Electronic Supplementary Material (ESI) for ChemComm.

Selective Difluoroalkylation of Alkenes by Using Visible Light Photoredox Catalysis

Chunghyeon Yu, Naeem Iqbal, Sehyun Park, and Eun Jin Cho*

Department of Applied Chemistry and Bionanotechnology, Hanyang University, Ansan, Kyeonggi-do 426-791, Republic of Korea

Email: echo@hanyang.ac.kr

Supporting Information

Contents

General considerations

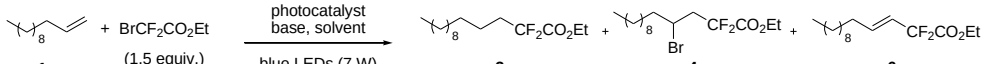
General reagent information

Anhydrous DCM and DMF were purchased from Sigma-Aldrich chemical company in Sure-Seal bottles and degassed by repeated sonication reduced vacuum and replenishing the atmosphere with argon. All reagents including *fac*-[$Ir(ppy)_3$] and $BrCF_2CO_2Et$ were purchased from Sigma-Aldrich, Alfa Aesar, or TCI chemical companies. Flash column chromatography was performed using Merck silica gel 60 (70-230 mesh).

General analytical information

The synthesized alkenes were characterized by ^1H, ^{13}C NMR, and FT-IR spectroscopy, and difluoroalkylated products were characterized by ^1H, ^{13}C, and ^{19}F NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Bruker 400 MHz instrument (400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR, and 377 MHz for ^{19}F NMR). Copies of ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra can be found at the end of the Supporting Information. ^1H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^1H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using KBr plates. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.

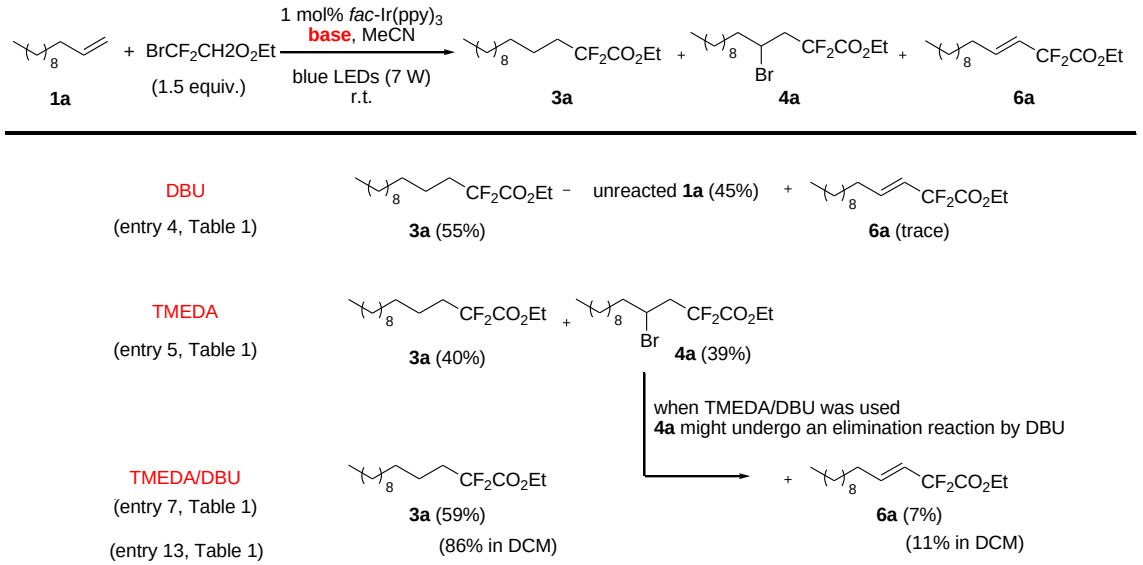
Table S1. Additional Optimization Studies for Selective Difluoroalkylation



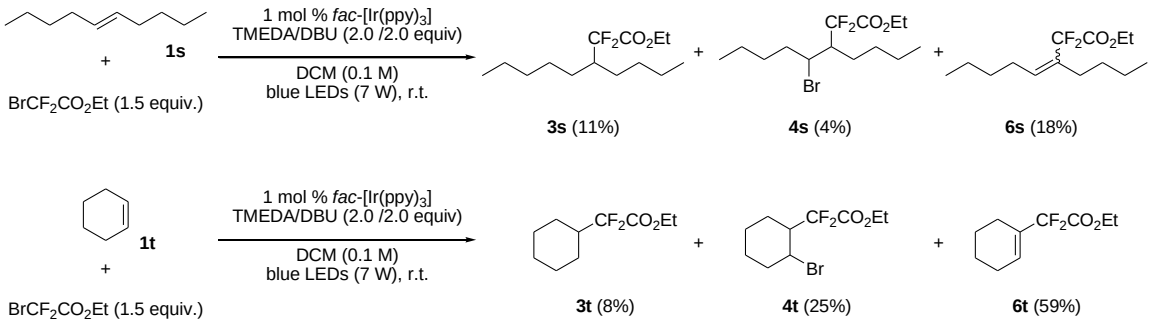
1a **3a** **4a** **6a**

entry	photocatalyst (1 mol%)	base (2 equiv.)	Stoichimetry $BrCF_2CO_2Et$	solvent (0.1 M)	Yield (%)[b]		
					3a	**4a**	**6a**
1	$[Ru(bpy)_3]Cl_2$	TMEDA		MeCN (0.2 M)	30	47	trace
2	$[Ru(bpy)_3]Cl_2$ (0.5 mol%)	TMEDA		MeCN (0.2 M)	25	51	trace
3	$[Ru(bpy)_3]Cl_2$	TMEDA		DCM (0.2 M)	16	39	trace
4	$[Ru(bpy)_3]Cl_2$	TMEDA		THF (0.2 M)	trace	-	trace
5	$[Ru(bpy)_3]Cl_2$	TMEDA		MeOH (0.2 M)	trace	-	trace
6	$[Ru(bpy)_3]Cl_2$	TEA		MeCN (0.2 M)	10	44	trace
7	$[Ru(bpy)_3]Cl_2$	DIPEA		MeCN (0.2 M)	10	17	-
8	$[Ru(bpy)_3]Cl_2$	Lutidine		MeCN (0.2 M)	-	-	trace
9	$[Ru(bpy)_3]Cl_2$	DBU		MeCN (0.2 M)	21	-	-
10	$[Ru(bpy)_3]Cl_2$	DBU		MeCN	30	-	trace
11	$[Ru(phen)_3]Cl_2$	DBU		MeCN	25	-	trace
12	*fac*-$[Ir(dFppy)_3]$	DBU		MeCN	35	-	trace
13	*fac*-$[Ir(ppy)_3]$	DBU		MeCN	55	-	trace
14	*fac*-$[Ir(ppy)_3]$	DBU		DCM	59	6	9
15	*fac*-$[Ir(ppy)_3]$	TMEDA		MeCN	40	39	trace
16	*fac*-$[Ir(ppy)_3]$	K_2CO_3		MeCN	-	99	-
17	*fac*-$[Ir(ppy)_3]$	K_2CO_3		DMF	-	99	-
18	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		MeCN	59	trace	7
19	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		DMF	41	trace	trace
20	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		DMSO	trace	-	-
21	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		THF	34	trace	trace
22	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		1,4-dioxane	75	8	8
23	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		MeOH	80[c]	3	10
24	***fac*-$[Ir(ppy)_3]$**	DBU/TMEDA (2eq : 2eq)		**DCM**	**86**	-	**11**
25	*fac*-$[Ir(ppy)_3]$	DBU/TEA (2eq : 2eq)		DCM	21	7	20
26	*fac*-$[Ir(ppy)_3]$	DBU/DIPEA (2eq : 2eq)		DCM	65	7	10
27	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)		DCM (0.2 M)	46	-	trace
28	*fac*-$[Ir(ppy)_3]$ (0.5 mol%)	DBU/TMEDA (2eq : 2eq)		DCM	40	-	8
29	*fac*-$[Ir(ppy)_3]$ (2.0 mol%)	DBU/TMEDA (2eq : 2eq)		DCM	83	-	10
30	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)	1.0 equiv.	DCM	35	-	-
31	*fac*-$[Ir(ppy)_3]$	DBU/TMEDA (2eq : 2eq)	2.0 equiv.	DCM	78	19	-
32	*fac*-$[Ir(ppy)_3]$	-		DCM	trace	-	-
33	-	DBU/TMEDA (2eq : 2eq)		DCM	-	-	-
34	*fac*-$[Ir(ppy)_3]$(no light)	DBU/TMEDA (2eq : 2eq)		DCM	-	-	-
35	*fac*-$[Ir(ppy)_3]$	K_2CO_3/DBU (2eq : 2eq)		MeCN	49	-	15
36	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		MeCN	-	-	95(16[e])
37	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		1,4-dioxane	trace	(35[e])	96(58[e])
38	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		DMF	trace	-	97(96[e])
39	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		DMSO	trace	(32[e])	87(60[e])
40	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		THF	trace	(24[e])	88(49[e])
41	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		DMF (0.25 M)	trace	-	96(95[e])
42	*fac*-$[Ir(ppy)_3]$	K_2CO_3; DBU (2eq : 2eq)[d]		DMF (0.5 M)	trace	-	98(96[e])

[a]Conditions: **1a** (0.1 mmol), $BrCF_2CO_2Et$ (0.15 mmol), 24 h. [b]Yields were determined by using gas chromatography and ^{19}F NMR spectroscopy with internal standards dodecane and 4-fluorotoluene, respectively. [c]CF_2CO_2Me substituted alkane was formed. [d]DBU was added after complete conversion of **1a** to **4a**. [e]In parenthesis are yields after 1 h reaction times.



Scheme S1. **Base selection for the hydrodifluoroalkylation.**



Scheme S2. **Difluoroalkylations of internal alkenes.**

Experimental Details

Synthesis of hydrodifluoroalkylation of alkenes

An oven-dried resealable tube equipped with a magnetic stir bar was charged with an alkene (0.5 mmol), *fac*-[Ir(ppy)$_3$] (1 mol%, 0.005 mmol), TMEDA (1.0 mmol), DBU (1.0 mmol), and $BrCF_2CO_2Et$ (0.75 mmol) in dichloromethane (5.0 mL, 0.1 M). The tube was sealed with a silicone septum screw cap, and the solution was degassed by bubbling argon through the mixture. The test tube was placed under blue LEDs (7 W) at room temperature for 18-24 h, and the reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with dichloromethane and washed with saturated NH_4Cl solution and brine. The organic

layers were dried over $MgSO_4$, concentrated in vacuo, and purified by flash column chromatography to give the hydrodifluoroalkylated alkane.

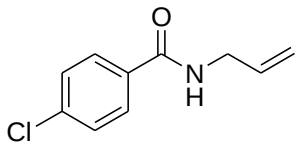
Alkenyl-difluoroalkylations

An oven-dried resealable tube equipped with a magnetic stir bar was charged with an alkene (1.0 mmol), *fac*-[$Ir(ppy)_3$] (1 mol%, 0.01 mmol), K_2CO_3 (2.0 mmol), and $BrCF_2CO_2Et$ (1.5 mmol) in DMF (10.0 mL, 0.1 M). The tube was sealed with a silicone septum screw cap, and the mixture was degassed by bubbling argon through the reaction. The test tube was placed under blue LEDs (7 W) at room temperature. After 1-2 h, DBU (2.0 mmol) was added to the mixture, and the reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with ethyl acetate and washed with saturated NH_4Cl solution and brine. The organic layers were dried over $MgSO_4$, concentrated in vacuo, and purified by flash column chromatography to give the difluoroalkylated alkene.

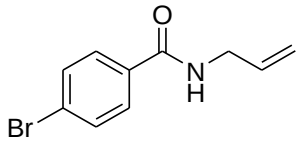
Alkenyl-difluoroalkylations of electron-rich aromatic alkenes

An oven-dried resealable tube equipped with a magnetic stir bar was charged with an alkene (1.0 mmol), *fac*-[$Ir(ppy)_3$] (1 mol%, 0.01 mmol), K_2CO_3 (3.0 mmol), and $BrCF_2CO_2Et$ (1.5 mmol) in DMF (10.0 mL, 0.1 M). The tube was sealed with a silicone septum screw cap, and the mixture was degassed by bubbling argon through the reaction. The test tube was placed under blue LEDs (7 W) at room temperature for 5 h, and the reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with ethyl acetate and washed with saturated NH_4Cl solution and brine. The organic layers were dried over $MgSO_4$, concentrated in vacuo, and purified by flash column chromatography to give the difluoroalkylated alkene.

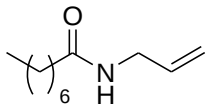
Analytic Data for synthesized alkenes



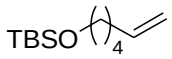
1b: white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.24 (bs, 1H), 5.87 (ddt, *J* = 17.0, 10.2, 5.6 Hz, 1H), 5.20 (ddt, *J* = 17.0, 1.6, 1.2 Hz, 1H), 5.12 (ddt, *J* = 10.2, 1.6, 1.2 Hz, 1H), 4.03-3.98 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.75, 137.65, 134.02, 132.84, 128.70, 128.65, 116.52, 42.57; **IR (neat)**: ν_{max} = 3329, 3076, 1631, 1540, 1300, 1093 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{10}H_{10}ClNO$ [M^+] 195.0451, found 195.0450; R_f 0.33 (hex/EtOAc, 2/1).



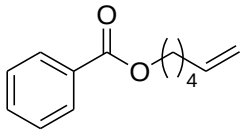
1c: white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.39 (bs, 1H), 5.87 (ddt, *J* = 17.0, 10.2, 5.6 Hz, 1H), 5.19 (ddt, *J* = 17.0, 1.6, 1.2 Hz, 1H), 5.13 (ddt, *J* = 10.2, 1.6, 1.2 Hz, 1H), 4.02-3.96 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.85, 133.97, 133.24, 131.64, 128.82, 126.11, 116.49, 42.54; **IR (neat)**: ν_{max} = 3295, 3074, 2248, 1633, 1538 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{10}H_{10}BrNO$ [M^+] 238.9946, found 238.9946; R_f 0.28 (hex/EtOAc, 2/1).



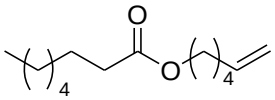
1d: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.18 (bs, 1H), 5.77 (ddt, *J* = 17.2, 10.0, 5.6 Hz, 1H), 5.11 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H), 5.05 (ddt, *J* = 10.0, 1.6, 1.2 Hz, 1H), 3.83-3.78 (m, 2H), 2.15 (t, *J* = 7.6 Hz, 2H), 1.58 (tt, *J* = 7.6, 7.6 Hz, 2H), 1.30-1.16 (m, 8H), 0.82 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.37, 134.54, 166.10, 41.92, 36.76, 31.78, 29.38, 29.12, 25.93, 22.68, 14.13; **IR (neat)**: ν_{max} = 3289, 2927, 1644, 1547 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{11}H_{21}NO$ [M^+] 183.1623, found 183.1624; R_f 0.30 (hexanes:EtOAc, 2/1).



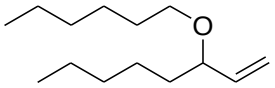
1e: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.81 (ddt, *J* = 16.9, 10.0, 7.0 Hz, 1H), 5.00 (ddt, *J* = 16.9, 2.0, 1.6 Hz, 1H), 4.94 (ddt, *J* = 10.0, 2.0, 1.2 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.06 (dtdd, *J* = 7.0, 6.9, 1.6, 1.2 Hz, 2H), 1.57-1.49 (m, 2H), 1.47-1.38 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.16, 114.57, 63.29, 33.76, 32.52, 26.20, 25.38, 18.59, -5.06; **IR (neat)**: ν_{max} = 2930, 2859, 1472, 1255, 1103 cm^{-1}; R_f 0.83 (only hexanes).



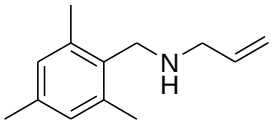
1f: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.55 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.43 (dd, *J* = 8.4, 7.6 Hz, 2H), 5.82 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1H), 5.04 (ddt, *J* = 17.0, 2.0, 1.6 Hz, 1H), 4.98 (ddt, *J* = 10.0, 2.0, 1.2 Hz, 1H), 4.33 (t, *J* = 6.4 Hz, 2H), 2.13 (tddd, *J* = 6.9, 6.8, 1.6, 1.2 Hz, 2H), 1.83-1.75 (m, 2H), 1.60-1.51 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.79, 138.50, 132.98, 130.64, 129.70, 128.49, 115.05, 65.04, 33.50, 28.34, 25.48; **IR (neat)**: ν_{max} = 2938, 2861, 1720, 1641, 1452, 1274 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{13}H_{16}O_2$ [M^+] 204.1150, found 204.1153; R_f 0.63 (hex/EtOAc, 8/1).



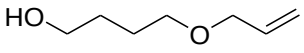
1g: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.79 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.01 (ddt, *J* = 17.2, 2.0, 1.6 Hz, 1H), 4.96 (ddt, *J* = 10.0, 2.0, 1.2 Hz, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 2.08 (tddd, *J* = 6.9, 6.8, 1.6, 1.2 Hz, 2H), 1.68-1.58 (m, 2H), 1.50-1.41 (m, 2H), 1.35-1.25 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.93, 138.37, 114.87, 64.17, 34.44, 33.39, 31.78, 29.22, 29.04, 28.21, 25.32, 25.11, 22.70, 14.12; **IR (neat)**: ν_{max} = 2929, 2858, 1740, 1641, 1459, 1168 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{14}H_{26}O_2$ [M^+] 226.1933, found 226.1936; R_f 0.70 (hex/EtOAc, 8/1).



1h: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.71-5.63 (m, 1H), 5.17 -5.11 (m, 2H), 3.57 (ddd, *J* = 7.2, 7.0, 6.8 Hz, 1H), 3.47 (dt, *J* = 9.2, 6.8 Hz, 1H), 3.23 (dt, *J* = 9.2, 6.8 Hz, 1H), 1.60-1.49 (m, 4H), 1.45-1.20 (m, 12H), 0.88 (t, *J* = 6.2 Hz, 3H), 0.87 (t, *J* = 6.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.96, 116.23, 81.54, 68.75, 35.68, 31.99, 31.90, 30.07, 26.11, 25.28, 22.82, 22.80, 14.22; **IR (neat)**: ν_{max} = 2931, 2859, 1466, 1097, 922 cm^{-1}; R_f 0.61 (only hexanes).



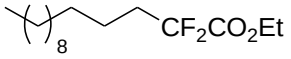
1i: solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.86 (s, 2H), 5.99 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.27 (ddt, *J* = 16.8, 1.6, 1.6 Hz, 1H), 5.18 (ddt, *J* = 10.4, 1.6, 1.2 Hz, 1H), 3.77 (s, 2H), 3.38 (bs, 1H), 3.34 (ddd, *J* = 6.4, 1.6, 1.6 Hz, 2H), 2.39 (s, 6H), 2.26 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.32, 137.04, 135.04, 132.38, 129.23, 117.39, 52.35, 46.47, 21.06, 19.80; **IR (neat)**: ν_{max} = 2916, 2858, 1613, 1448 cm^{-1}; R_f 0.69 (only hexanes).



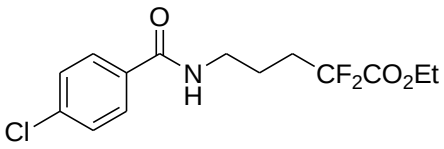
1j: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.64 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 4.93 (ddt, *J* = 17.2, 1.6, 1.2 Hz, 1H), 4.83 (ddt, *J* = 10.4, 1.6, 1.2 Hz, 1H), 3.91 (bs, 1H), 3.63 (ddd, *J* = 5.6, 1.2, 1.2 Hz, 2H), 3.25 (t, *J* = 6.2 Hz, 2H), 3.13 (t, *J* = 6.0 Hz, 2H), 1.37-1.23 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.51, 116.51, 71.54, 70.01, 61.86, 29.41, 26.17; **IR (neat)**: ν_{max} = 3384, 2940, 2886, 1647, 1347, 1061 cm^{-1}; **HRMS** m/z (FAB) calc. for $C_7H_{15}O_2$ $[M+H]^+$ 131.1072, found 131.1070; R_f 0.18 (hex/EtOAc, 4/1).

Analytic Data for Synthesized Difluoroalkylated Products

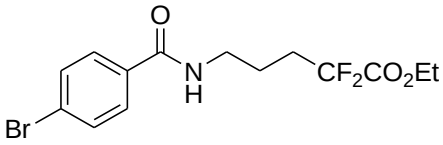
Analytic Data for hydrodifluoroalkylated products



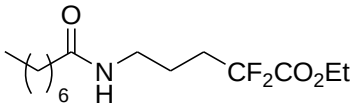
3a: colorless oil; **^{1}H NMR (400 MHz, CDCl3)** δ 4.31 (q, *J* = 7.2, 2H), 2.16-1.96 (m, 2H), 1.34 (t, *J* = 7.2, 3H), 1.38-1.21 (m, 20H), 0.87 (t, *J* = 6.8, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.29 (t, *J* = 33.2 Hz), 116.55 (t, *J* = 248.3 Hz), 62.75, 34.68 (t, *J* = 23.3 Hz), 32.1, 29.81, 29.76, 29.57, 29.53, 29.42, 29.24, 28.31, 22.85, 21.62 (t, *J* = 4.4 Hz), 14.2, 14.05; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.97; **IR (neat)**: ν_{max} = 2927, 2856, 1771, 1467, 1192, 1093 cm^{-1}; ***R*$_f$** 0.54 (only hexanes).



3b: yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.49 (bs, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.48 (td, *J* = 6.8, 6.4 Hz, 2H), 2.14 (tt, *J* = 16.8, 7.6 Hz, 2H), 1.86-1.76 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.87, 164.29 (t, *J* = 32.7 Hz), 137.95, 132.89, 129.00, 128.51, 116.17 (t, *J* = 251.3 Hz), 63.20, 39.37, 32.03 (t, *J* = 23.7 Hz), 22.07 (t, *J* = 4.0 Hz), 14.10; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.77; **IR (neat)**: ν_{max} = 3307, 1762, 1639, 1095 cm^{-1}; ***R*$_f$** 0.49 (hex/EtOAc, 2/1).

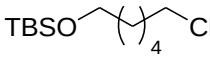


3c: yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 6.46 (bs, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.48 (td, *J* = 6.8, 6.4 Hz, 2H), 2.15 (tt, *J* = 16.8, 7.6 Hz, 2H), 1.86-1.76 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.95, 164.27 (t, *J* = 32.9 Hz), 133.31, 131.97, 128.67, 126.39, 116.14 (t, *J* = 251.2 Hz), 63.20, 39.35, 32.00 (t, *J* = 23.7 Hz), 22.04 (t, *J* = 4.0 Hz), 14.09; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.77; ***R*$_f$** 0.43 (hex/EtOAc, 2/1).

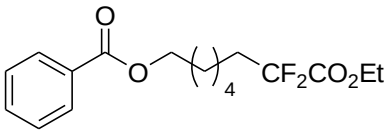


3d: yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.60 (bs, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.27 (td, *J* = 6.8, 6.0 Hz, 2H), 2.12 (t, *J* = 7.3 Hz, 2H), 2.03 (tt, *J* = 16.4, 8.4 Hz, 2H), 1.72-1.67 (m, 2H) , 1.67-1.58 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.28-1.20 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.57, 164.31 (t, *J* = 33.3 Hz), 116.19 (t, *J* = 251.5 Hz), 63.15, 38.65, 36.98, 32.02 (t, *J* = 24.2 Hz), 31.85, 29.43, 29.19, 25.94, 22.78, 22.18 (t, *J* = 4.0 Hz), 14.24,

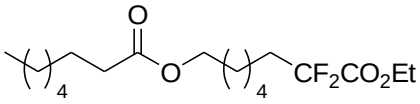
14.13; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.95; **IR (neat)**: ν_{max} = 3370, 1637, 1142 cm^{-1}; $\boldsymbol{R_f}$ 0.41 (hex/EtOAc, 2/1).



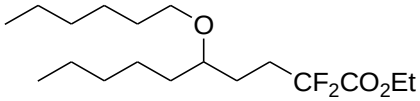
3e: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.35 (q, *J* = 7.0 Hz, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.03 (tt, *J* = 16.8, 7.6 Hz, 2H), 1.60-1.40 (m, 4H), 1.39-1.27 (m, 4H), 1.34 (t, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.61 (t, *J* = 35.5 Hz), 137.93, 116.56 (t, *J* = 250.7 Hz), 63.22, 62.86, 34.64 (t, *J* = 23.2 Hz), 32.75, 29.06, 26.15, 25.67, 21.64 (t, J = 4.3 Hz), 18.54, 14.15, -5.12; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.97; **IR (neat)**: ν_{max} = 2933, 2859, 1771, 1256, 1100 cm^{-1}; $\boldsymbol{R_f}$ 0.62 (only hexanes).



3f: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 7.4, 7.2 Hz, 2H), 4.29 (q, *J* = 7.0 Hz), 4.28 (t, *J* = 6.8 Hz), 2.01 (tt, *J* = 16.4, 7.2 Hz, 2H), 1.86-1.68 (m, 2H), 1.63-1.52 (m, 2H), 1.52-1.35 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.71, 164.46 (t, *J* = 33.1 Hz), 132.97, 130.55, 129.63, 128.46, 116.43 (t, *J* = 250.9 Hz), 64.93, 62.83, 34.49 (t, *J* = 23.2 Hz), 28.82, 28.61, 25.85, 21.49 (t, *J* = 4.1 Hz), 14.05; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.93; **IR (neat)**: ν_{max} = 2942, 1768, 1720, 1276, 1114 cm^{-1}; $\boldsymbol{R_f}$ 0.58 (hex/EtOAc, 4/1).

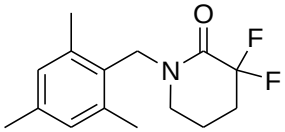


3g: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.29 (q, *J* = 7.2 Hz, 2H), 4.02 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.03 (tt, *J* = 16.4, 7.6 Hz, 2H), 1.65-1.53 (m, 4H), 1.53-1.46 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.29-1.18 (m, 12H), 0.84 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.13, 164.55 (t, *J* = 32.8 Hz), 116.46 (t, *J* = 250.9 Hz), 64.25, 62.91, 34.54, 34.50 (t, *J* = 19.1 Hz), 31.84, 29.29, 29.10, 28.86, 28.60, 25.81, 25.18, 22.77, 21.53 (t, *J* = 4.2 Hz), 14.22, 14.14 (t, *J* = 2.8 Hz); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -105.99; **IR (neat)**: ν_{max} = 2932, 2859, 1770, 1736, 1183 cm^{-1}; $\boldsymbol{R_f}$ 0.61 (hex/EtOAc, 4/1).



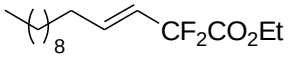
3h: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.30 (q, *J* = 7.2 Hz, 2H), 3.45-3.31 (m, 2H), 3.30-3.25 (m, 1H), 2.24-2.00 (m, 2H), 1.73-1.64 (m, 2H), 1.61-1.45 (m, 4H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.37-1.22 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.54 (t, *J* = 33.3 Hz), 140.51 (t, *J* = 8.2 Hz), 116.73 (t, *J* = 250.7

Hz), 78.22, 69.12, 62.88, 33.90, 32.13, 31.85, 30.47 (t, *J* = 23.3 Hz), 30.37, 26.09, 25.63, 24.98, 22.79, 22.72, 14.18; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -104.69; **IR (neat)**: ν_{max} = 2934, 2870, 1771, 1141, 1091 cm^{-1}; ***R**$_f$* 0.57 (only hexanes).

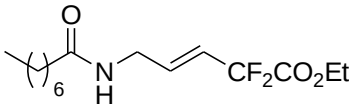


3i: colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.87 (s, 2H), 4.14 (s, 2H), 3.00 (t, *J* = 6.2 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 6H), 1.88 (tt, *J* = 9.2, 4.0 Hz, 2H), 1.25 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.69 (t, *J* = 29.3), 138.32, 137.99, 129.65, 128.33, 112.92 (t, *J* = 242.5, Hz), 44.55, 43.53, 32.12 (t, *J* = 22.9, Hz), 21.11, 20.16, 19.28 (t, *J* = 5.2, Hz); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -99.95; **HRMS** *m/z* (EI) calc. for $C_{15}H_{19}F_2NO$ [M$^+$] 267.1435, found 267.1430; ***R**$_f$* 0.51 (hex/EtOAc, 4/1).

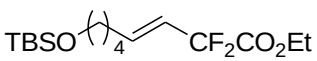
Analytic Data for alkenyl-CF_2CO_2Et compounds



6a: colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.27 (dtt, *J* = 15.8, 6.8, 2.6 Hz, 1H), 5.66 (dtt, *J* = 15.8, 11.1, 1.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.18-2.08 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.46-1.21 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.43 (t, *J* = 34.9 Hz), 140.26 (t, *J* = 8.9 Hz), 121.12 (t, *J* = 25.1 Hz), 112.62 (t, *J* = 248.4 Hz), 63.06, 32.11, 29.79, 29.75, 29.59, 29.53, 29.25, 28.33, 22.89, 14.32, 14.15; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -103.01; **IR (neat)**: ν_{max} = 2926, 2855, 1769, 1674, 1083 cm^{-1}; ***R**$_f$* 0.75 (hex/EtOAc, 8/1).

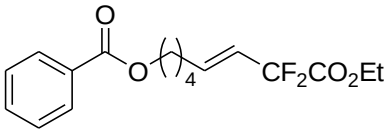


6d: yellow oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.26 (dtt, *J* = 15.8, 5.2, 1.8 Hz, 1H), 5.79 (dtt, *J* = 15.8, 11.2, 3.6 Hz, 1H), 5.66 (bs, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.02-3.95 (m, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.67-1.57 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.31-1.22(m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.35, 163.87 (t, *J* = 35.8 Hz), 135.80 (t, *J* = 8.8 Hz), 122.21 (t, *J* = 25.6 Hz), 112.21 (t, *J* = 249.2 Hz), 63.34, 39.96, 36.80, 31.84, 29.42, 29.17, 25.86, 22.77, 14.23, 14.09; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -103.42; **IR (neat)**: ν_{max} = 3288, 2870, 1768, 1650, 1142 cm^{-1}; **HRMS** *m/z* (FAB) calc. for $C_{10}H_{16}F_2NO_3$ [M+H]$^+$ 236.1020, found 236.1100; ***R**$_f$* 0.59 (hex/EtOAc, 1/1).

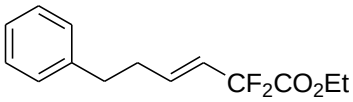


6e: colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.27 (dtt, *J* = 15.6, 6.8, 2.8 Hz, 1H), 5.67 (dtt, *J* = 15.6, 11.2, 1.6 Hz, 1H), 4.32 (q, *J* =

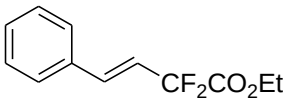
7.2 Hz, 2H), 3.60 (t, *J* = 6.0 Hz, 2H), 2.20-2.12 (m, 2H), 1.57-1.43 (m, 4H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.37 (t, *J* = 35.0 Hz), 139.98 (t, *J* = 8.9 Hz), 121.32 (t, *J* = 25.1 Hz), 112.56 (t, *J* = 248.3 Hz), 63.06, 62.96, 32.32, 31.85, 26.15, 24.69, 18.55, 14.14, -5.11; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.01; **IR (neat)**: ν_{max} = 2932, 2860, 1770, 1134, 1099 cm^{-1}; ***R*$_f$** 0.71 (hex/EtOAc, 4/1).



