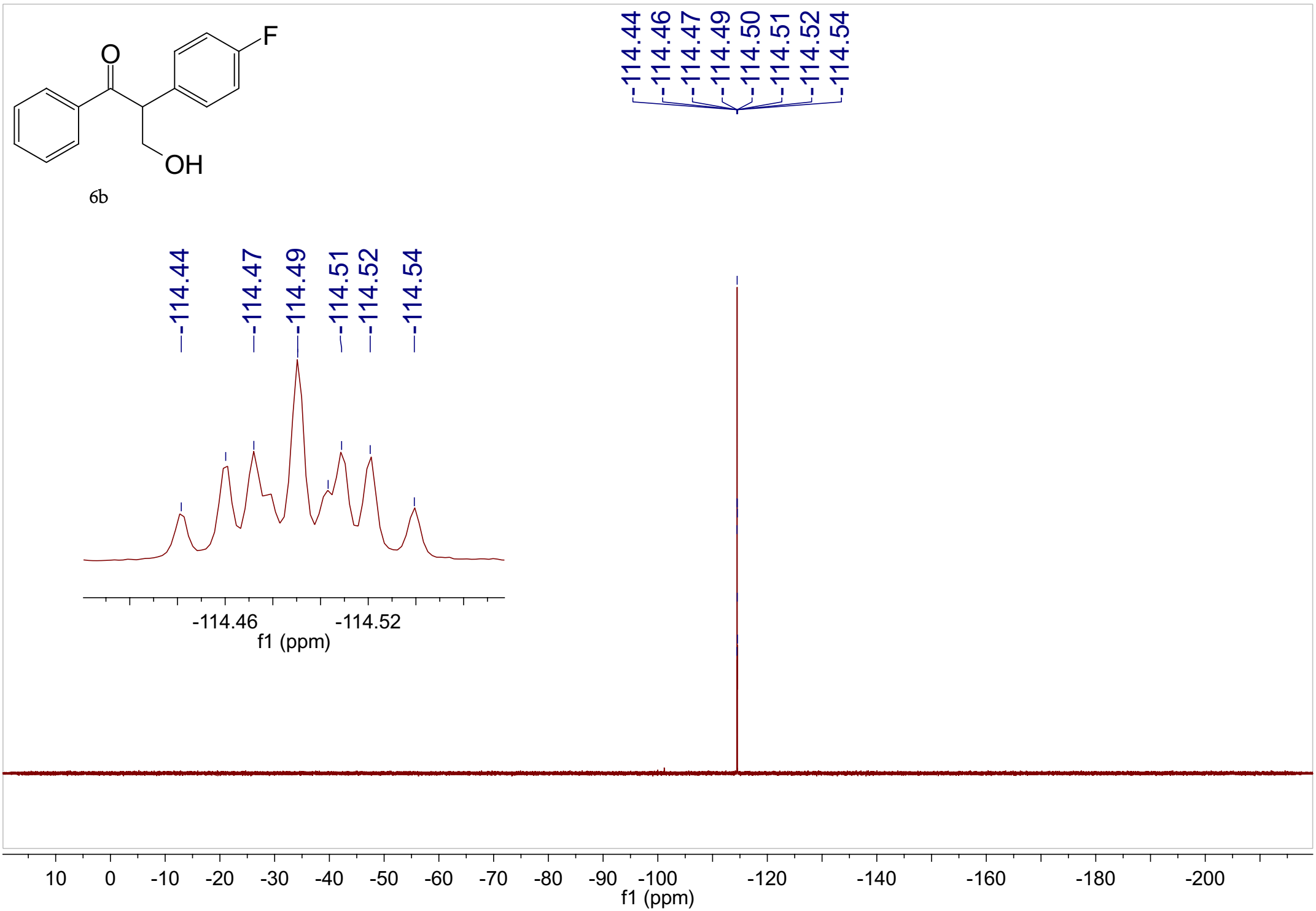
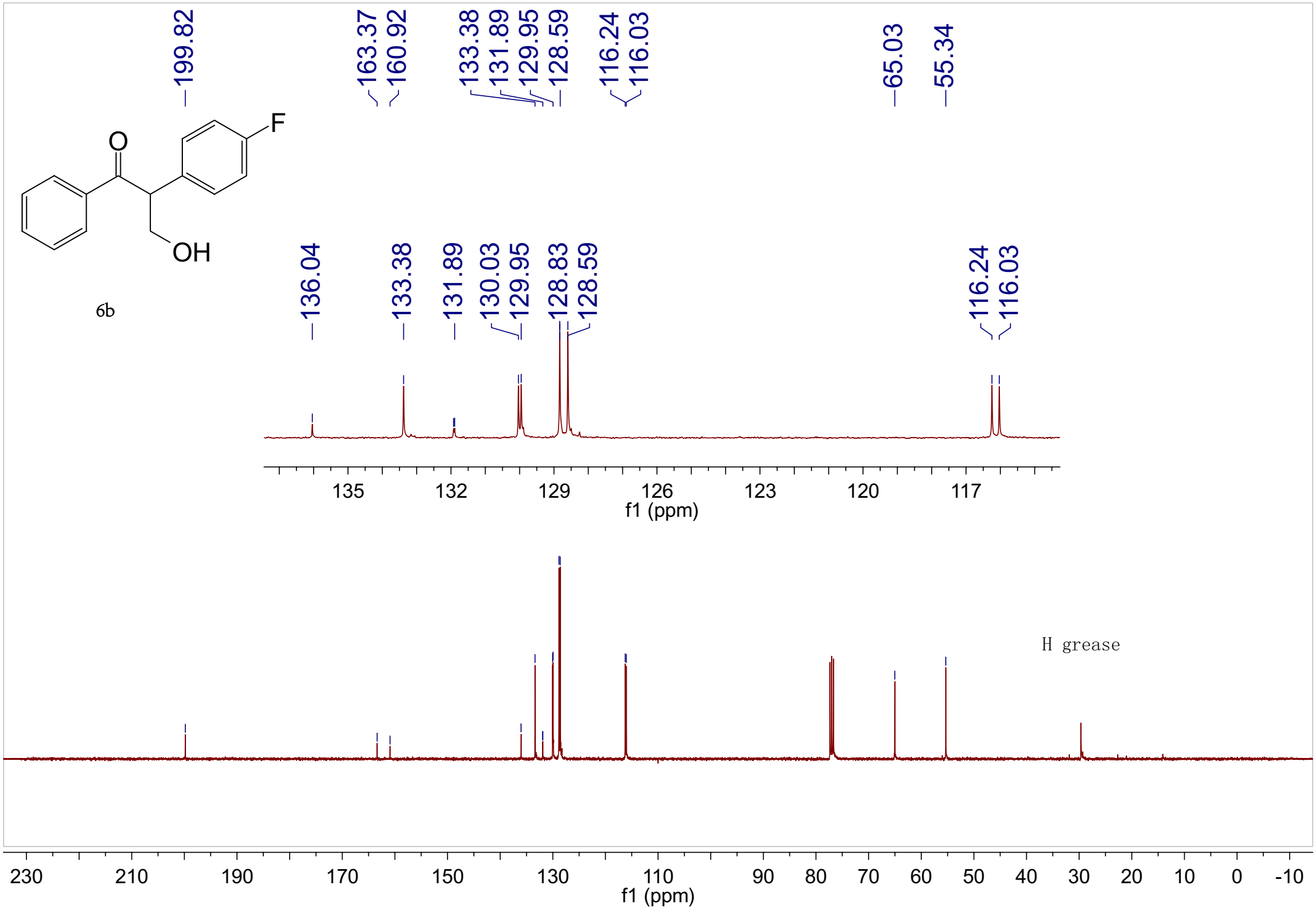
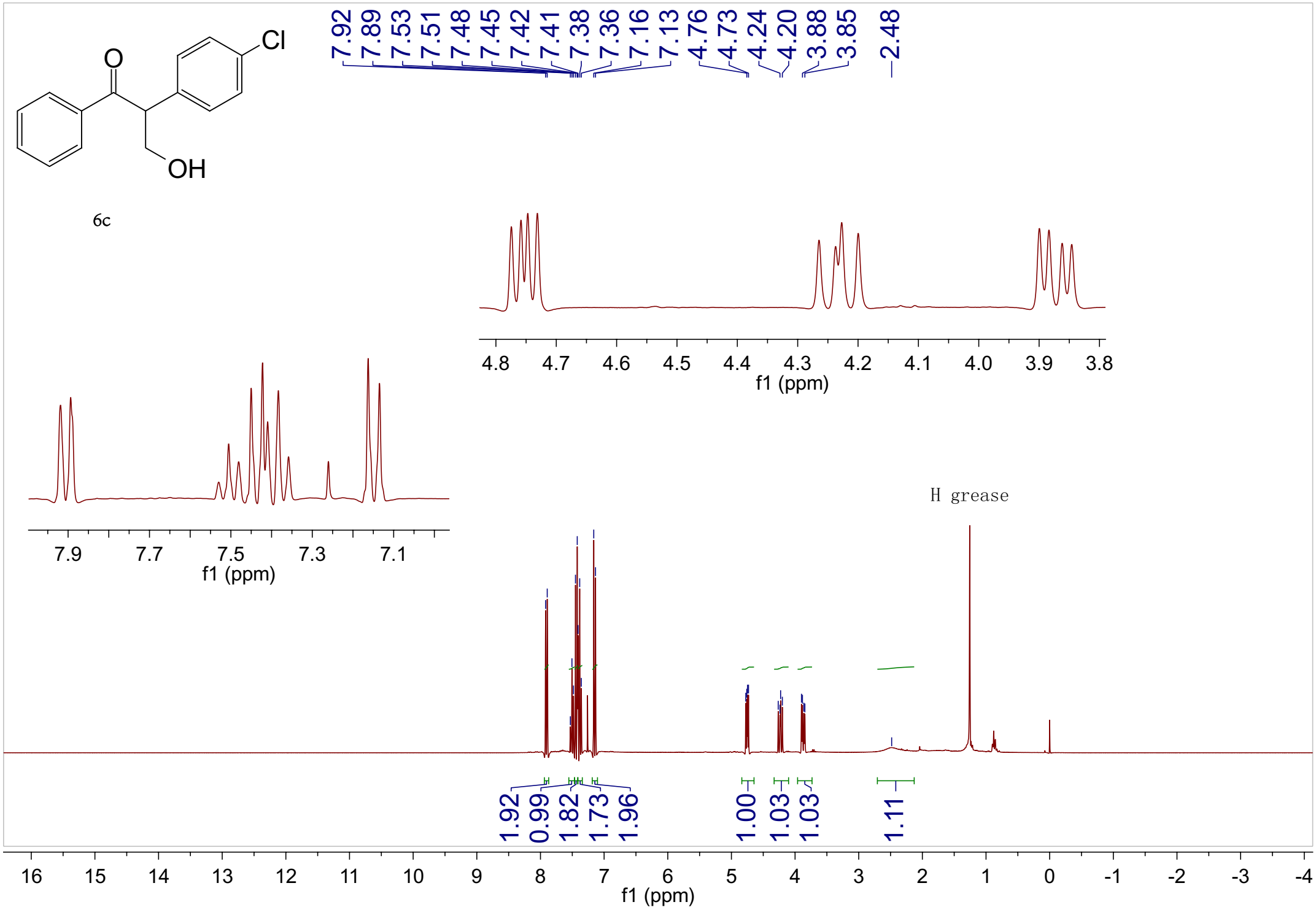
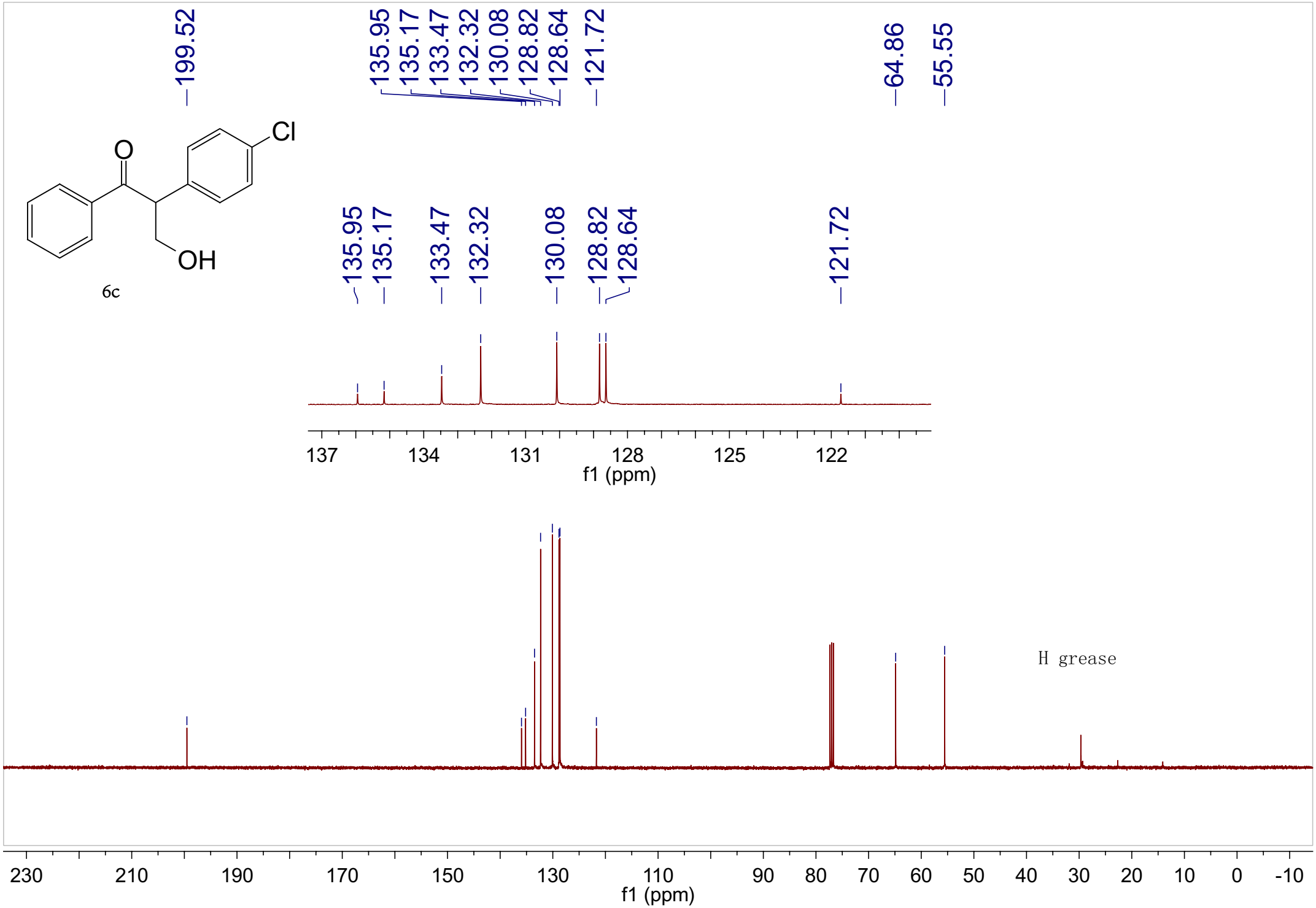
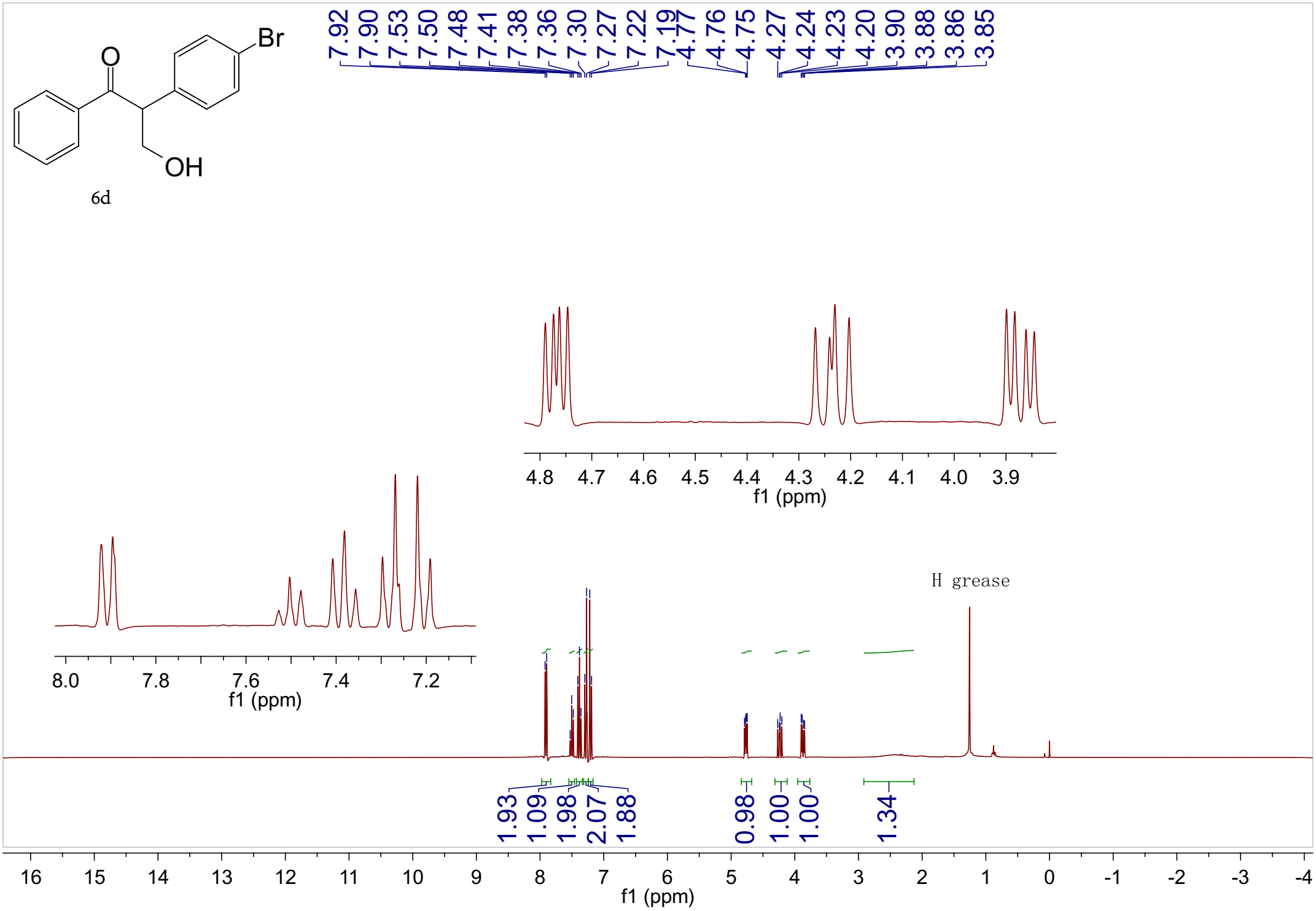
7.91
7.52
7.50
7.47
7.41
7.38
7.36
7.26
7.26
7.25
7.24
7.22
7.03
7.00
6.97
6.96
4.78
4.76
4.21
3.88
3.84
2.43
F
O
OH
6b
8.0
7.7
7.4
7.1
f1 (ppm)
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
f1 (ppm)
H grease
1.95
1.07
2.03
2.11
1.89
1.00
1.01
0.99
1.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

