SUPPORTING INFORMATION

(*Z*)- or (*E*)-Selective Hydrogenation of Potassium (3,3,3-trifluoroprop-1-yn-1-yl)trifluoroborate: Route to Either Isomer of β-Trifluoromethylstyrenes

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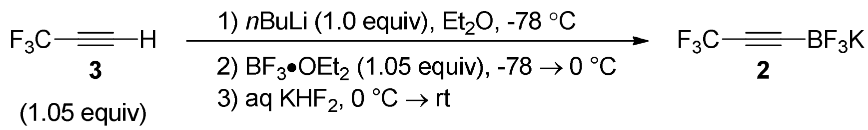
Experimental and Characterization Data

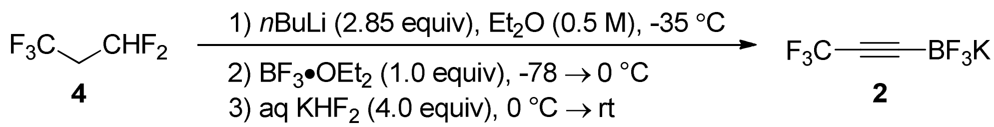
General Supporting Information

Reagents were purchased from Sigma-Aldrich, Fisher-Acros, Strem Chemical, Oakwood Chemical, or Alfa-Aesar, and were used without further purification, unless otherwise noted. All solvents were distilled prior to use, unless otherwise noted. All reactions were performed at room temperature and under a nitrogen atmosphere in either flame or oven-dried glassware, unless otherwise noted. All TLC analysis was performed using aluminum-backed thin-layer chromatography plates (Dynamic Absorbent Inc., 200 μm thickness, F-254 Indicator). All solvent systems are given as volume/volume ratios. Flash chromatography was performed using 230-400 mesh, 60Å pore diameter flash chromatography gel. All chromatography elutions were gradient in nature, eluting first with hexanes, followed by incorporating more polar solvents as appropriate. ^{1}H, ^{11}B, ^{13}C, and ^{19}F spectra were recorded at room temperature, on Varian INOVA 300 MHz or Bruker 400 MHz. Chemical shifts (δ values) are reported in parts per million, and are referenced to tetramethylsilane. ^{11}B and ^{19}F NMR is referenced internal to the spectrometer. Data are reported as: δ value, multiplicity, and integration, (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, h=hextet). ^{1}H and ^{19}F NMR were used to measure of *E*:*Z* ratio of alkenes by comparing the relative integration values of the vinylic protons and alkenyl CF_3 groups.

Preparation of $CF_3C{\equiv}CBF_3K$

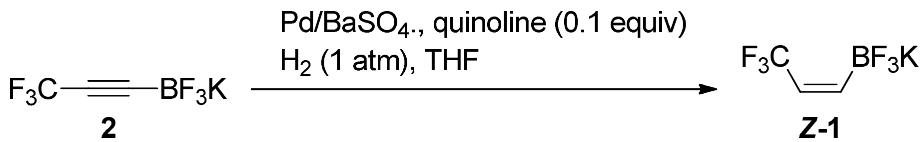


Potassium (3,3,3-trifluroprop-1-yn-1-yl)trifluoroborate (2): (From 3,3,3-trifluoroprop-1-yne). *n*BuLi (2.4 mL, 2.5 M in hexane) was added to a solution of **3** (586.3mg, 6.2 mmol) in Et_2O (12.5 mL) in a 50 mL RB flask at -78 °C. After stirring for 10 min, $BF_3{\cdot}OEt_2$ (0.77 mL, 6.2 mmol) was added, and the mixture was stirred for 10 min, followed by stirring at 0 °C for additional 30 min. Aqueous saturated KHF_2 (1.86 g, 23.8 mmol) was added to the mixture and stirred for 20 min at 0 °C, 1 h at rt, and opened to air. The residue, after removal of solvents, was extracted with acetone, filtered, concentrated, and precipitated with CH_2Cl_2. The solid was filtered and washed with CH_2Cl_2 to yield 1.05 g (89%) of **2** (white solid). ^{11}B NMR (96 MHz, CD_3CN) δ -2.04 (q, J = 28.8 Hz). ^{13}C NMR (101 MHz, CD_3CN) δ 115.1(q, J = 255.5 Hz), 101.3, 76.9. ^{19}F NMR (376 MHz, CD_3CN) δ -46.2 (s, 3F), -133.8 (q, J = 29.5 Hz, 3F). Mass (ESI-) calcd for $[M-K]^-$ 161.0, found 161.0.