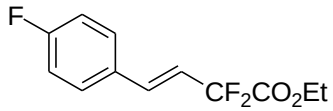
6f: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.55 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.43 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.28 (dtt, *J* = 15.8, 6.8, 2.6 Hz, 1H), 5.76 (dtt, *J* = 15.8 11.0, 1.6 Hz, 1H), 4.32 (t, *J* = 6.4 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.27-2.18 (m, 2H), 1.78 (tt, *J* = 7.0, 6.8 Hz, 2H), 1.60 (tt, *J* = 7.6, 7.0 Hz, 2H), 1.32 (t, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.74, 164.22 (t, *J* = 34.9 Hz), 139.31 (t, *J* = 9.1 Hz), 133.08, 130.44, 129.67, 128.52, 121.70 (t, *J* = 25.1 Hz), 112.41 (t, *J* = 253.6 Hz), 64.68, 63.07, 31.59, 28.28, 24.83, 14.07; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.06; **IR (neat)**: ν_{max} = 2942, 2864, 1767, 1719, 1275 cm^{-1}; ***R*$_f$** 0.50 (hex/EtOAc, 4/1).



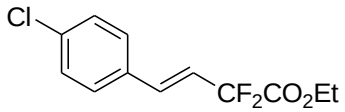
6k: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.24-7.16 (m, 3H), 6.33 (dtt, *J* = 15.6, 6.8, 2.6 Hz, 1H), 5.72 (dtt, *J* = 15.6, 11.0, 1.6 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.52-2.44 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.23 (t, *J* = 34.8 Hz), 140.87, 138.98 (t, *J* = 9.0 Hz), 128.63, 128.58, 126.35, 121.87 (t, *J* = 25.1 Hz), 112.44 (t, *J* = 248.6 Hz), 63.09, 34.68, 33.80, 14.11; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.17; **IR (neat)**: ν_{max} = 2988, 2870, 1767, 1142, 1077 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{14}H_{16}F_2O_2$ [M^+] 254.1118, found 254.1120; ***R*$_f$** 0.63 (hex/EtOAc, 4/1).



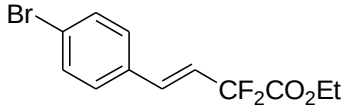
6l: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.42-7.33 (m, 3H), 7.09 (dt, *J* = 16.4, 2.4 Hz, 1H), 6.32 (dt, *J* = 16.4, 11.4 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.13 (t, *J* = 35.0 Hz), 137.03 (t, *J* = 9.4 Hz), 129.85, 129.04, 128.40, 127.65, 119.01 (t, *J* = 25.1 Hz), 112.94 (t, *J* = 249.5 Hz), 63.33, 14.15; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.24; **IR (neat)**: ν_{max} = 2987, 2871, 1767, 1075 cm^{-1}; ***R*$_f$** 0.63 (hex/EtOAc, 4/1).



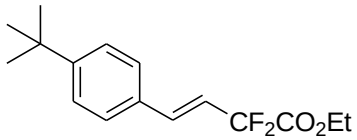
6m: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.06 (dd, *J* = 8.6, 8.6 Hz, 2H), 7.04 (dt, *J* = 16.2, 2.6 Hz, 1H), 6.23 (dt, *J* = 16.2, 11.2 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.07 (t, *J* = 35.0 Hz), 163.68 (d, *J* = 251.5 Hz), 135.82 (t, *J* = 9.5 Hz), 130.52 (d, *J* = 3.0 Hz), 129.46 (d, *J* = 8.0 Hz), 118.79 (td, *J* = 25.3, 2.0 Hz), 116.13 (d, *J* = 22.2 Hz), 112.83 (t, *J* = 249.6 Hz), 63.38, 14.15; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.21, -110.87; **IR (neat)**: ν_{max} = 2987, 1767, 1511, 1225, 1077 cm^{-1}; R_f 0.60 (hex/EtOAc, 4/1).



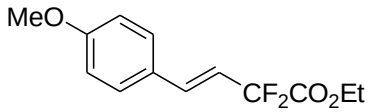
6n: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.03 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.28 (dt, *J* = 16.2, 11.4 Hz, 1H), 3.85 (q, *J* = 7.2 Hz, 2H) 1.36 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.96 (t, *J* = 34.9 Hz), 135.75 (t, *J* = 9.5 Hz), 135.71, 132.77, 129.28, 128.85, 119.62 (t, *J* = 25.1 Hz), 112.73 (t, *J* = 249.7 Hz), 63.41, 14.14; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.34; **IR (neat)**: ν_{max} = 2985, 1767, 1658, 1493, 1075 cm^{-1}; ***R_f*** 0.65 (hex/EtOAc, 4/1).



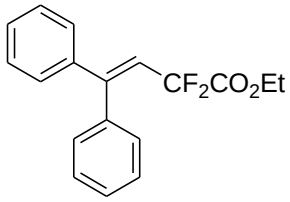
6o: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.02 (dt, *J* = 16.0, 2.4 Hz, 1H), 6.30 (dt, *J* = 16.0, 11.4 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.36(t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.94 (t, *J* = 34.8 Hz), 135.84 (t, *J* = 9.5 Hz), 133.21, 132.25, 129.11, 124.00, 119.75 (t, *J* = 25.1 Hz), 112.71 (t, *J* = 249.8 Hz), 63.43, 14.16; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.39; ***R_f*** 0.62 (hex/EtOAc, 4/1).



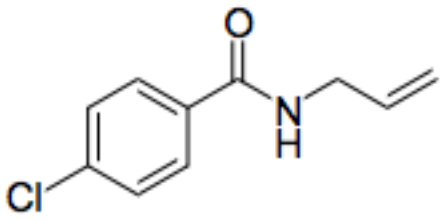
6p: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (s, 4H), 7.06 (dt, *J* = 16.2, 2.6 Hz, 1H), 6.27 (dt, *J* = 16.2, 11.6 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.25 (t, *J* = 35.4 Hz), 153.29, 136.83 (t, *J* = 9.1 Hz), 131.57, 127.45, 126.01, 118.19 (t, *J* = 25.3 Hz), 113.08 (t, *J* = 249.5 Hz), 63.27, 35.00, 31.40, 14.18; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -103.14; **IR (neat)**: ν_{max} = 2969, 2870, 1768, 1142, 1074 cm^{-1}; **HRMS** *m/z* (EI) calc. for $C_{16}H_{20}F_2O_2$ [M^+] 282.1431, found 282.1428; ***R_f*** 0.68 (hex/EtOAc, 4/1).



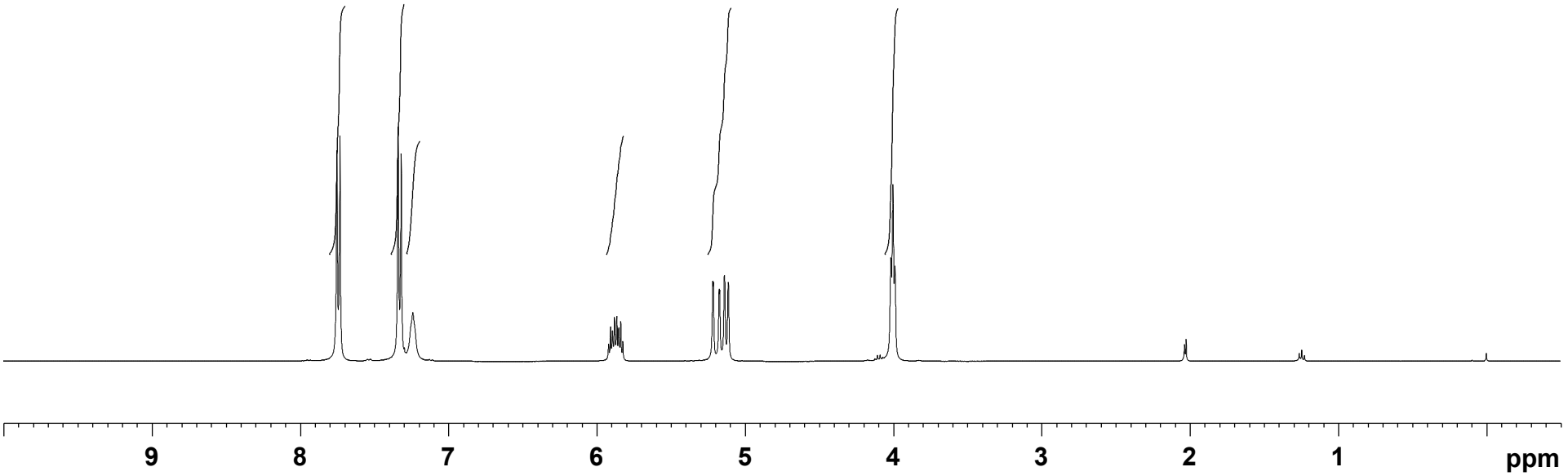
6q: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.02 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.89 (d, *J* = 8.8, Hz, 2H), 6.17 (dt, *J* = 16.2, 11.2 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.26 (t, *J* = 35.3 Hz), 160.95, 136.47 (t, *J* = 9.5 Hz), 129.08, 126.93, 116.48 (t, *J* = 25.1 Hz), 114.39, 113.16 (t, *J* = 249.2 Hz), 63.20, 55.47, 14.10; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -102.64; **IR (neat)**: ν_{max} = 1766, 1607, 1514, 1076 cm^{-1}; ***R*$_f$** 0.51 (hex/EtOAc, 4/1).

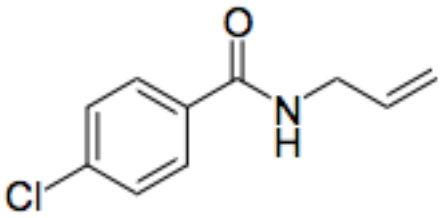


6r: colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.31 (m, 3H), 7.31-7.21 (m, 5H), 7.21-7.16 (m, 2H), 6.25 (t, *J* = 11.6 Hz, 1H), 3.87 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.57 (t, *J* = 34.1 Hz), 151.14 (t, *J* = 9.5 Hz), 140.58, 137.21, 129.99, 129.25, 128.73, 128.54, 128.15, 128.03, 119.63 (t, *J* = 28.5 Hz), 112.71 (t, *J* = 245.8 Hz), 62.89, 13.80; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.76; **IR (neat)**: ν_{max} = 1771, 1637, 1102, 1066 cm^{-1}; ***R*$_f$** 0.56 (hex/EtOAc, 4/1).