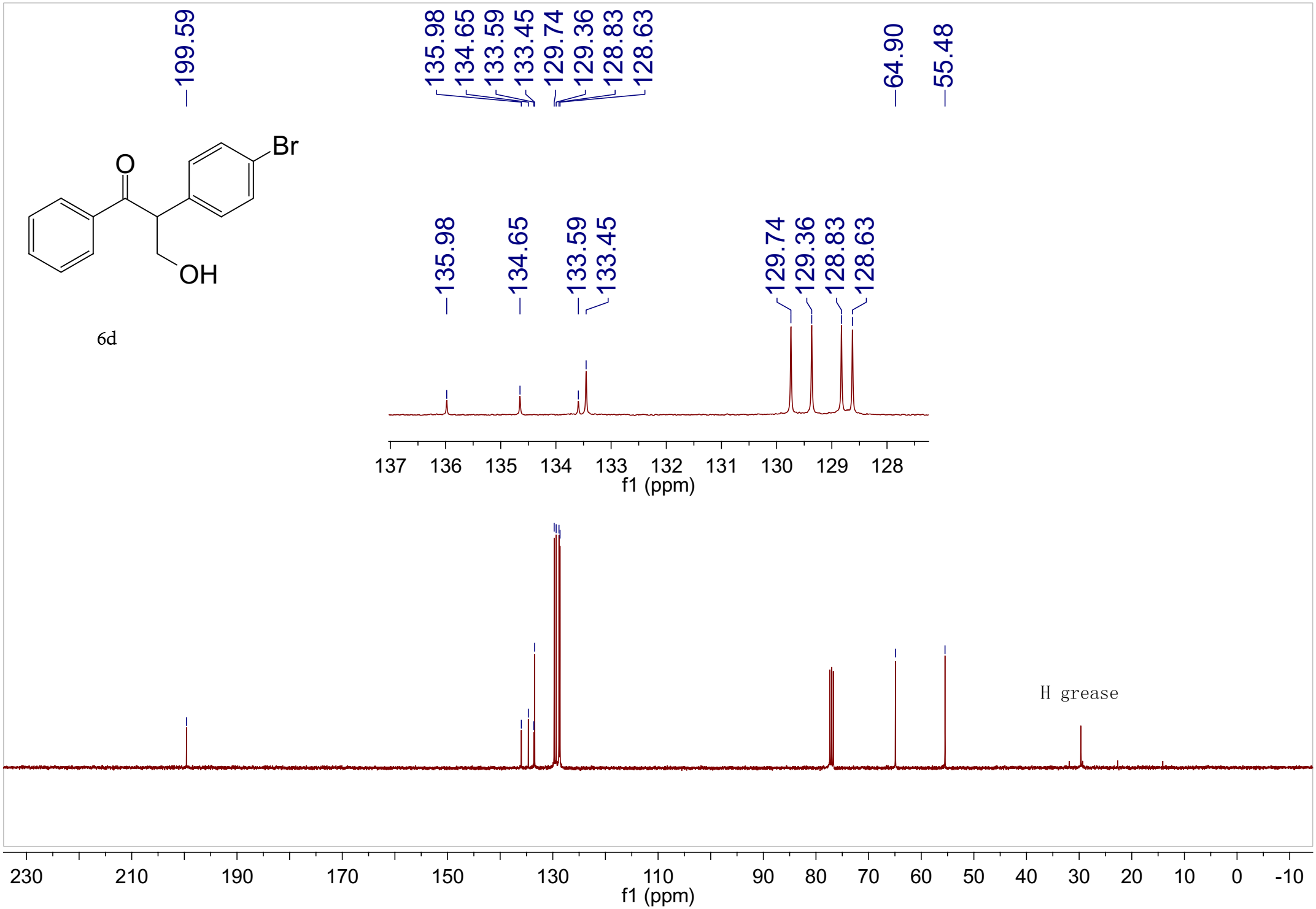

O
F
OH
6b
-114.44
-114.46
-114.47
-114.49
-114.50
-114.51
-114.52
-114.54
-114.44
-114.47
-114.49
-114.51
-114.52
-114.54
-114.46
-114.52
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

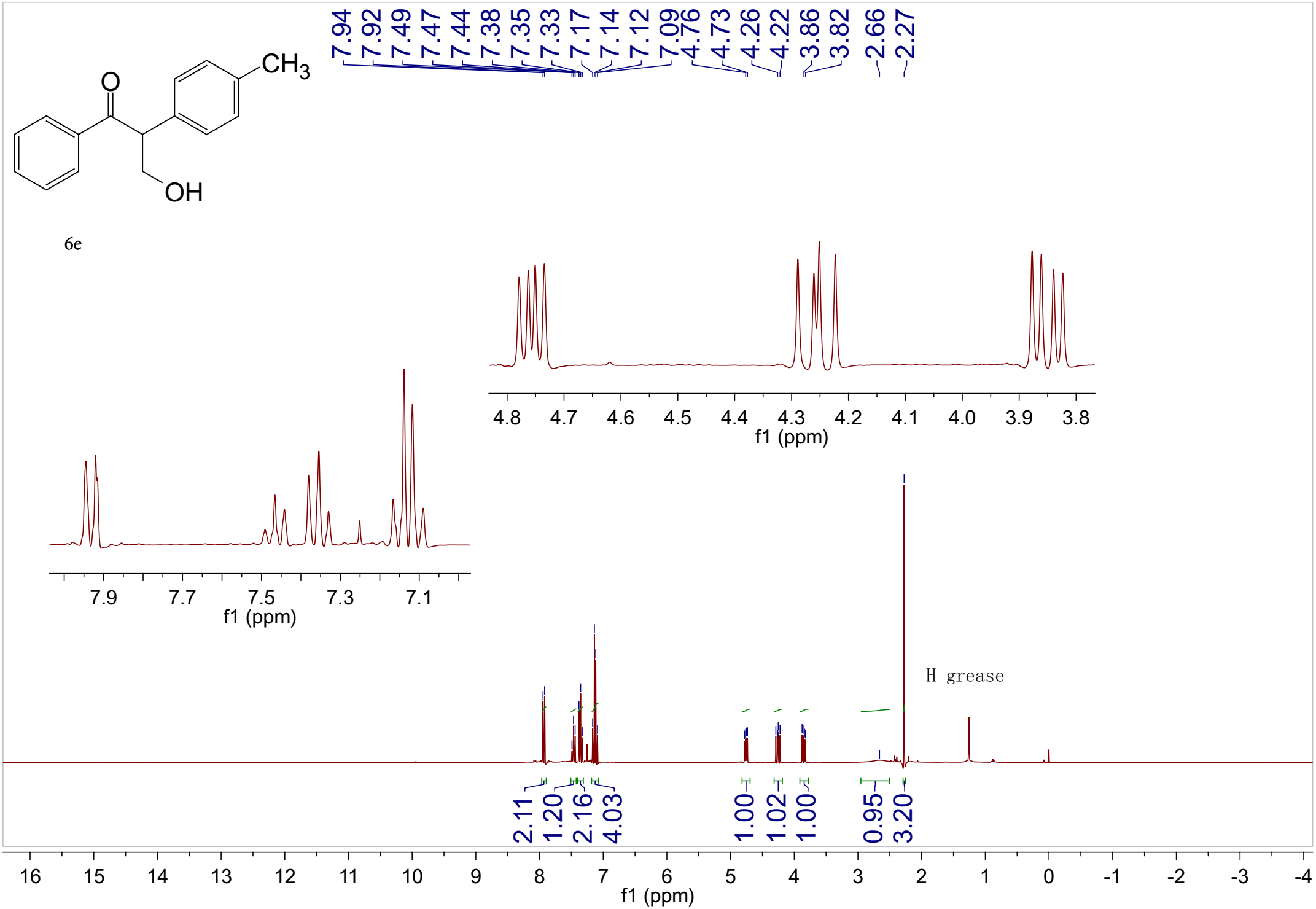

199.82
163.37
160.92
133.38
131.89
129.95
128.59
116.24
116.03
65.03
55.34
F
O
OH
6b
136.04
133.38
131.89
130.03
129.95
128.83
128.59
116.24
116.03
135
132
129
126
123
120
117
f1 (ppm)
H grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

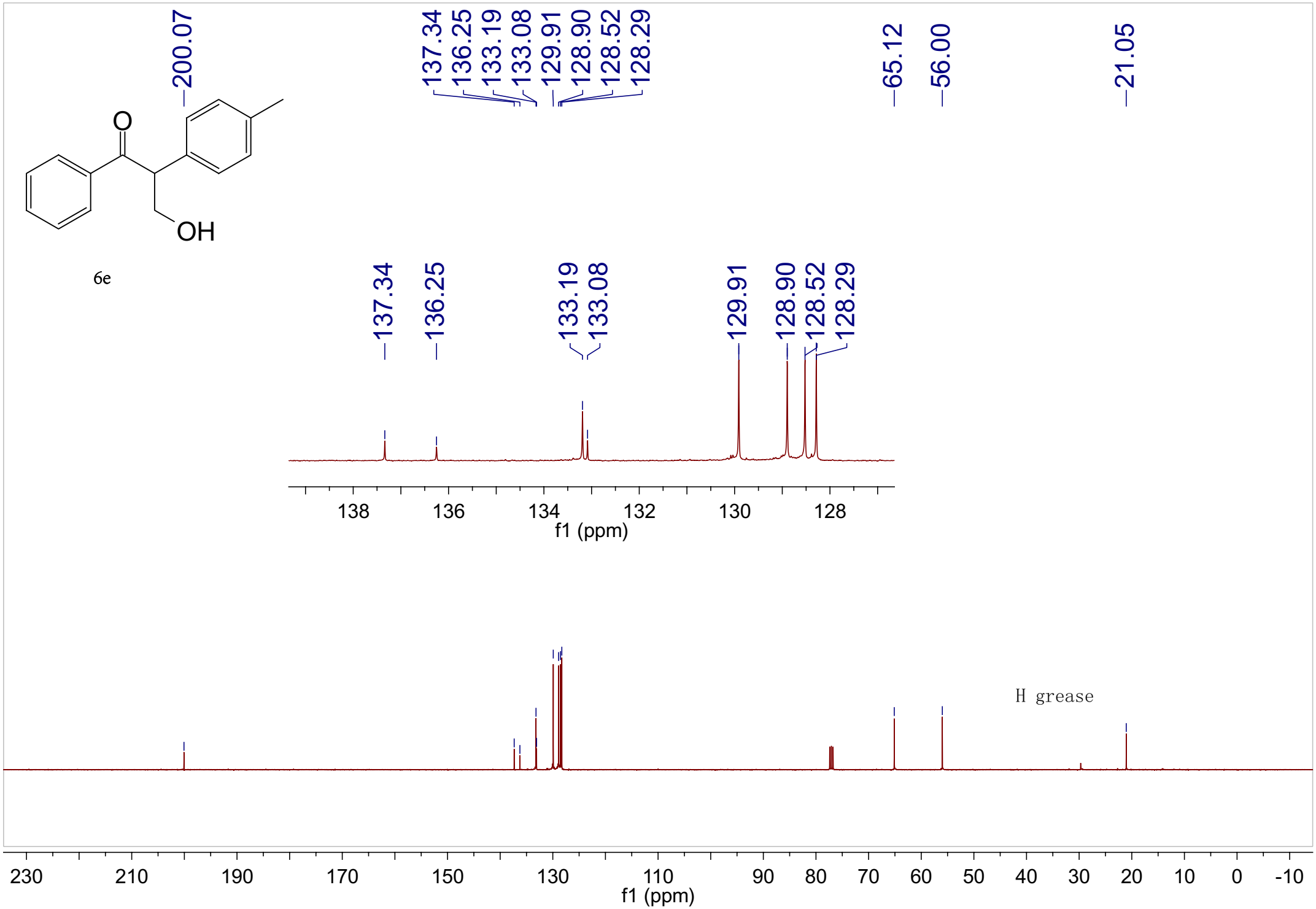

7.92
7.89
7.53
7.51
7.48
7.45
7.42
7.41
7.38
7.36
7.16
7.13
4.76
4.73
4.24
4.20
3.88
3.85
2.48
Cl
O
OH
6c
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
f1 (ppm)
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
H grease
1.92
0.99
1.82
1.73
1.96
1.00
1.03
1.03
1.11
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


199.52
135.95
135.17
133.47
132.32
130.08
128.82
128.64
121.72
64.86
55.55
Cl
O
OH
6c
135.95
135.17
133.47
132.32
130.08
128.82
128.64
121.72
137
134
131
128
125
122
f1 (ppm)
H grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Br
O
OH
6d
7.92
7.90
7.53
7.50
7.48
7.41
7.38
7.36
7.30
7.27
7.22
7.19
4.77
4.76
4.75
4.27
4.24
4.23
4.20
3.90
3.88
3.86
3.85
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
f1 (ppm)
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
H grease
1.93
1.09
1.98
2.07
1.88
0.98
1.00
1.00
1.34
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