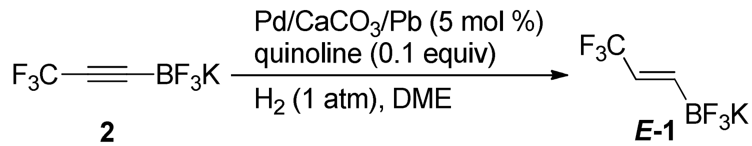
Potassium (3,3,3-trifluroprop-1-yn-1-yl)trifluoroborate (2): (From 1,1,1,3,3-petnafluoropropane, HFC-245fa). *n*BuLi (800 mL, 2.5 M in hexane) was slowly added to a solution of **4** (67.2 mL, 0.702 mol) in Et_2O (1.4 L) in a 5 L RB flask at -35 °C. After stirring for 1 h, $BF_3 \cdot OEt_2$ (86.6 mL, 0.702 mol) was added at -78 °C, and the mixture was stirred for 10 min, followed by stirring at 0 °C for additional 30 min. Aqueous KHF_2 (219 g, 2.81 mol, in 600 mL H_2O) was added to the mixture and stirred for 20 min at 0 °C, 1 h at rt, and opened to air. The residue, after removal of solvents, was extracted with acetone, filtered, concentrated, and precipitated with CH_2Cl_2. The solid was filtered and washed with CH_2Cl_2 to yield 68.3 g (51%) of **2** (White Solid).

Preparation of (*Z*)-$CF_3CH{=}CHBF_3K$



Potassium [(*Z*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (*Z*-1). THF was added to **2** (10.0 g, 50.0 mmol), Pd/$BaSO_4$ (5.32 g, 2.5 mmol, 5 wt%) and quinoline (0.59 mL, 5.0 mmol). The reaction mixture was stirred under H_2 at rt and monitored by ^{19}F NMR. The reaction was completed after stirring for 2 h 35 min, the reaction mixture was filtered through Celite® which was washed with EtOAc. The product was precipitated with minimal amount of CH_2Cl_2, after removing the solvents, and recrystallized from *i*PrOH (250 mL) to obtain white solid ***Z*-1** (6.07 g, 59 %, *Z*:*E*:alkane = 98:1.5:0.5). ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ 6.20 (m, 1H), 5.84 (m, 1H). ^{11}B NMR [96 MHz, $(CD_3)_2SO$] δ 5.50 (q, J = 47.7 Hz). ^{13}C NMR [101 MHz, $(CD_3)_2CO$] δ 149.4, 125.0 (q, J = 34.3, 4.0 Hz), 124.9 (q, J = 270.5 Hz). ^{19}F NMR [282 MHz, $(CD_3)_2SO$] δ -54.72 – -54.94 (m, 3F), -132.82 (q, J =46.7 Hz, 3F). HRMS (ESI-) calcd for $[M\text{-}K]^-$ 163.0154, found 163.0163.

Preparation of (*E*)-$CF_3CH{=}CHBF_3K$



Potassium [(*E*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (*E*-1). A similar reaction as above for 3 h 52 min in DME using Pd/$CaCO_3$/Pb (5.32 g, 2.5 mmol, 5 wt %) as the catalyst to **2** (10.0 g, 50.0 mmol), yielded white solid ***E*-1** (7.06 g, 56 %, *Z*:*E*:alkane = 1:80:19). ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ 6.37 (d, *J* = 17.1 Hz, 1H), 5.85 – 5.71 (m, 1H). ^{11}B NMR [96 MHz, $(CD_3)_2CO$] δ 2.79 (d, J = 47.3 Hz). ^{13}C NMR [101 MHz, $(CD_3)_2CO$] δ 145.0, 125.0 (q, *J* = 269.3 Hz), δ 124.0 (m). ^{19}F NMR [282 MHz, $(CD_3)_2SO$] δ -61.67 – -61.81 (m, 3F), -139.82 – -141.30 (m, 3F). HRMS (ESI-) calcd for $[M-K]^-$ 163.0154, found 163.0163.