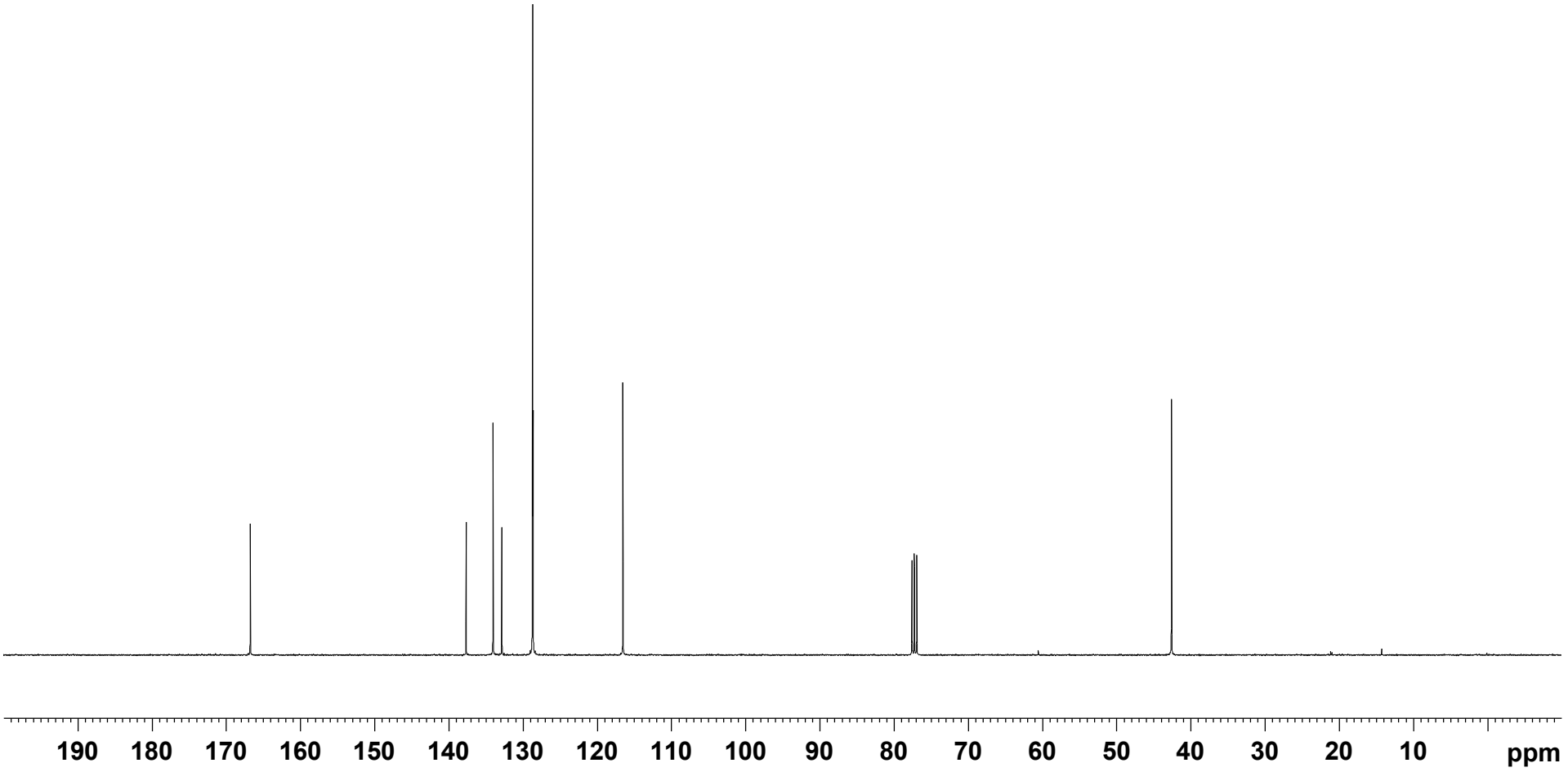


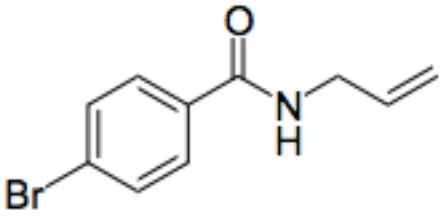
1b : ^{1}H NMR



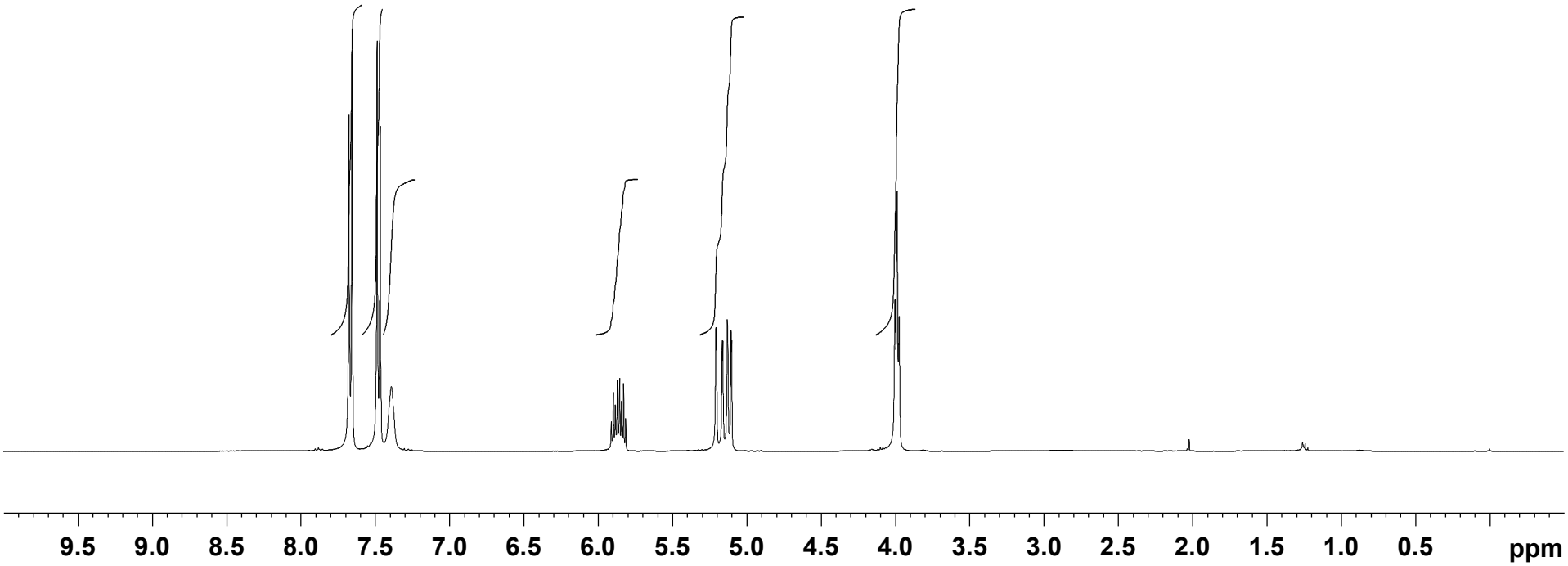

O
N
H
Cl

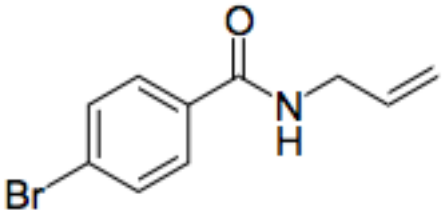
1b : ^{13}C NMR


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

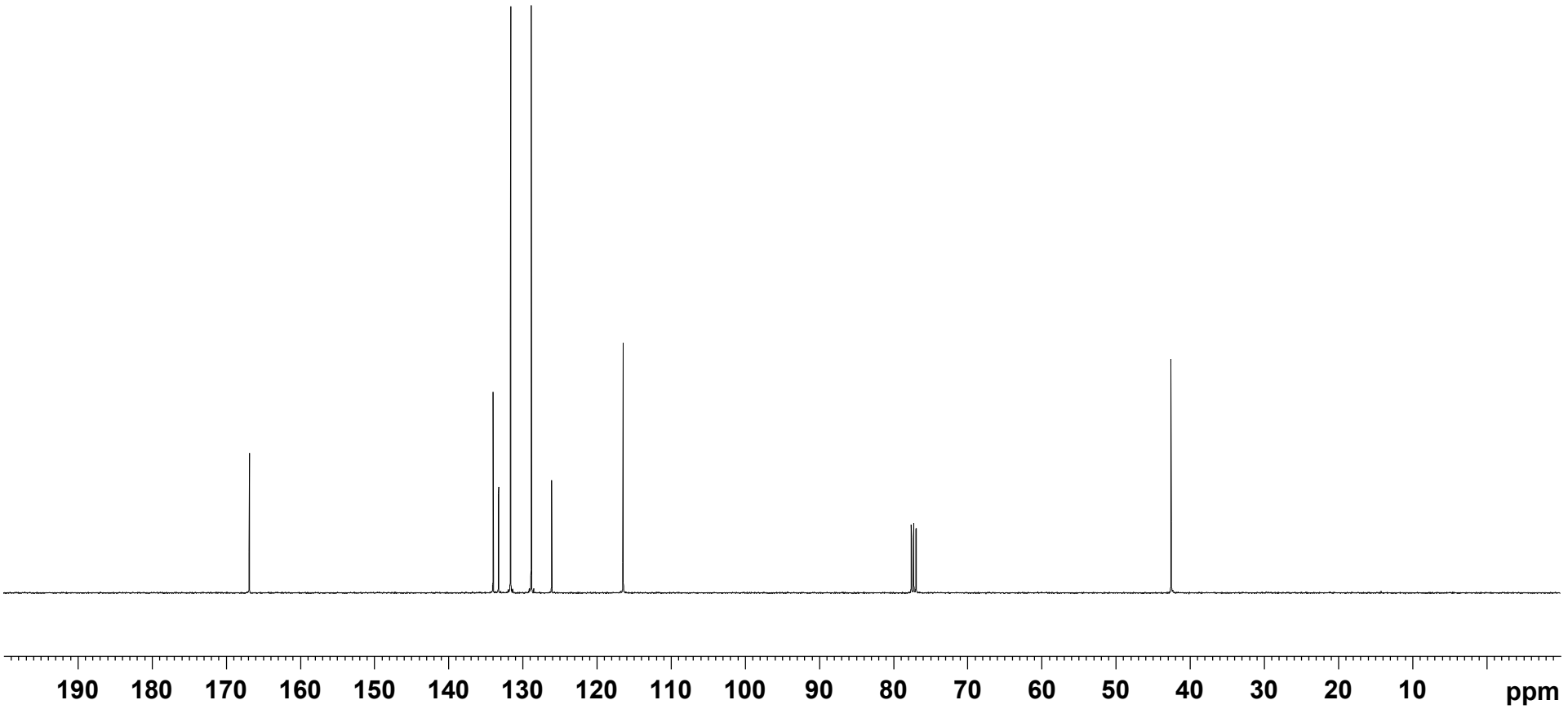


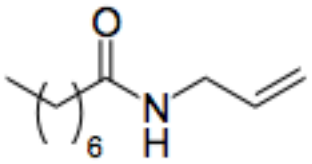
1c : ^{1}H NMR



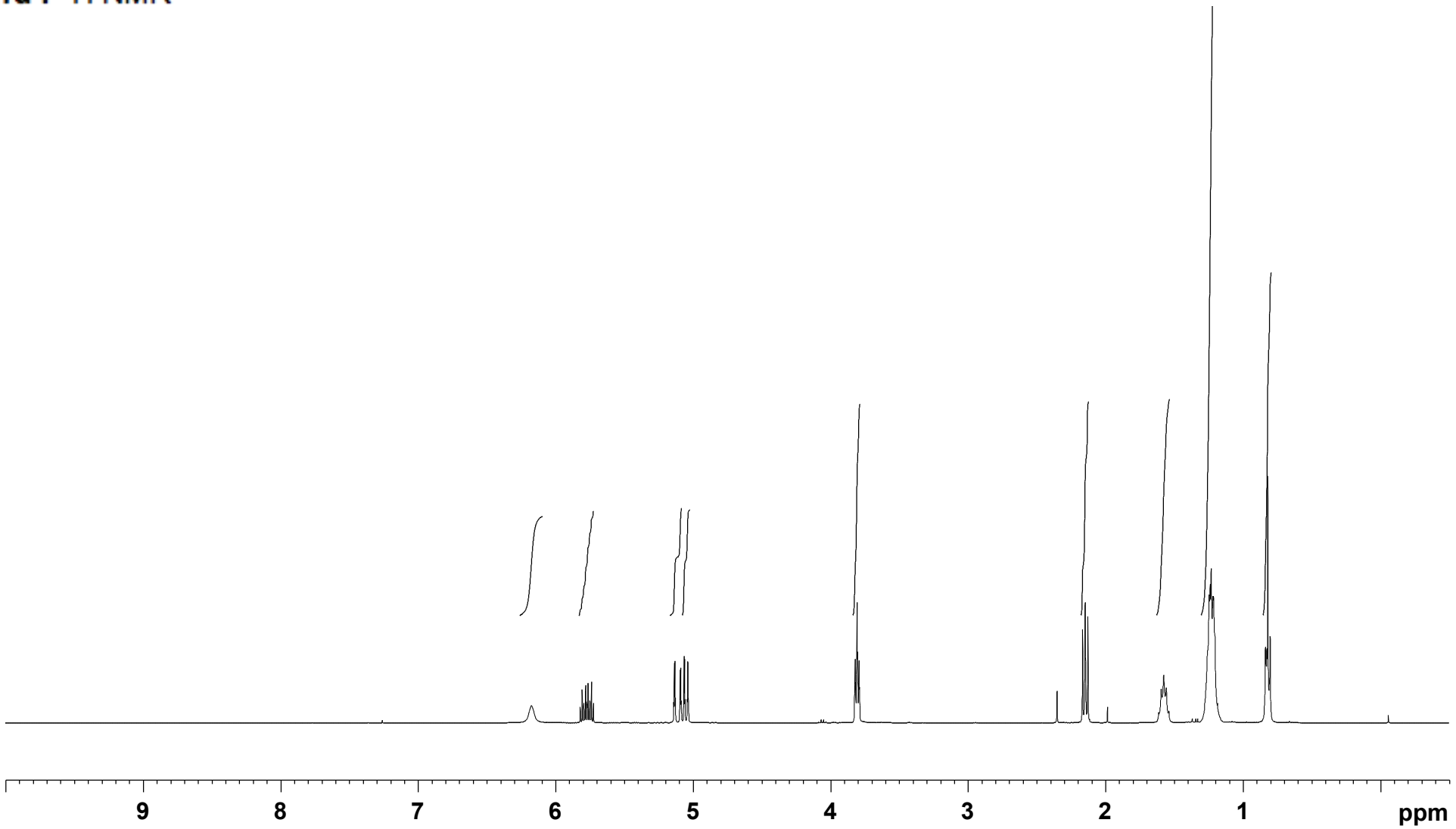

O
N
H
Br

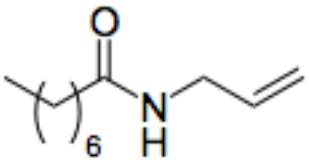
1c : ^{13}C NMR


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

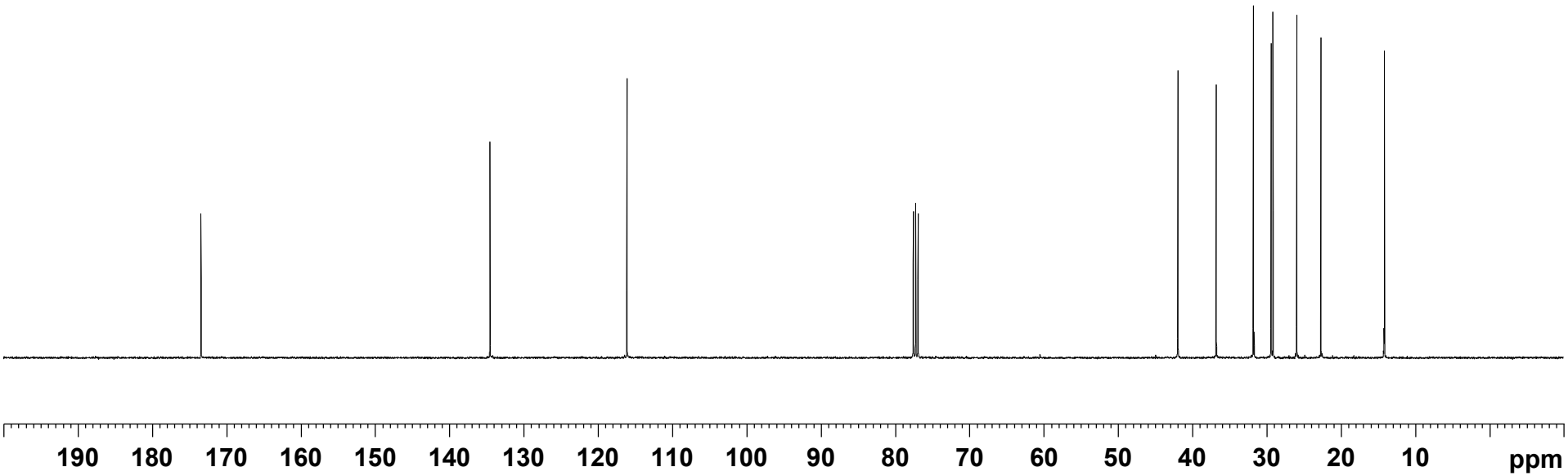


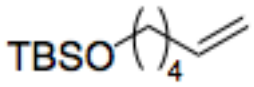
1d : ^{1}H NMR



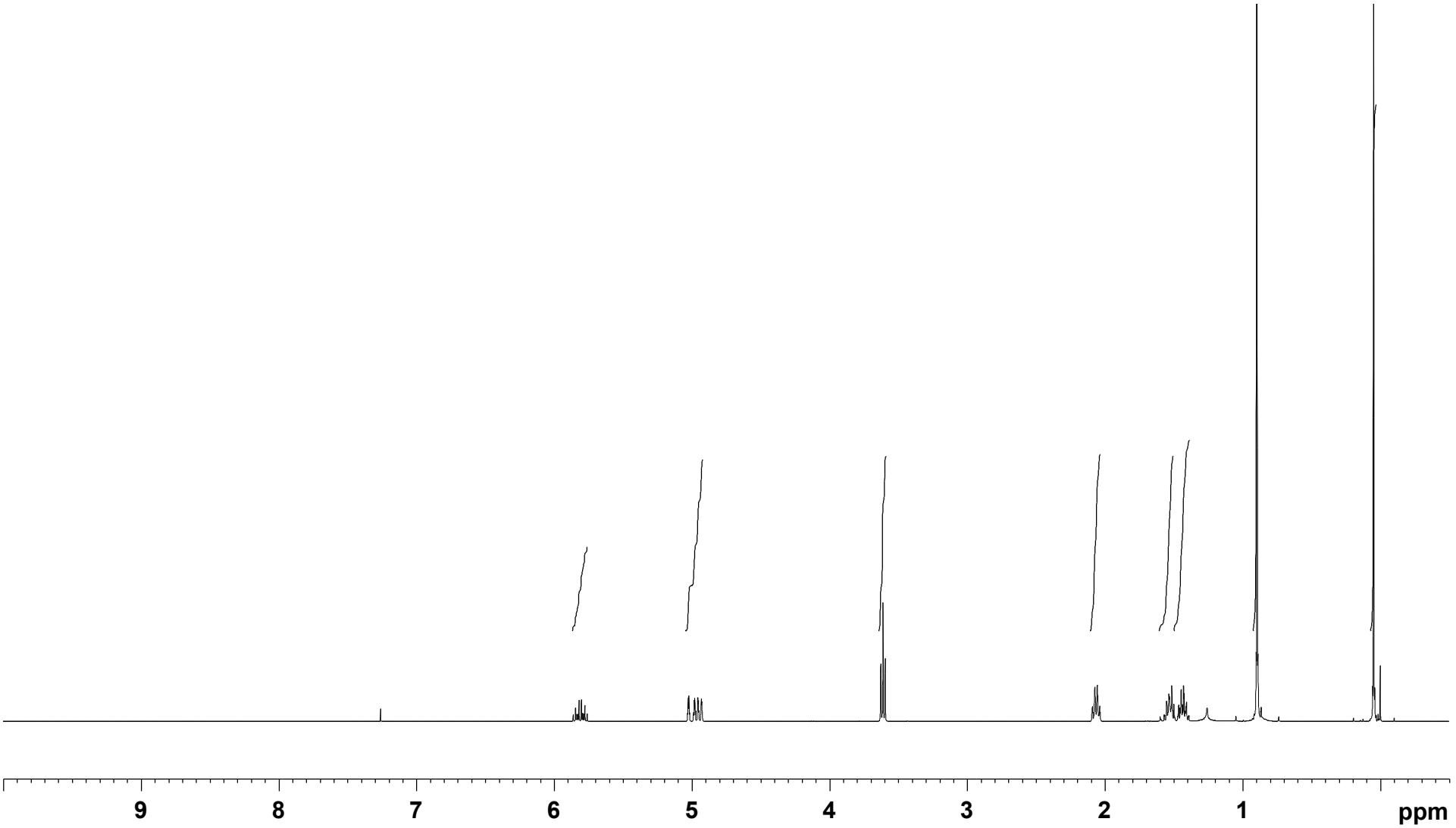

O
N
H
6

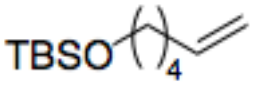
1d : ^{13}C NMR


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

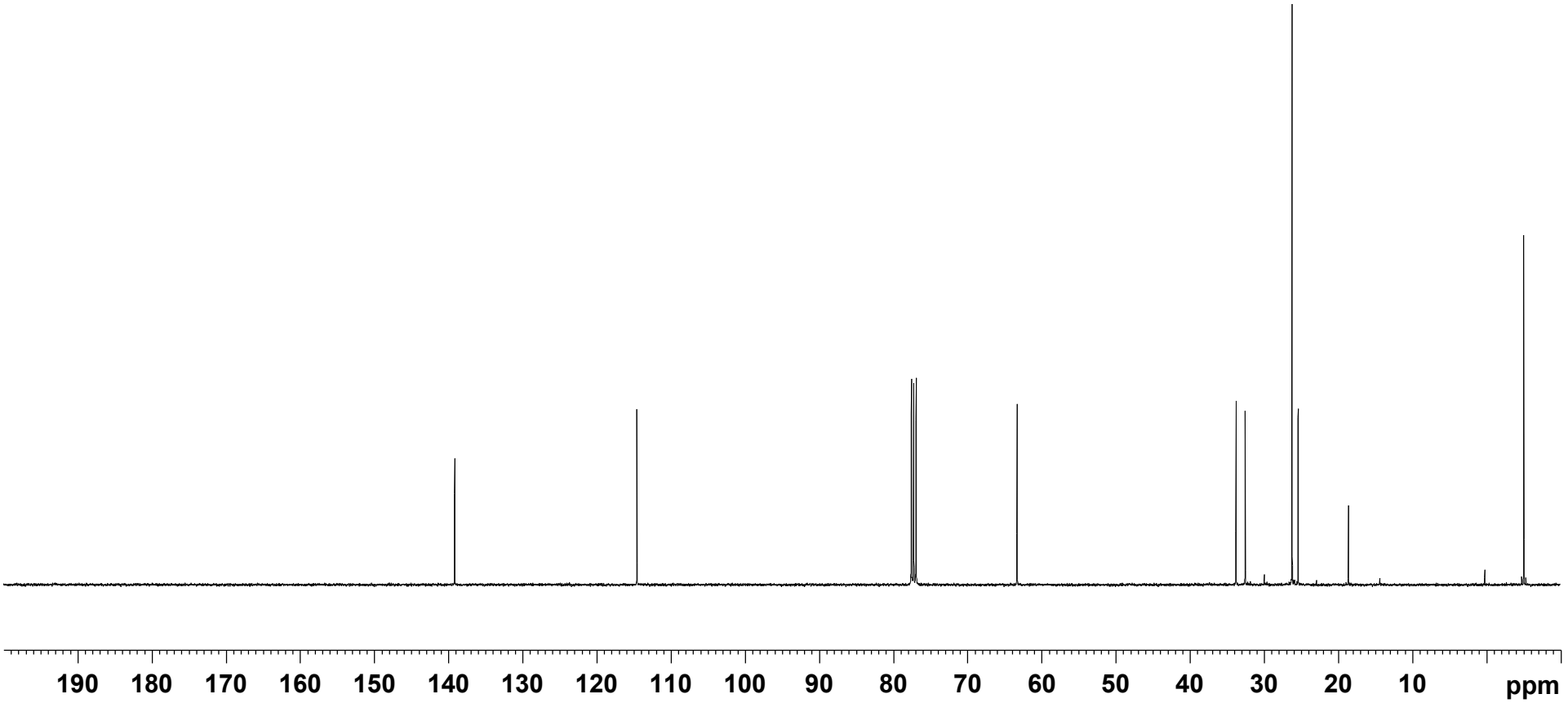


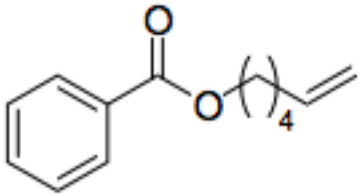
1e : ^{1}H NMR



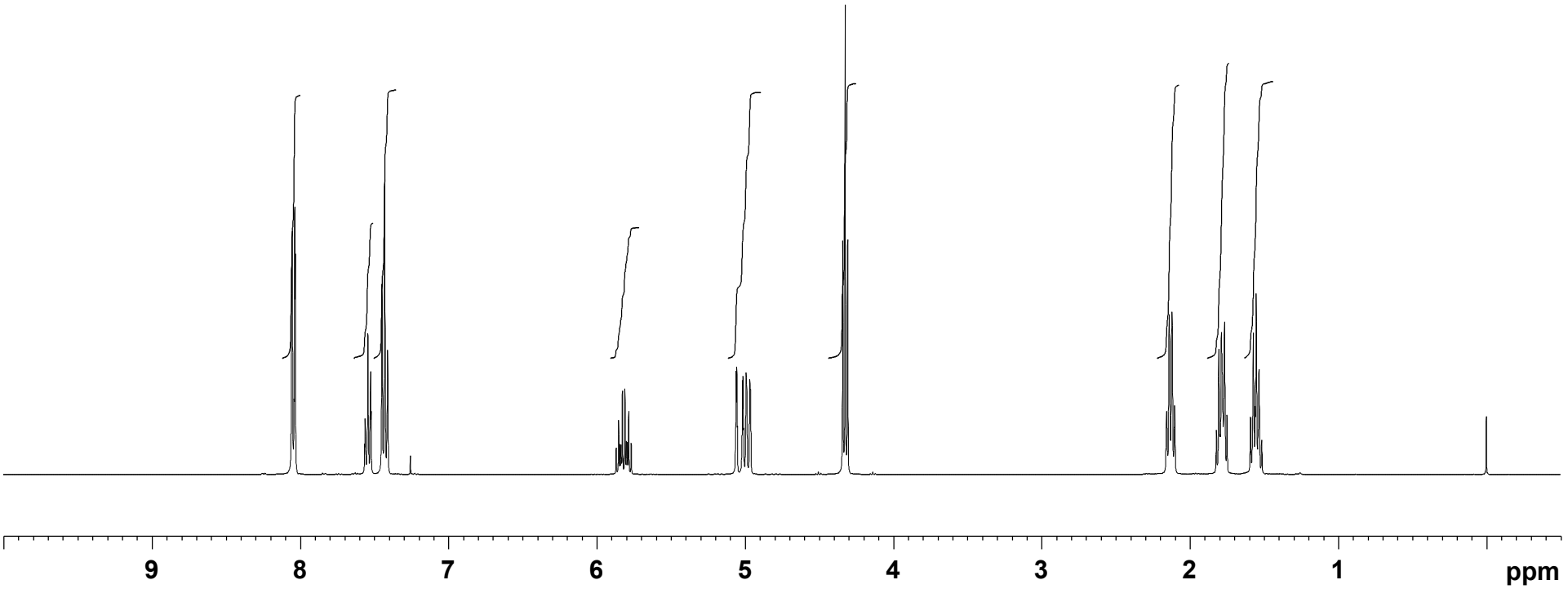

TBSO
4

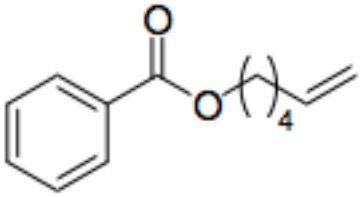
1e : ^{13}C NMR


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

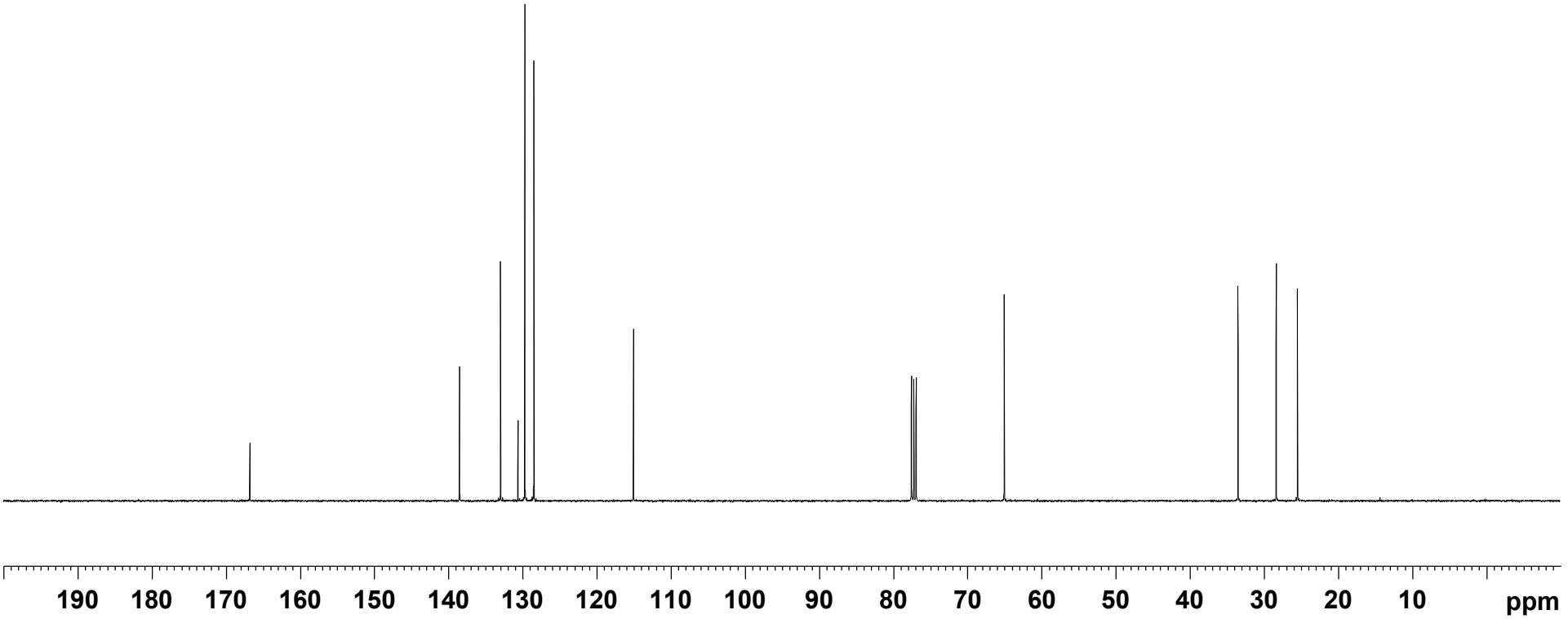


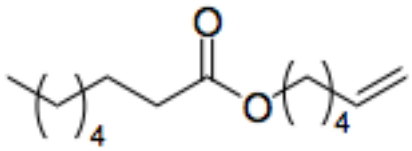
1f : ^{1}H NMR



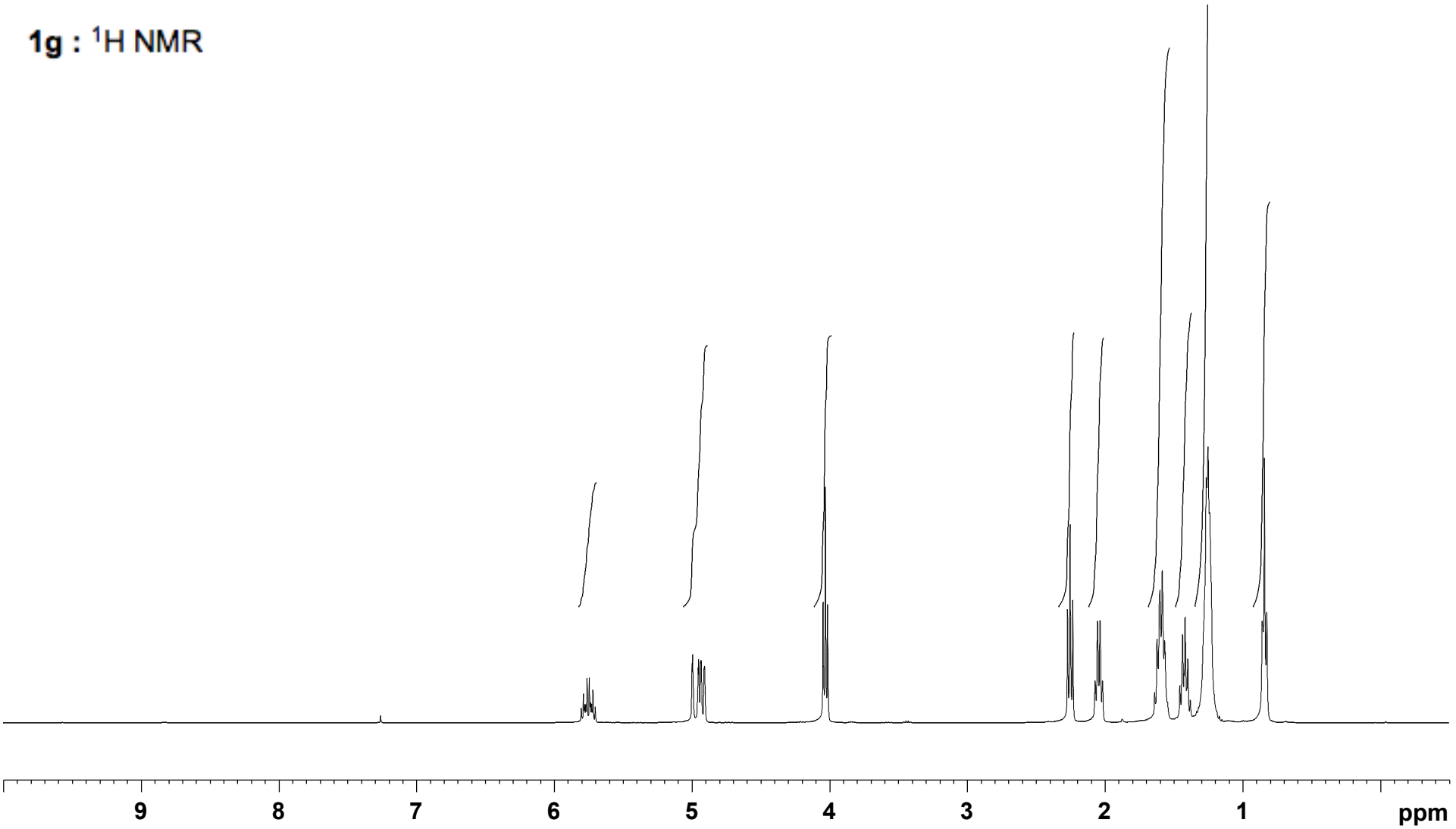


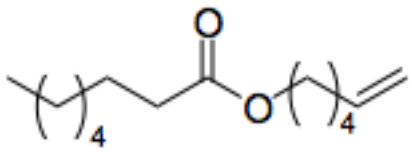
1f : ^{13}C NMR


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

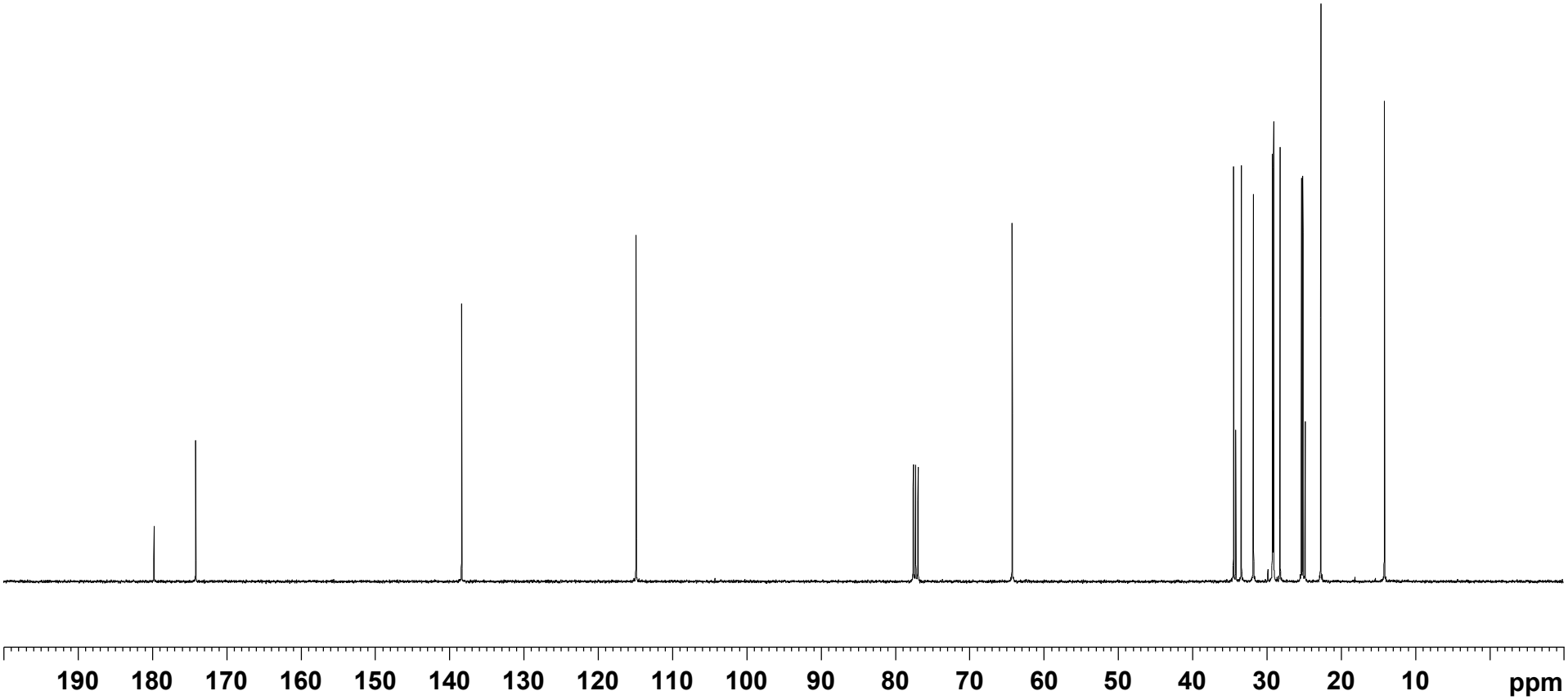


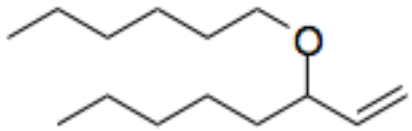
1g : ^{1}H NMR



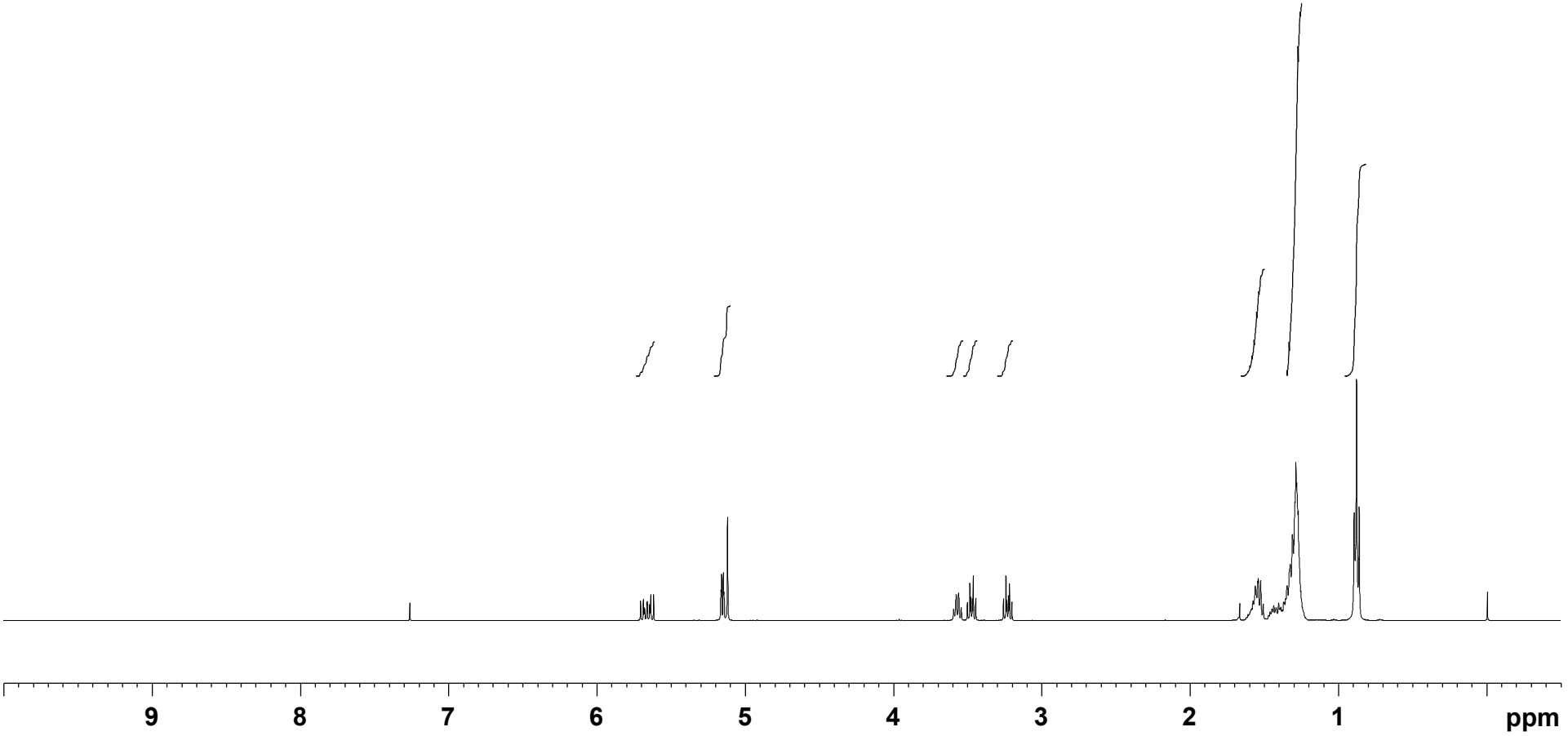

O
O
4
4

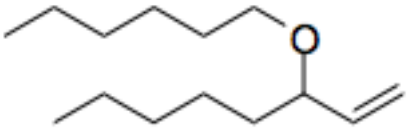
1g : ^{13}C NMR


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

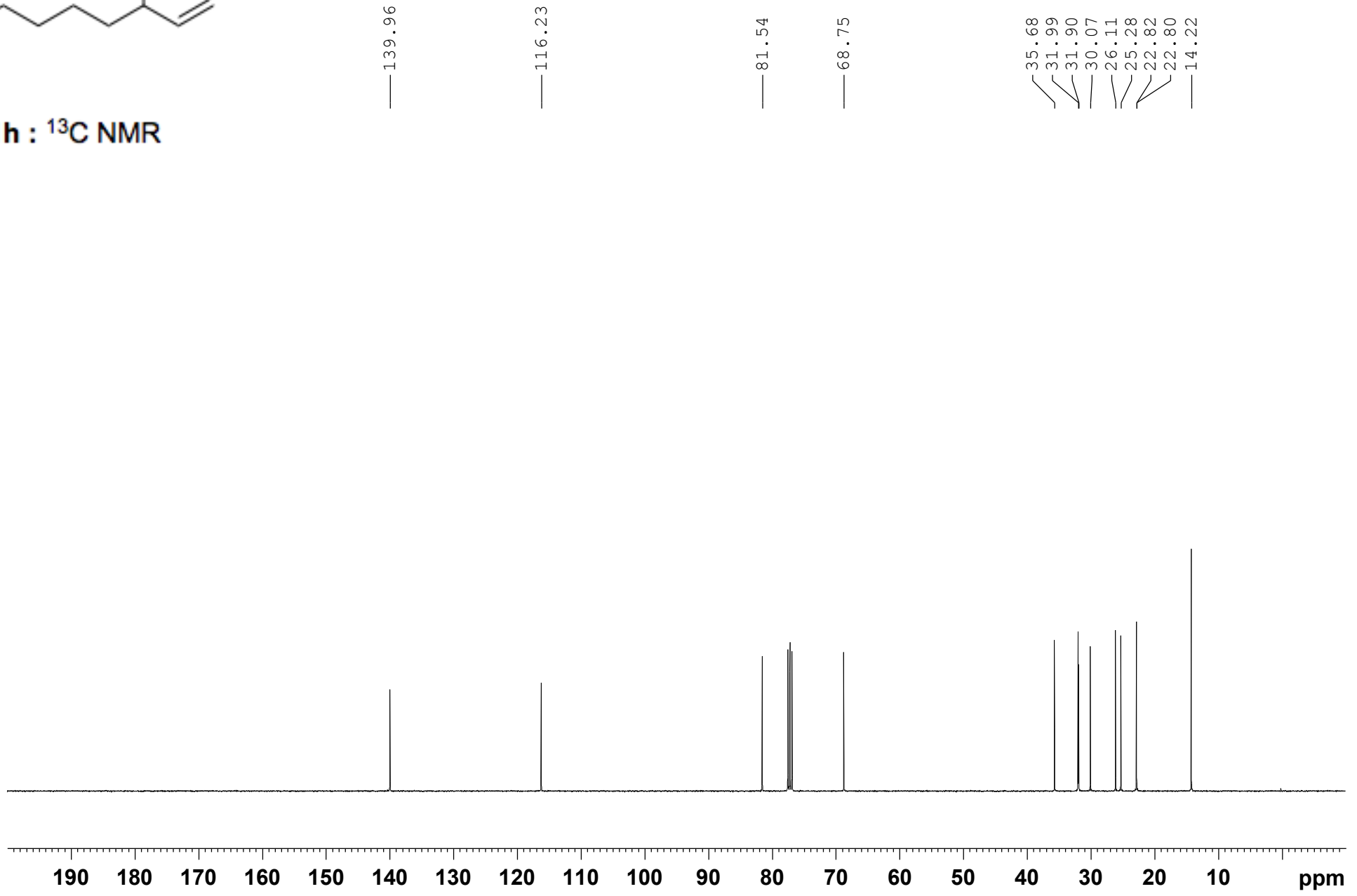


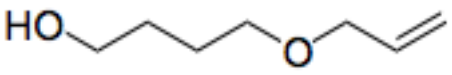
1h : ^{1}H NMR



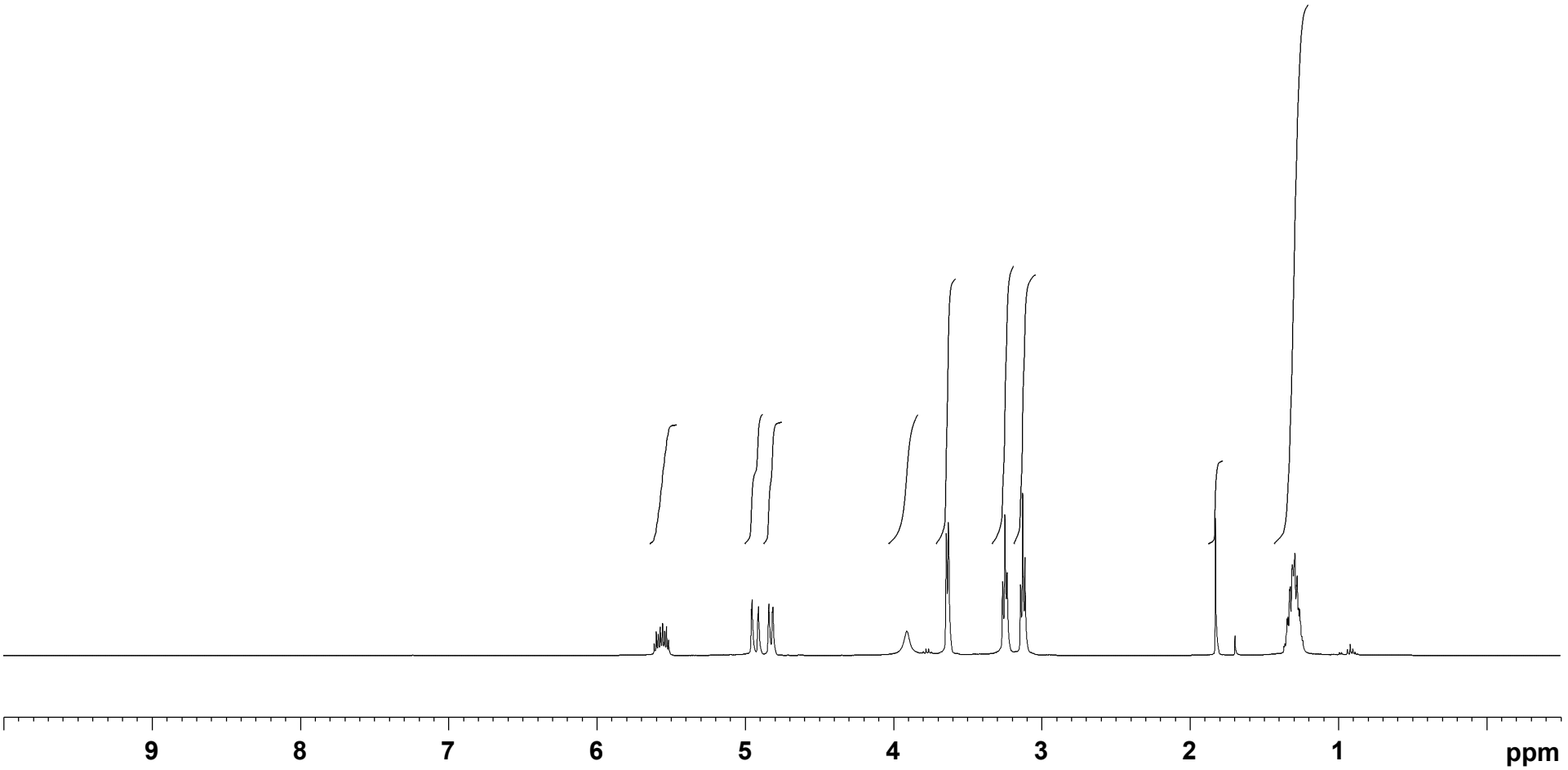


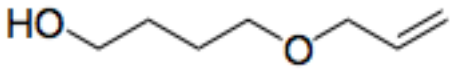
1h : ^{13}C NMR


139.96
116.23
81.54
68.75
35.68
31.99
31.90
30.07
26.11
25.28
22.82
22.80
14.22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