199.59
135.98
134.65
133.59
133.45
129.74
129.36
128.83
128.63
64.90
55.48
Br
O
OH
6d
135.98
134.65
133.59
133.45
129.74
129.36
128.83
128.63
137 136 135 134 133 132 131 130 129 128
f1 (ppm)
H grease
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.94
7.92
7.49
7.47
7.44
7.38
7.35
7.33
7.17
7.14
7.12
7.09
4.76
4.73
4.26
4.22
3.86
3.82
2.66
2.27
O
CH3
OH
6e
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
7.9 7.7 7.5 7.3 7.1
f1 (ppm)
H grease
2.11
1.20
2.16
4.03
1.00
1.02
1.00
0.95
3.20
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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136.25
133.19
133.08
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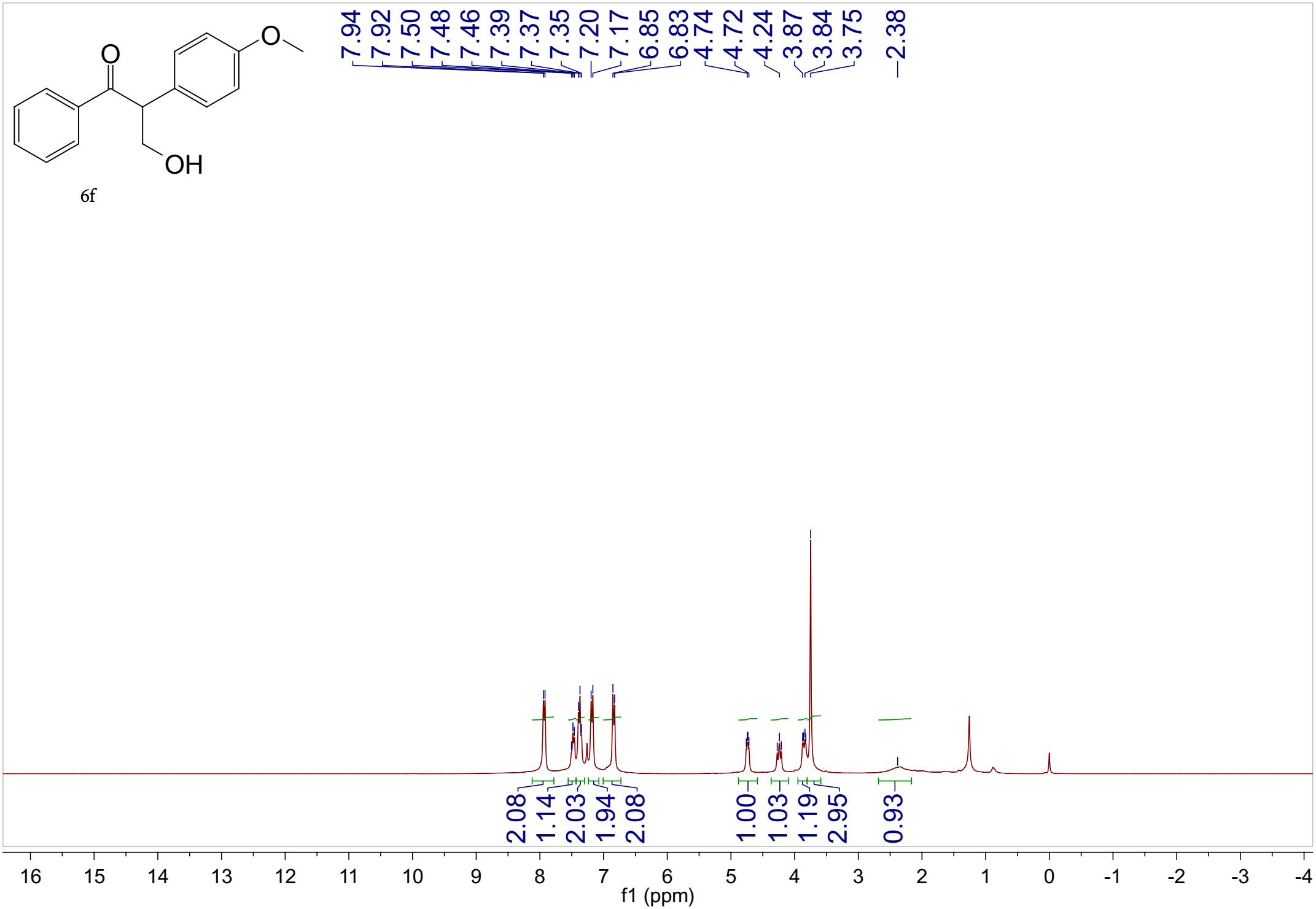
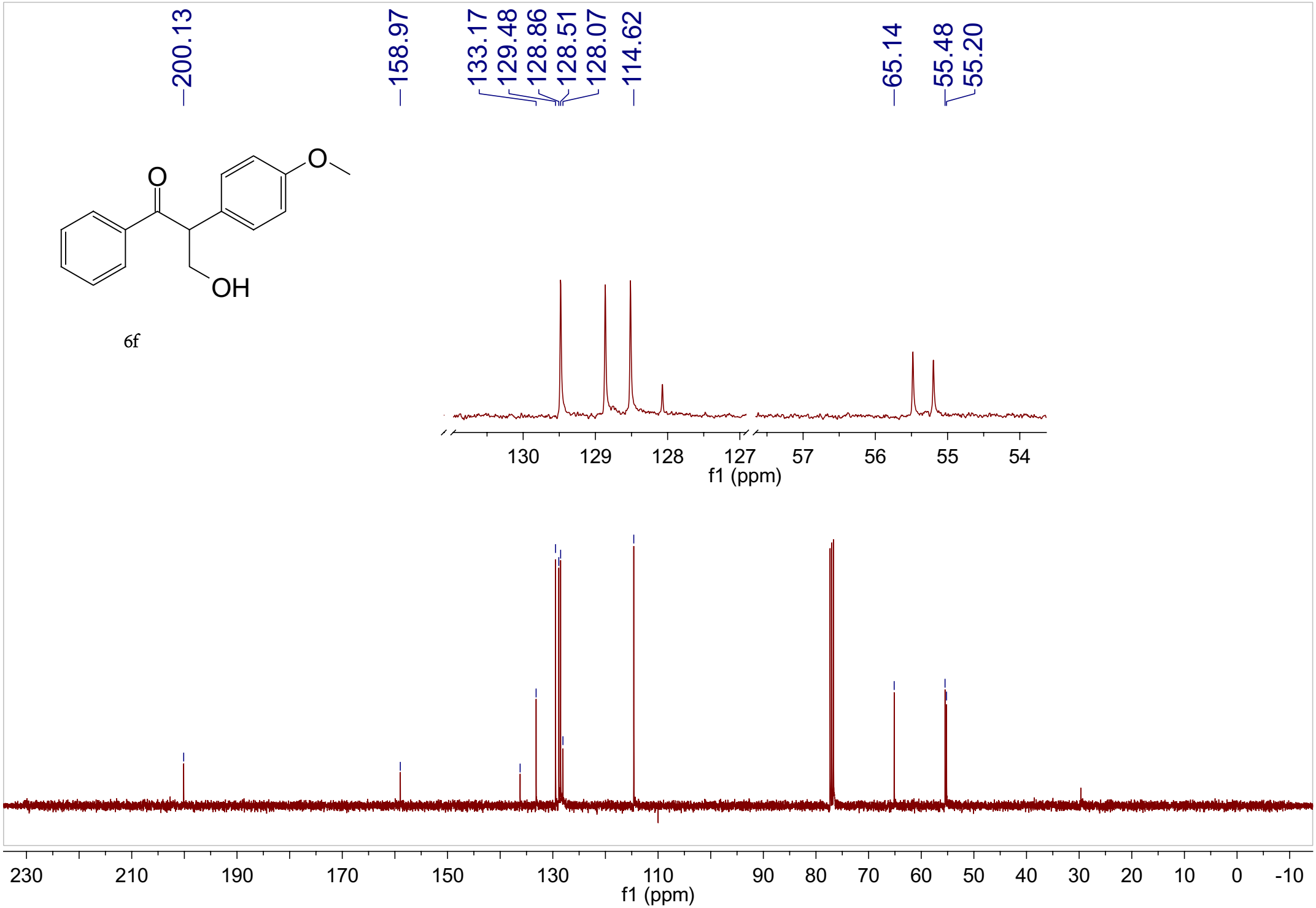
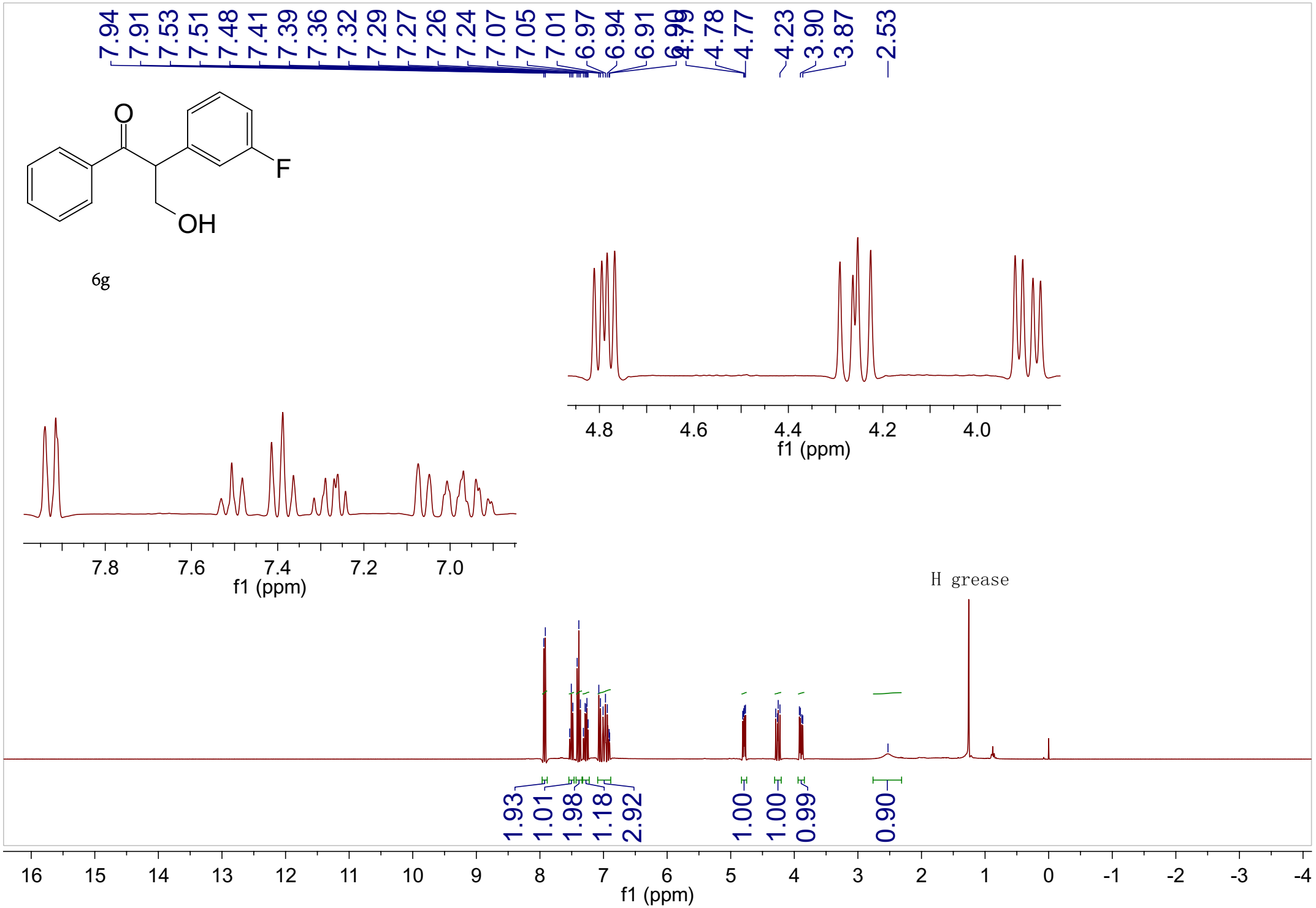
128.90
128.52
128.29
65.12
56.00
21.05
O
OH
6e
137.34
136.25
133.19
133.08
129.91
128.90
128.52
128.29
138
136
134
132
130
128
f1 (ppm)
H grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
OH
7.94
7.92
7.50
7.48
7.46
7.39
7.37
7.35
7.20
7.17
6.85
6.83
4.74
4.72
4.24
3.87
3.84
3.75
2.38
2.08
1.14
2.03
1.94
2.08
1.00
1.03
1.19
2.95
0.93
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

6f


200.13
158.97
133.17
129.48
128.86
128.51
128.07
114.62
65.14
55.48
55.20
O
O
OH
6f
130
129
128
127
57
56
55
54
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.51
7.48
7.41
7.39
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7.32
7.29
7.27
7.26
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7.07
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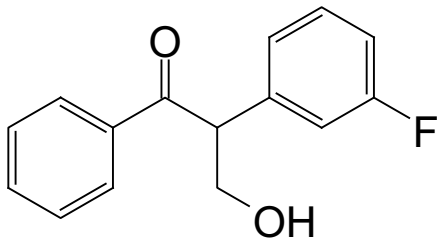
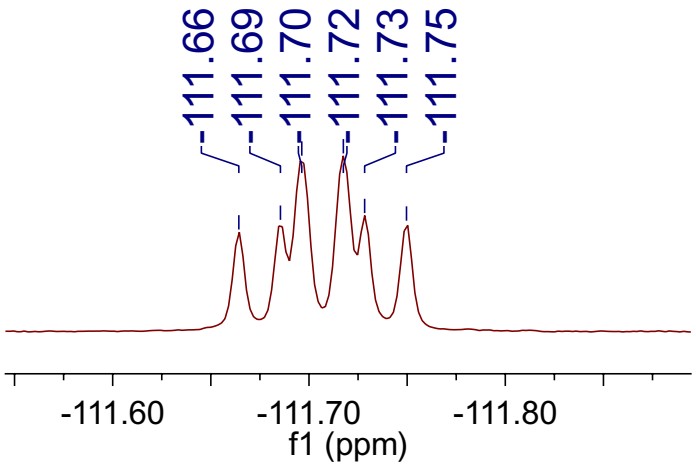
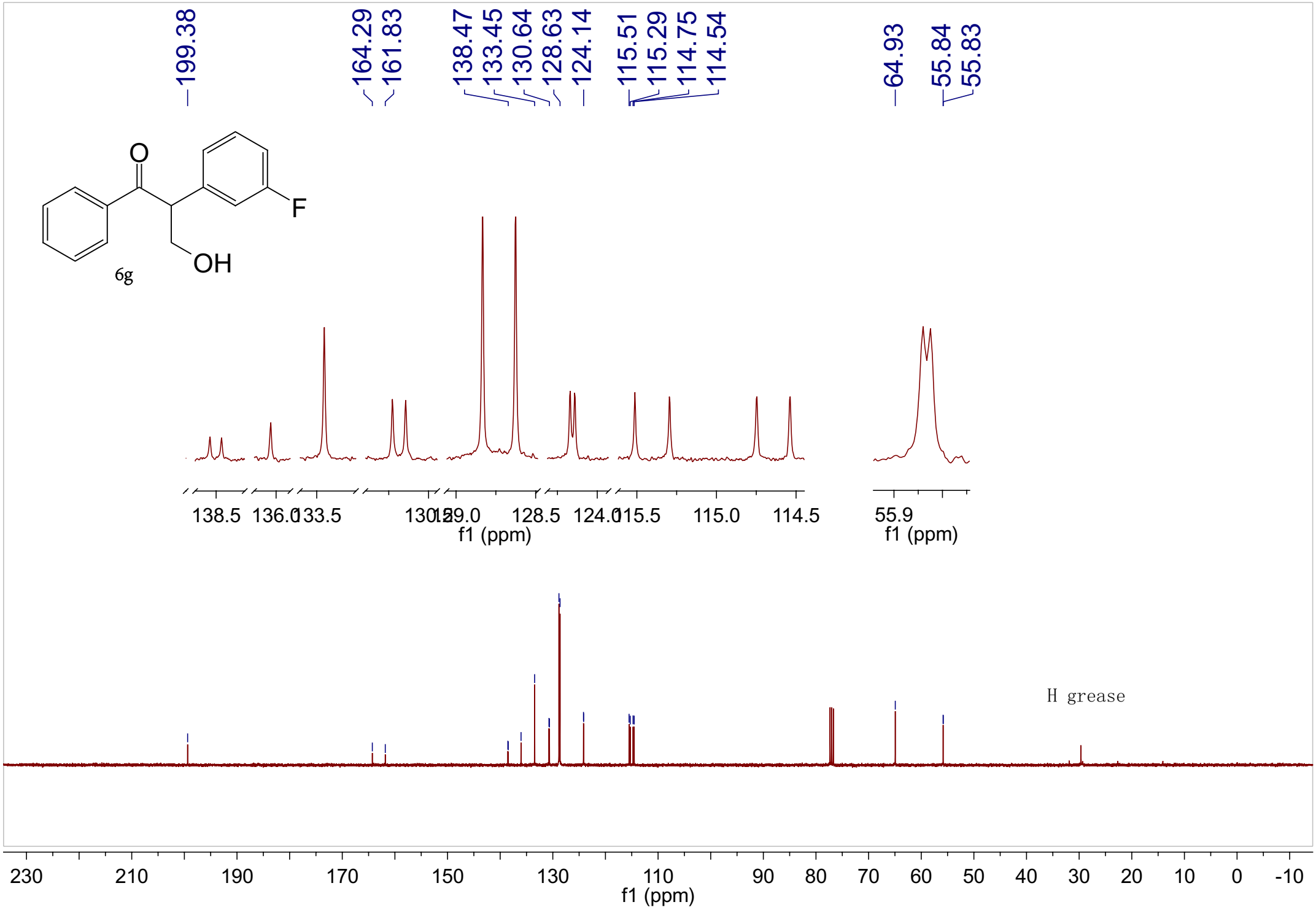
7.01
6.97
6.94
6.91
4.78
4.77
4.23
3.90
3.87
2.53
O
F
OH
6g
4.8
4.6
4.4
4.2
4.0
f1 (ppm)
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
H grease
1.93
1.01
1.98
1.18
2.92
1.00
1.00
0.99
0.90
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