Optimization of the Selective Semi-hydrogenation

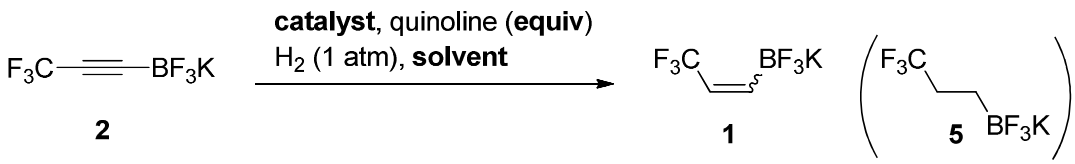


Table 1. Reaction conditions and ratios of 1-2 mmol scale hydrogenation.

no.	catalyst[a]	solvent	catalyst (mol %)	quionline (mol %)	concn (M)	time (h)	product ratio			
							2	***Z*-1**	***E*-1**	**5**
1	L	THF	5	5.5	0.3	1.5	77	21	2	0
						3.5	0	13	59	28
2[b]	L	THF	5	10	0.3	3	0	69	23	8
3	L	MeOH	5	10	0.25	1.5	0	0	67	33
4	L	MeOH	1	5	0.3	1.5	0	3	73	24
5	L	THF	5	5	0.3	1.5	0	2	80	18
6	L	DME	0.5	5	0.5	1.0	0	75	20	5
			+4.5			1.5	0	0	76	24
7	L	DME	10	15	0.25	0.5	0	43	44	13
						1.0	0	0	76	24
8	L	DME	0.1	1	0.5	0.5	94	6	0	0
						2.5	69	29	2	0
9	L	DME	5	20	0.3	0.5	78	22	0	0
						1.0	28	67	3	2
						1.75	0	0	71	29
10	L	DME	5	10	0.3	0.5	68	32	0	0
						1h10m	0	22	50	17
						1h25m	0	2	73	25
						crude[d]	0	1	78	21
11	L	DME	0.5	5	1.0	0.5h	37	60	3	0
						1.0h	9	79	9	3
						1.5h	0	44	42	14

12	R	DME	5	10	0.3	0.5h	46	52	2	0
						1.0h	1	79	14	6
						3h	0	6	60	34
						3.25h	0	2	63	35
13	B	DME	5	10	0.3	1.0h	34	57	5	4
						1.5h	0	0	56	44
14[c]	R	DME	1	5	0.5	1h05m	78	22	0	0
						2h05m	37	58	2	3
						3h05m	15	75	5	5
						4h05m	8	77	8	7
						4h35m	3	76	12	9
15	R	THF	5	10	0.5	0.5h	41	56	2	1
						1.0h	0	87	8	5
						crude[d]	0	89	8	3
						recry.[e]	0	96	3	1
						3h	0	6	63	31
						3.25h	0	4	65	31
16	R	EtOAc	5	10	0.5	0.5h	41	56	2	1
						1.0h	0	63	23	14
17	R	THF	5	10	0.5	0.5h	84	16	0	0
						1h25m	16	78	4	2
						1h55m	0	89	8	3
						crude[d]	0	95.5	3.5	1.0
21[f]	L	DME	2.5	50	0.3	1h	0	12	62	26
22	R	THF	5	-	0.3	0.5h	0	0	59	41
23	R	THF	2	-	0.3	0.5h	0	0	70	30
24	R	THF	2	1	0.3	0.5h	54	42	3	1
						1h	0	0	54	46
25	R	acetone	5	-	0.1	20m	28	27	34	11
						40m	0	0	65	35
26	R	acetone	2	-	0.1	30m	5	16	59	17
						40m	4	13	64	20
						1h	3	11	67	19

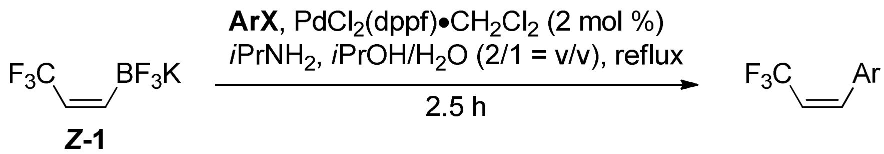
a) L: $Pd/CaCO_3/Pb$, R: $Pd/BaSO_4$, B: $Pd/BaCO_3$. b) 5 equiv of 1-octene was added as a scavenger. c) 3 equiv of 1-octene was added as a scavenger. d) Filtered through Celite®. e) Recrystallization from *i*PrOH/EtOAc. f) Reaction at 0 °C.

Table 2. Reaction conditions and ratios of large-scale reactions.