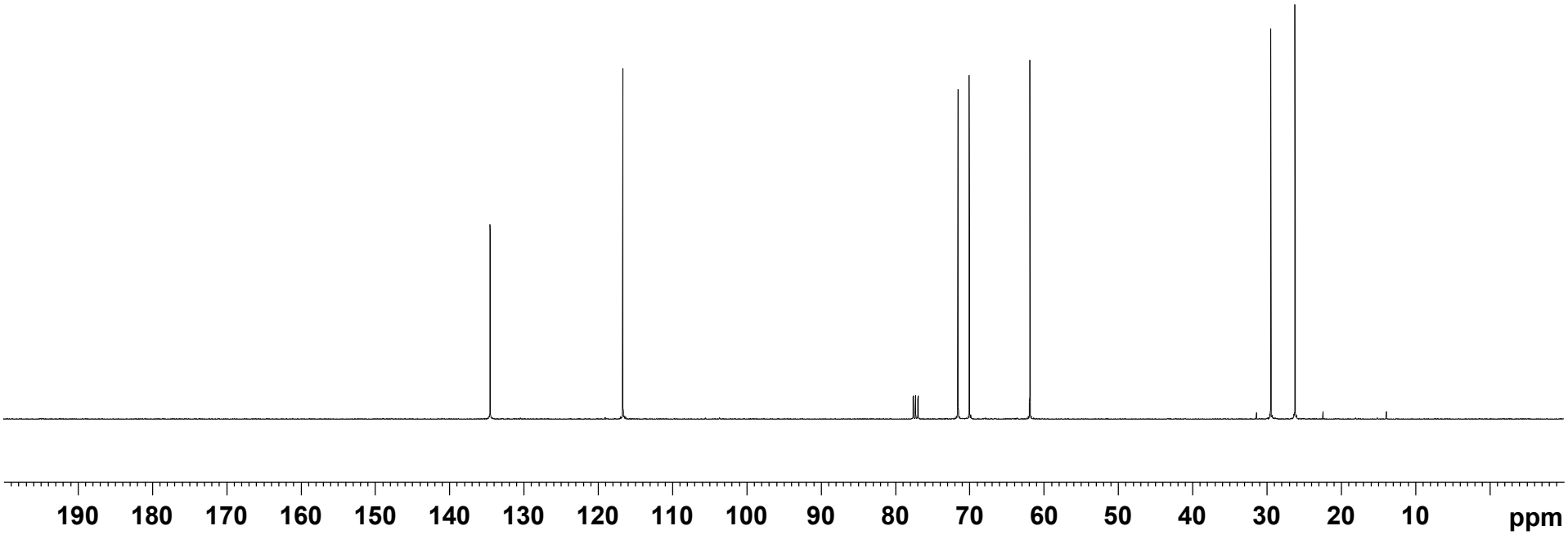


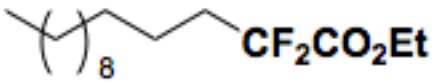
1j : ^{1}H NMR



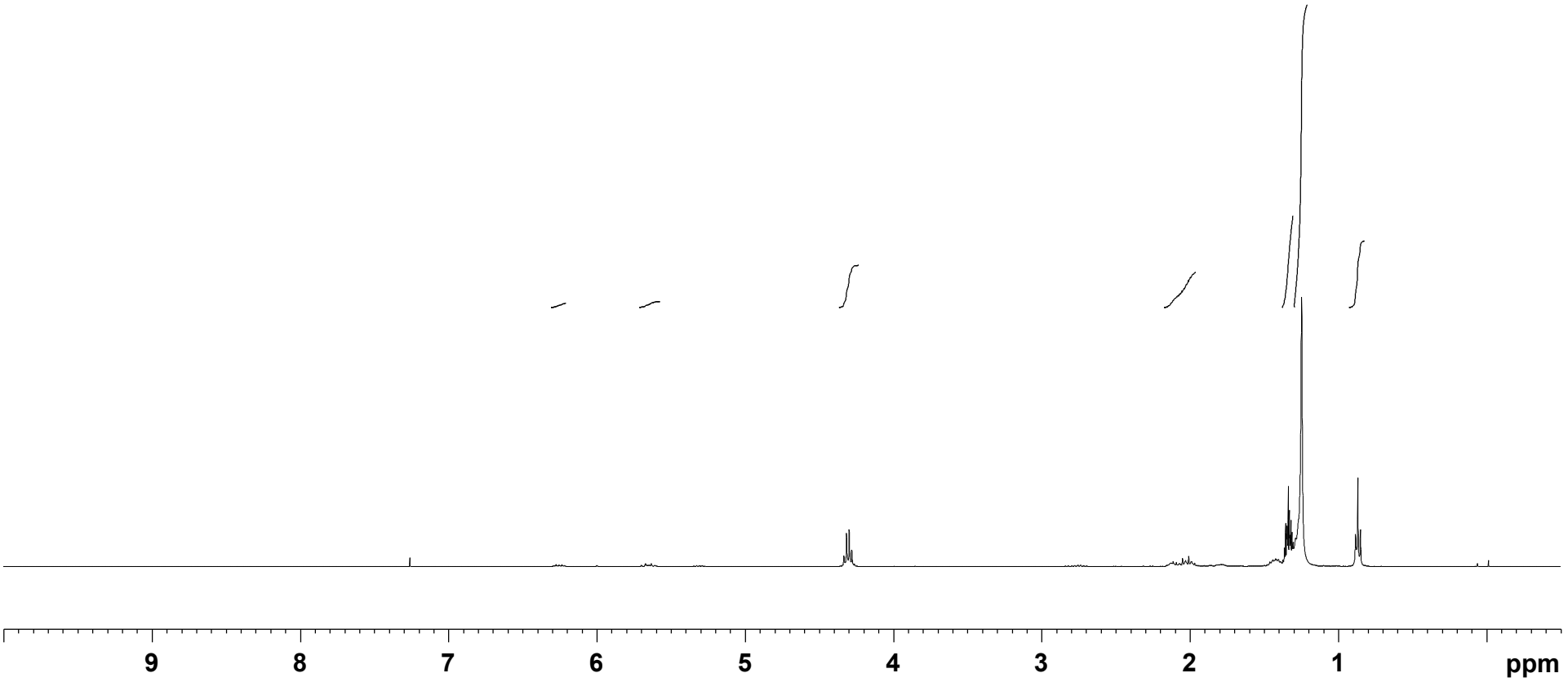

HO
O

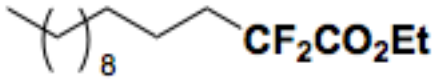
1j : ^{13}C NMR


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



3a : ^{1}H NMR (3a/6a = 4:1)



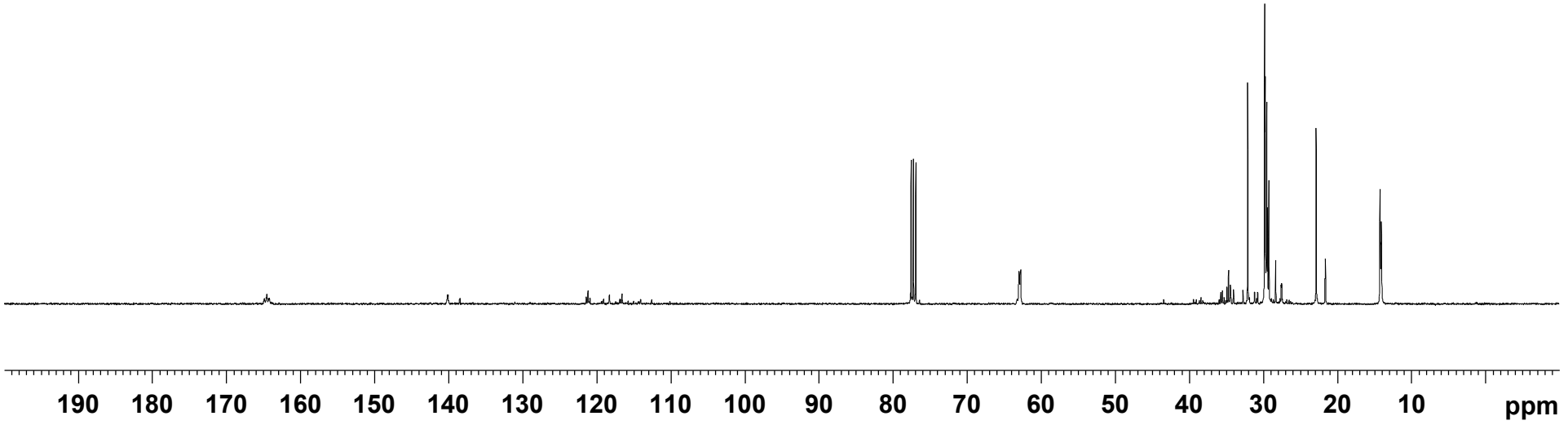


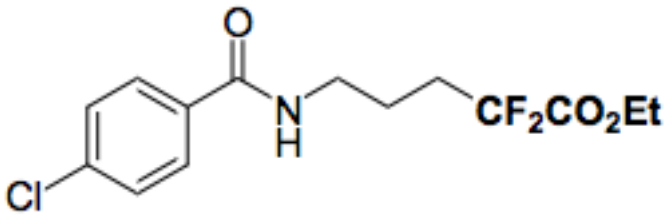
3a : ^{13}C NMR (3a/6a = 4:1)

119.03
116.55
114.07

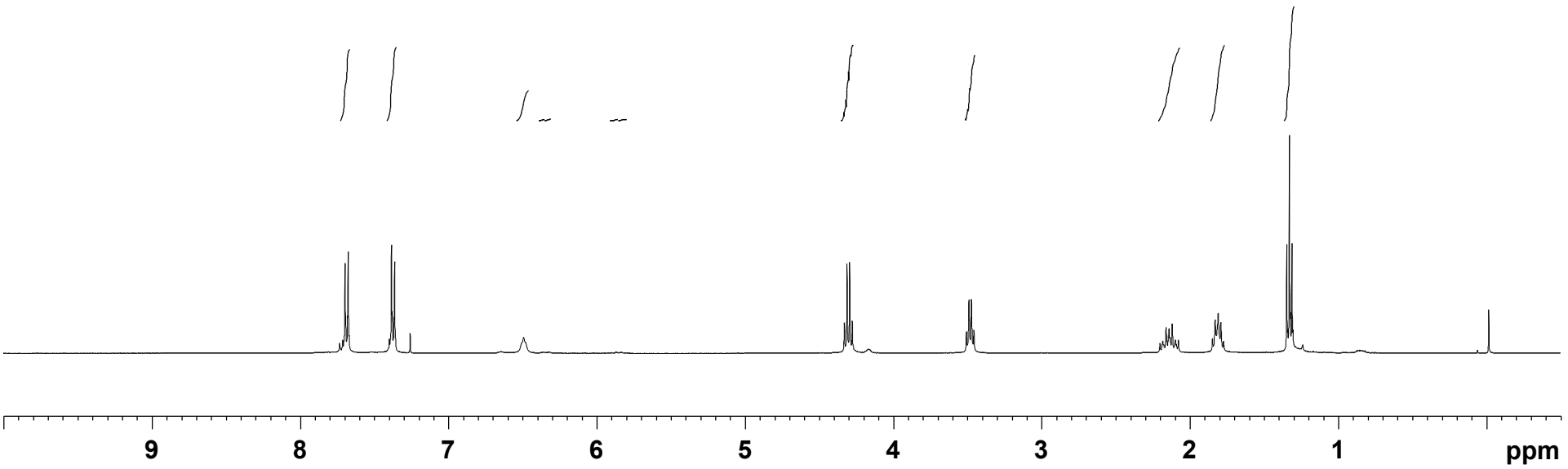
62.75

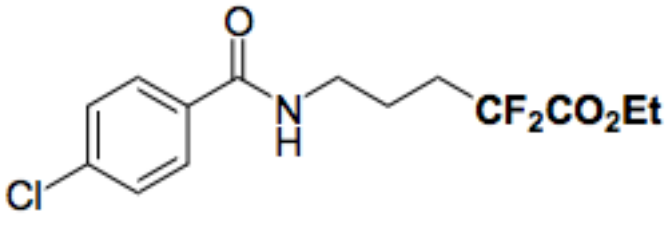
34.91
34.68
34.44
32.10
29.81
29.76
29.57
29.53
29.42
29.24
28.31
22.85
21.66
21.62
21.58
14.20
14.05





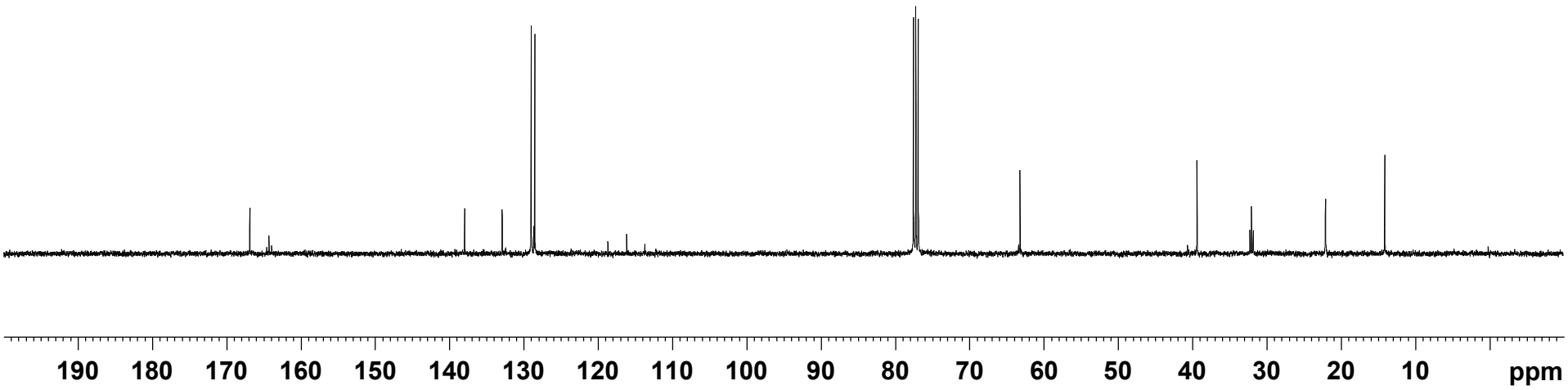
3b : ^{1}H NMR (3b/6b = 11:1)

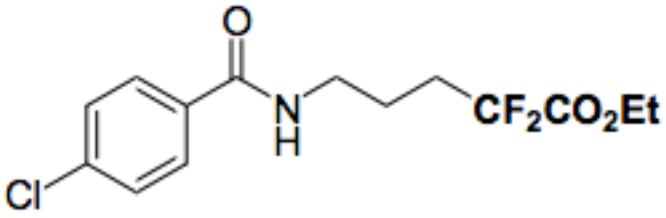




137.95
132.89
128.99
128.51
118.65
116.17
113.68
63.20
39.36
32.26
32.03
31.79
22.11
22.07
22.03
14.09

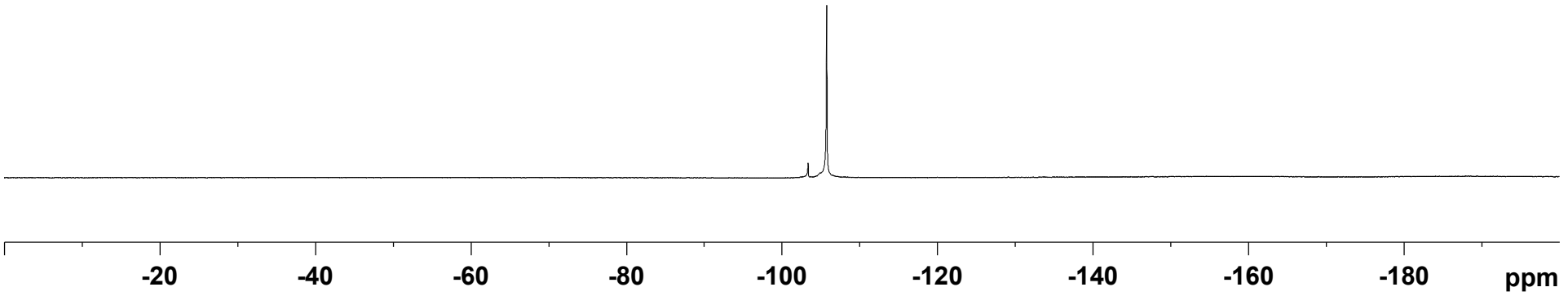
3b : ^{13}C NMR (3b/6b = 11:1)

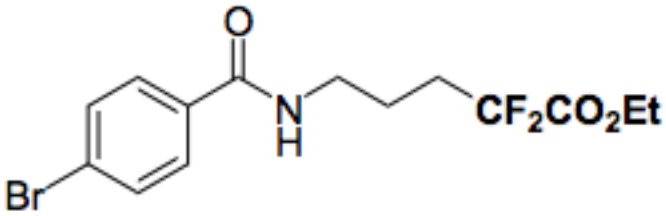




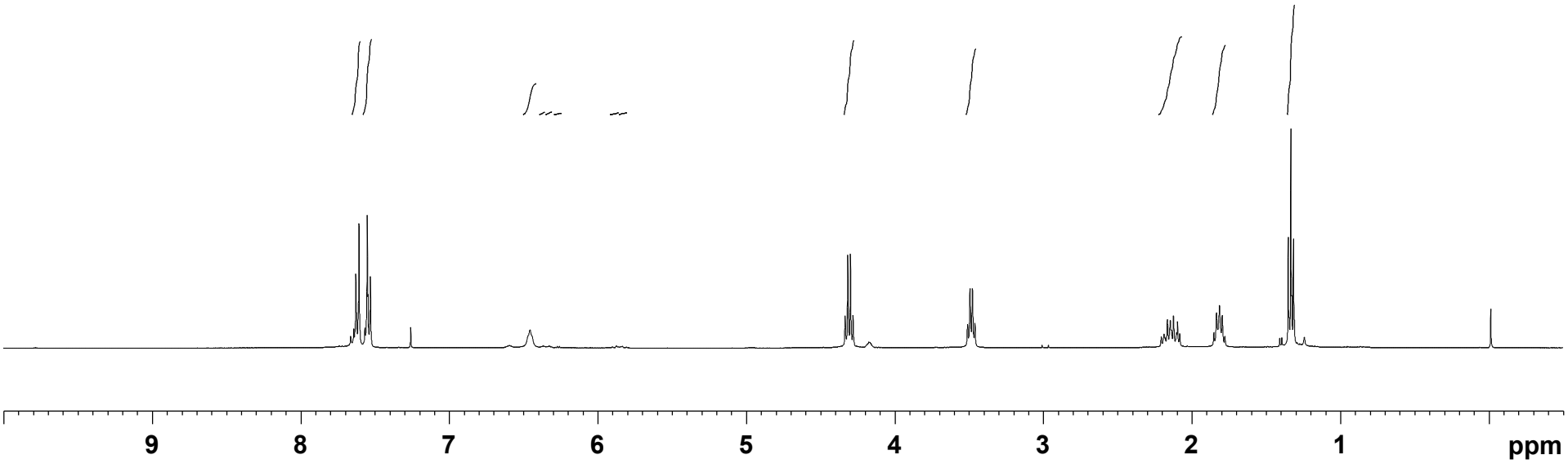
-103.37
-105.77

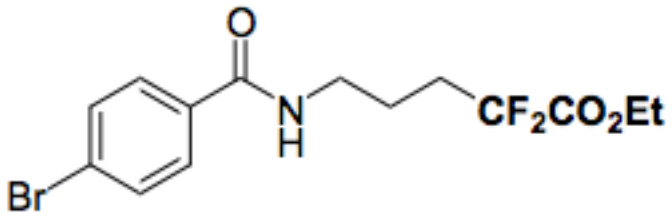
3b : ^{19}F NMR (3b/6b = 11:1)





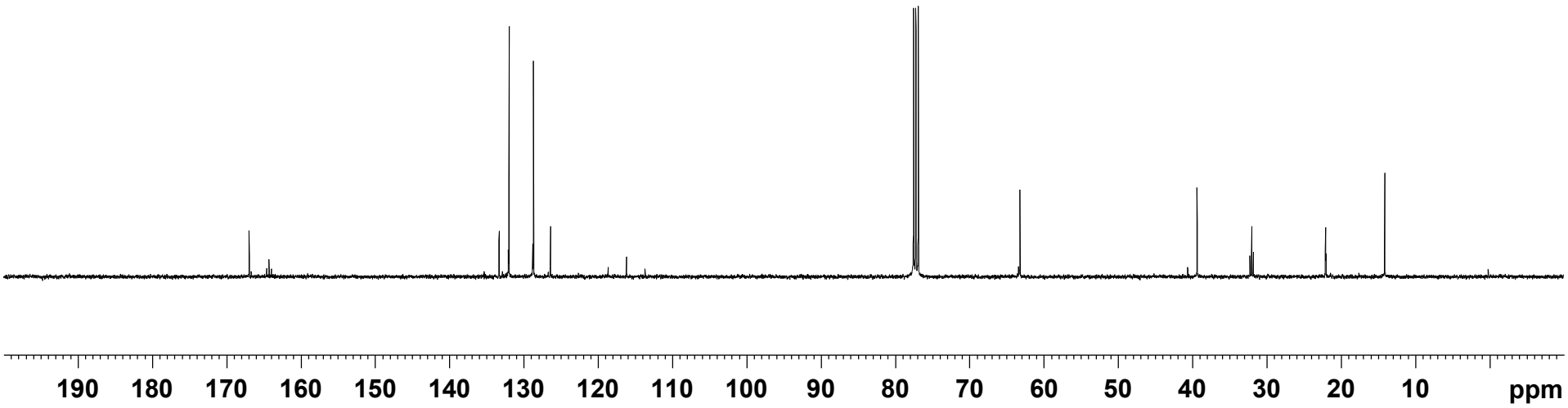
3c : ^{1}H NMR (3c/6c = 8:1)

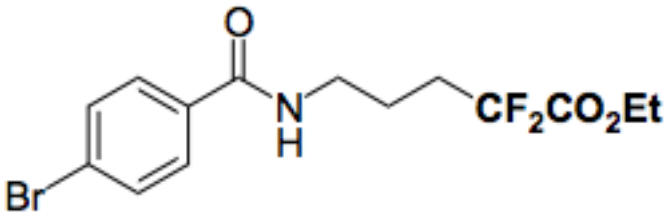




133.306
131.970
128.670
126.394
118.630
116.143
113.654
63.199
39.348
32.233
31.998
31.764
22.081
22.041
22.002
14.092

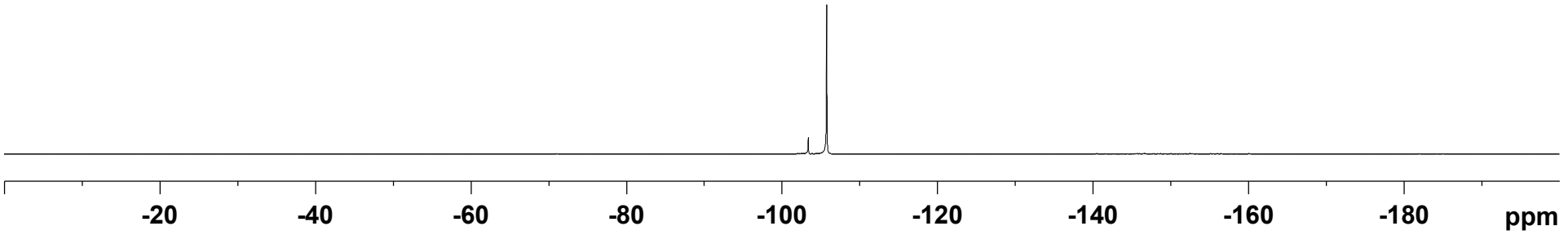
3c : ^{13}C NMR (3c/6c = 8:1)

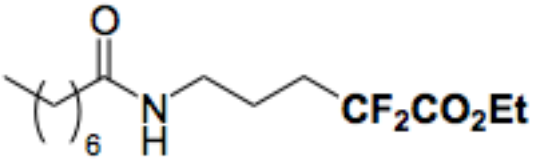




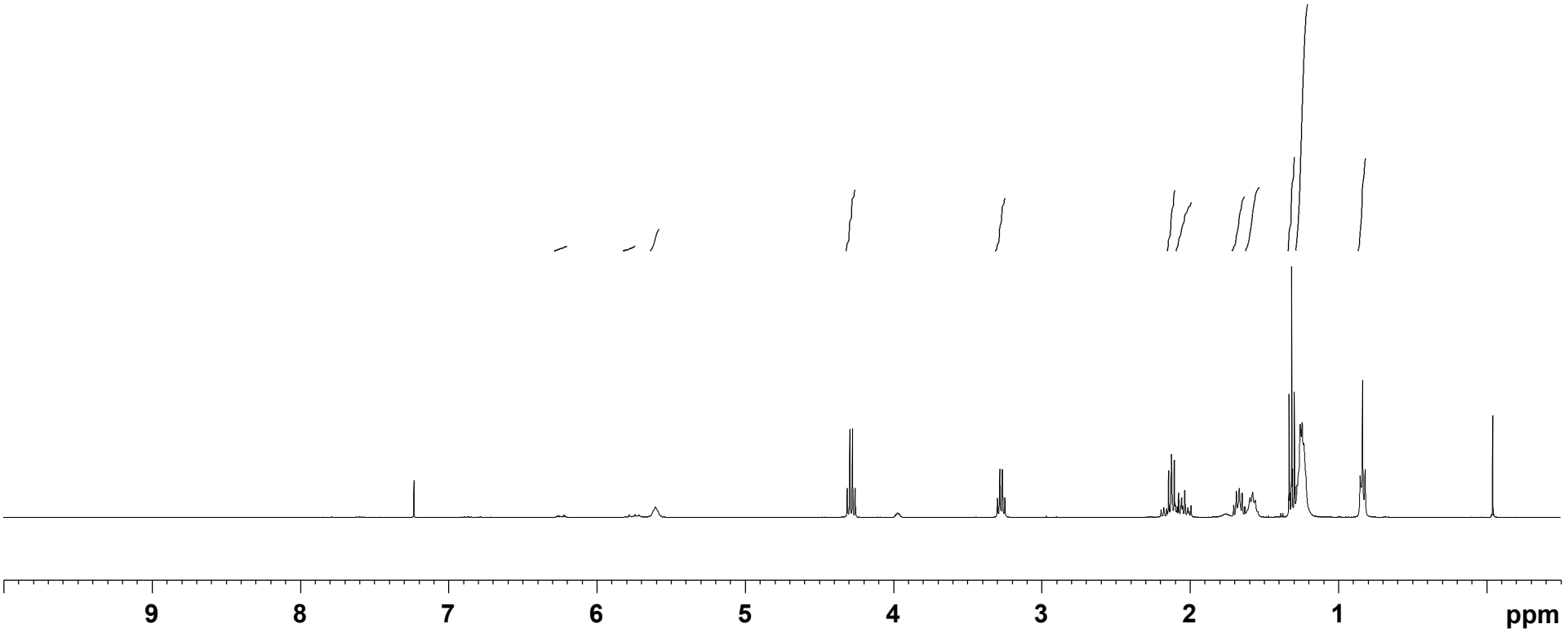
-103.40
-105.77

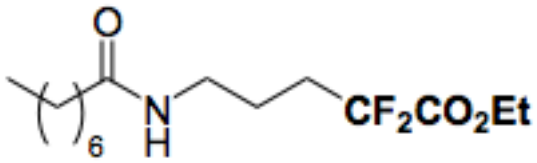
3c : ^{19}F NMR (3c/6c = 8:1)



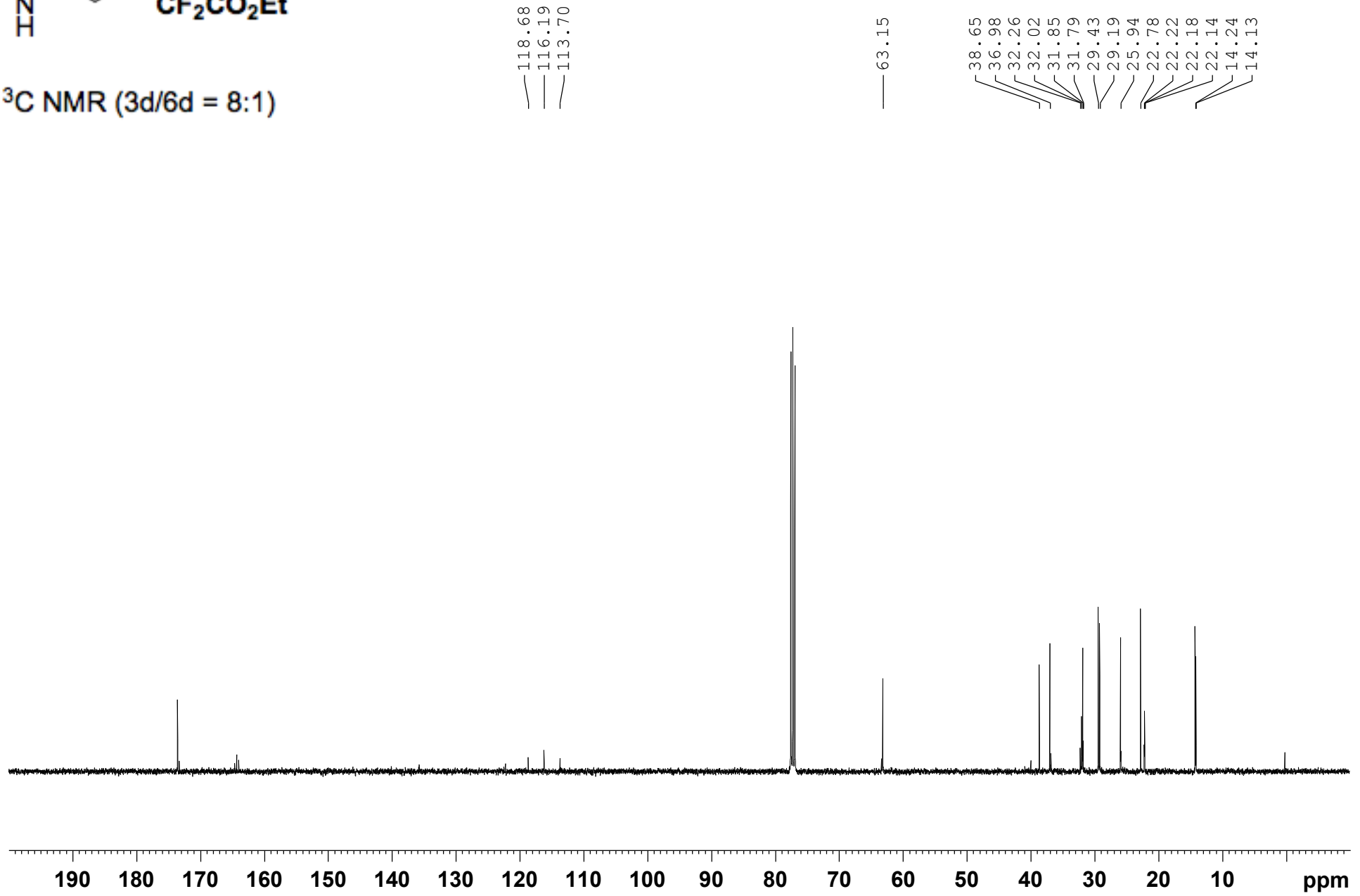


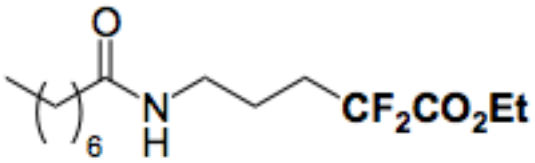
3d : ^{1}H NMR (3d/6d = 8:1)





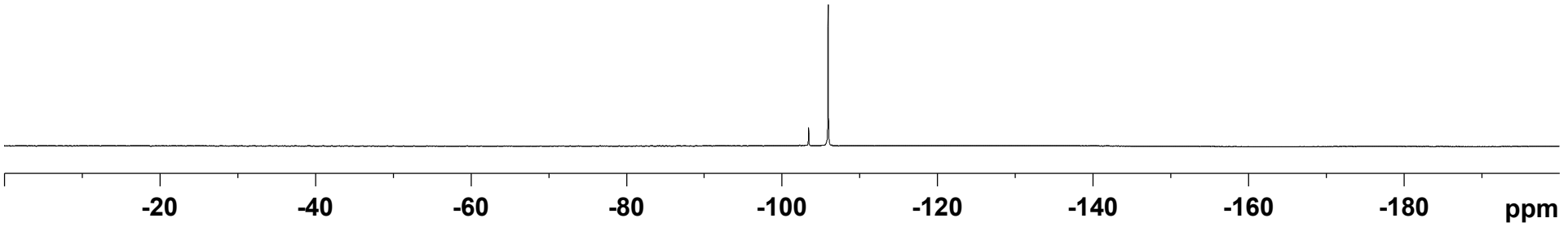
3d : ^{13}C NMR (3d/6d = 8:1)