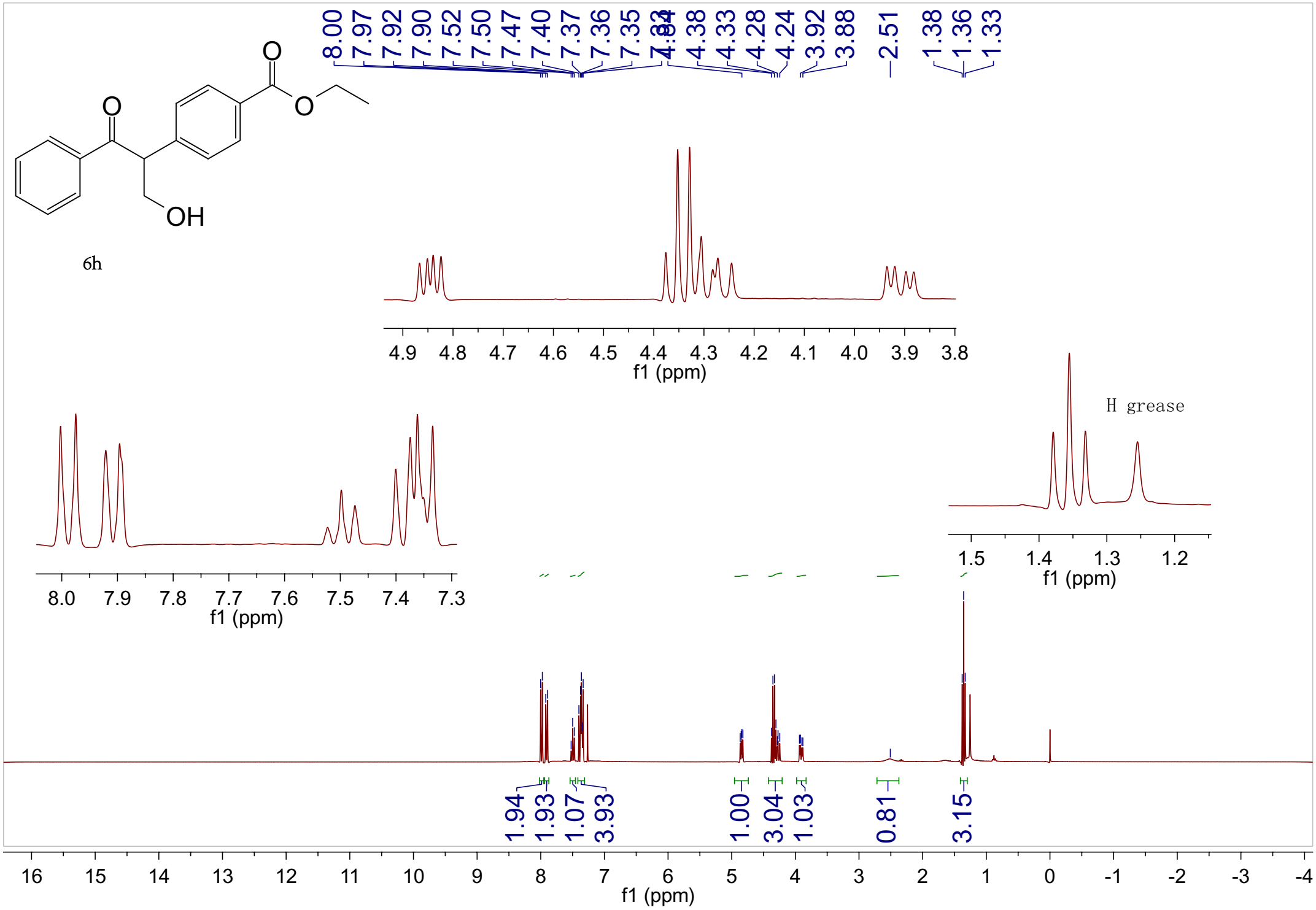


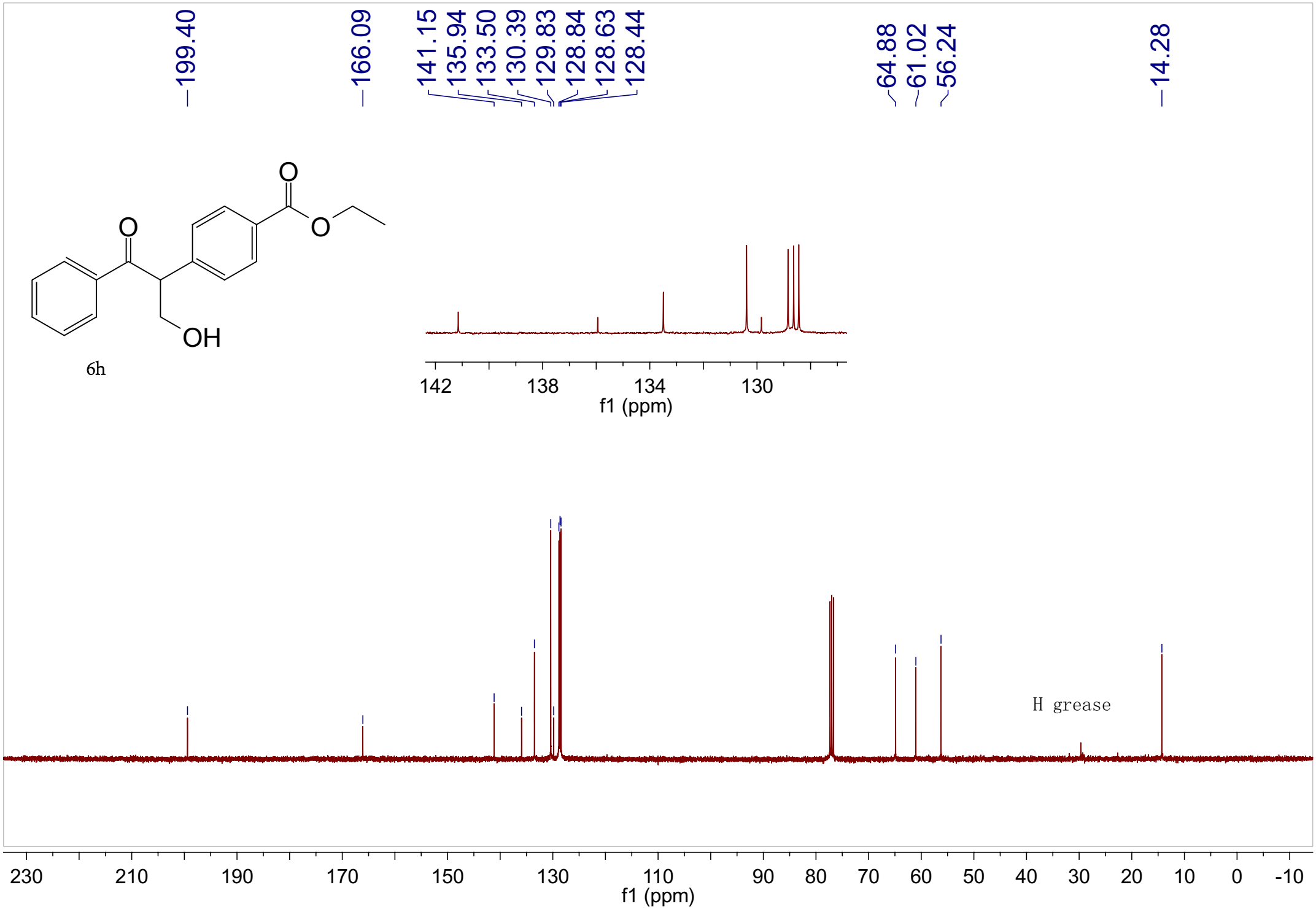
6g

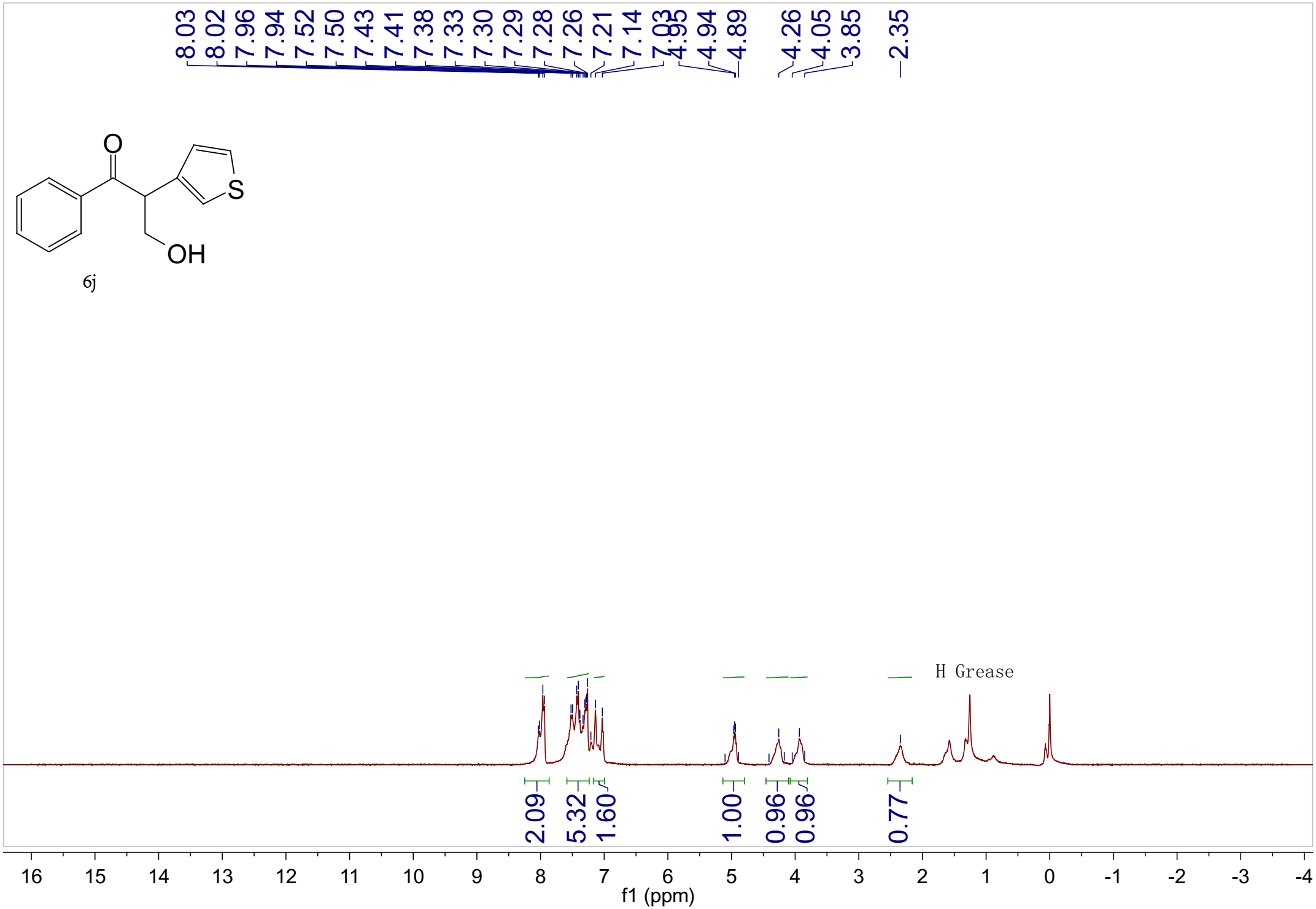
-111.66
-111.69
-111.70
-111.72
-111.73
-111.75



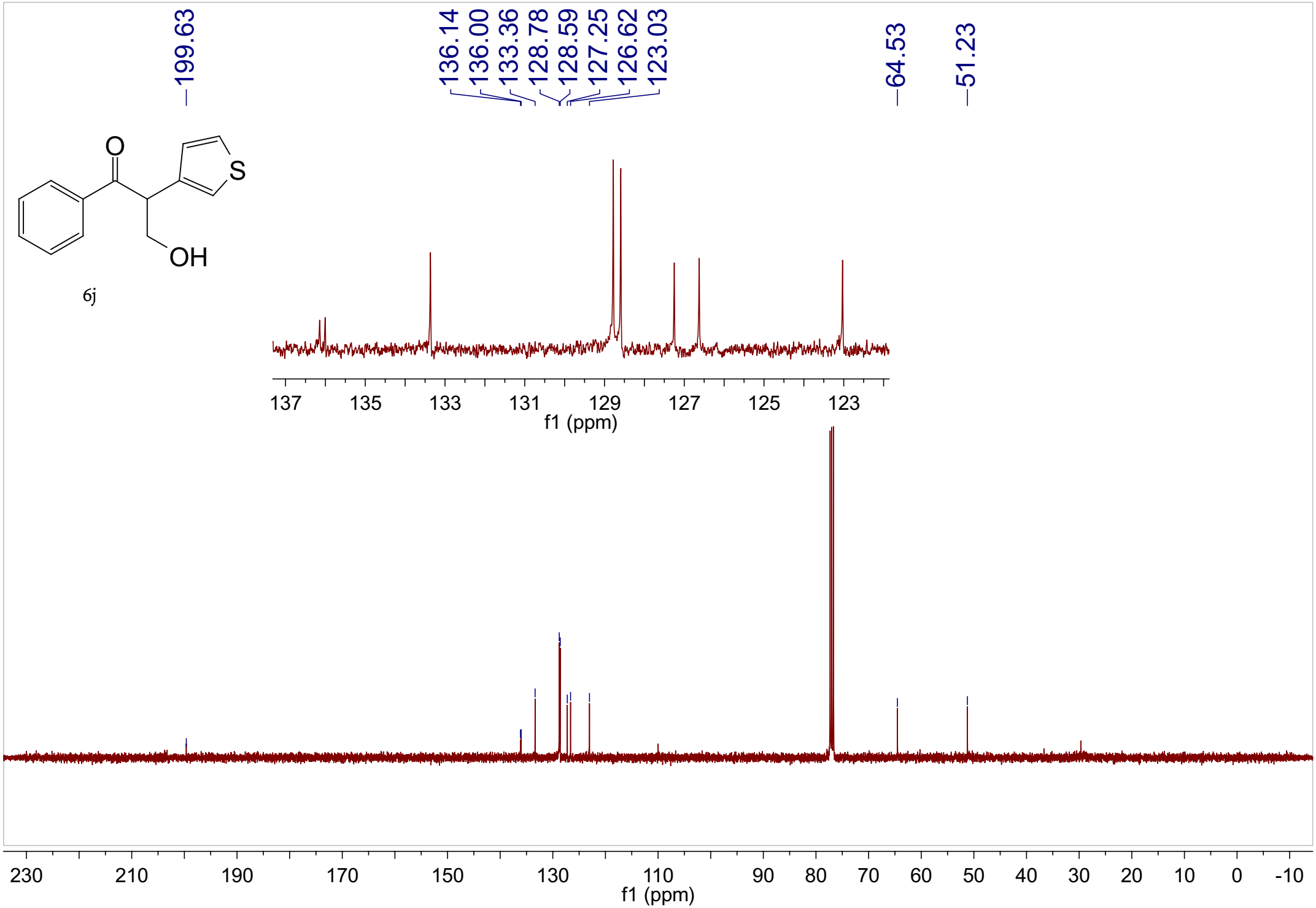

199.38
164.29
161.83
138.47
133.45
130.64
128.63
124.14
115.51
115.29
114.75
114.54
64.93
55.84
55.83
O
F
OH
6g
138.5
136.0
133.5
130.0
129.0
128.5
124.0
115.5
115.0
114.5
f1 (ppm)
55.9
f1 (ppm)
H grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