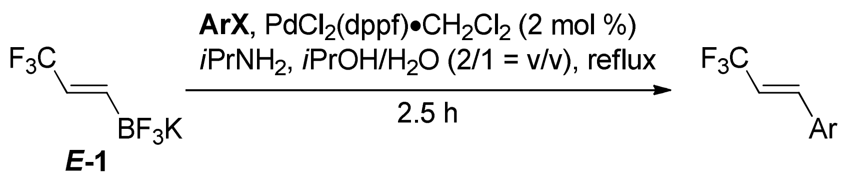
no.	catalyst[a]	solvent	catalyst (mol %)	quionline (mol %)	concn (M)	time (h)	product ratio			
							2	***Z*-1**	***E*-1**	**5**
1	R	THF	5	10	0.5	53m	34	62	3	1
						1h13m	0	90	6	4
						crude[b]	0	95	4	1
						recry.[c]	0	98[d]	1.5	0.5
2	R	THF	5	10	0.5	55m	83	3	73	24
						1h50m	45	55	0	0
						2h35m	0	92	5	3
						recry.[c]	0	98[e]	1.5	0.5
3	L	DME	5	10	0.3	1h	78	22	0	0
						2h06m	34	57	5	4
						2h36m	24	64	5	6
						3h06m	7	76	9	8
						3h36m	0	19	59	22
						3h50m	0	2	71	27
						crude[b] 3h52m	0	1	80[f]	19

a) L: $Pd/CaCO_3/Pb$, R: $Pd/BaSO_4$. b) Filtered through Celite®. c) Recrystallization from *i*PrOH. d) 15 mmol scale, 53 % yield. e) 50 mmol scale, 59% yield. f) 50 mmol scale, 56%.

General Procedure for Suzuki coupling

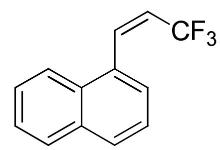


(*Z*)-β-trifluoromethylstyrenes. To a solution of potassium [(*Z*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***Z*-1**) (98%, *E*/*Z* = 1.5/98.5), 208.0 mg, 1.03 mmol), $PdCl_2$(dppf)•CH_2Cl_2 (16.3 mg, 0.02 mmol), aryl halide* (1.00 mmol) in degassed (freeze-pump-thaw) *i*PrOH/H_2O (2/1 = v/v, 10 mL) was added *i*$PrNH_2$ (0.265 mL, 3.09 mmol) under N_2 (*liquid aryl halide was dissolved in the solvents and added via cannulation). The reaction mixture was stirred at reflux for 2.5 h, diluted with H_2O (15 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers was washed with brine (15 mL), filtered through Na_2SO_4, concentrated, and the crude product was purified by column chromatography to obtain (*Z*)-β-trifluoromethylstyrenes.

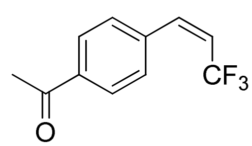


(*E*)-β-trifluoromethylstyrenes. To a solution of potassium [(*E*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***E*-1**) (80%, *E*:*Z* = 99:1), 343.3 mg, 1.7 mmol), $PdCl_2$(dppf)•CH_2Cl_2 (16.3 mg, 0.02 mmol), aryl halide* (1.00 mmol) in degassed (freeze-pump-thaw) *i*PrOH/H_2O (2/1 = v/v, 10 mL) was added *i*$PrNH_2$ (0.265 mL, 5.1 mmol) under N_2 (*liquid aryl halide was dissolved in the solvents and added via cannulation). The reaction mixture was stirred at reflux for 2.5 h, diluted with H_2O (15 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers was washed with brine (15 mL), filtered through Na_2SO_4, concentrated, and the crude product was purified by column chromatography to obtain (*E*)-β-trifluoromethylstyrenes.

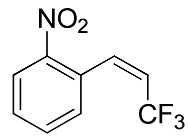
Characterization Data



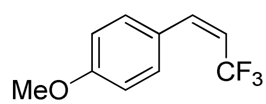
(*Z*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (*Z*-7a). Yellow oil. 189.0 mg, 85% yield, *E*:*Z* = 1:99. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.65 (m, 3H), 7.43 – 7.39 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 12.2 Hz, 1H), 5.92 (dq, *J* = 12.2, 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (q, *J* = 5.5 Hz), 133.3, 131.5, 131.0, 129.2, 128.6, 126.6, 126.4, 126.2, 125.2, 124.4, 123.0 (q, *J* = 272.7 Hz), 120.6 (q, *J* = 33.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.00 (d, *J* = 8.2 Hz). HRMS (EI+) calcd for $C_{13}H_9F_3$ (M^+) 222.0651, found 222.0641.



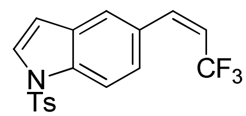
(*Z*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (*Z*-7b). Yellow oil. 200.9 mg, 94% yield (from ArBr, **6b**), 195.4 mg, 91% yield (from ArI, **6b'**), *E*:*Z* = 1:99. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 12.6 Hz, 1H), 5.87 (dq, *J* = 12.6, 8.9 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 138.7 (q, *J* = 5.6 Hz), 138.4, 137.2, 129.1, 128.3, 122.7 (q, *J* = 271.5 Hz), 120.0 (q, *J* = 34.9 Hz), 26.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.22 (d, *J* = 8.9 Hz). HRMS (EI+) calcd for $C_{11}H_9OF_3$ (M^+) 214.0600, found 214.0593.