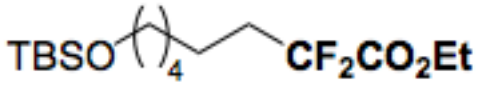




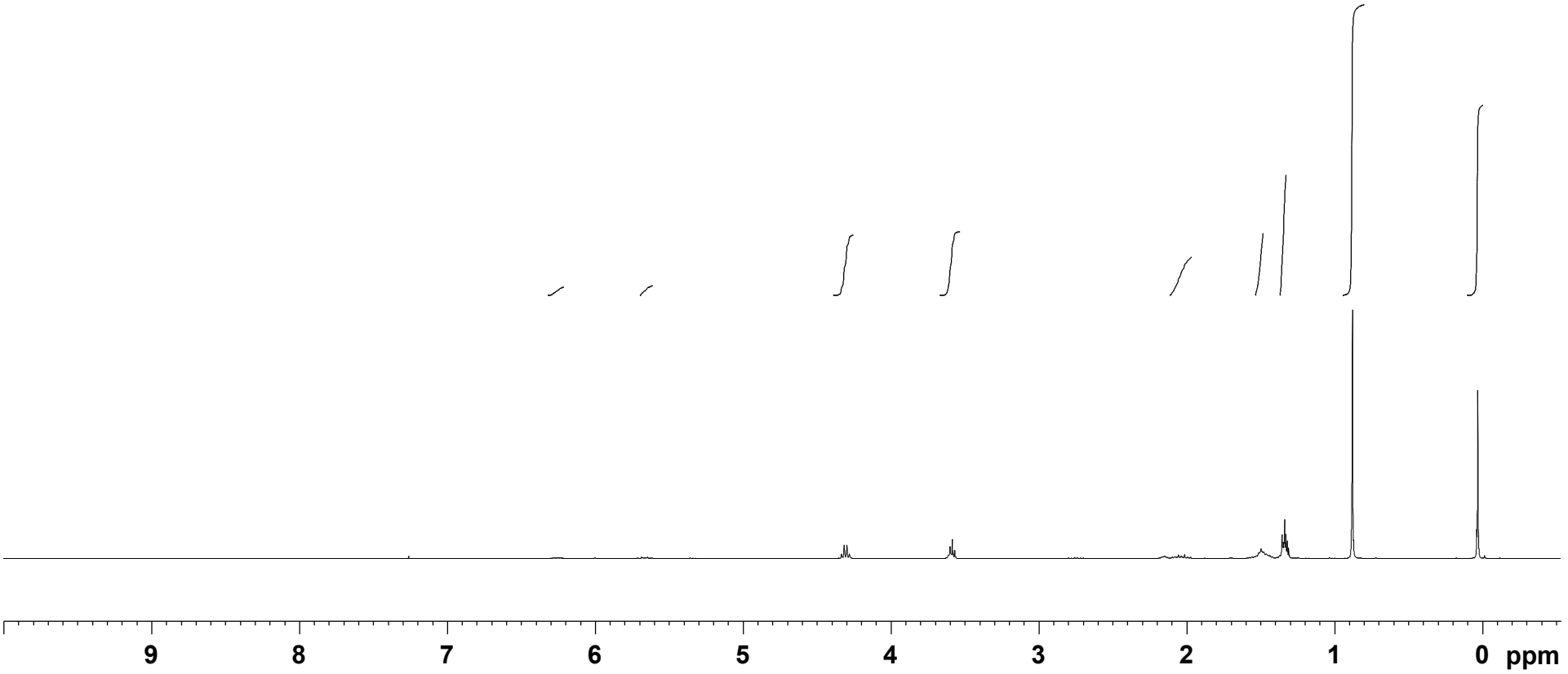
-103.44
-105.95

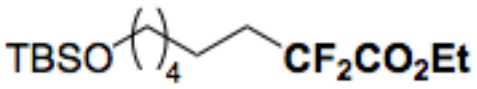
3d : ^{19}F NMR (3d/6d = 8:1)



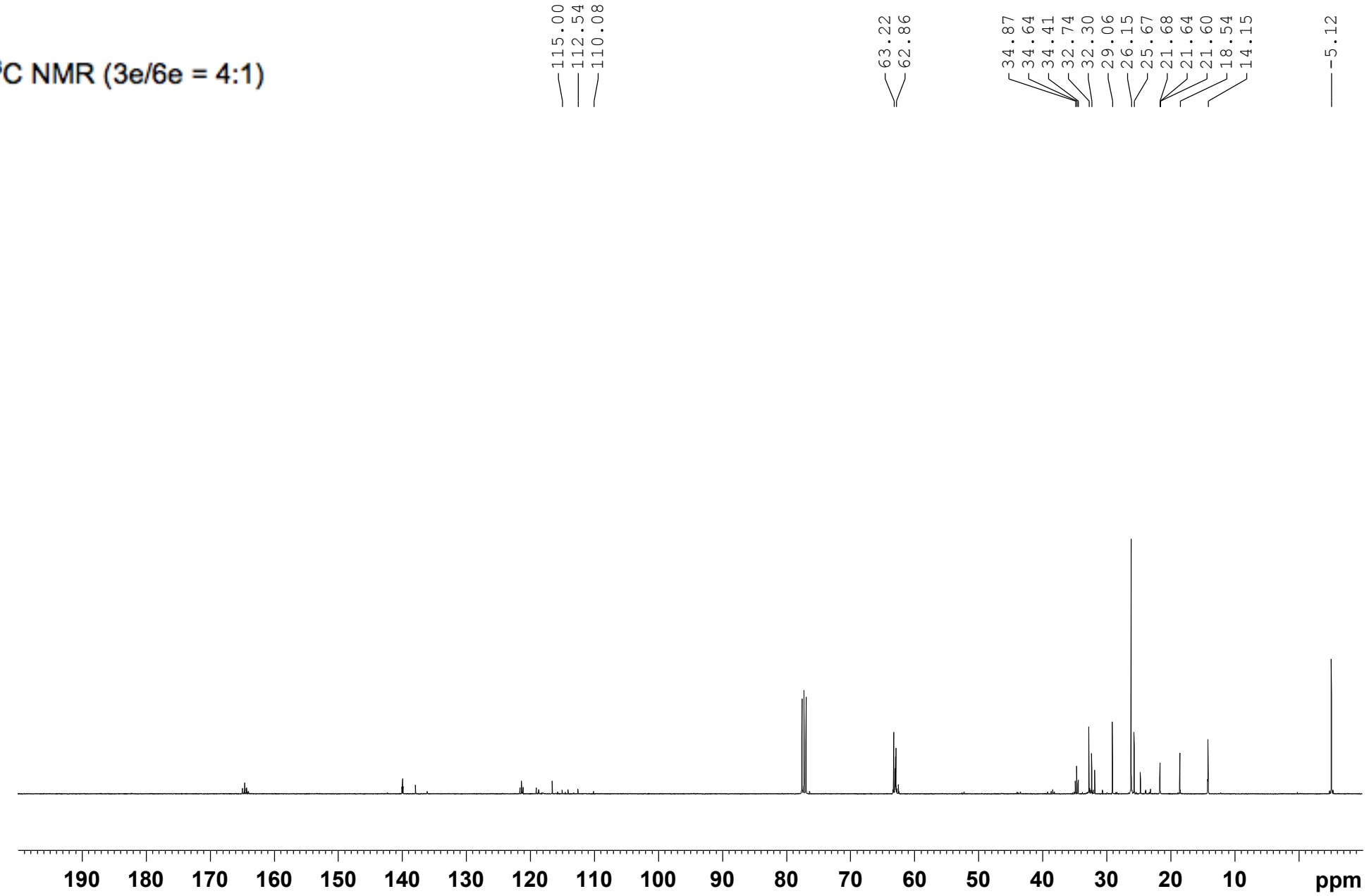


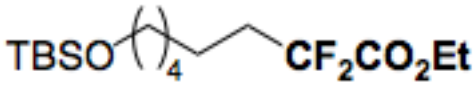
3e : ^{1}H NMR (3e/6e = 4:1)





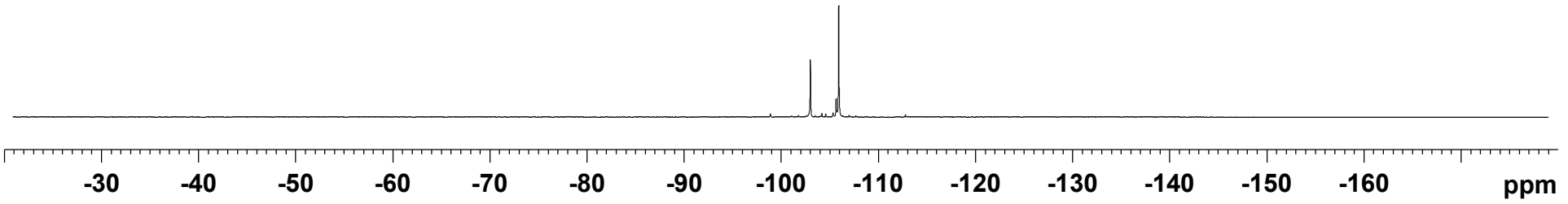
3e : ^{13}C NMR (3e/6e = 4:1)

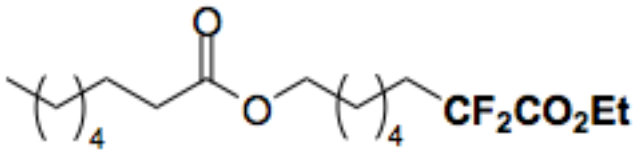




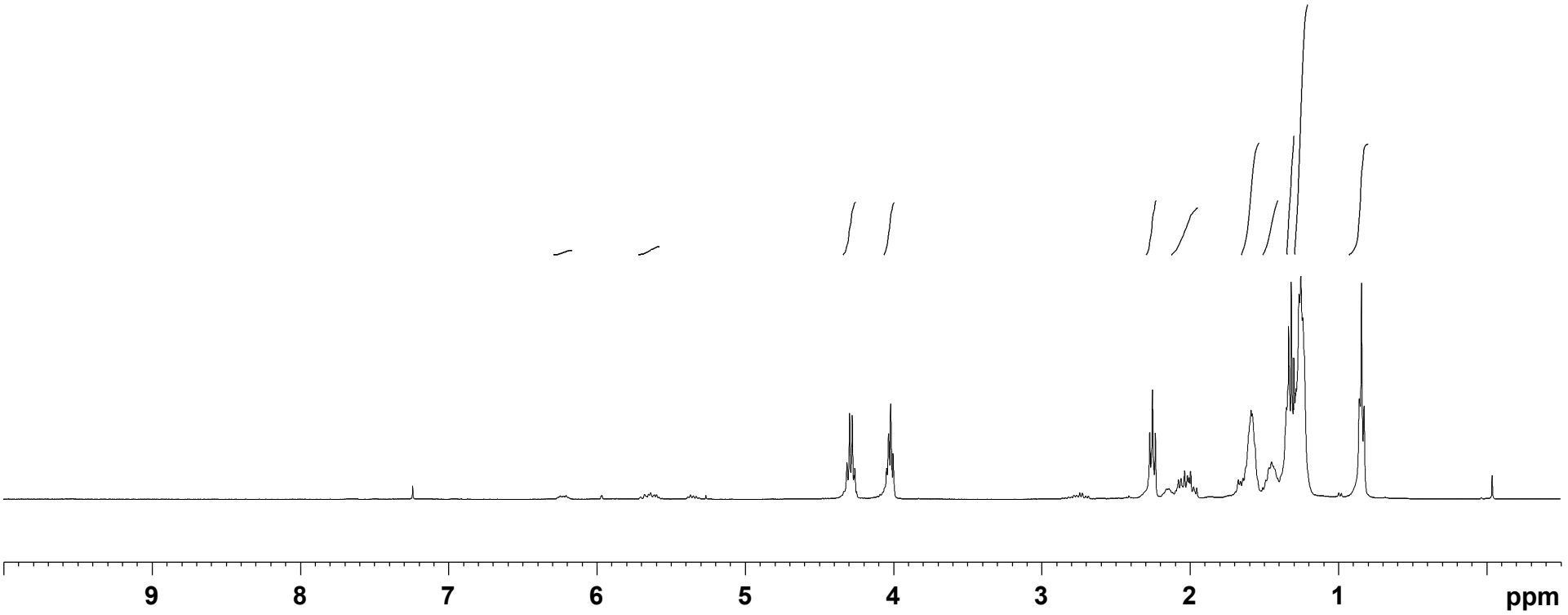
3e : ^{19}F NMR (3e/6e = 4:1)

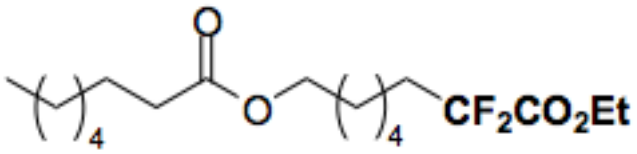
-103.02
-105.94





3g : ^{1}H NMR (3g/6g = 6:1)



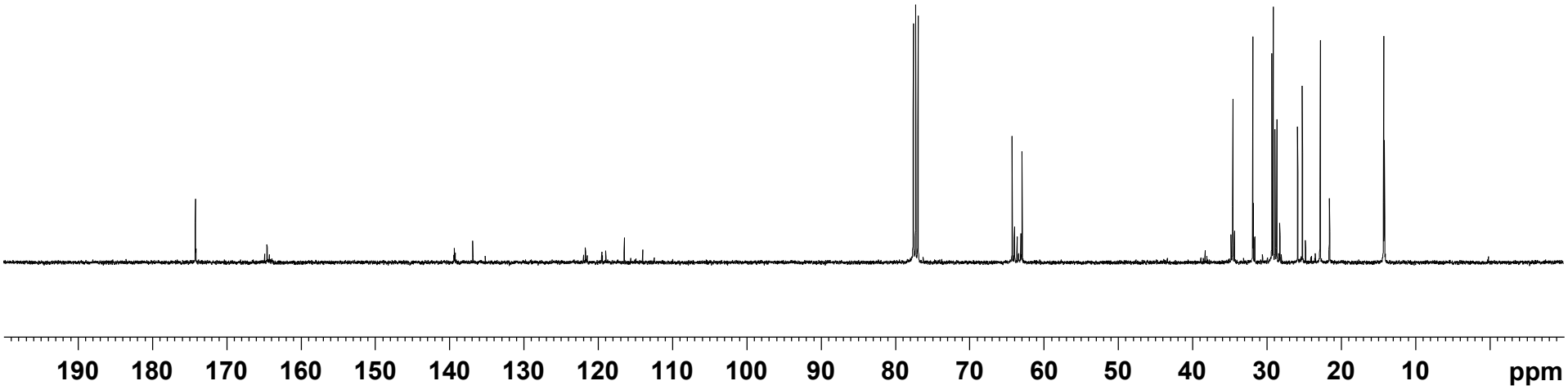


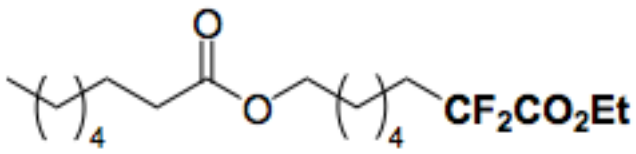
118.95
116.46
113.98

64.25
62.91

34.78
34.53
34.50
34.32
31.84
29.29
29.10
28.86
28.60
25.81
25.18
22.77
21.57
21.53
21.49
14.22
14.17
14.14
14.10

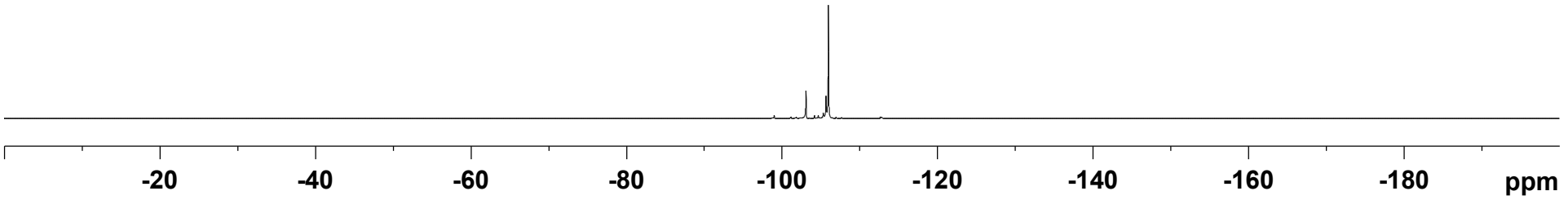
3g : ^{13}C NMR (3g/6g = 6:1)

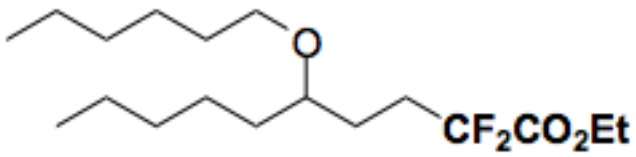




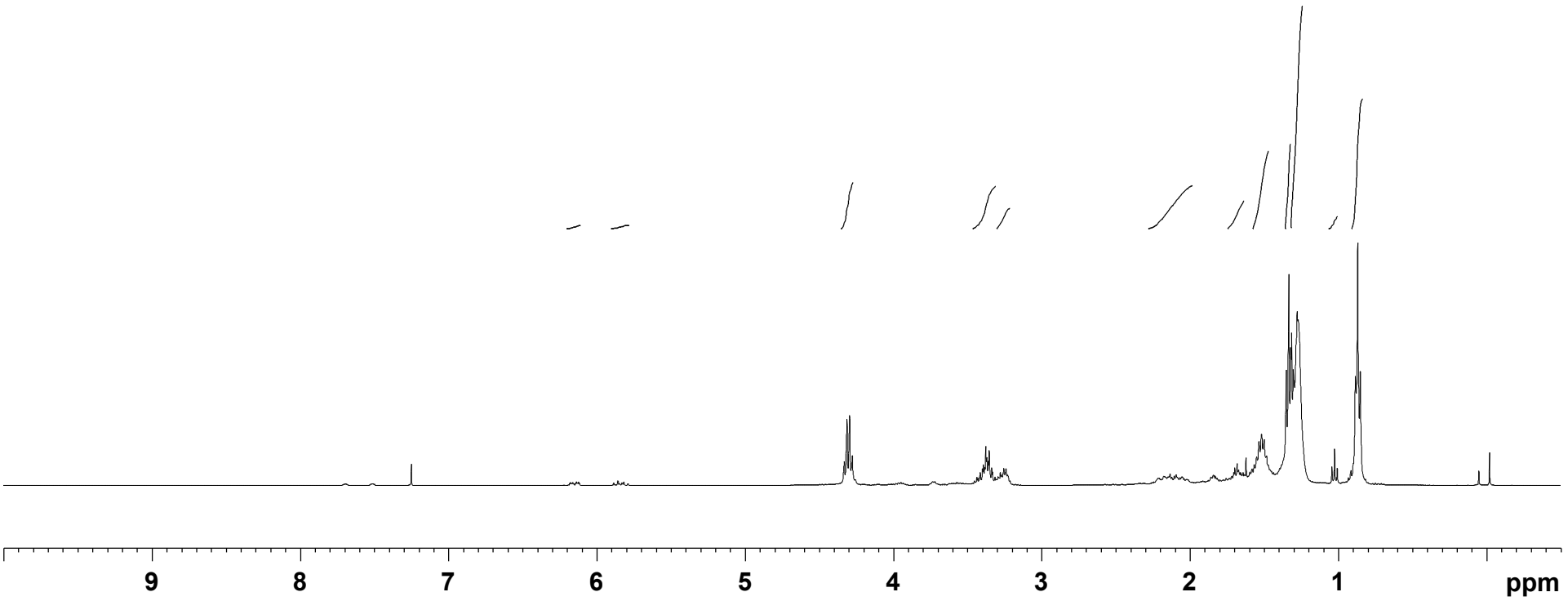
-103.11
-105.99

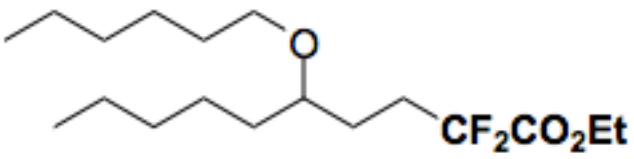
3g : ^{19}F NMR (3g/6g = 6:1)





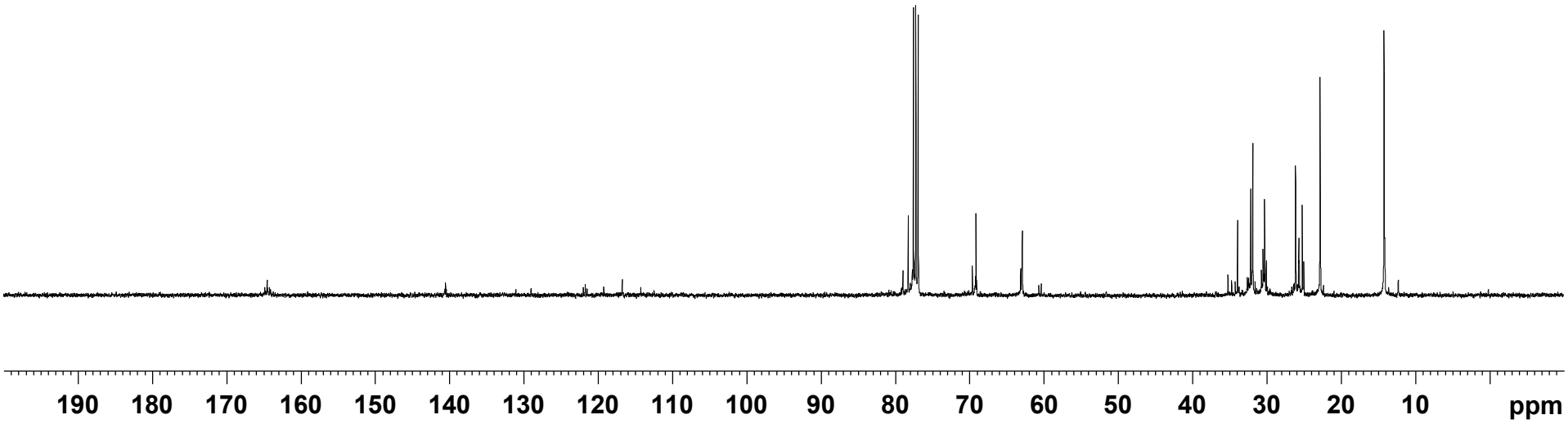
3h : ^{1}H NMR (3h/6h = 11:1)

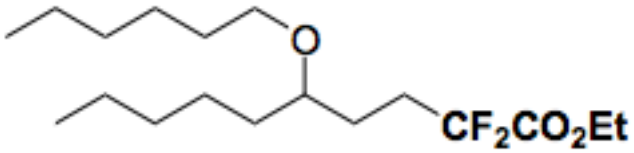




140.51
140.43
121.97
121.72
121.47
119.22
116.73
114.25
78.22
69.12
62.93
62.88
33.90
32.13
31.85
30.47
30.29
30.23
30.03
26.09
25.63
25.20
22.79
14.18

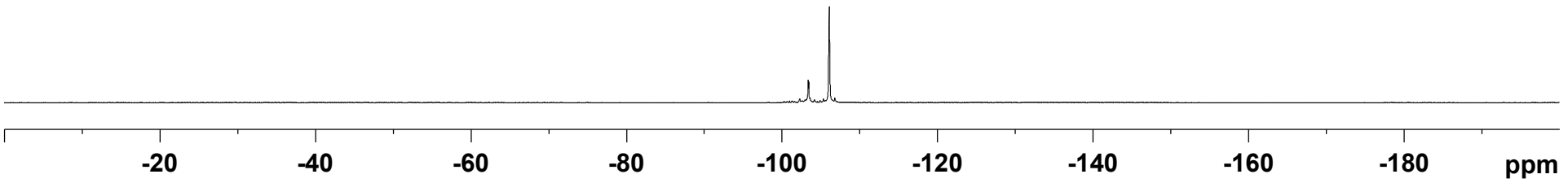
3h : ^{13}C NMR (3h/6h = 11:1)

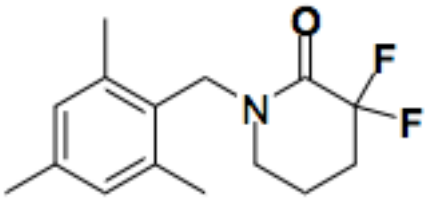




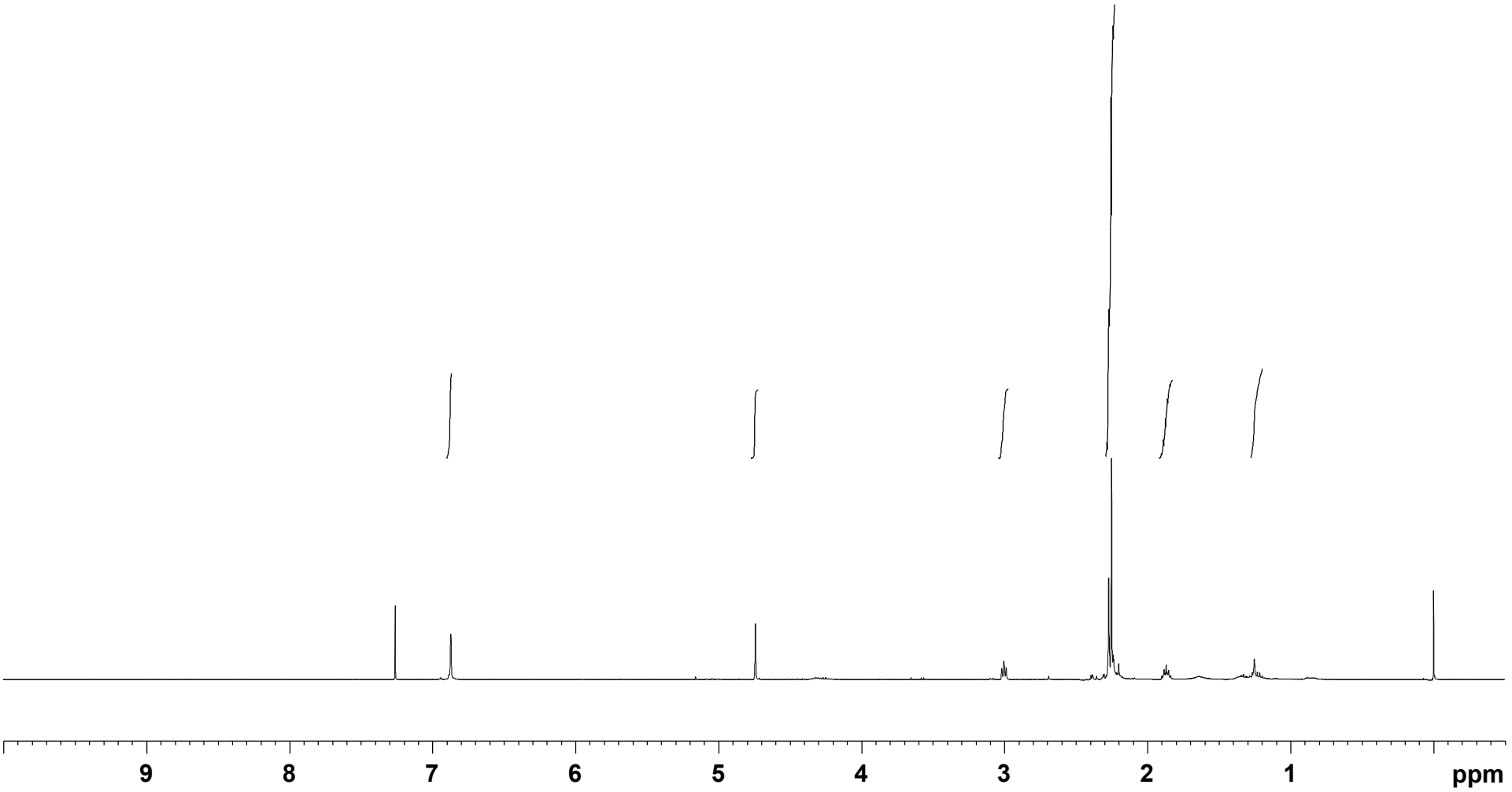
-103.39
-106.11

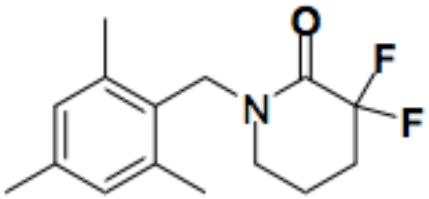
3h : ^{19}F NMR (3h/6h = 11:1)



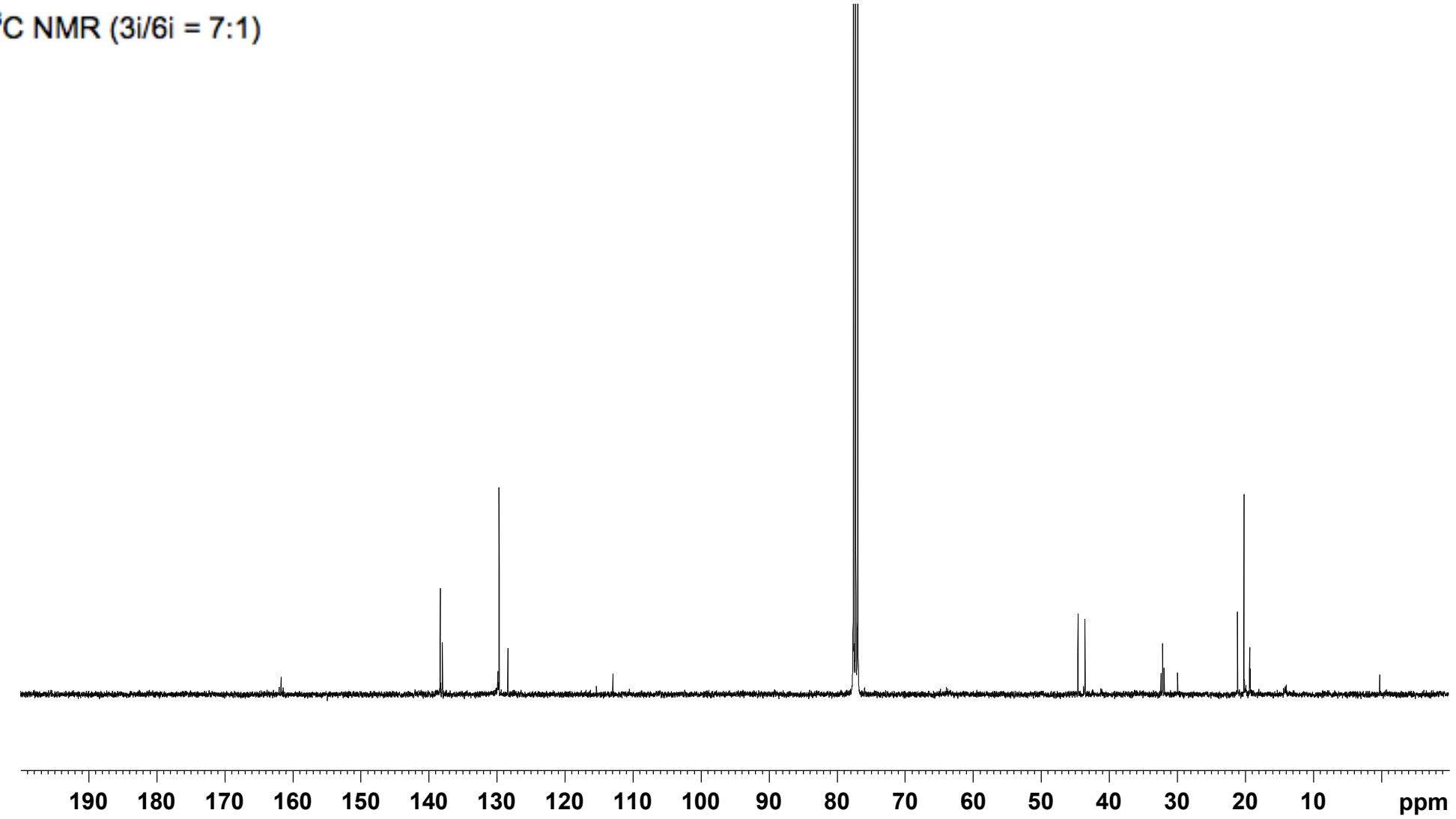


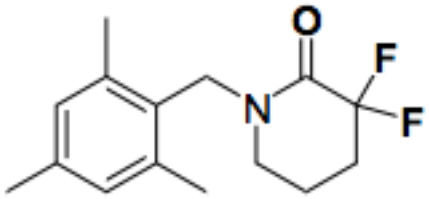
3i : ^{1}H NMR (3i/6i = 7:1)





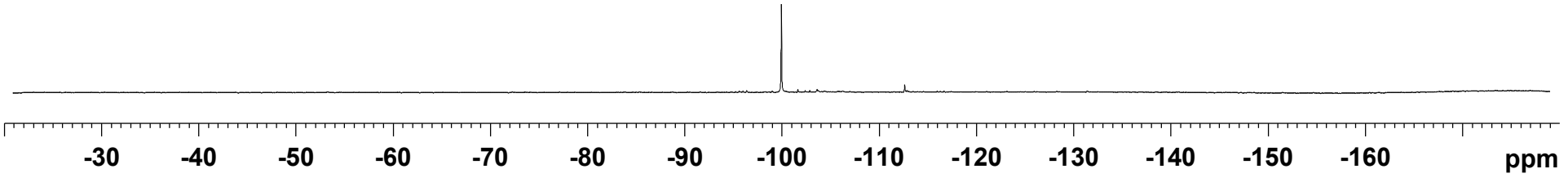
3i : ^{13}C NMR (3i/6i = 7:1)