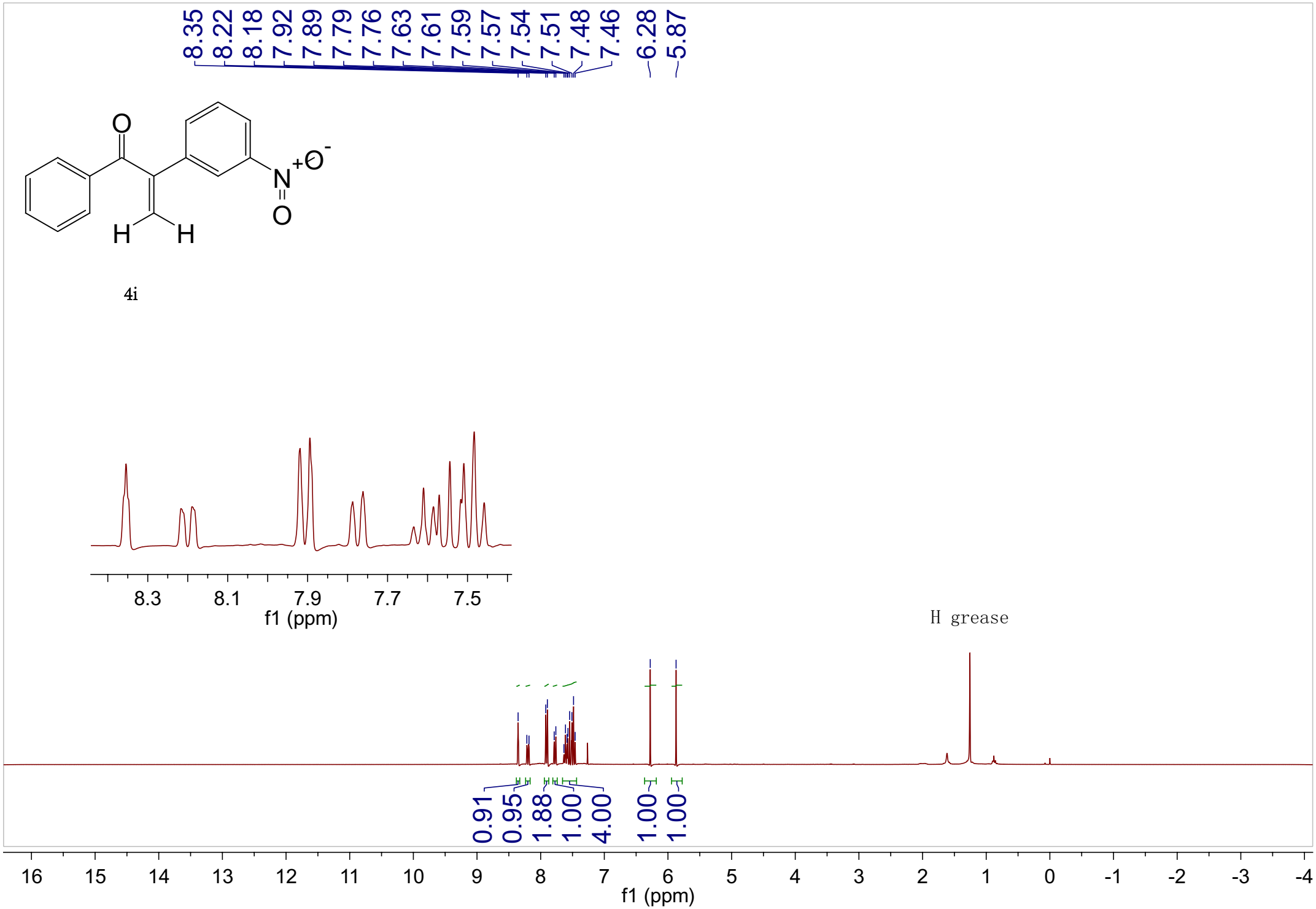

8.00
7.97
7.92
7.90
7.52
7.50
7.47
7.40
7.37
7.36
7.35
4.38
4.33
4.28
4.24
3.92
3.88
2.51
1.38
1.36
1.33
O
O
O
OH
6h
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
H grease
1.5 1.4 1.3 1.2
f1 (ppm)
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.94
1.93
1.07
3.93
1.00
3.04
1.03
0.81
3.15
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

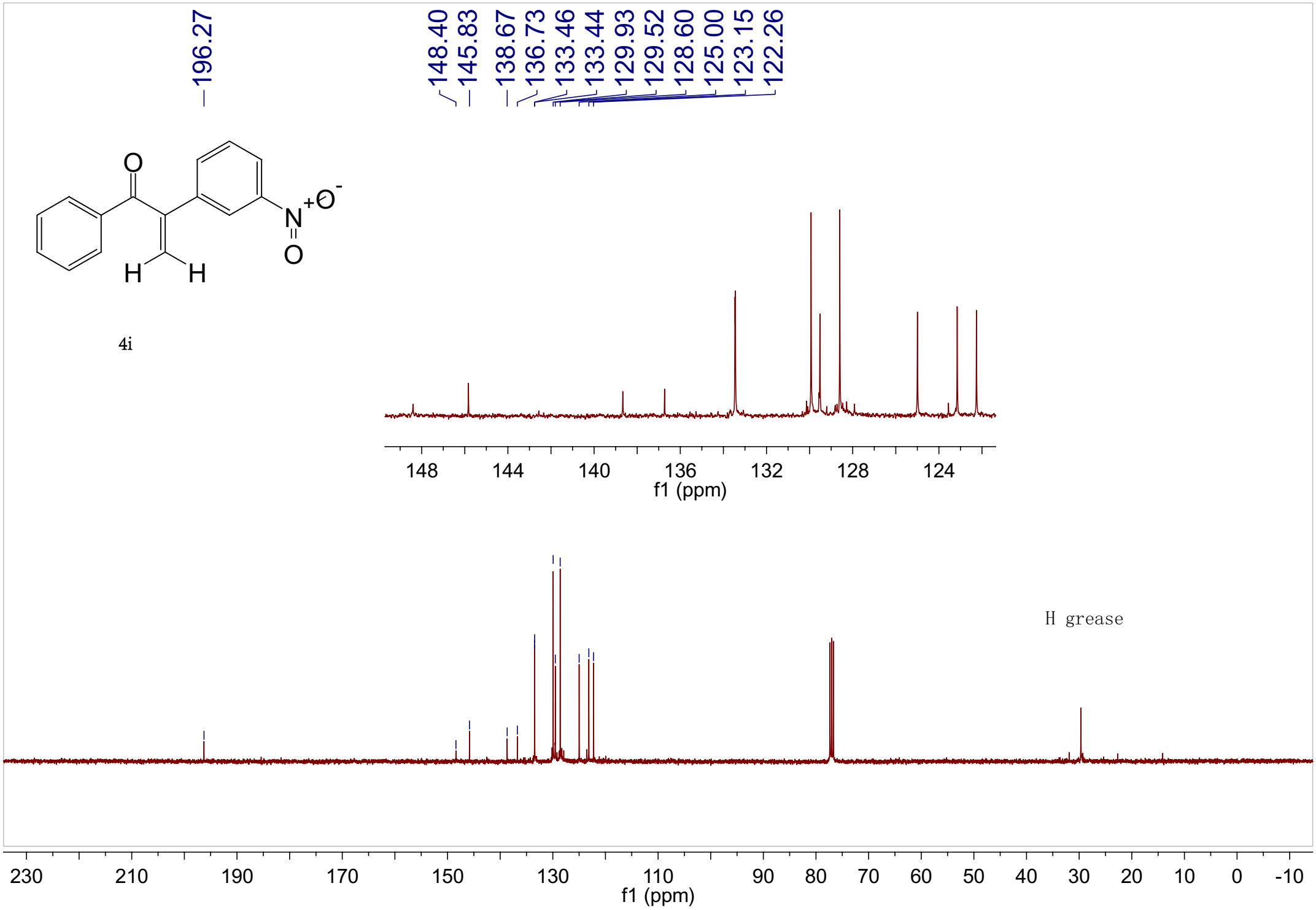

199.40
166.09
141.15
135.94
133.50
130.39
129.83
128.84
128.63
128.44
64.88
61.02
56.24
14.28
O
O
O
OH
6h
142
138
134
130
f1 (ppm)
H grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

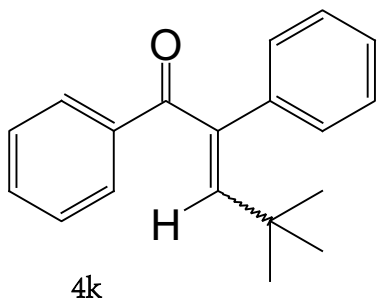

8.03
8.02
7.96
7.94
7.52
7.50
7.43
7.41
7.38
7.33
7.30
7.29
7.28
7.26
7.21
7.14
7.03
4.95
4.94
4.89
4.26
4.05
3.85
2.35
O
S
OH
H Grease
2.09
5.32
1.60
1.00
0.96
0.96
0.77
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

6j


199.63
136.14
136.00
133.36
128.78
128.59
127.25
126.62
123.03
64.53
51.23
O
S
OH
6j
137
135
133
131
129
127
125
123
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

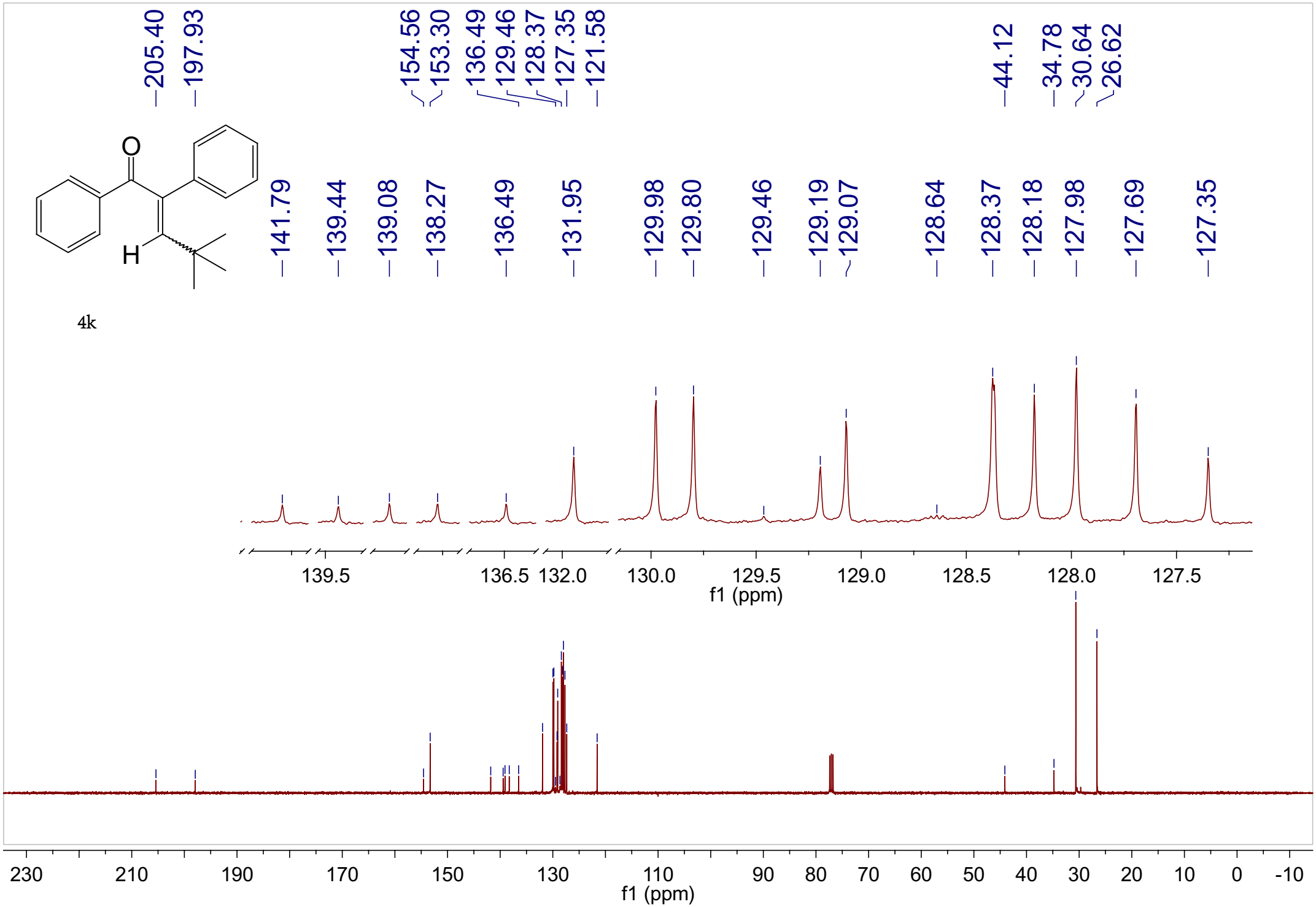

8.35
8.22
8.18
7.92
7.89
7.79
7.76
7.63
7.61
7.59
7.57
7.54
7.51
7.48
7.46
6.28
5.87
O
N
O
H
H
4i
8.3
8.1
7.9
7.7
7.5
f1 (ppm)
H grease
0.91
0.95
1.88
1.00
4.00
1.00
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

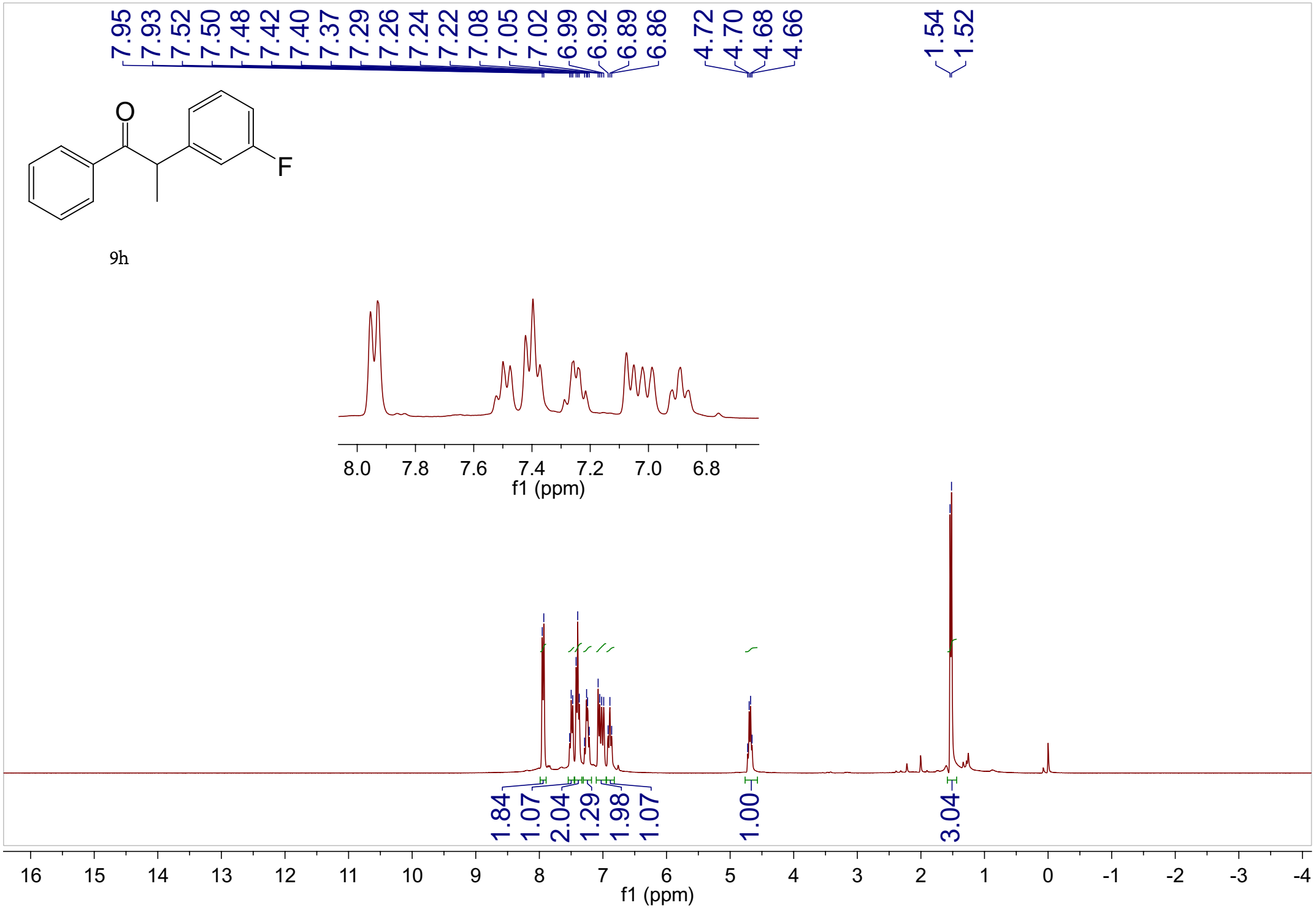

196.27
148.40
145.83
138.67
136.73
133.46
133.44
129.93
129.52
128.60
125.00
123.15
122.26
O
N+
O-
O
H
H
4i
148
144
140
136
132
128
124
f1 (ppm)
H grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