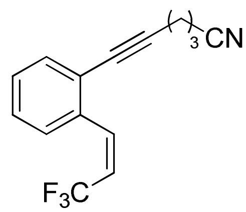
(Z)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (*Z*-7c). Orange oil. 185.8 mg, 86% yield, *E*:*Z* = 1:99. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 12.2 Hz, 1H), 5.95 (dq, *J* = 12.2, 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 136.7 (q, *J* = 5.3 Hz), 133.5, 131.0, 130.3, 129.6, 124.6, 122.5 (q, *J* = 271.7 Hz), 119.2 (q, *J* = 33.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.33 (d, *J* = 7.9 Hz). HRMS (EI+) calcd for $C_9H_6O_2NF_3$ (M^+) 217.0345, found 217.0339.



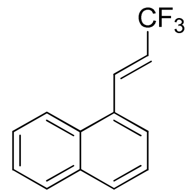
(*Z*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (*Z*-7d). Yellow oil. 153.4 mg (*E*/*Z* mixture) 69% yield, *E*:*Z* = 9:91. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 12.7 Hz, 1H), 5.60 (dq, *J* = 12.7, 9.4 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 139.3 (q, *J* = 5.8 Hz), 131.0, 126.1, 123.3 (q, *J* = 270.9 Hz), 115.6 (q, *J* = 35.1 Hz), 113.9, 55.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.05 (d, *J* = 9.4 Hz). Mass (ESI+) calcd for $[M+H]^+$ 189.1, found 189.1.



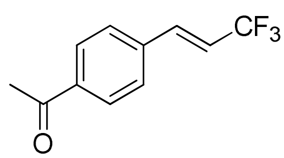
(*Z*)-1-tosyl-5-(3,3,3-trifluoroprop-1-en-1-yl)-1H-indole (*Z*-7e). The starting material was prepared by following the reported procedure.[1] White solid. 335.3 mg, 92 % yield, *E*:*Z* = 2:98. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 12.3 Hz, 1H), 6.63 (d, *J* = 3.1 Hz, 1H), 5.71 (dq, *J* = 12.3, 8.7 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 139.9 (q, *J* = 5.7 Hz), 135.1, 134.9, 130.9, 130.0, 128.9, 127.3, 126.8, 125.8, 123.1 (q, *J* = 272.7 Hz), 122.5, 117.0 (q, *J* = 34.8 Hz), 113.4, 109.2, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.64 (d, *J* = 8.7 Hz). HRMS (EI+) calcd for $C_{18}H_{14}O_2NF_3S$ (M^+) 365.0692, found 365.0689.



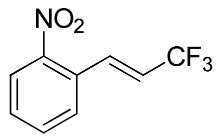
(*Z*)-6-(2-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)hex-5-ynenitrile (*Z*-7f). The starting material was prepared by following the reported procedure.[2] Yellow oil. 151.5 mg, 58 % yield, *E*:*Z* = 1:99. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.32 – 7.24 (m, 2H), 7.18 (s, 1H), 5.85 (dq, *J* = 12.4, 8.7 Hz, 1H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.01 – 1.81 (m, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (q, *J* = 5.3 Hz), 136.0, 132.1, 128.8, 128.7, 127.9, 127.0, 122.9 (q, *J* = 272.7 Hz), 119.2, 119.0 (q, *J* = 34.3 Hz), 93.2, 80.3, 24.5, 18.7, 16.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.23 (d, *J* = 8.7 Hz). HRMS (EI+) calcd for $C_{15}H_{12}NF_3$ (M^+) 263.0916, found 263.0925.



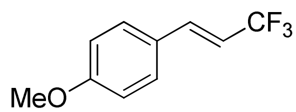
(*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (*Z*-7a). Yellow oil. 162.6 mg, 73% yield, *E*:*Z* = 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.92 (m, 2H), 7.92 – 7.85 (m, 3H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.51 – 7.45 (m, 1H), 6.27 (dq, *J* = 15.9, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (q, *J* = 6.7 Hz), 133.6, 131.0 (d, *J* = 17.8 Hz), 130.2, 128.8, 126.9, 126.3, 125.4, 124.8, 123.6 (q, *J* = 269.3 Hz), 123.1, 118.7 (q, *J* = 33.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.94 (d, *J* = 6.0 Hz). Mass (ESI+) calcd for $[M+H]^+$ 223.1, found 223.1.