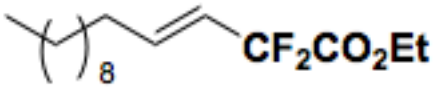




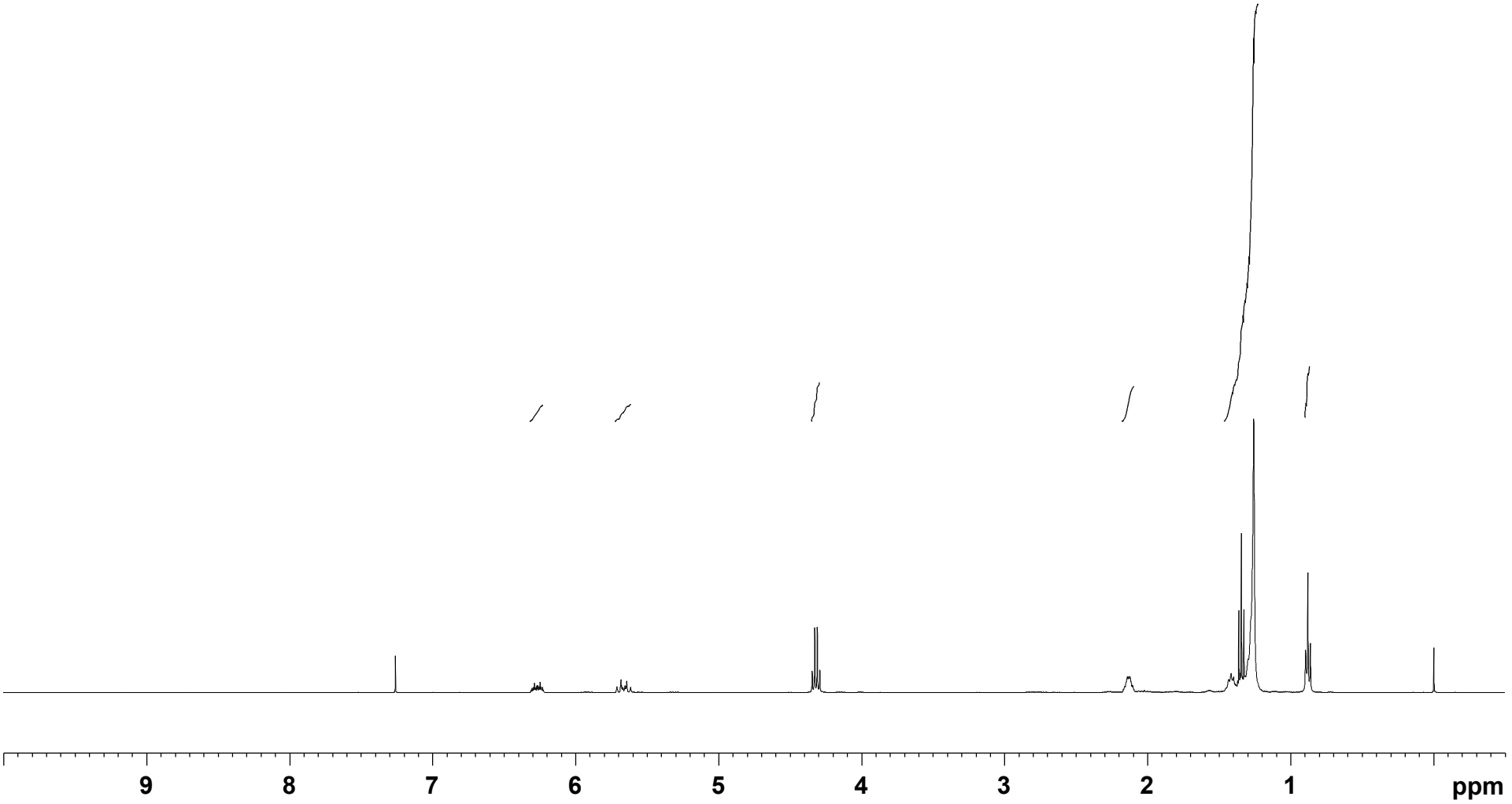
-99.95

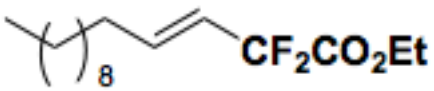
3i : ^{19}F NMR





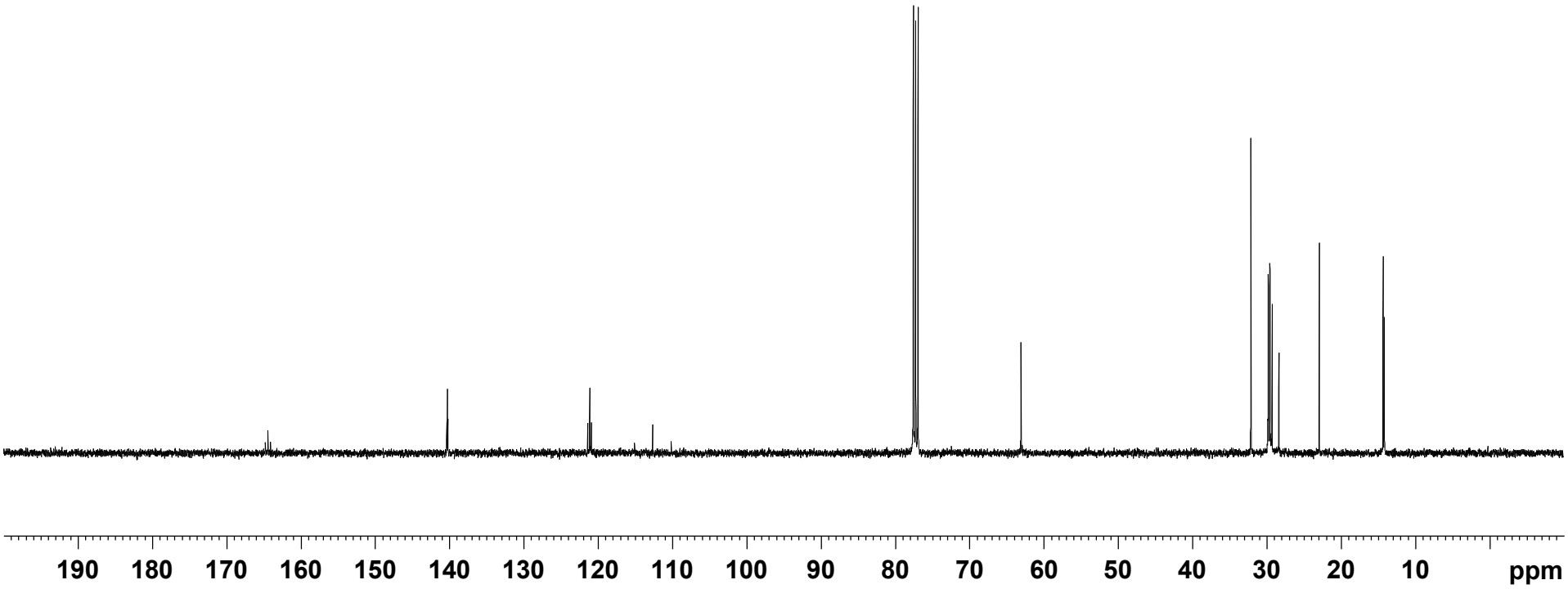
6a : ^{1}H NMR

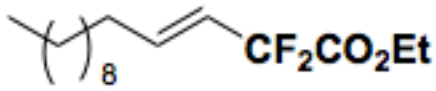




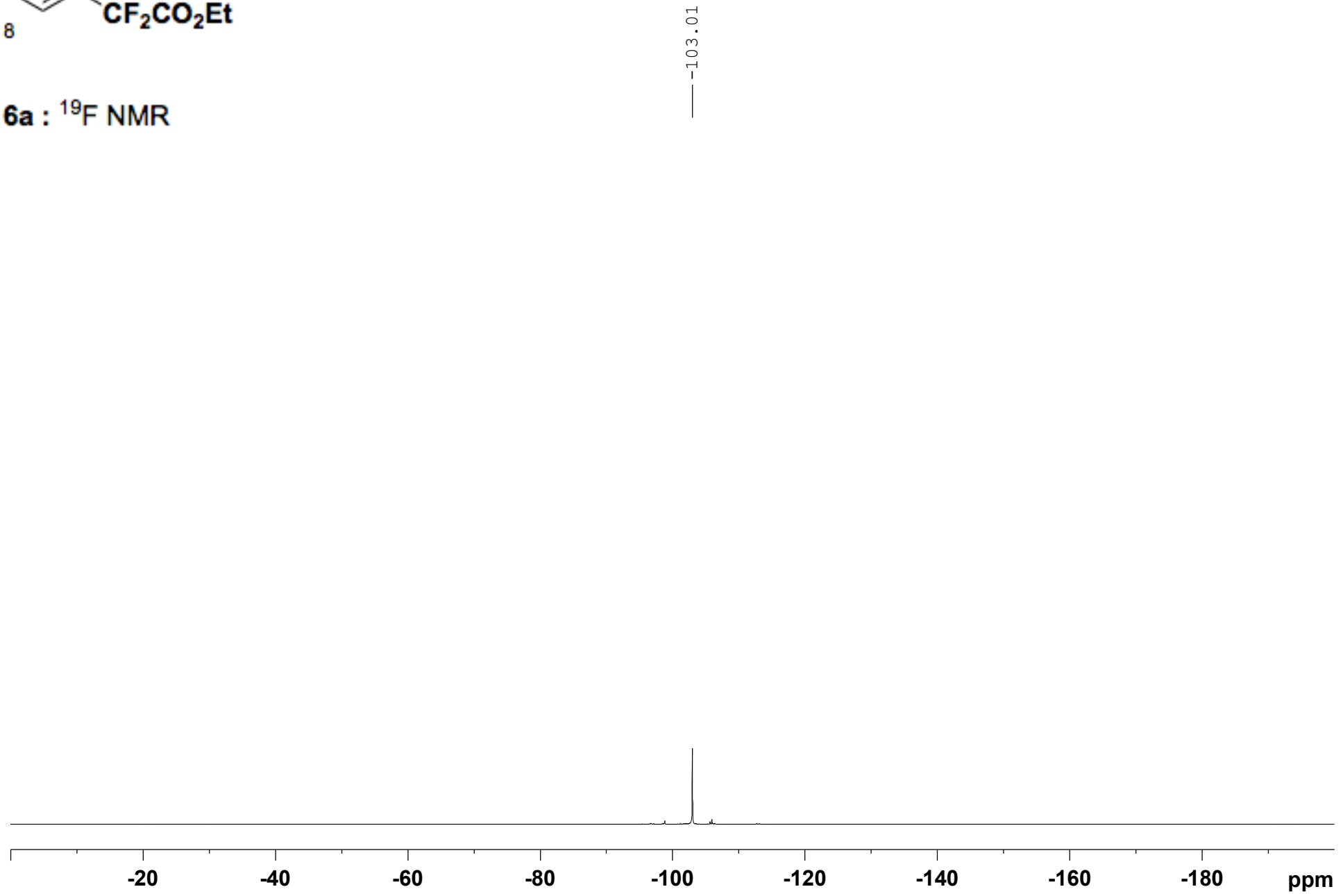
140.35
140.26
140.18
121.37
121.12
120.87
115.08
112.62
110.16
63.06
32.11
29.79
29.75
29.59
29.53
29.25
28.33
22.89
14.32
14.15

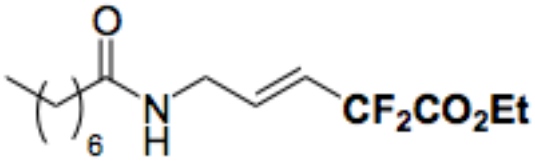
6a : ^{13}C NMR





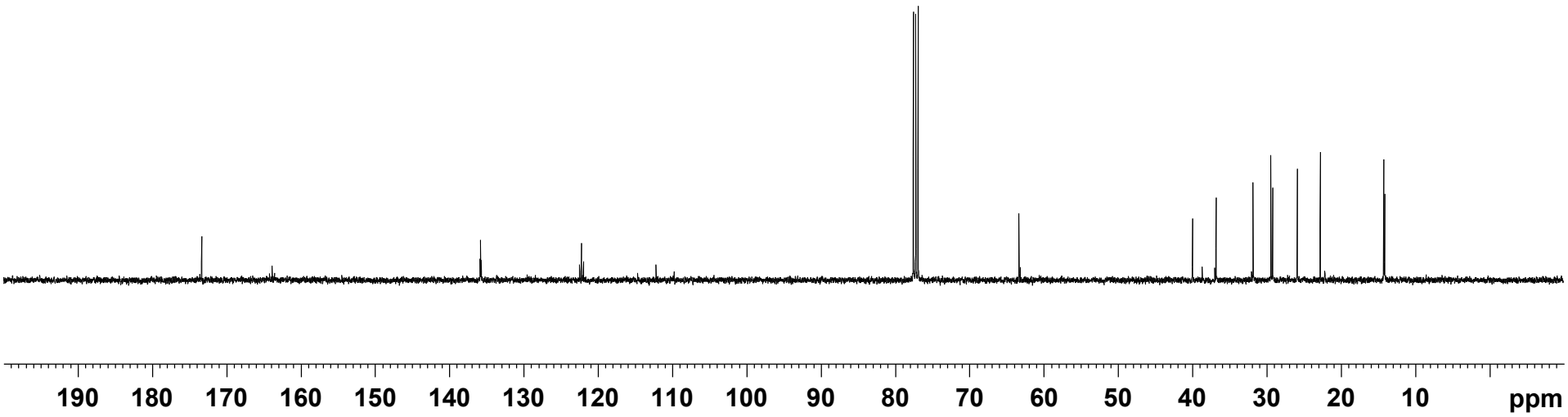
6a : ^{19}F NMR

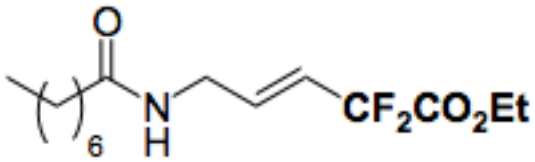




135.89
135.80
135.72
122.47
122.21
121.96
114.67
112.21
109.74
63.34
39.96
36.80
31.84
29.42
29.17
25.86
22.77
14.23
14.09

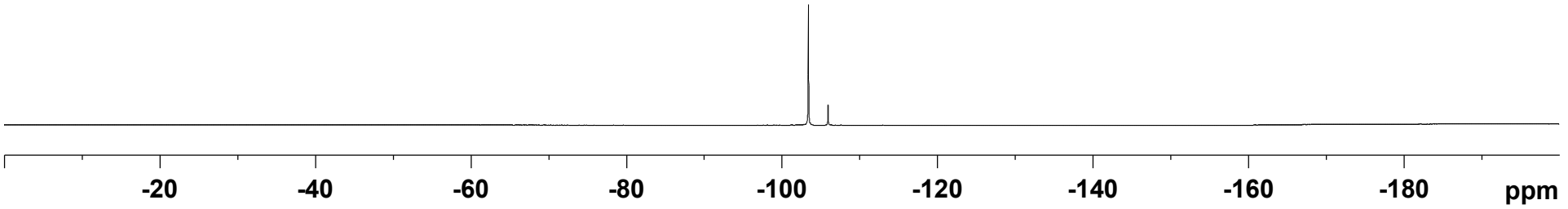
6d : ^{13}C NMR

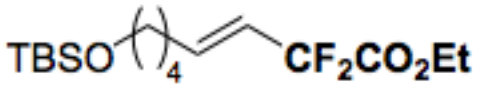




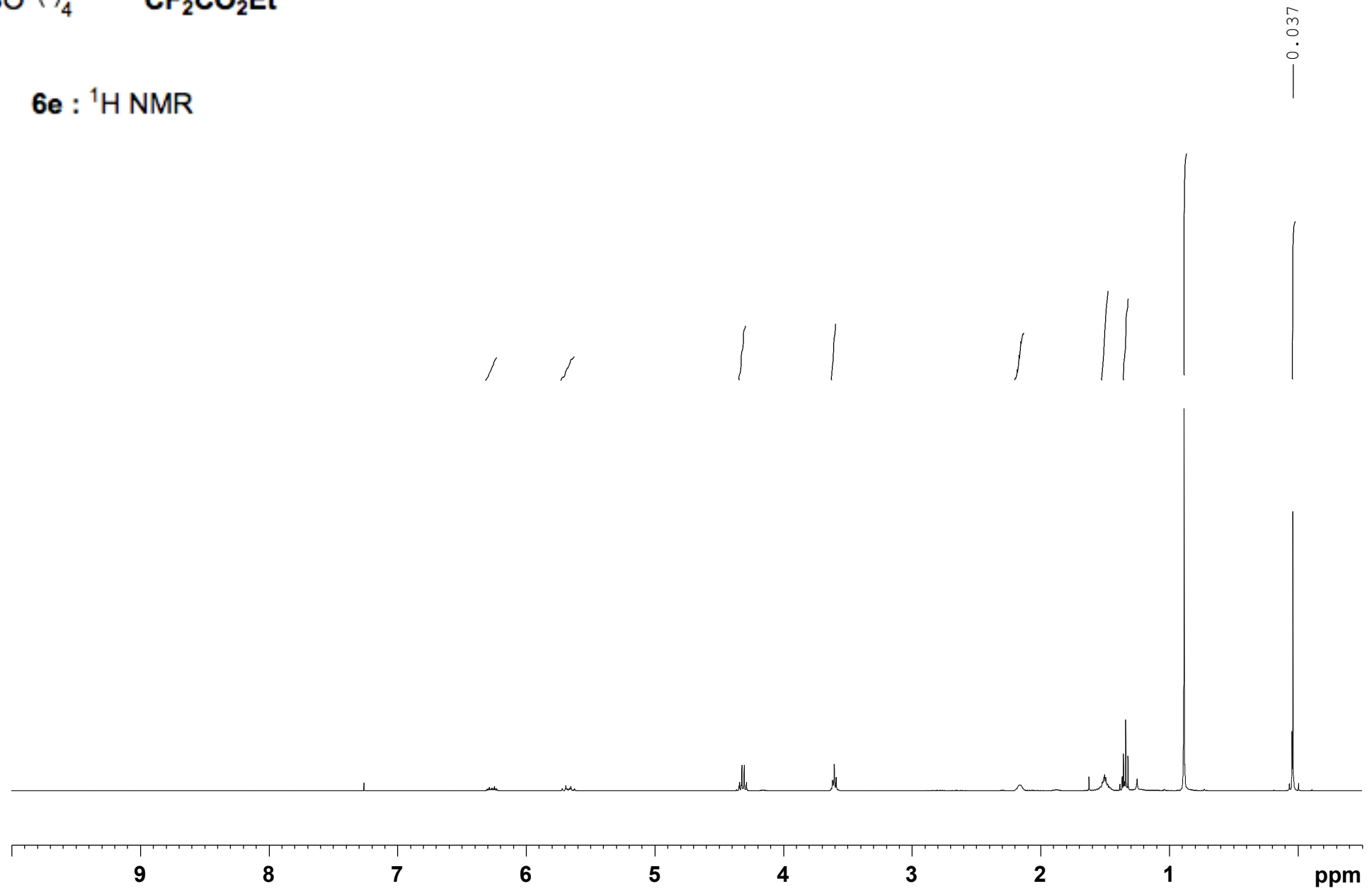
-103.42
-105.94

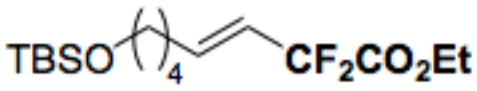
6d : ^{19}F NMR (6d/3d = 15:1)



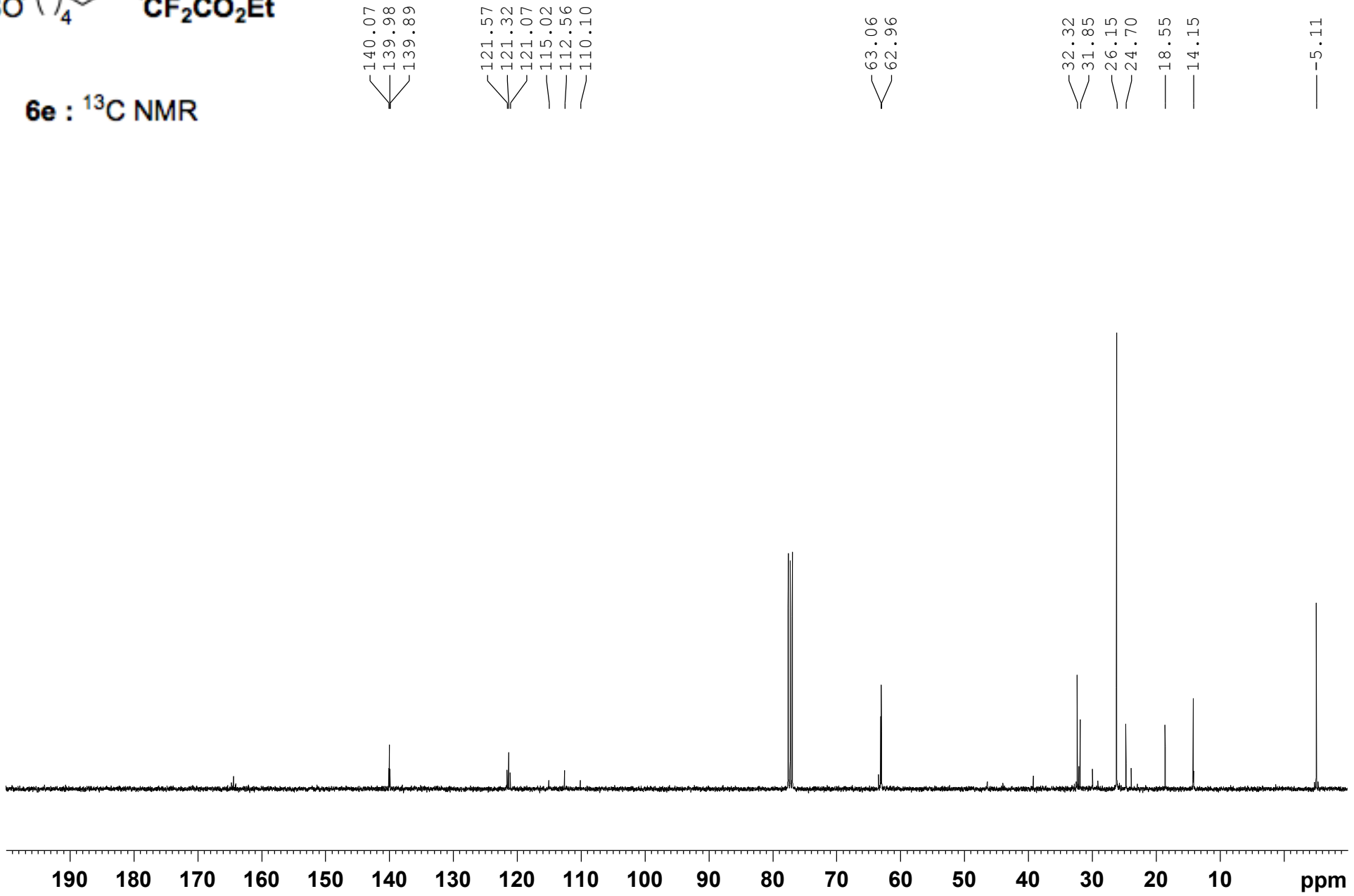


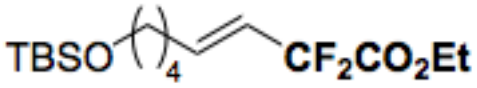
6e : ^{1}H NMR



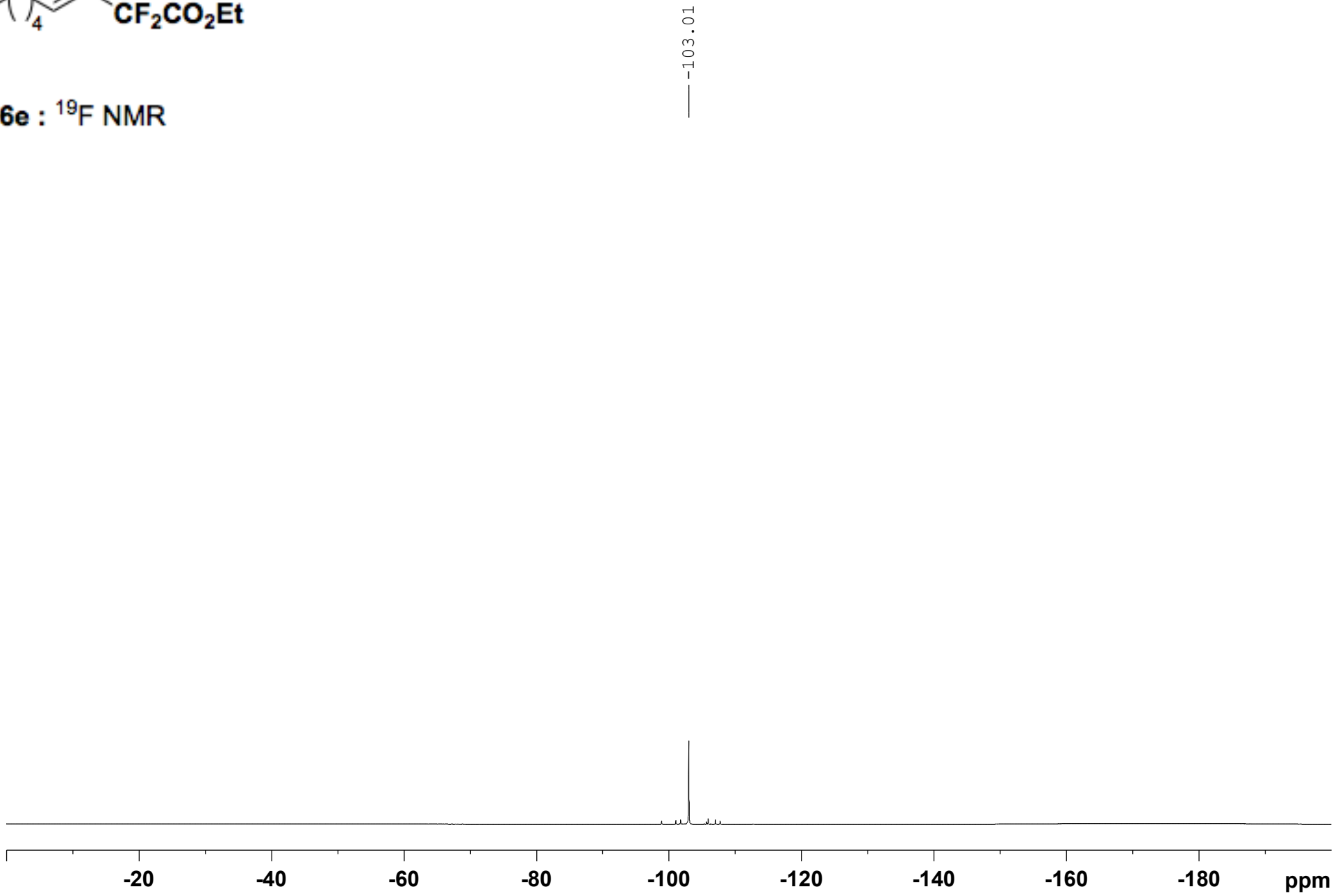

TBSO
4
CF2CO2Et

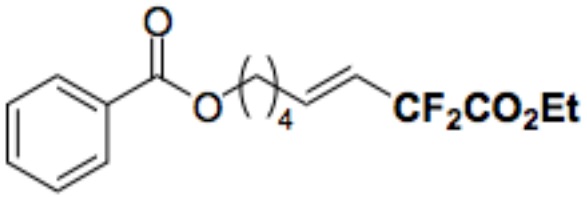
6e : ^{13}C NMR


140.07
139.98
139.89
121.57
121.32
121.07
115.02
112.56
110.10
63.06
62.96
32.32
31.85
26.15
24.70
18.55
14.15
-5.11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