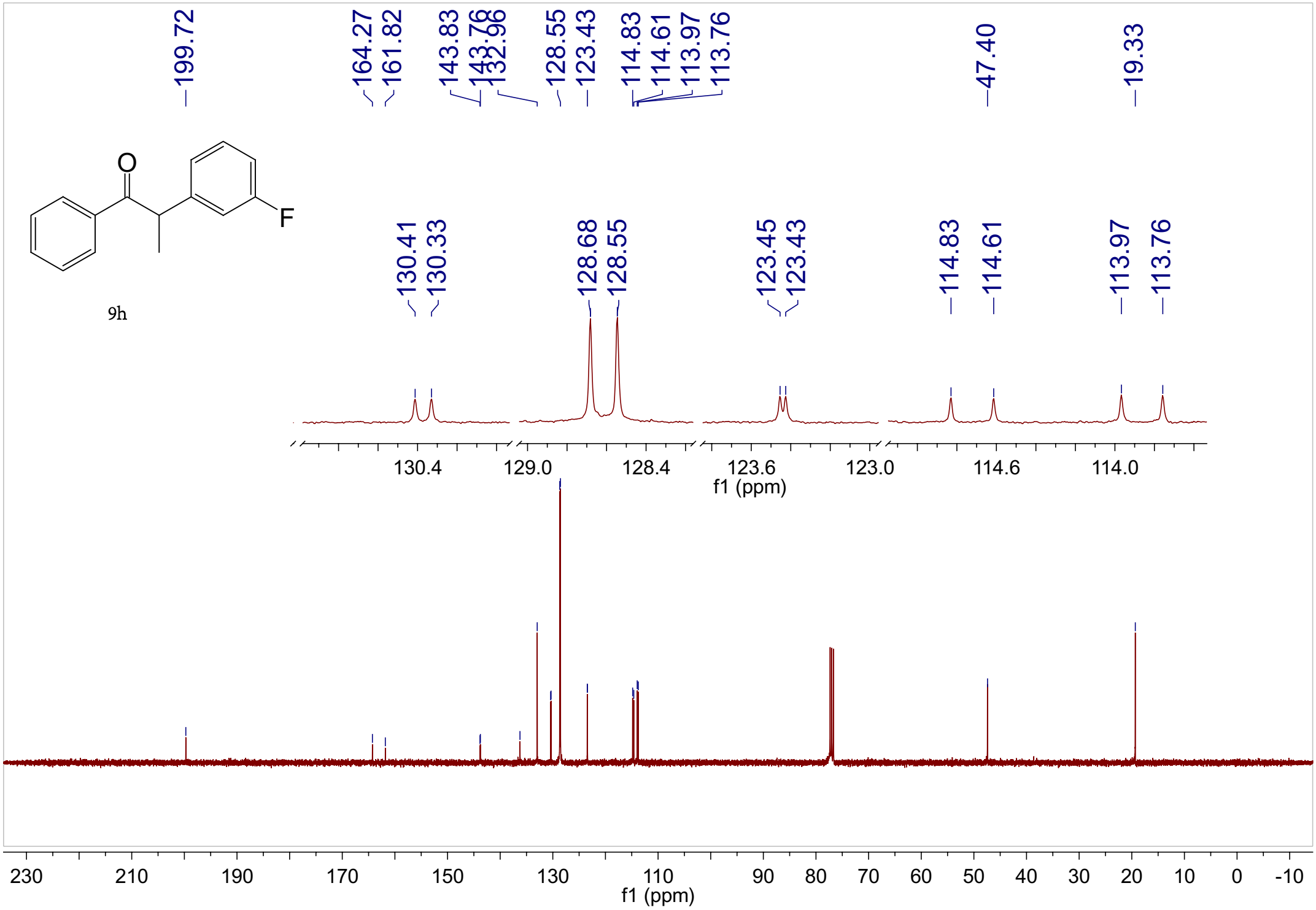

O
H

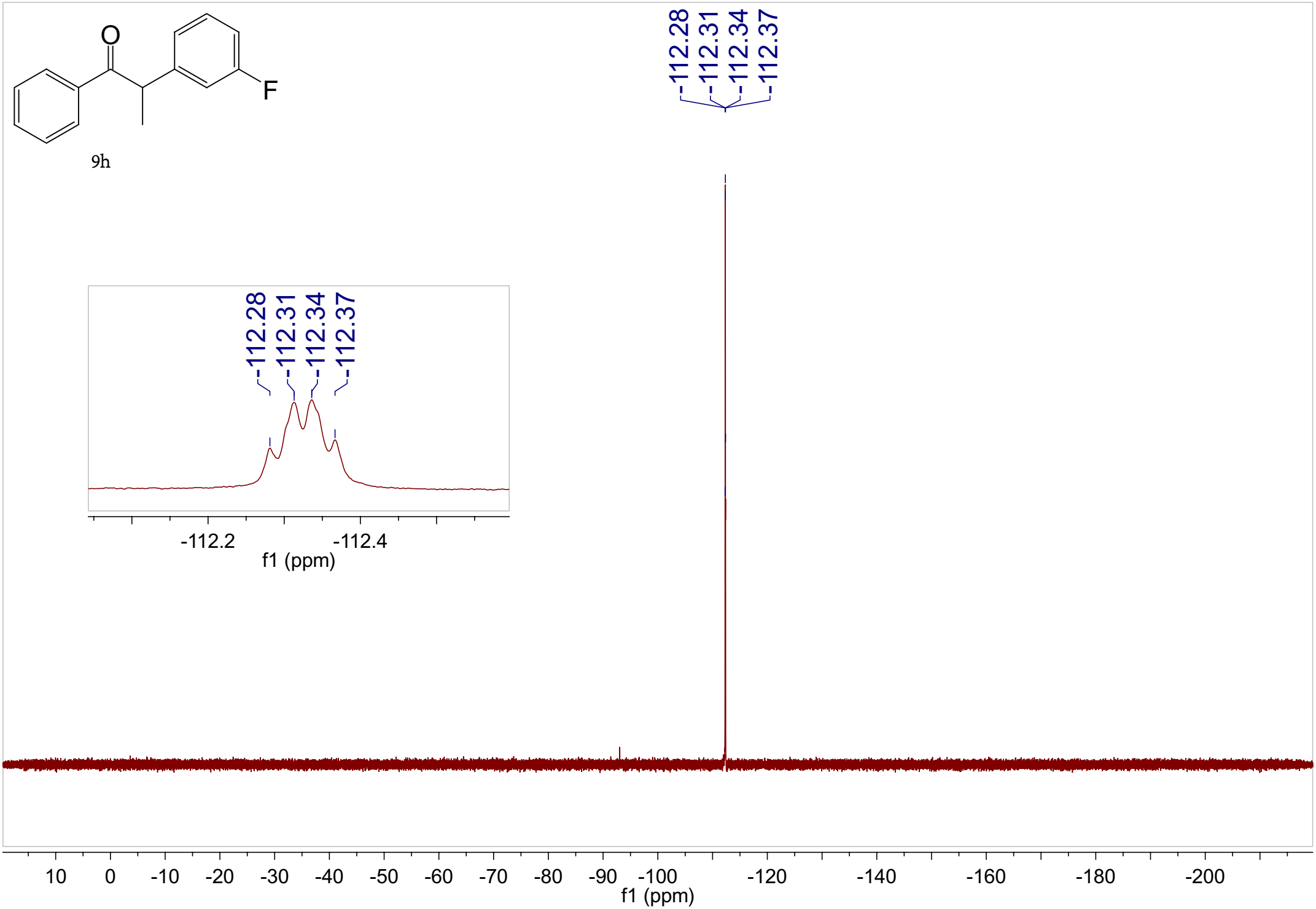
4k

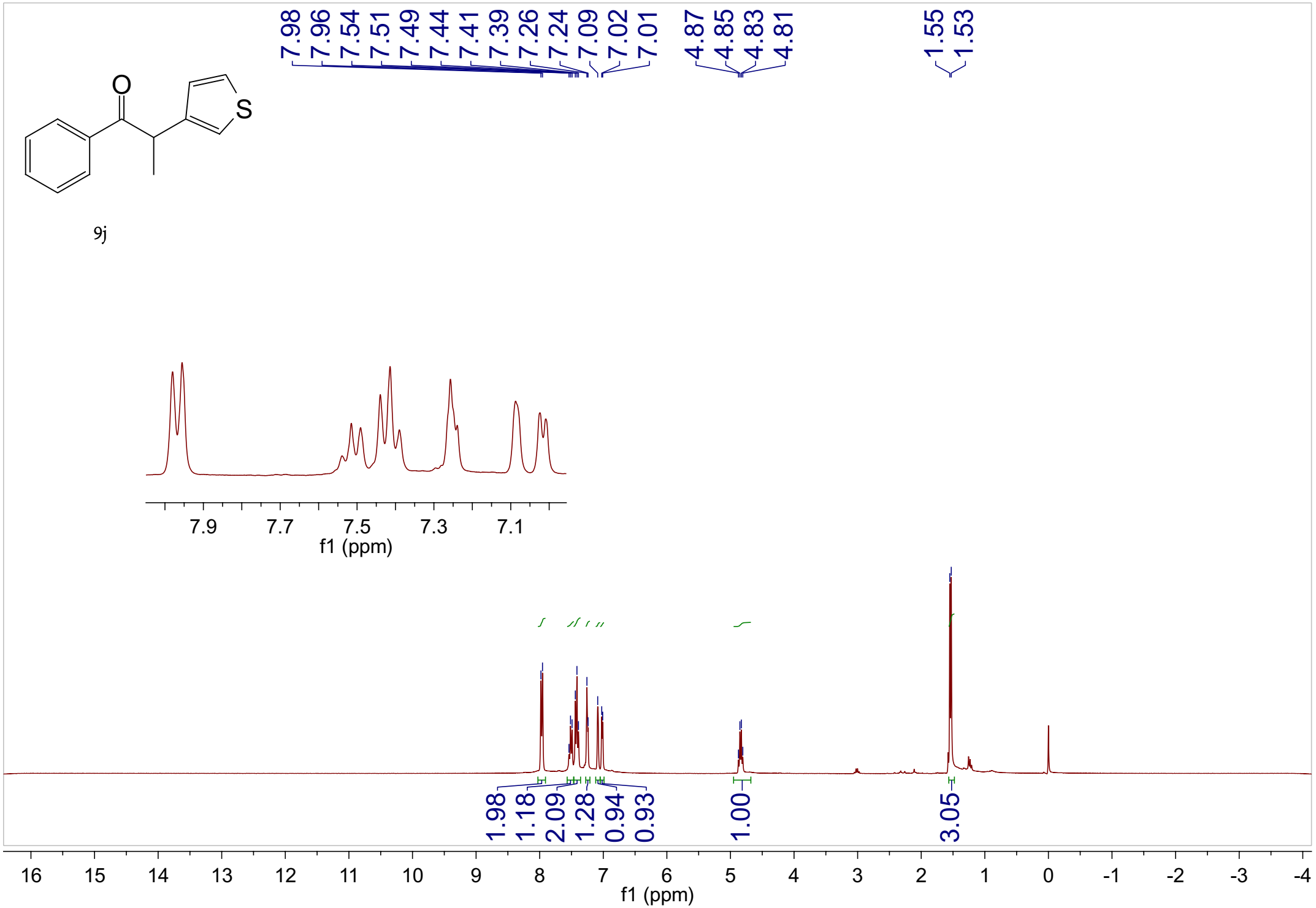
7.84
7.81
7.81
7.44
7.30
7.24
6.91
6.36
1.20
0.97
7.54
7.52
7.50
7.46
7.44
7.41
7.32
7.28
7.24
7.17
7.15
7.14
7.13
2.11
1.40
2.54
12.29
1.72
0.87
1.00
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
7.76
9.44
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

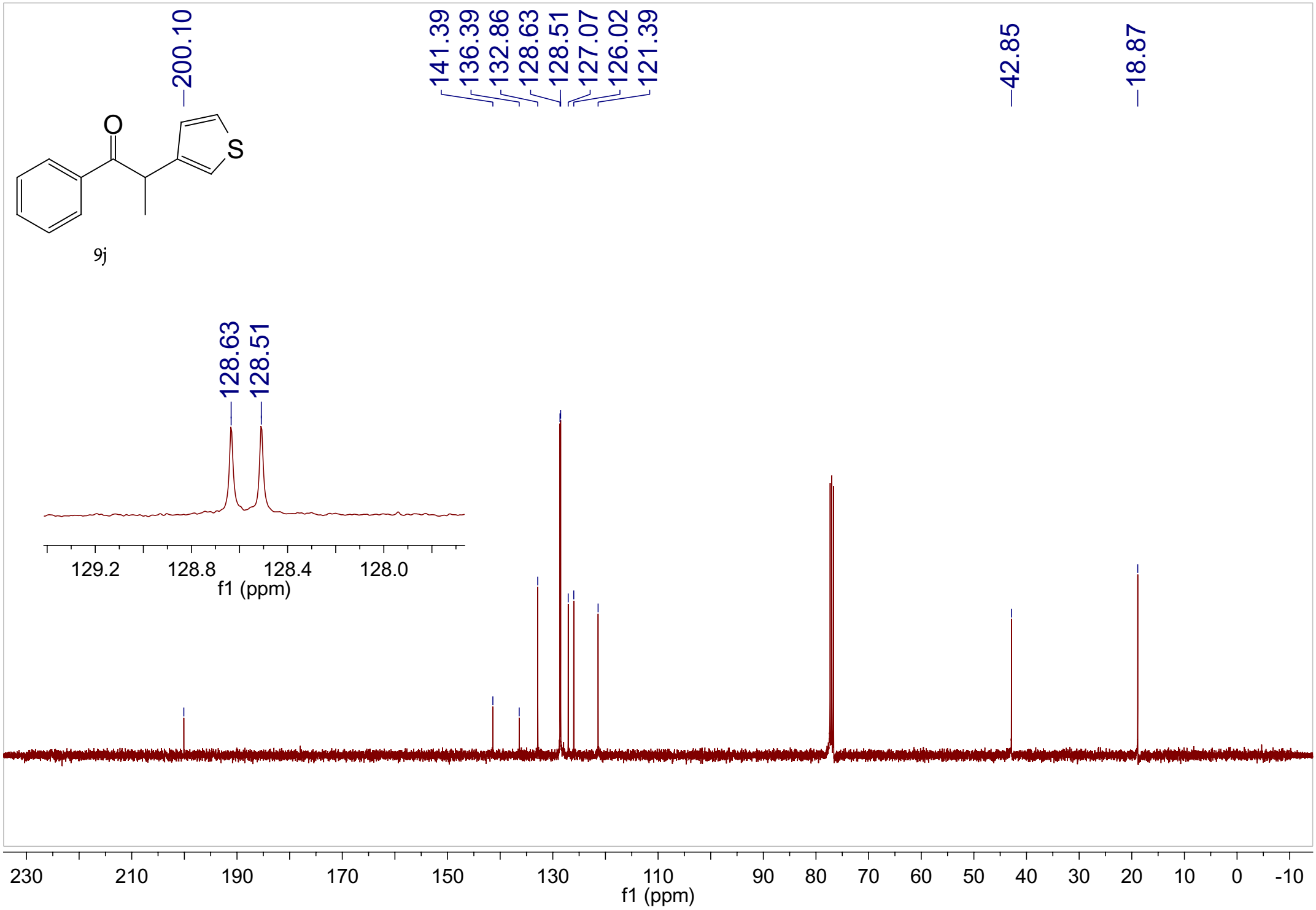

205.40
197.93
154.56
153.30
136.49
129.46
128.37
127.35
121.58
44.12
34.78
30.64
26.62
O
H
141.79
139.44
139.08
138.27
136.49
131.95
129.98
129.80
129.46
129.19
129.07
128.64
128.37
128.18
127.98
127.69
127.35
4k
139.5
136.5
132.0
130.0
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