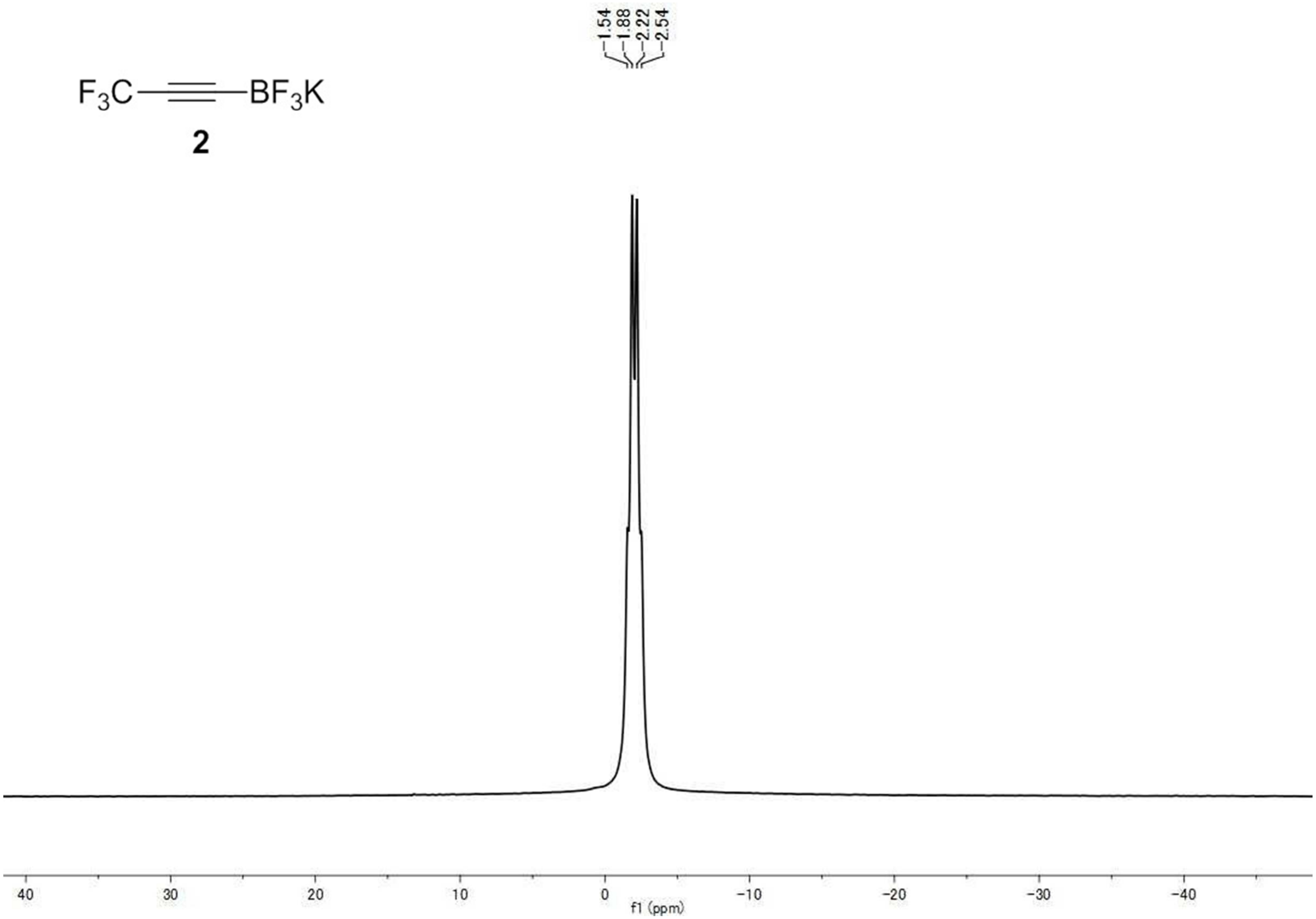
(*E*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (*E*-7b). White solid. 194.3 mg, 91% yield (from ArBr, **6b**), 181.5 mg, 85% yield (from ArI, **6b'**), *E*:*Z* = 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.16 (dd, *J* = 16.2, 1.9 Hz, 1H), 6.31 (dq, *J* = 16.2, 6.4 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 138.0, 137.6, 136.6 (q, *J* = 6.6 Hz), 128.9, 127.7, 123.3 (q, *J* = 269.2 Hz), 118.1 (q, *J* = 34.1 Hz), 26.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.24 (d, *J* = 5.6 Hz). Mass (ESI+) calcd for $[M+Na]^+$ 237.1, found 237.2.