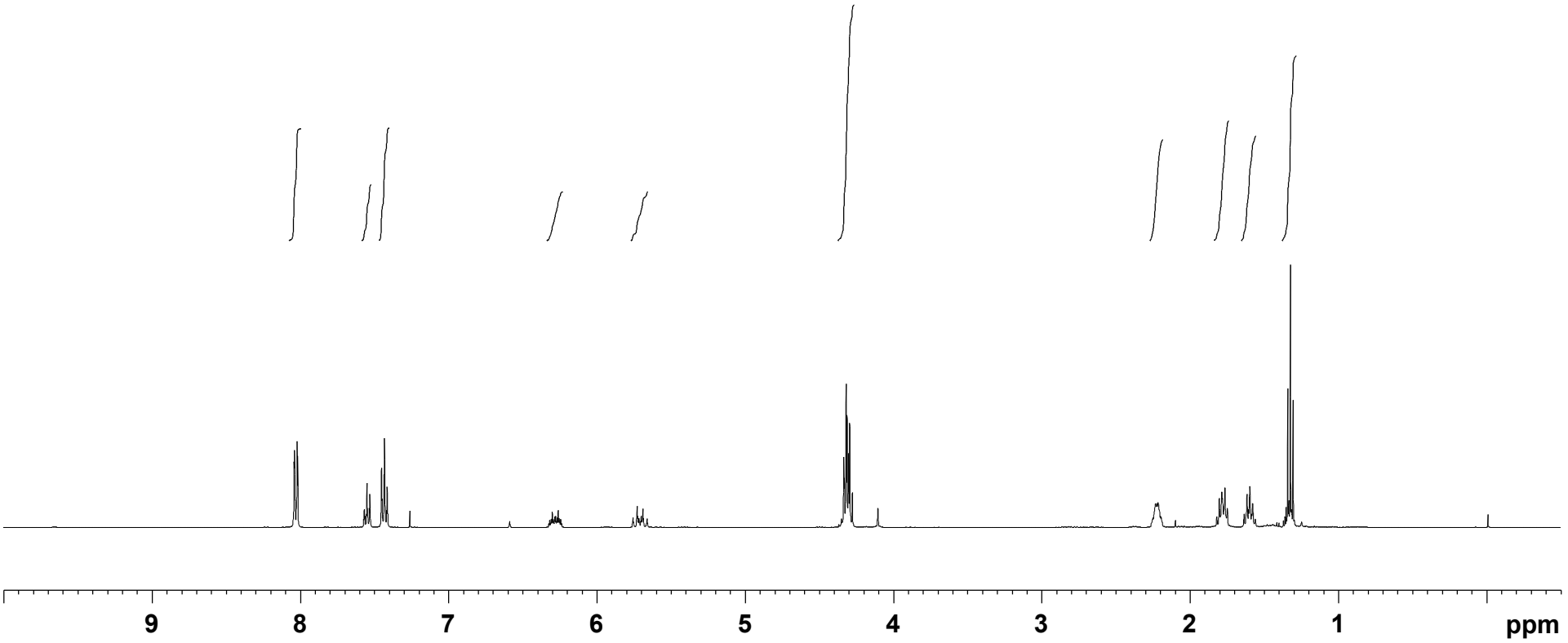


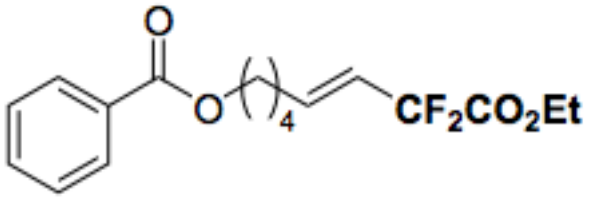
6e : ^{19}F NMR



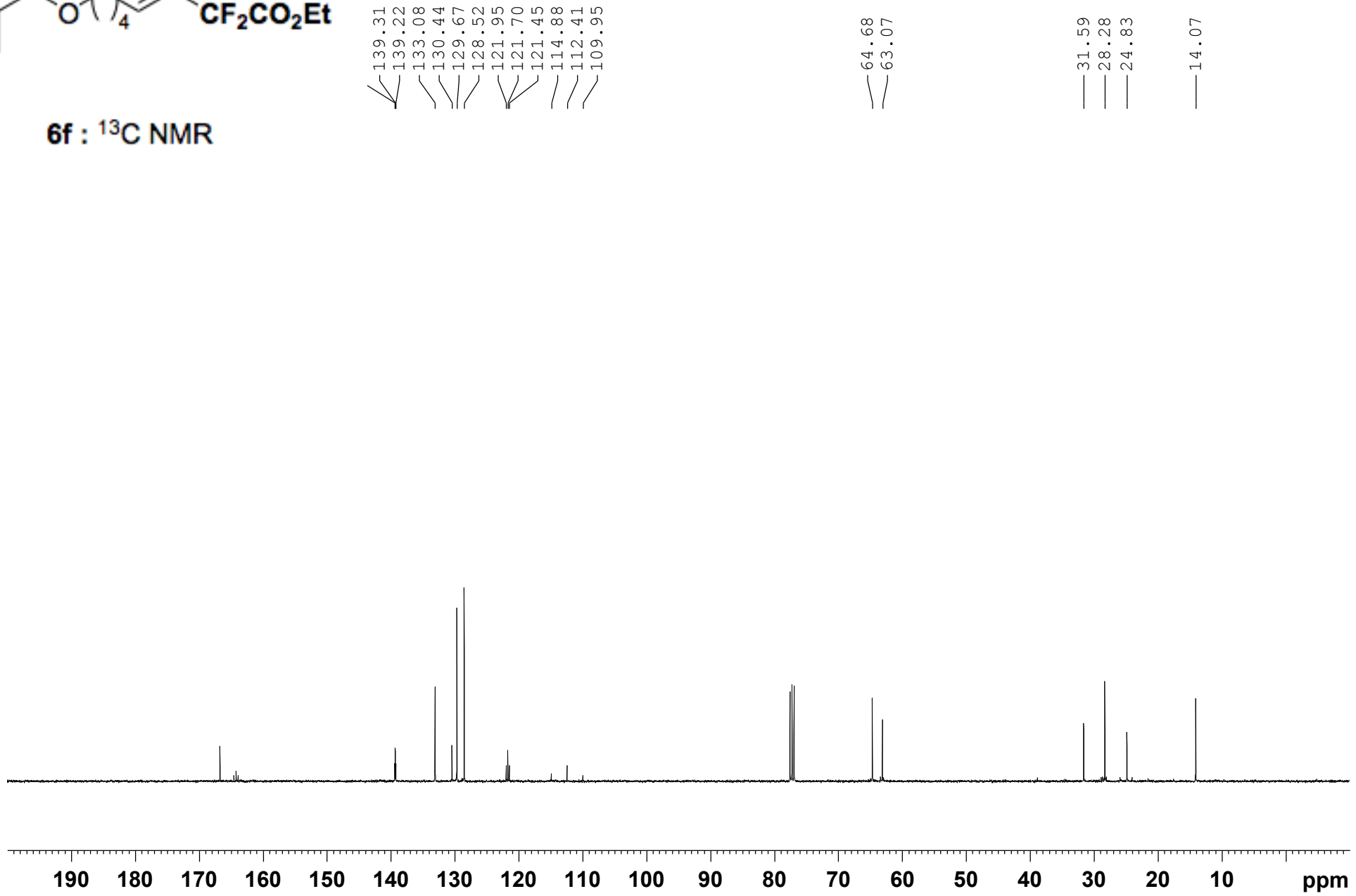


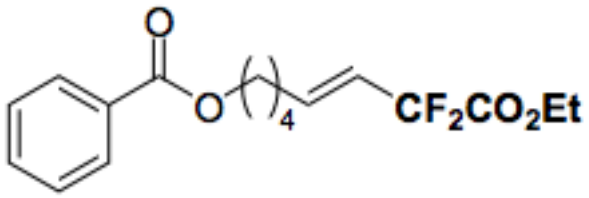
6f : ^{1}H NMR




O
O
4
CF2CO2Et

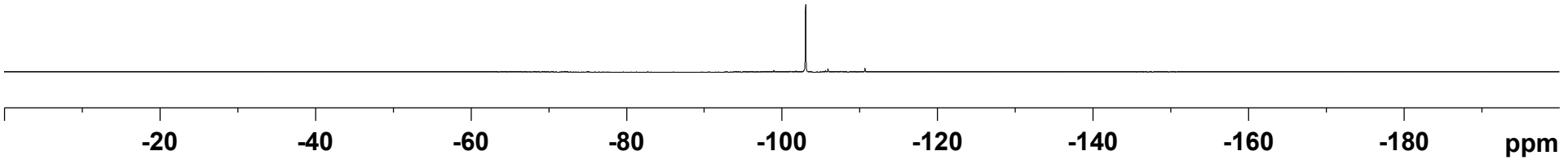
6f : ^{13}C NMR

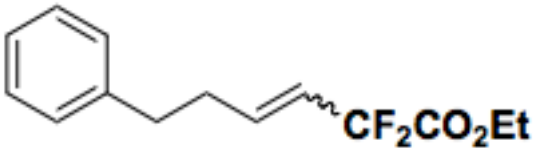

139.31
139.22
133.08
130.44
129.67
128.52
121.95
121.70
121.45
114.88
112.41
109.95
64.68
63.07
31.59
28.28
24.83
14.07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



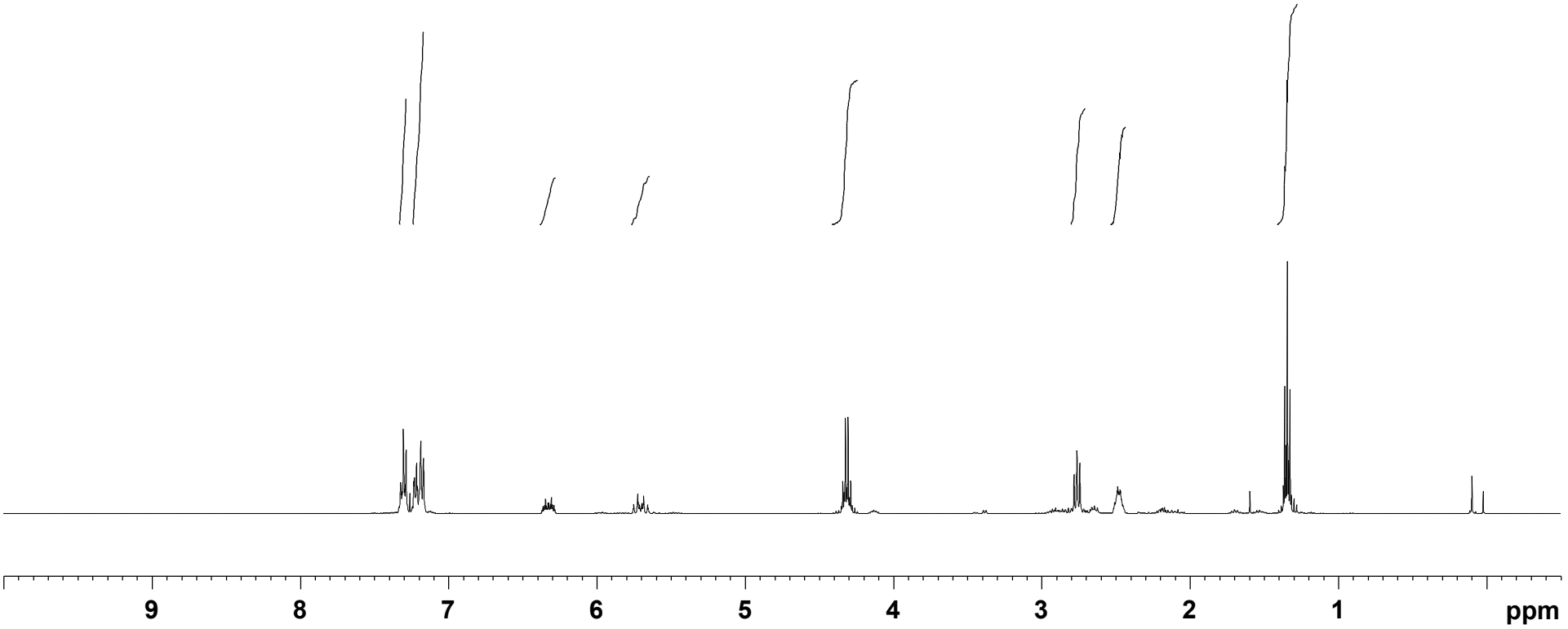
-103.06

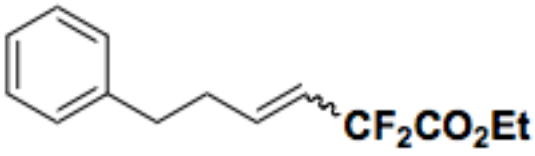
6f : ^{19}F NMR

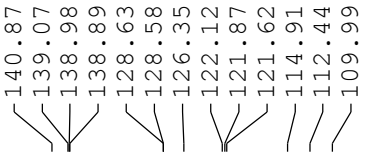


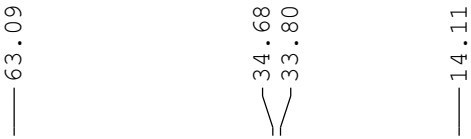


6k : ^{1}H NMR (*E*/*Z* = 15:1)

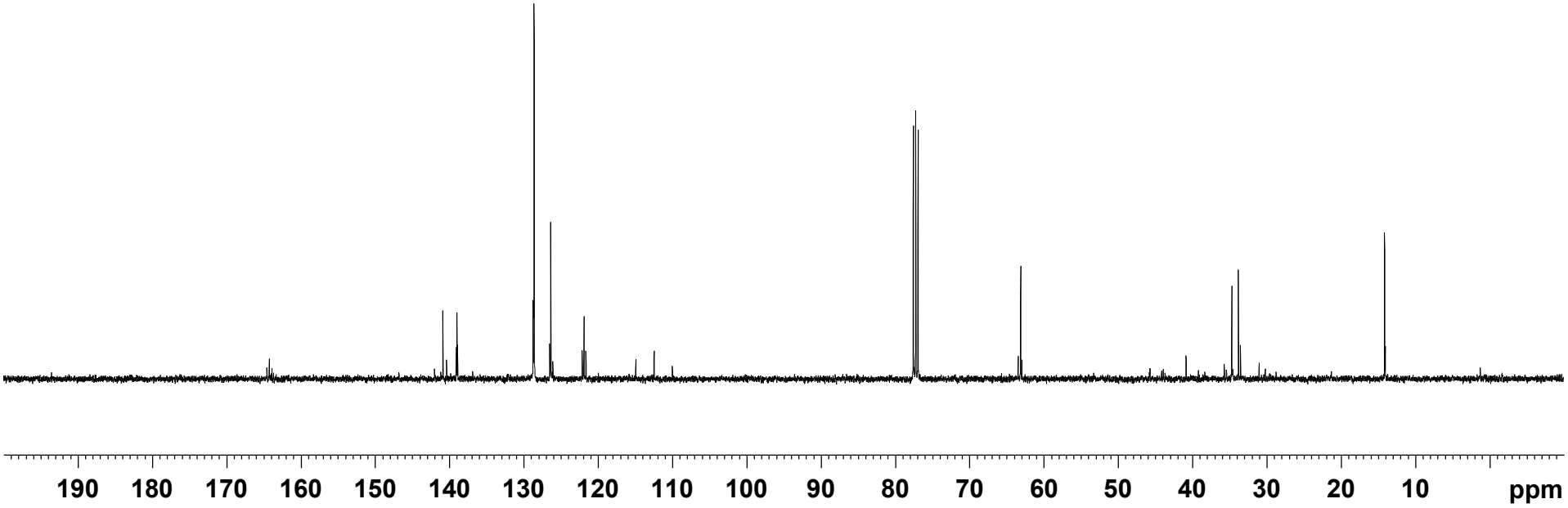


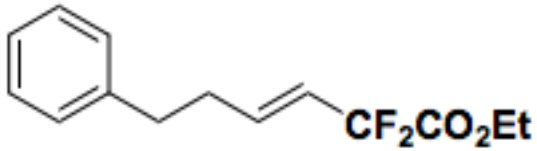




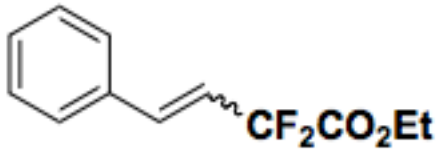


6k : ^{13}C NMR (*E*/*Z* = 15:1)

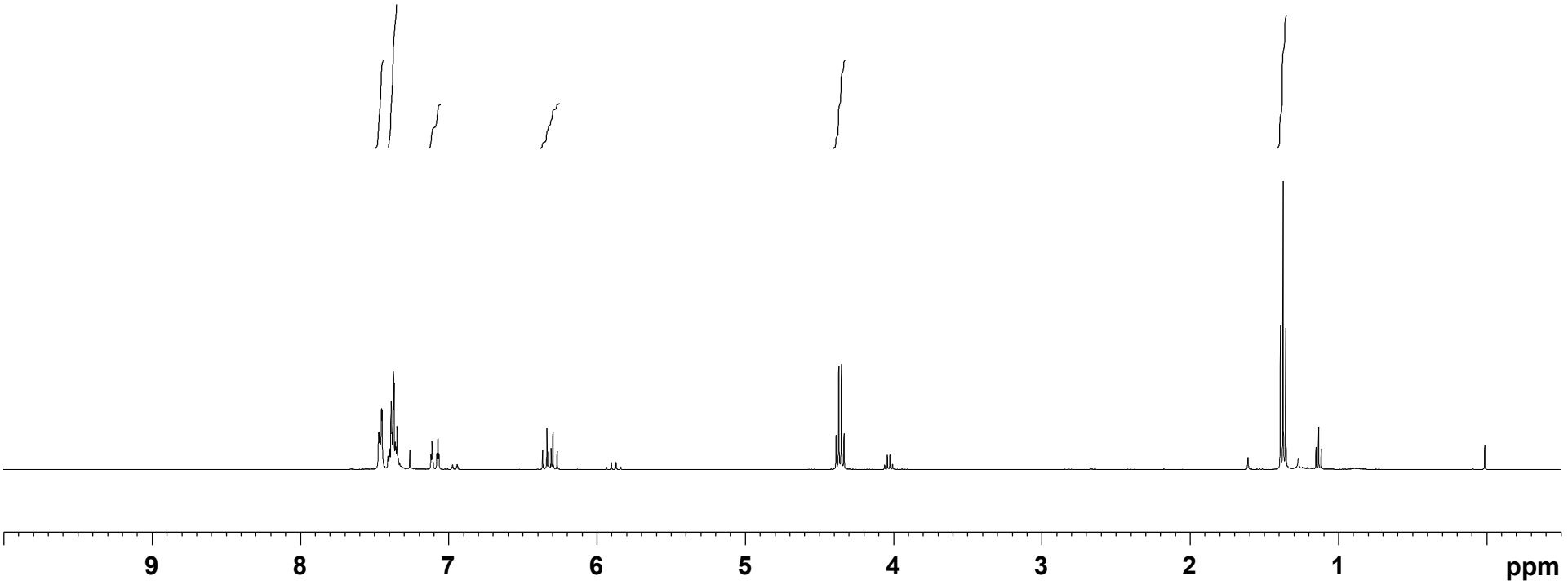


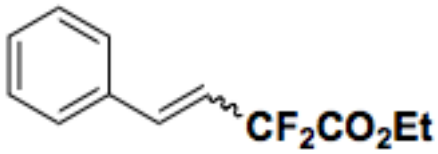


6k : ^{19}F NMR



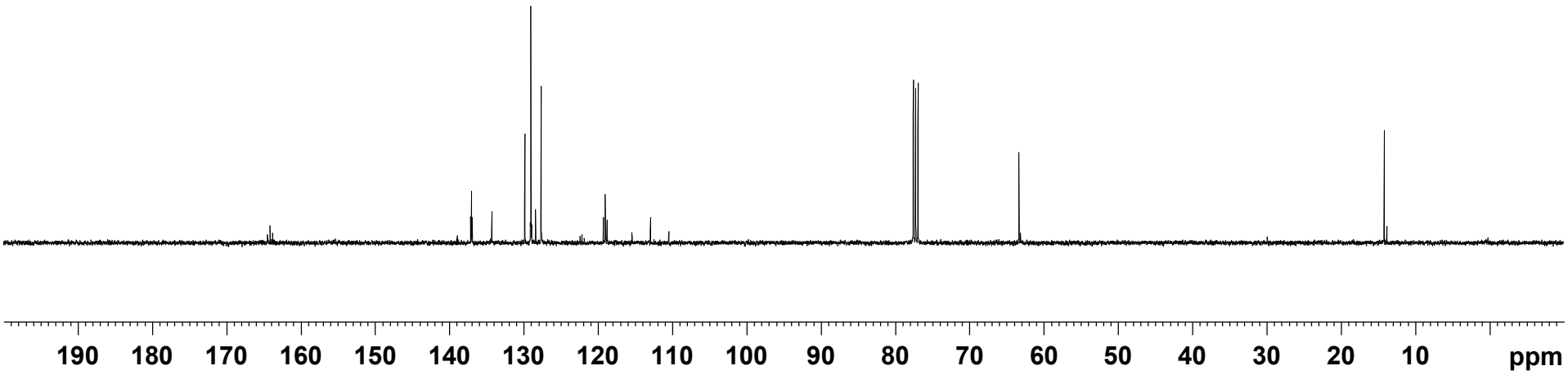
6l : ^{1}H NMR (*E*/*Z* = 11:1)

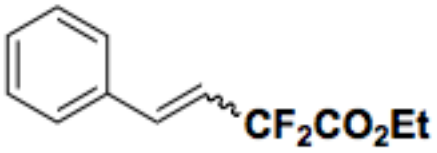




137.13
137.03
136.94
129.85
129.04
128.40
127.65
119.26
119.01
118.77
115.41
112.94
110.47
63.33
14.15

6l : ^{13}C NMR (*E*/*Z* = 11:1)

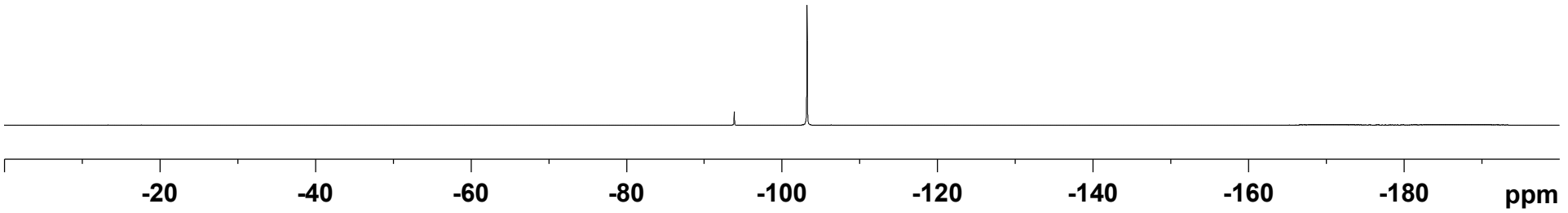


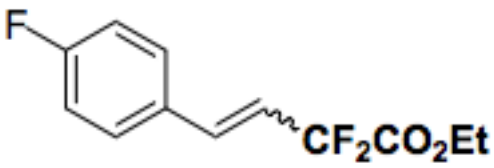


-93.89

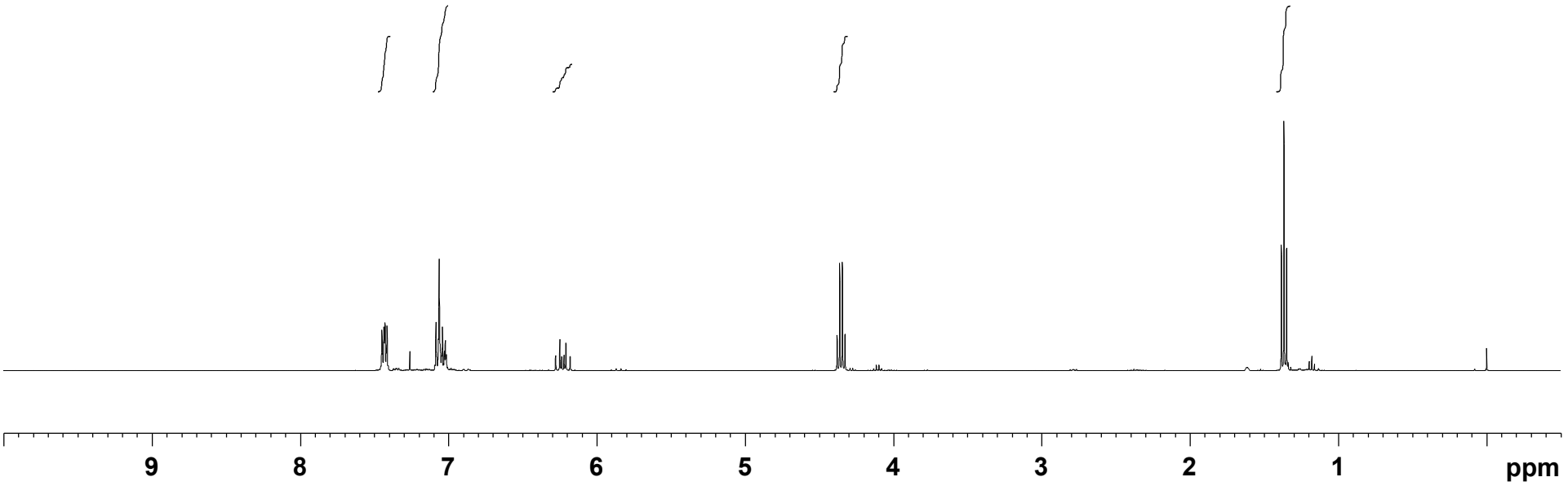
-103.24

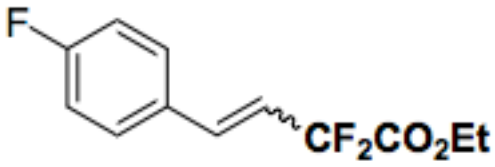
6l : ^{19}F NMR (*E*/*Z* = 11:1)





6m : ^{1}H NMR (*E*/*Z* = 25:1)



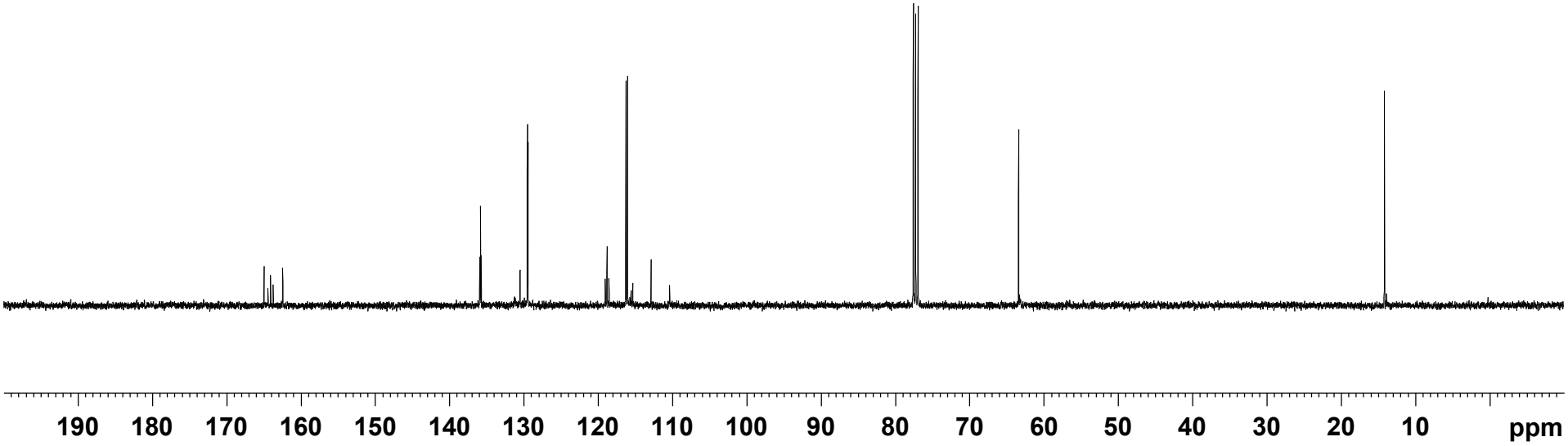


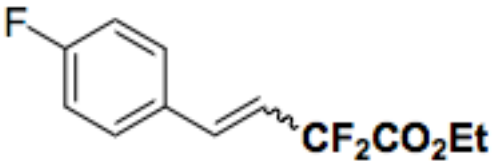
135.91
135.82
135.72
130.53
130.50
129.50
129.42
119.04
119.02
118.79
118.77
118.54
118.52
116.24
116.02
115.30
112.83
110.36

63.38

14.15

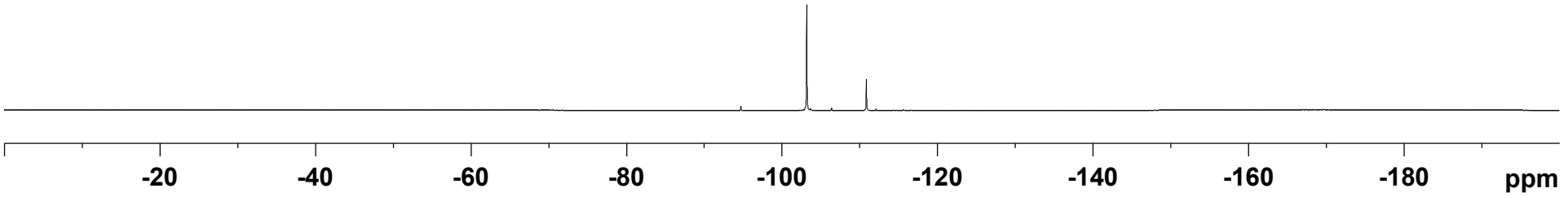
6m : ^{13}C NMR (*E*/*Z* = 25:1)

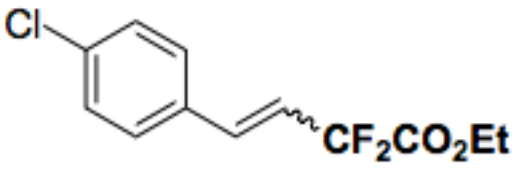




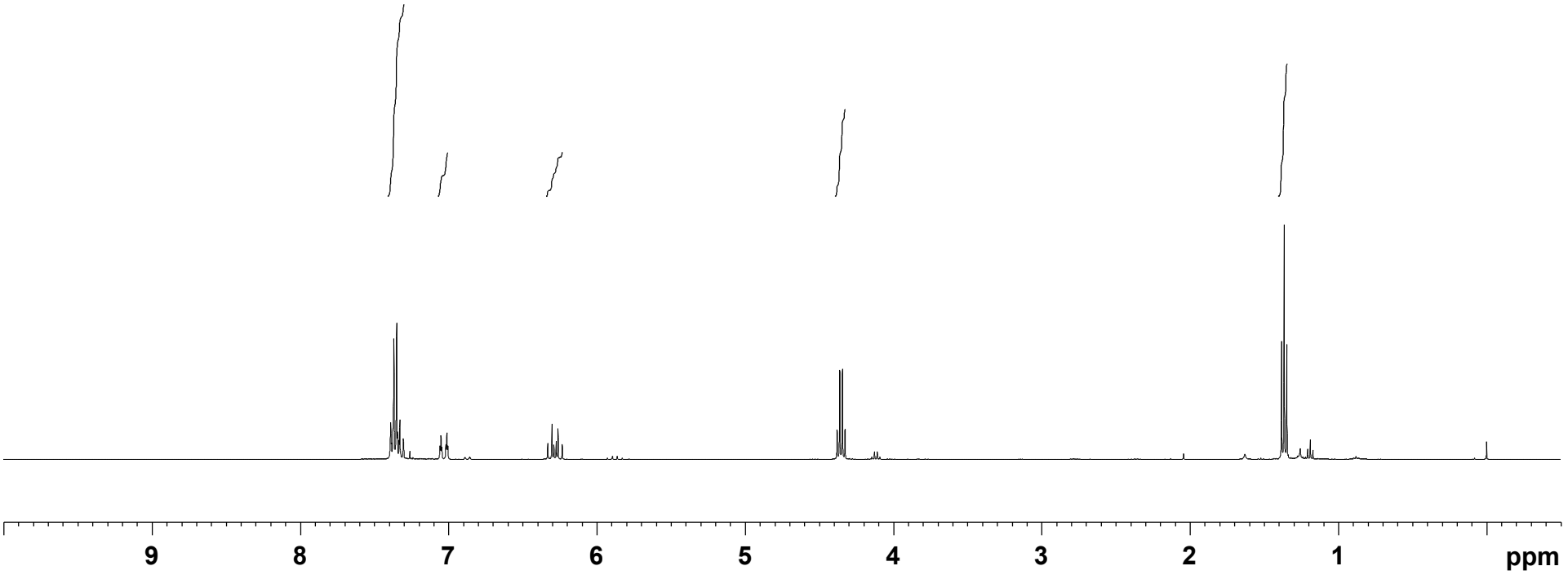
-94.72
-103.21
-110.87

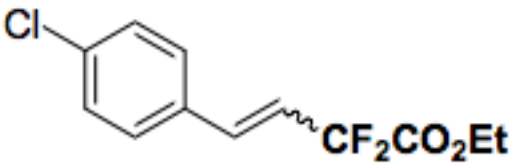
6m : ^{19}F NMR (*E*/*Z* = 25:1)





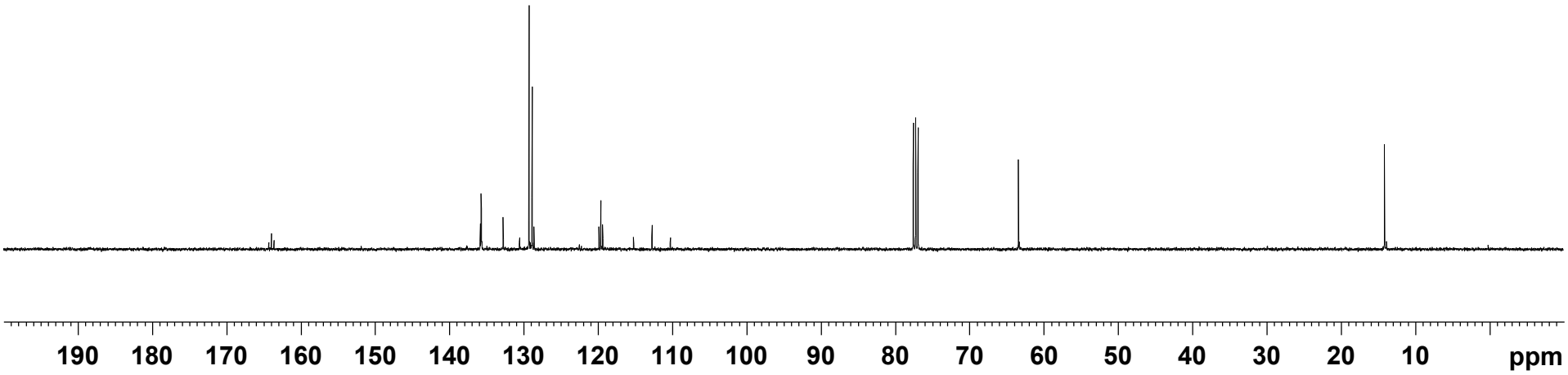
6n : ^{1}H NMR (*E*/*Z* = 19:1)

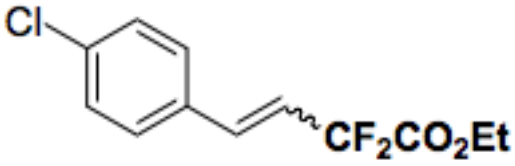




135.84
135.75
135.71
135.65
132.77
129.28
128.85
119.86
119.62
119.37
115.20
112.73
110.26
63.41
14.14