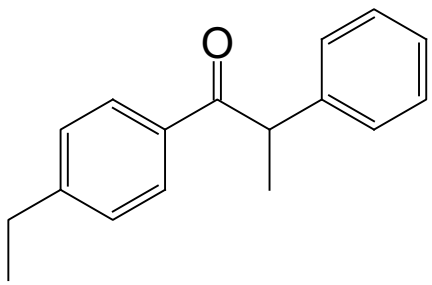

7.95
7.93
7.52
7.50
7.48
7.42
7.40
7.37
7.29
7.26
7.24
7.22
7.08
7.05
7.02
6.99
6.92
6.89
6.86
4.72
4.70
4.68
4.66
1.54
1.52
O
F
9h
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.84
1.07
2.04
1.29
1.98
1.07
1.00
3.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


199.72
164.27
161.82
143.83
143.76
132.96
128.55
123.43
114.83
114.61
113.97
113.76
47.40
19.33
O
F
9h
130.41
130.33
128.68
128.55
123.45
123.43
114.83
114.61
113.97
113.76
130.4
129.0
128.4
123.6
123.0
114.6
114.0
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
F
9h
-112.28
-112.31
-112.34
-112.37
-112.28
-112.31
-112.34
-112.37
-112.2
-112.4
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

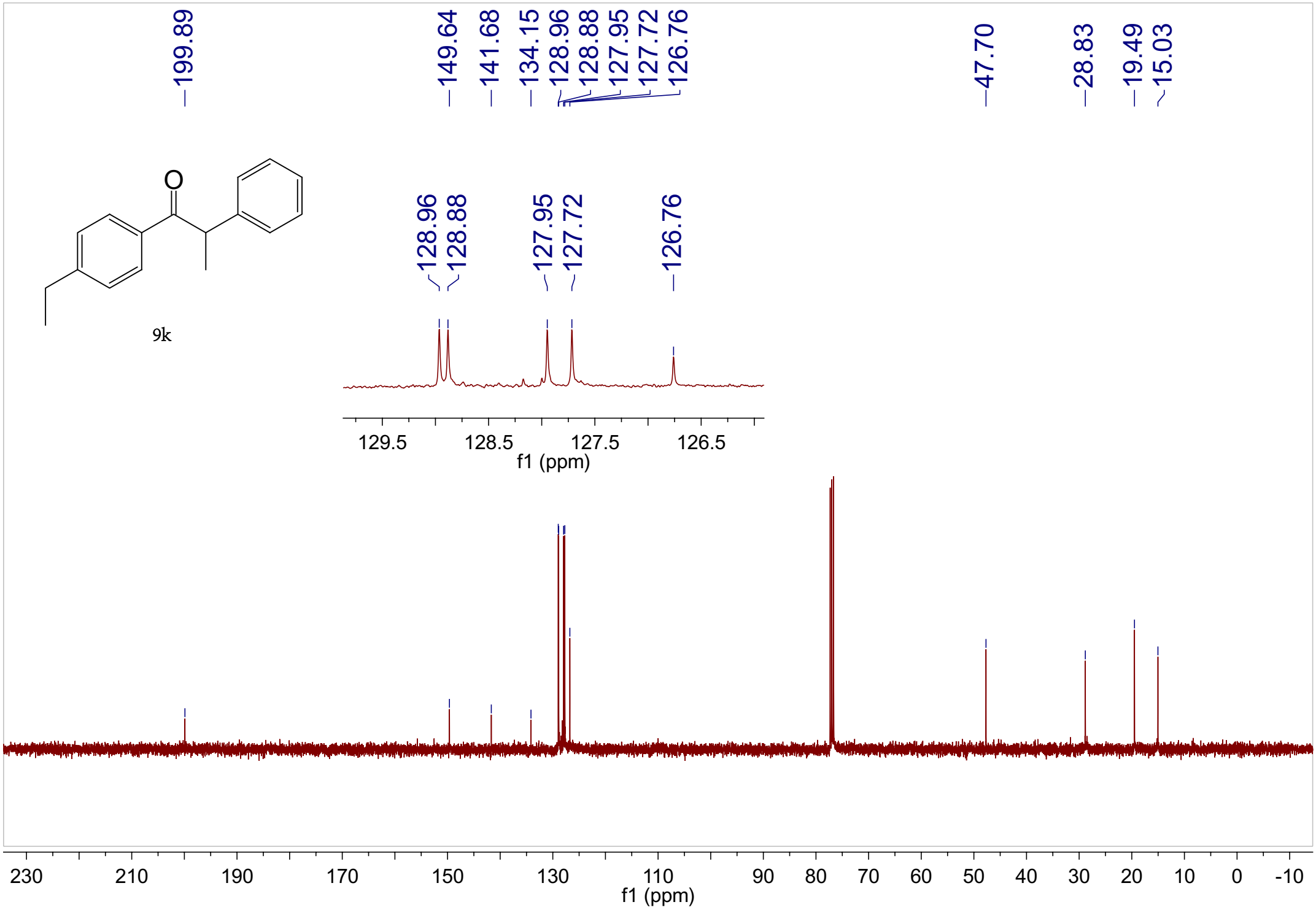

7.98
7.96
7.54
7.51
7.49
7.44
7.41
7.39
7.26
7.24
7.09
7.02
7.01
4.87
4.85
4.83
4.81
1.55
1.53
O
S
9j
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
1.98
1.18
2.09
1.28
0.94
0.93
1.00
3.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

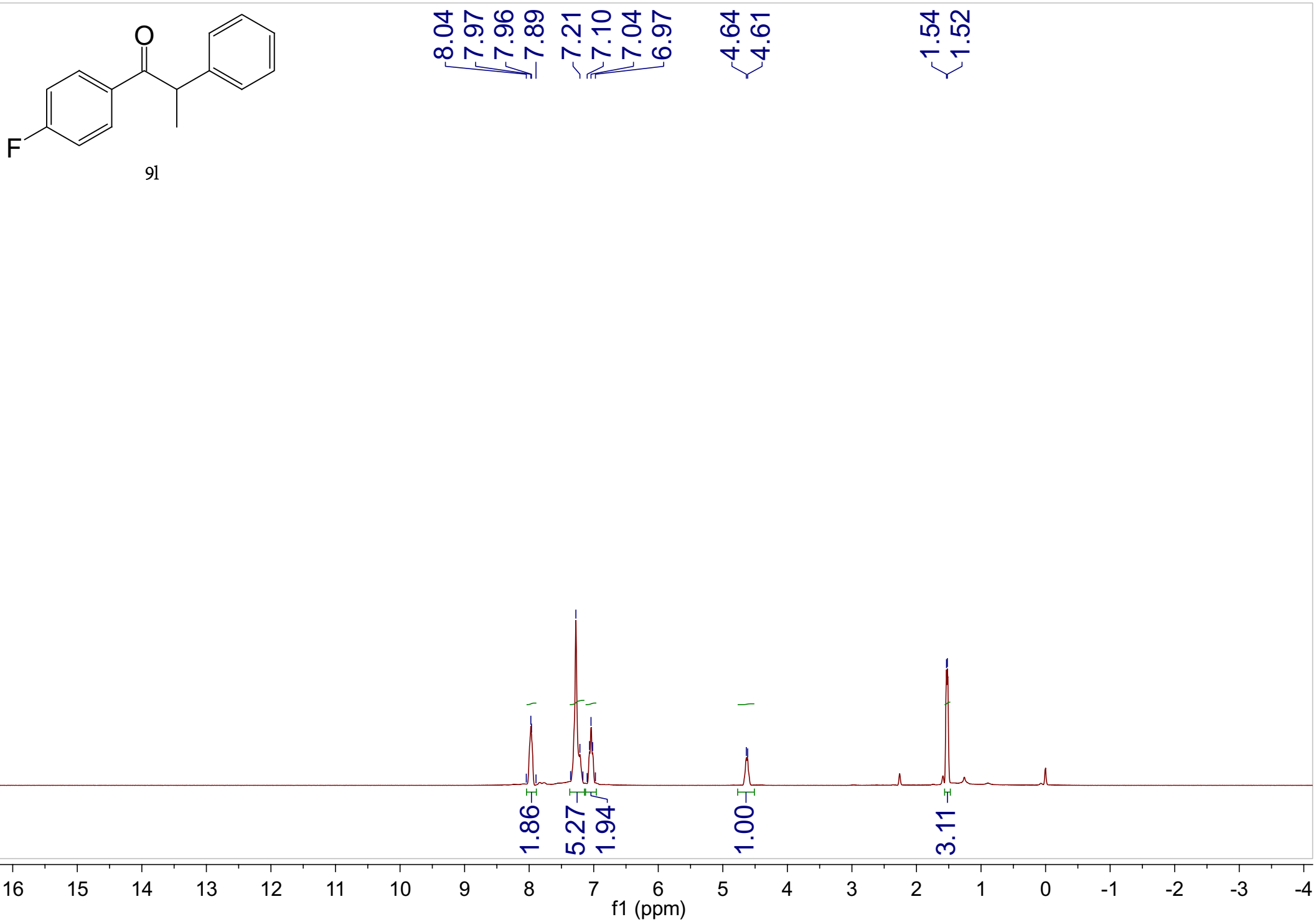

200.10
141.39
136.39
132.86
128.63
128.51
127.07
126.02
121.39
42.85
18.87
O
S
9j
128.63
128.51
129.2
128.8
128.4
128.0
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

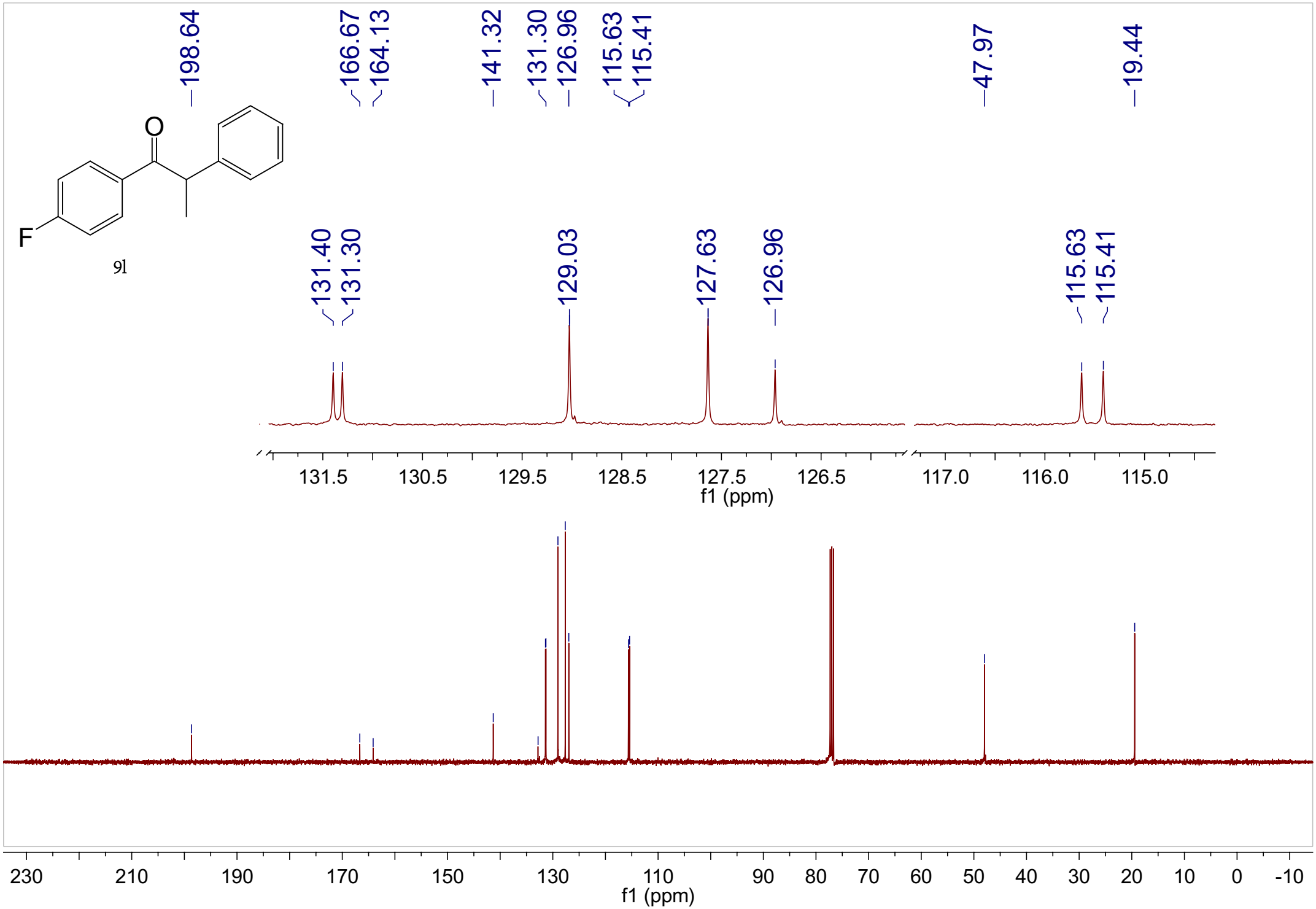


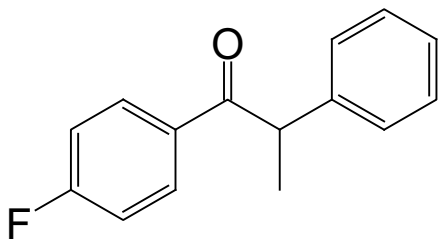
9k

7.90
7.87
7.28
7.21
7.19
4.71
4.68
4.66
4.64
2.65
2.63
2.60
1.53
1.51
1.23
1.21
1.18
2.08
4.40
2.80
1.00
2.07
2.97
3.33
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


199.89
149.64
141.68
134.15
128.96
128.88
127.95
127.72
126.76
47.70
28.83
19.49
15.03
O
9k
128.96
128.88
127.95
127.72
126.76
129.5
128.5
127.5
126.5
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
F
9l
8.04
7.97
7.96
7.89
7.21
7.10
7.04
6.97
4.64
4.61
1.54
1.52
1.86
5.27
1.94
1.00
3.11
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


198.64
166.67
164.13
141.32
131.30
126.96
115.63
115.41
47.97
19.44
O
F
91
131.40
131.30
129.03
127.63
126.96
115.63
115.41
131.5
130.5
129.5
128.5
127.5
126.5
117.0
116.0
115.0
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