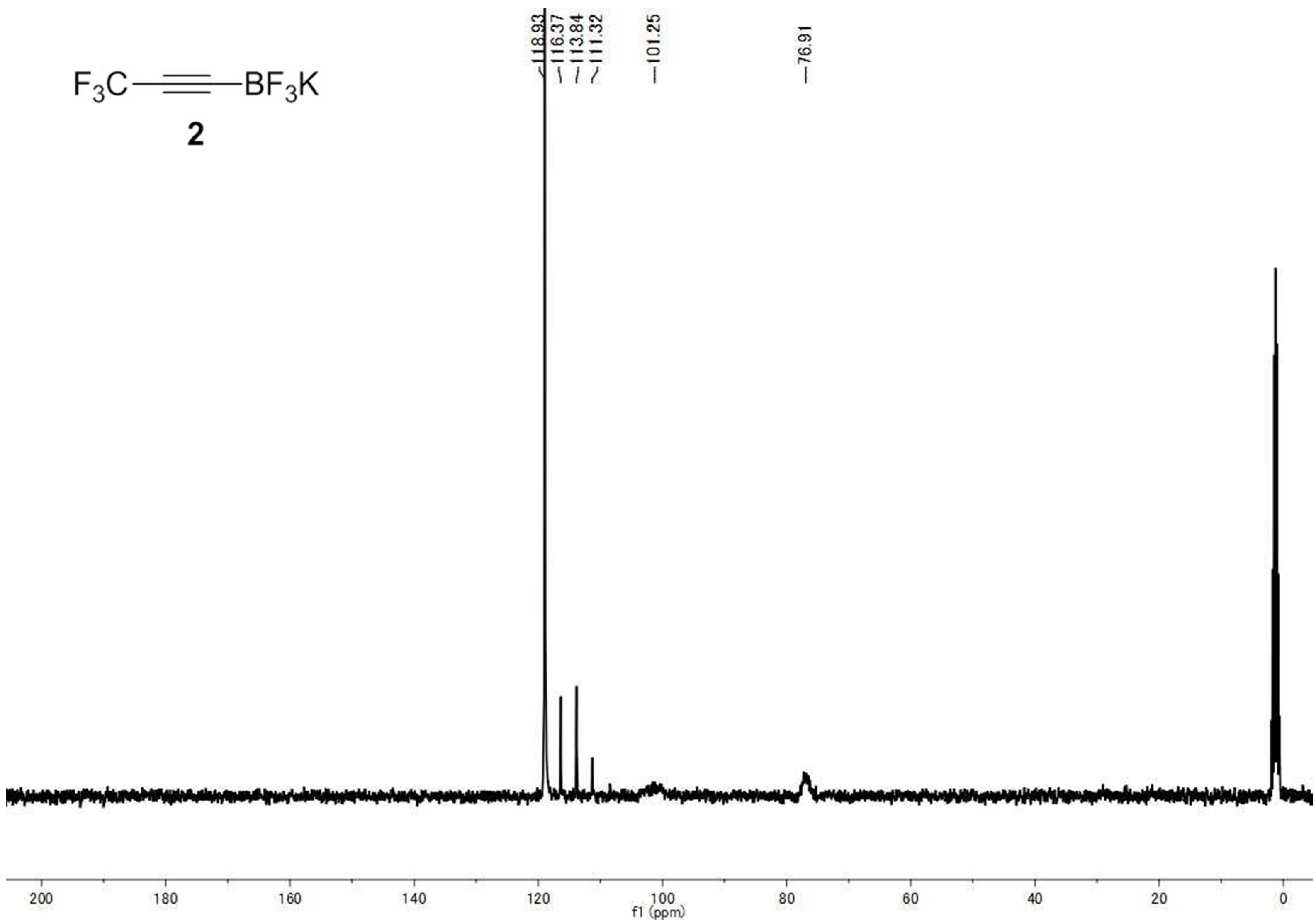
(*E*)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (*E*-7c). Orange oil. 193.7 mg, 89% yield, E:Z = 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 1H), 7.68 (m, 2H), 7.58 (m, 2H), 6.15 (dq, J = 15.9, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 134.5 (q, J = 7.0 Hz), 134.1, 130.6, 129.8, 129.4, 125.1, 122.9 (q, J = 269.6 Hz) 120.5 (q, J = 34.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.60 (d, J = 5.6 Hz). Mass (ESI+) calcd for $[M+H]^+$ 218.0, found 218.1; for $[M+Na]^+$ 240.0, found 240.2.