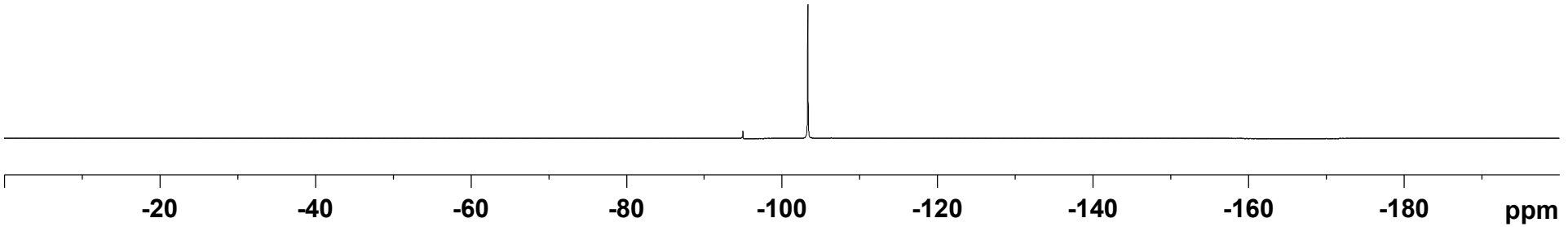
6n : ^{13}C NMR (*E*/*Z* = 19:1)

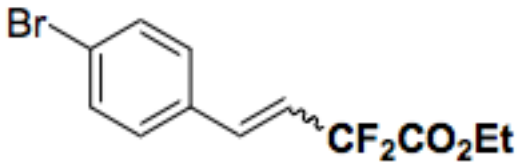




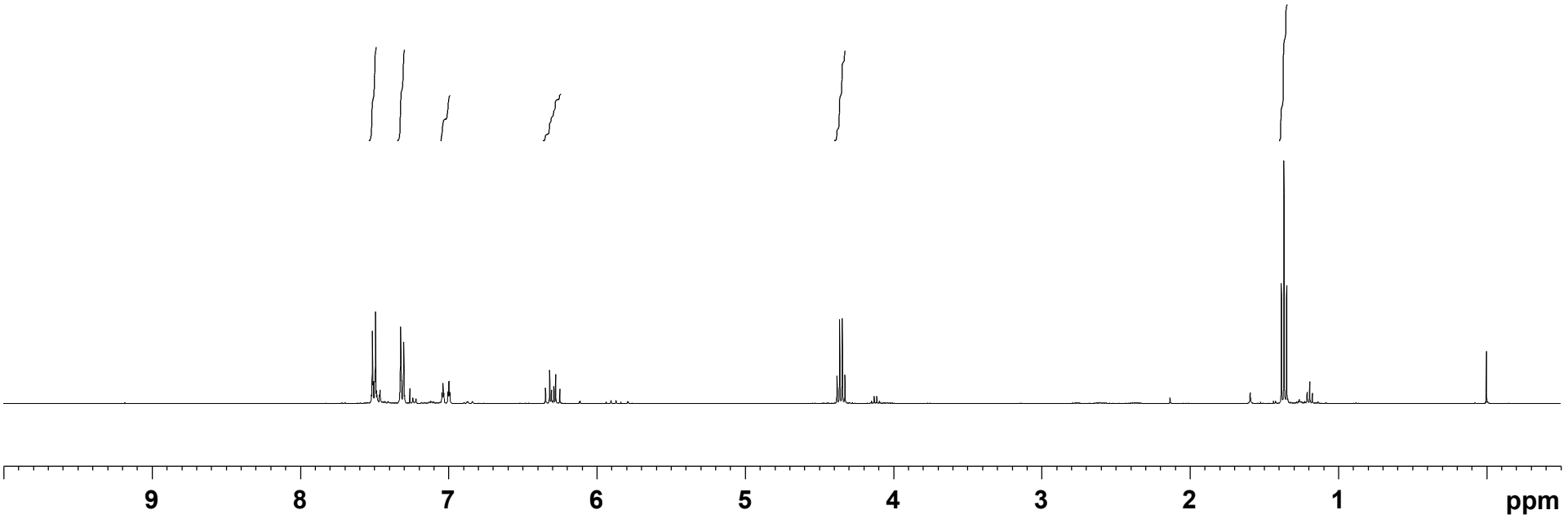
-94.99
-103.34

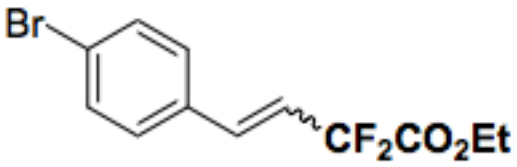
6n : ^{19}F NMR (*E*/*Z* = 29:1)





6o : ^{1}H NMR (*E*/*Z* = 11:1)



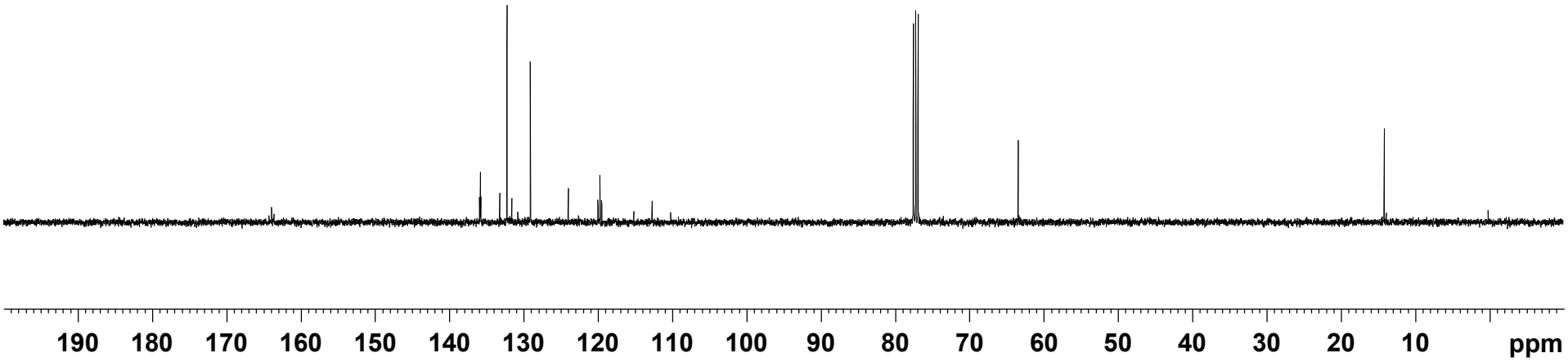


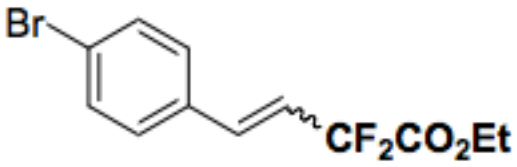
135.93
135.84
135.74
133.21
132.25
129.11
124.00
120.00
119.75
119.50
115.19
112.71
110.24

63.42

14.16

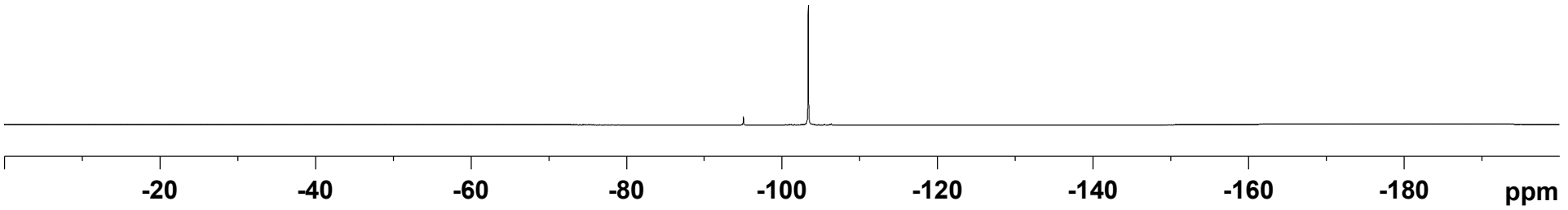
6o : ^{13}C NMR (*E*/*Z* = 11:1)

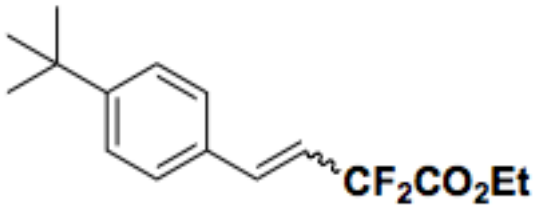




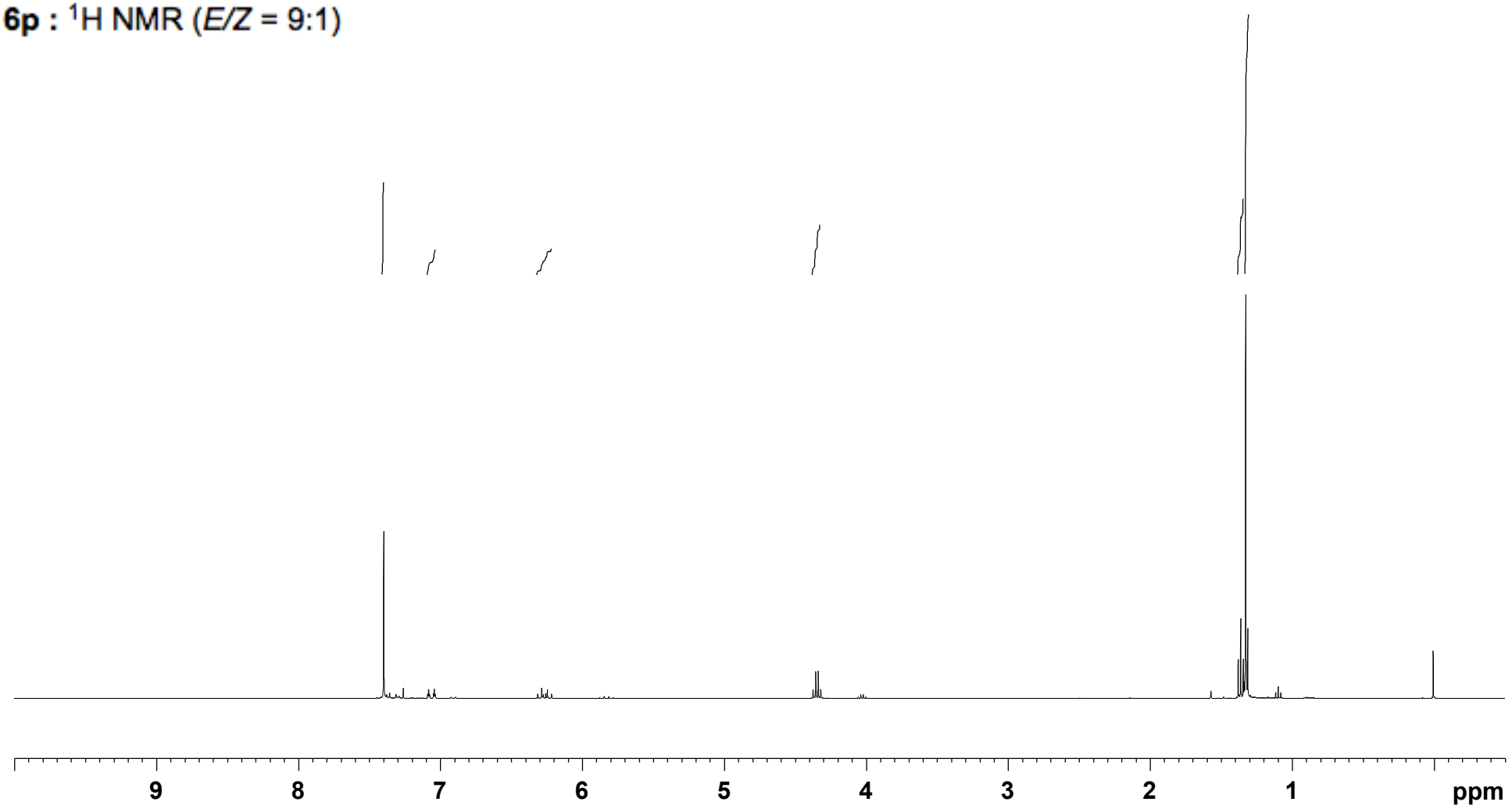
-95.05
-103.40

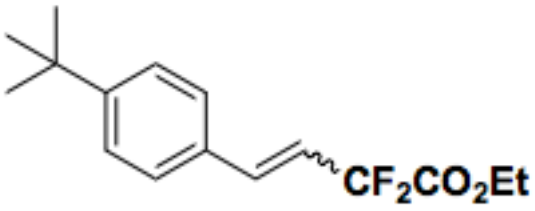
6o : ^{19}F NMR (*E*/*Z* = 11:1)





6p : ^{1}H NMR (*E*/*Z* = 9:1)





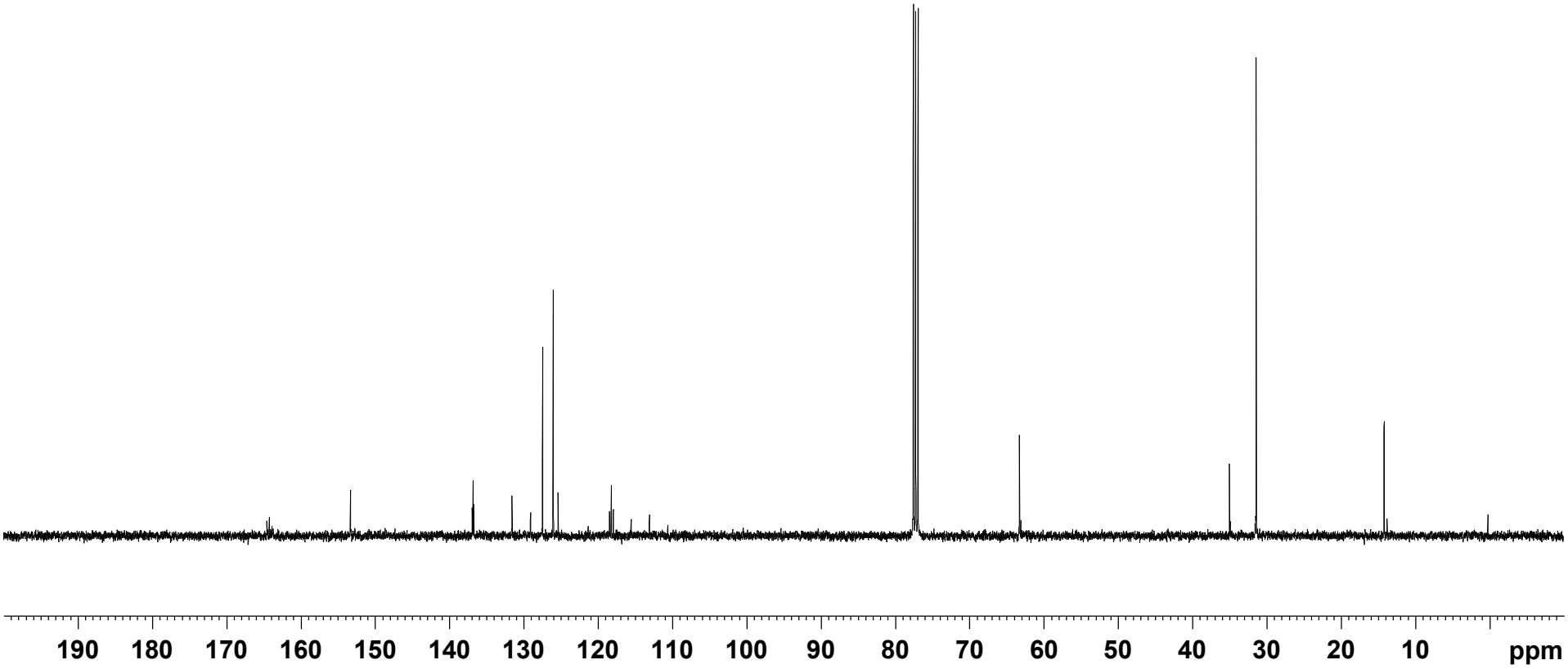
136.92
136.83
136.73
131.57
127.45
126.01
118.44
118.19
117.94
115.55
113.08
110.61

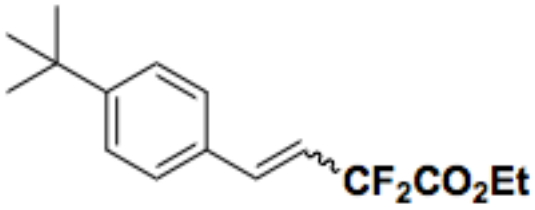
63.27

35.00
31.40

14.18

6p : ^{13}C NMR (*E*/*Z* = 9:1)

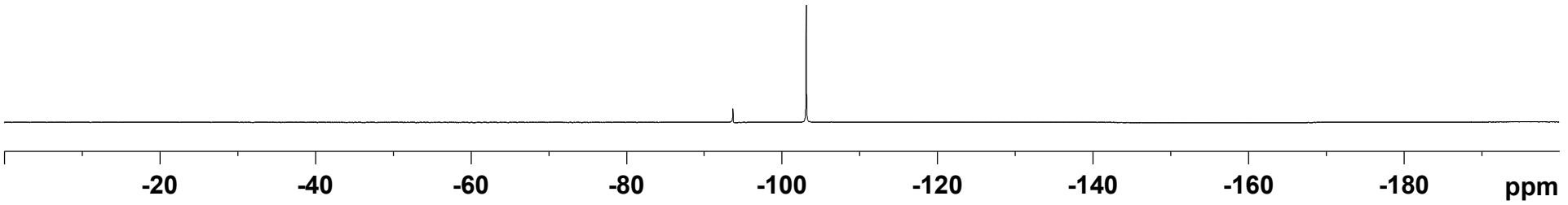


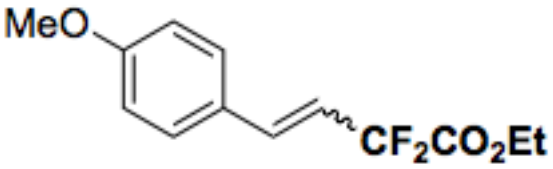


-93.70

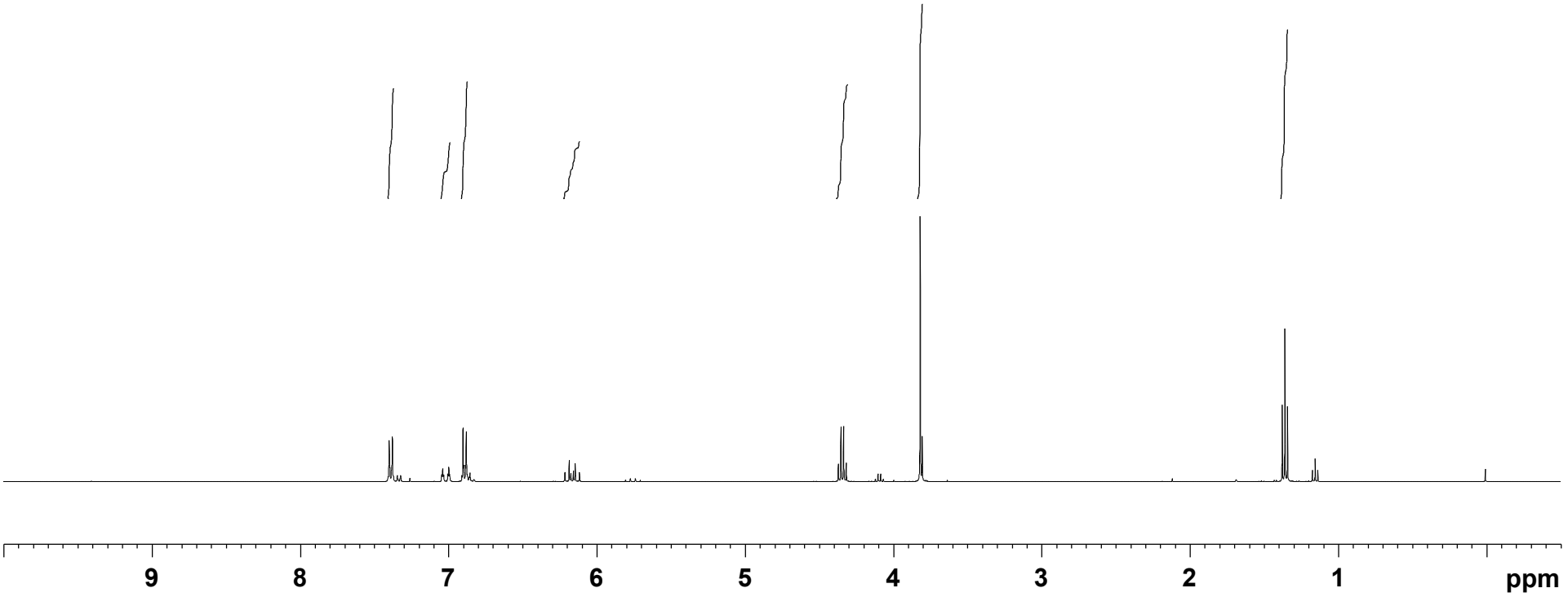
-103.14

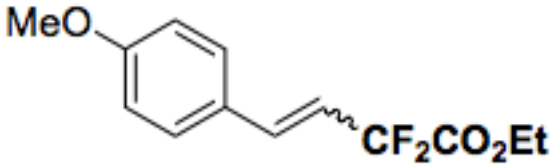
6p : ^{19}F NMR (*E*/*Z* = 9:1)





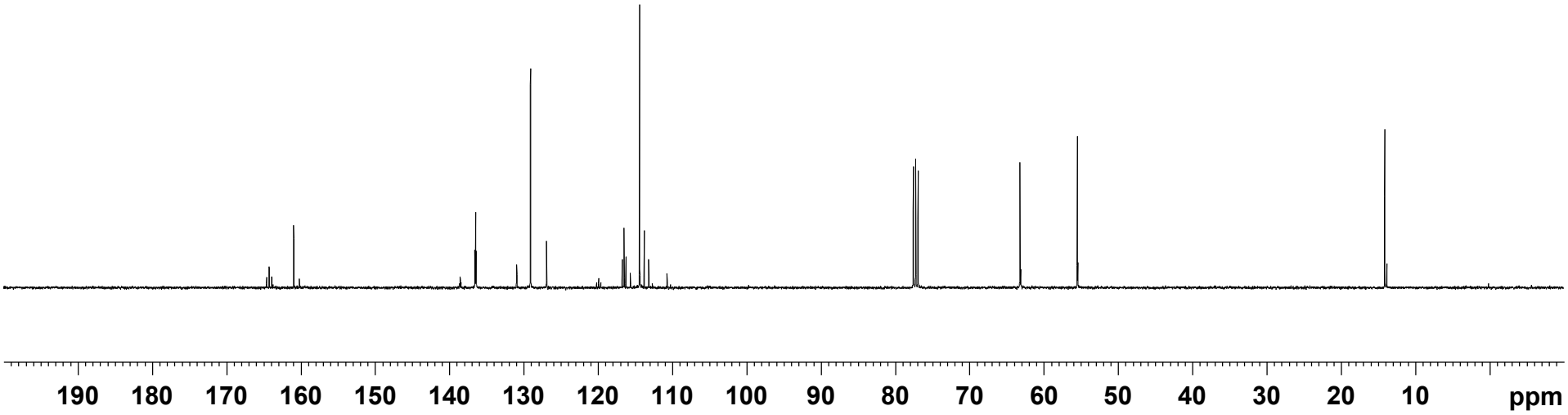
6q : ^{1}H NMR (*E*/*Z* = 9:1)

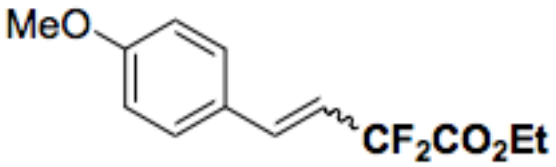




136.57
136.47
136.38
129.08
126.93
116.73
116.48
116.23
115.63
114.39
113.16
110.69
63.20
55.47
14.10

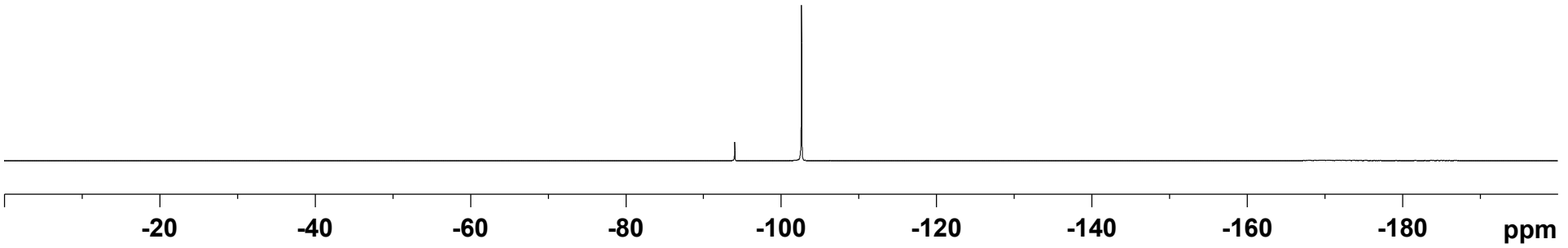
6q : ^{13}C NMR (*E*/*Z* = 9:1)

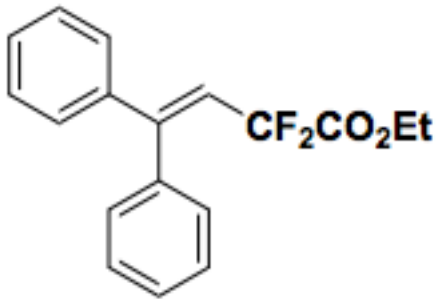




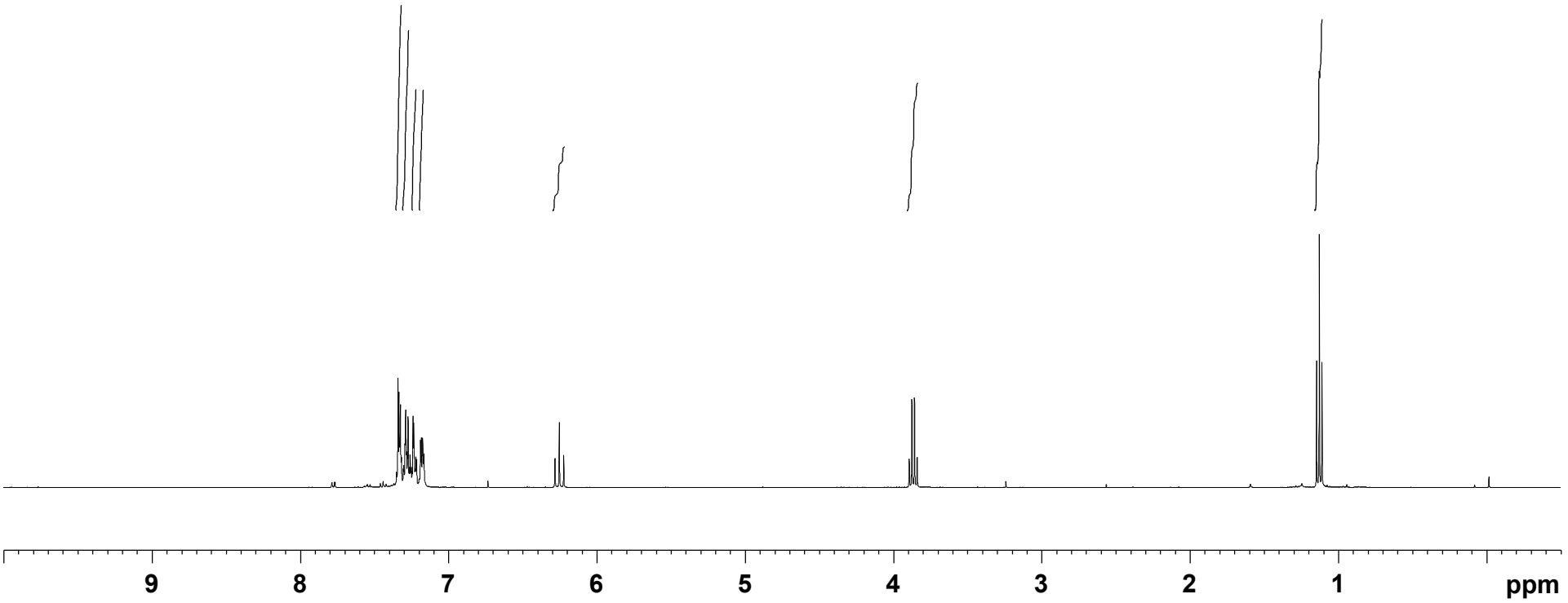
-94.04
-102.64

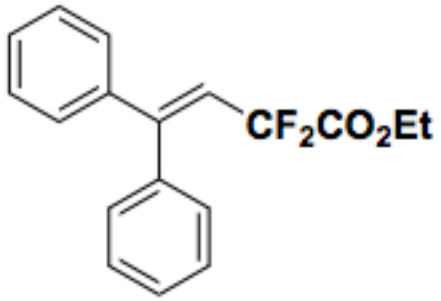
6q : ^{19}F NMR (*E*/*Z* = 9:1)





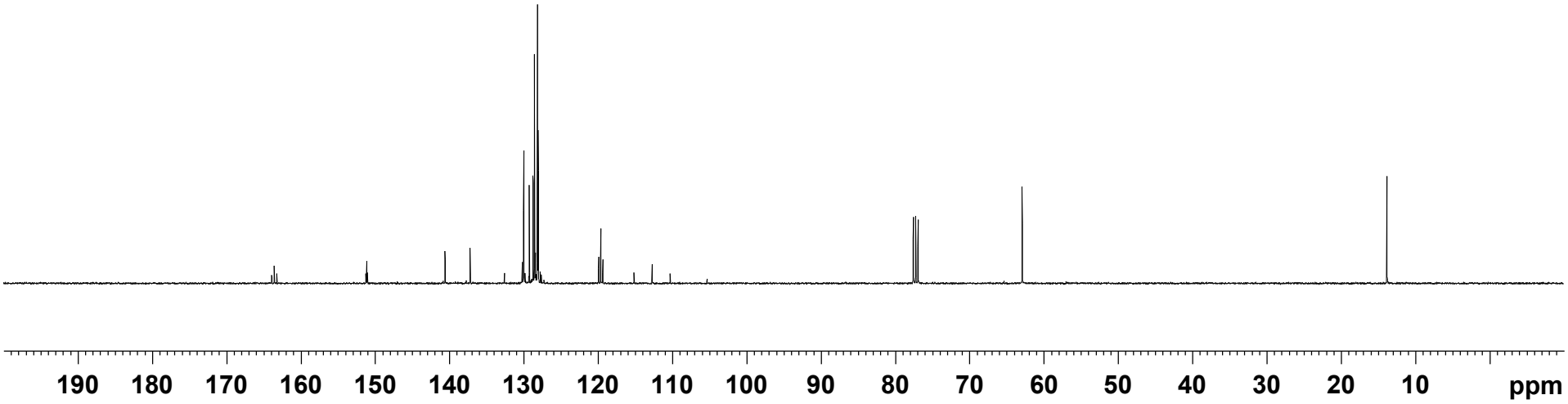
6r : ^{1}H NMR

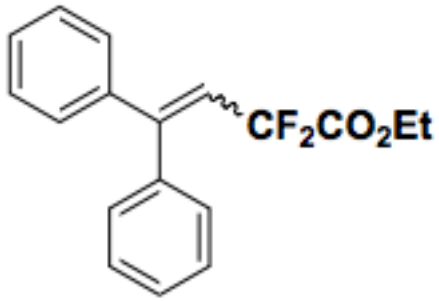




151.14
151.04
140.58
137.21
129.99
129.25
128.73
128.54
128.15
128.03
119.92
119.63
119.35
115.14
112.71
110.28
62.89
13.80

6r : ^{13}C NMR





6r : ^{19}F NMR