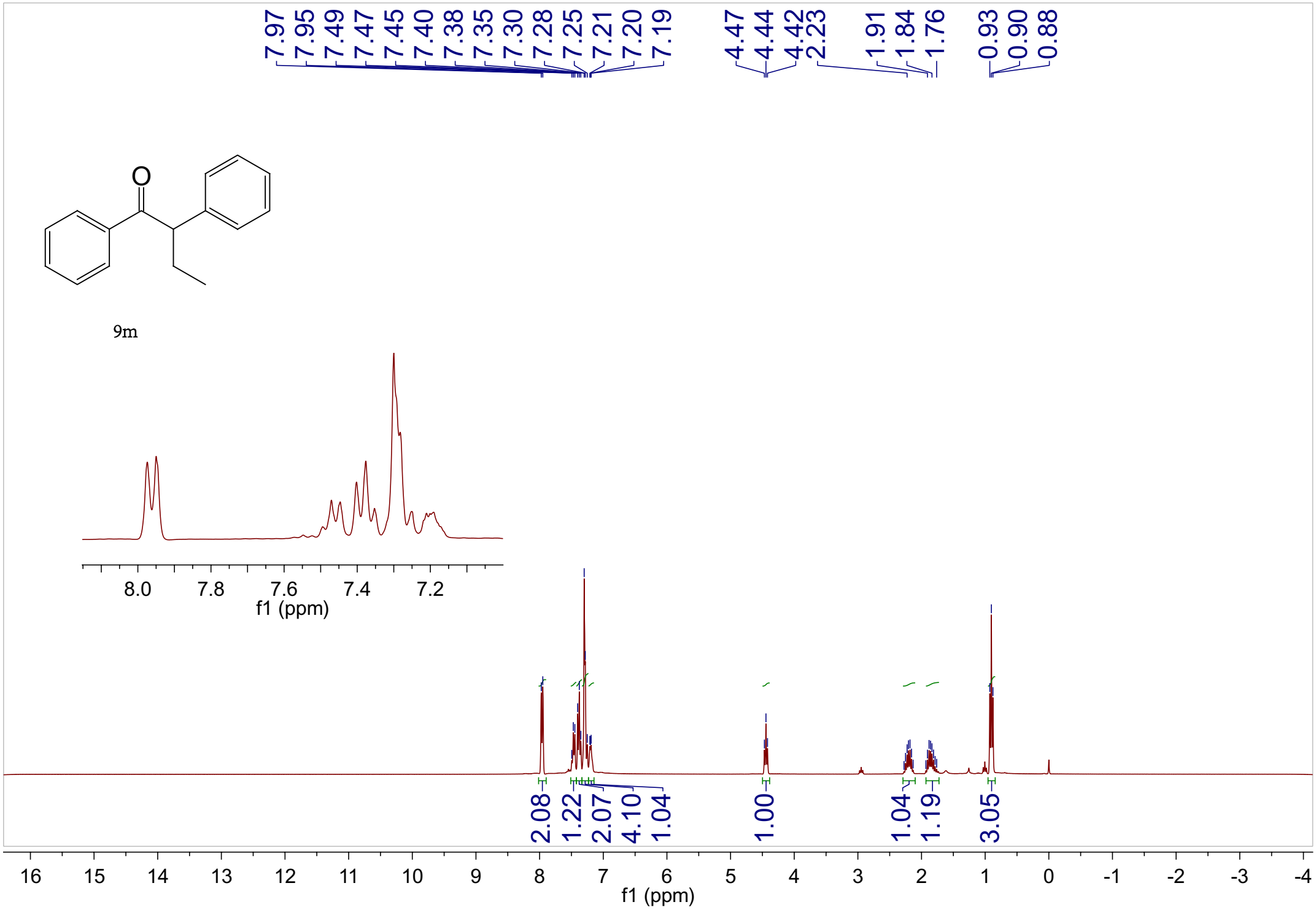


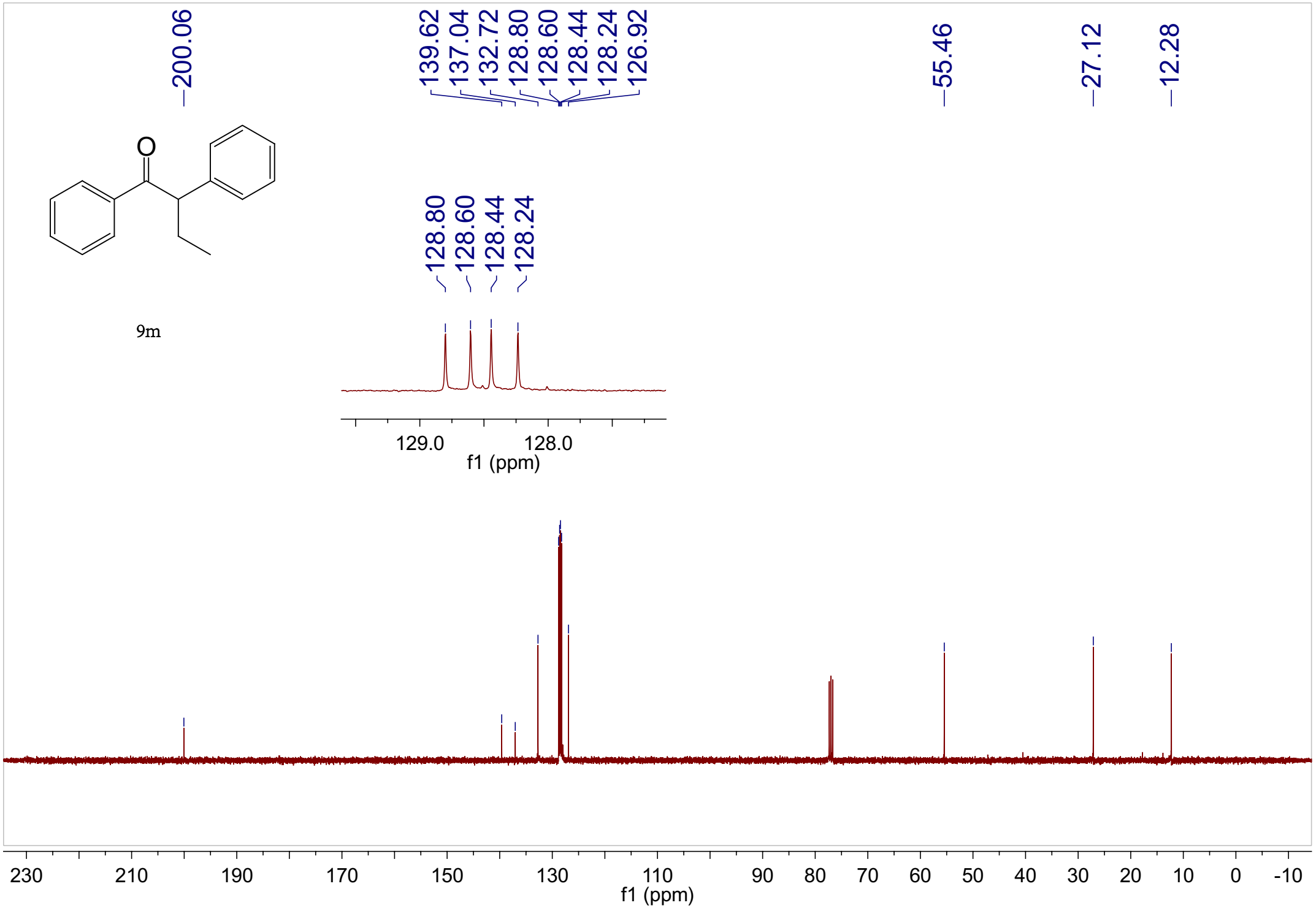
9l

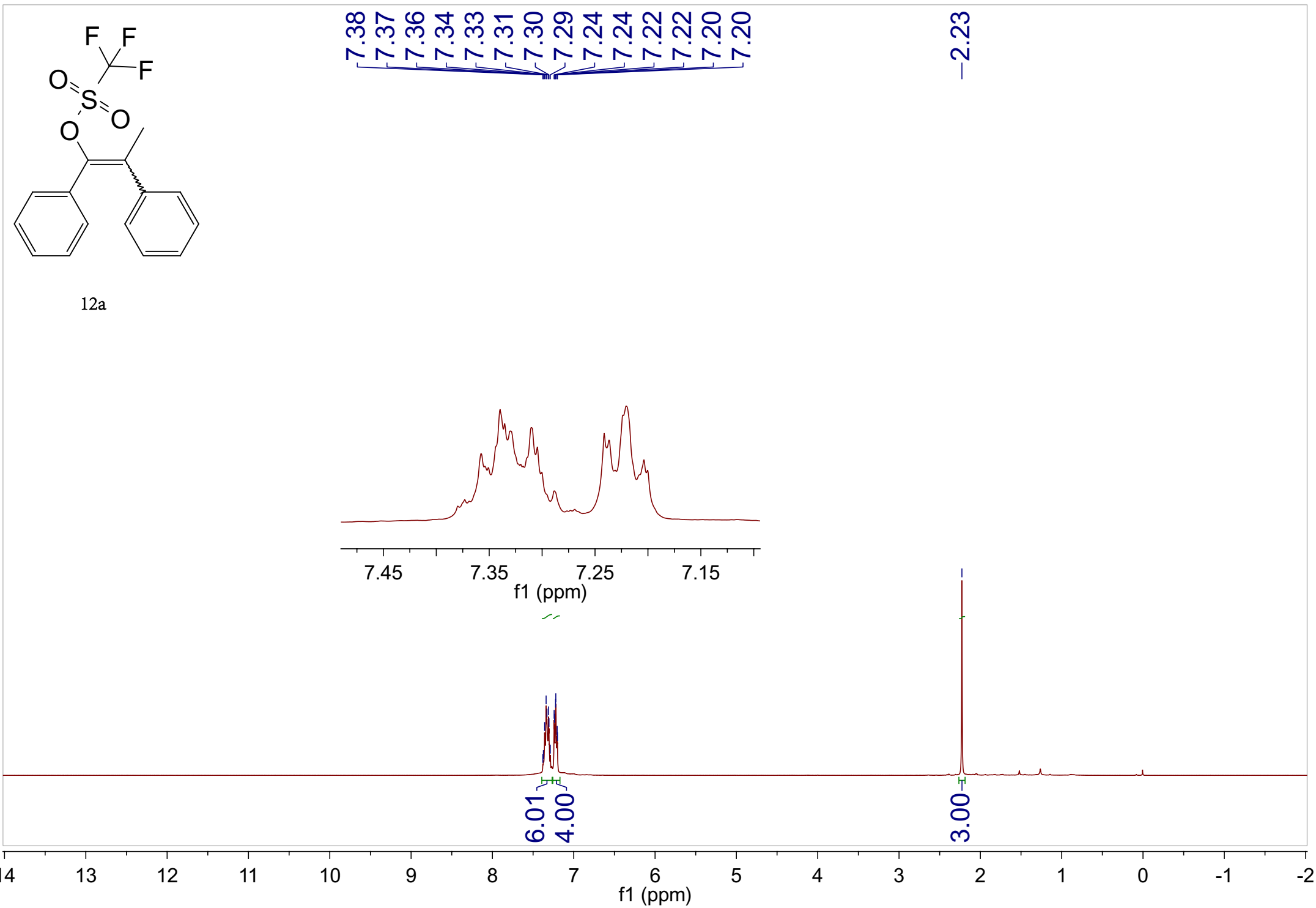
-105.58

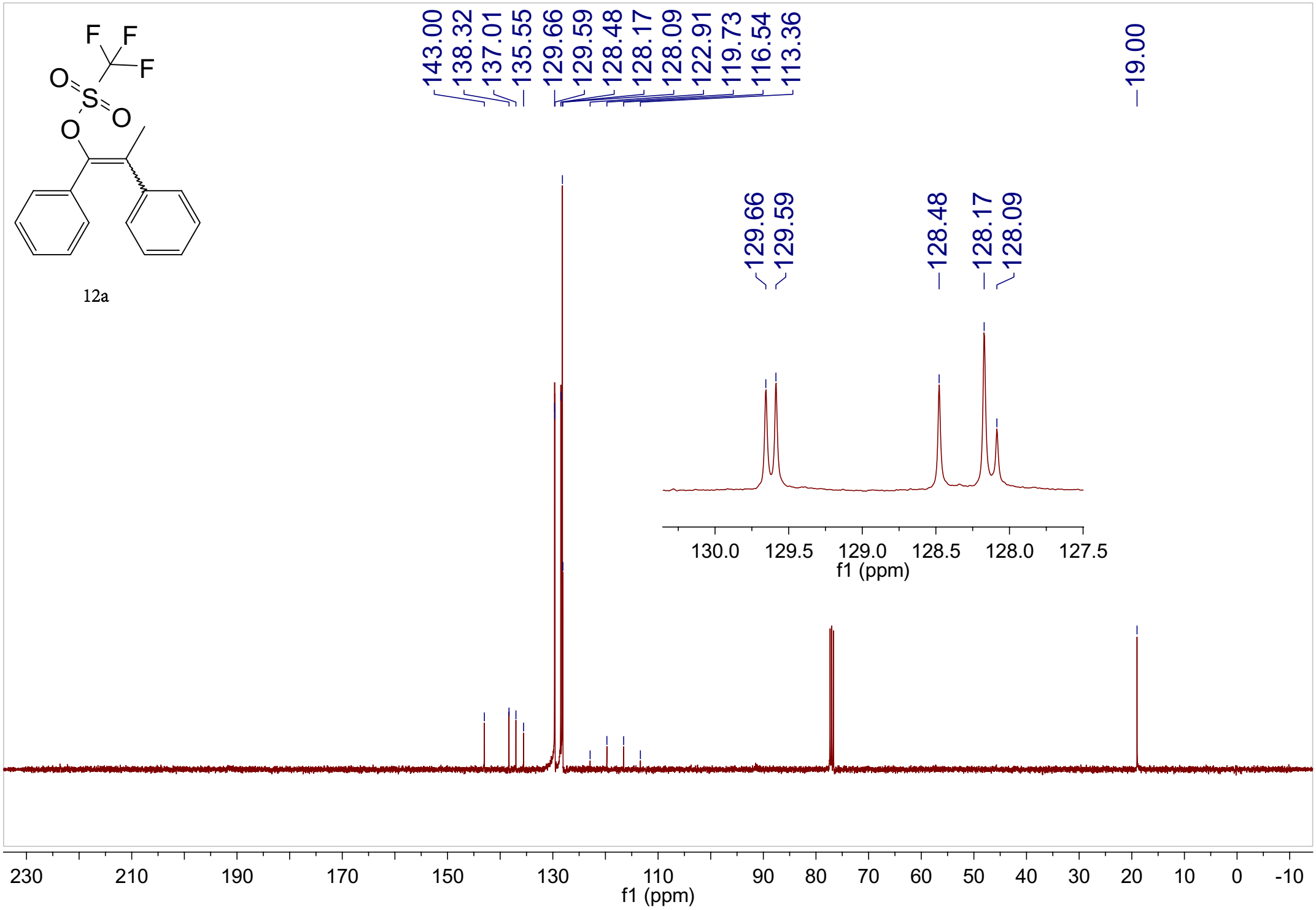
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200

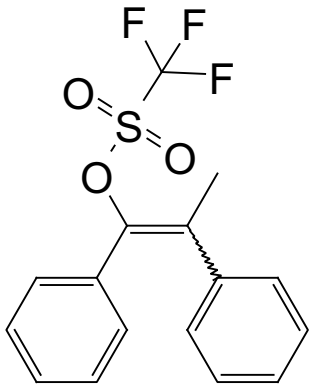
f1 (ppm)


7.97
7.95
7.49
7.47
7.45
7.40
7.38
7.35
7.30
7.28
7.25
7.21
7.20
7.19
4.47
4.44
4.42
2.23
1.91
1.84
1.76
0.93
0.90
0.88
O
9m
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
2.08
1.22
2.07
4.10
1.04
1.00
1.04
1.19
3.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


200.06
139.62
137.04
132.72
128.80
128.60
128.44
128.24
126.92
55.46
27.12
12.28
O
9m
128.80
128.60
128.44
128.24
129.0
128.0
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F F F
O S O
O
12a
7.38 7.37 7.36 7.34 7.33 7.31 7.30 7.29 7.24 7.24 7.22 7.22 7.20 7.20
2.23
7.45 7.35 7.25 7.15
f1 (ppm)
6.01 4.00
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


143.00
138.32
137.01
135.55
129.66
129.59
128.48
128.17
128.09
122.91
119.73
116.54
113.36
19.00
F F F
O S O
O
12a
129.66
129.59
128.48
128.17
128.09
130.0
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
F
F
O
S
O
O

12a

-75.11
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)