(*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (*E*-7d). White solid. 72.4 mg, 36% yield, E:Z = 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 7.07 (dq, J = 15.9, 1.7 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.04 (dq, J = 15.9, 5.9 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 137.2 (q, J = 6.8 Hz), 129.1, 126.1, 124.0 (q, J = 268.6 Hz), 114.4, 113.4 (q, J = 33.7 Hz), 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.38 (d, J = 5.9 Hz). Mass (ESI+) calcd for $[M+Na]^+$ 211.0, found 211.2.

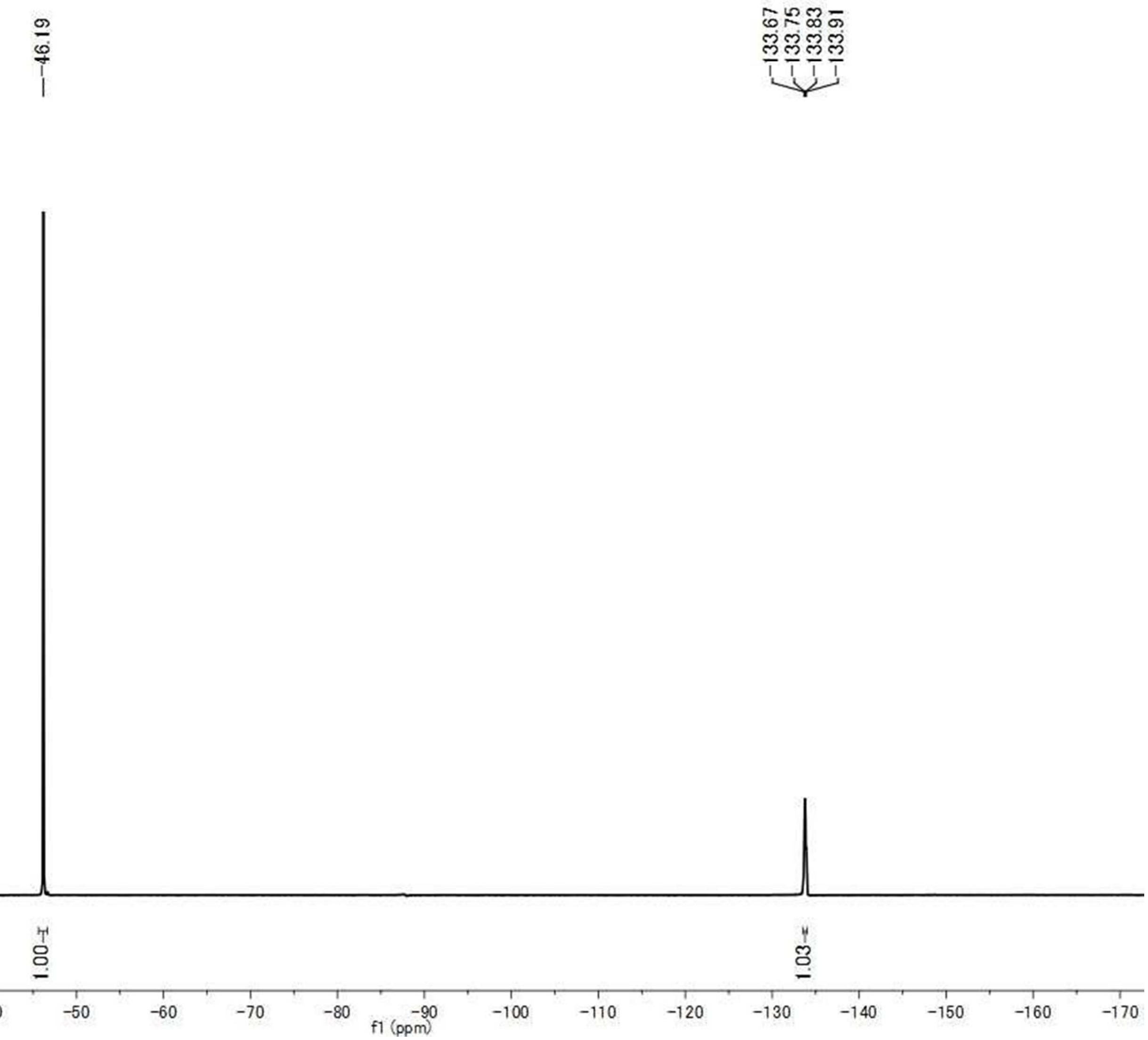


^{11}B NMR (96 MHz, CD_3CN) Potassium (3,3,3-trifluroprop-1-yn-1-yl)trifluoroborate (**2**)

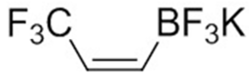


^{13}C NMR (101 MHz, CD_3CN) Potassium (3,3,3-trifluroprop-1-yn-1-yl)trifluoroborate (**2**)

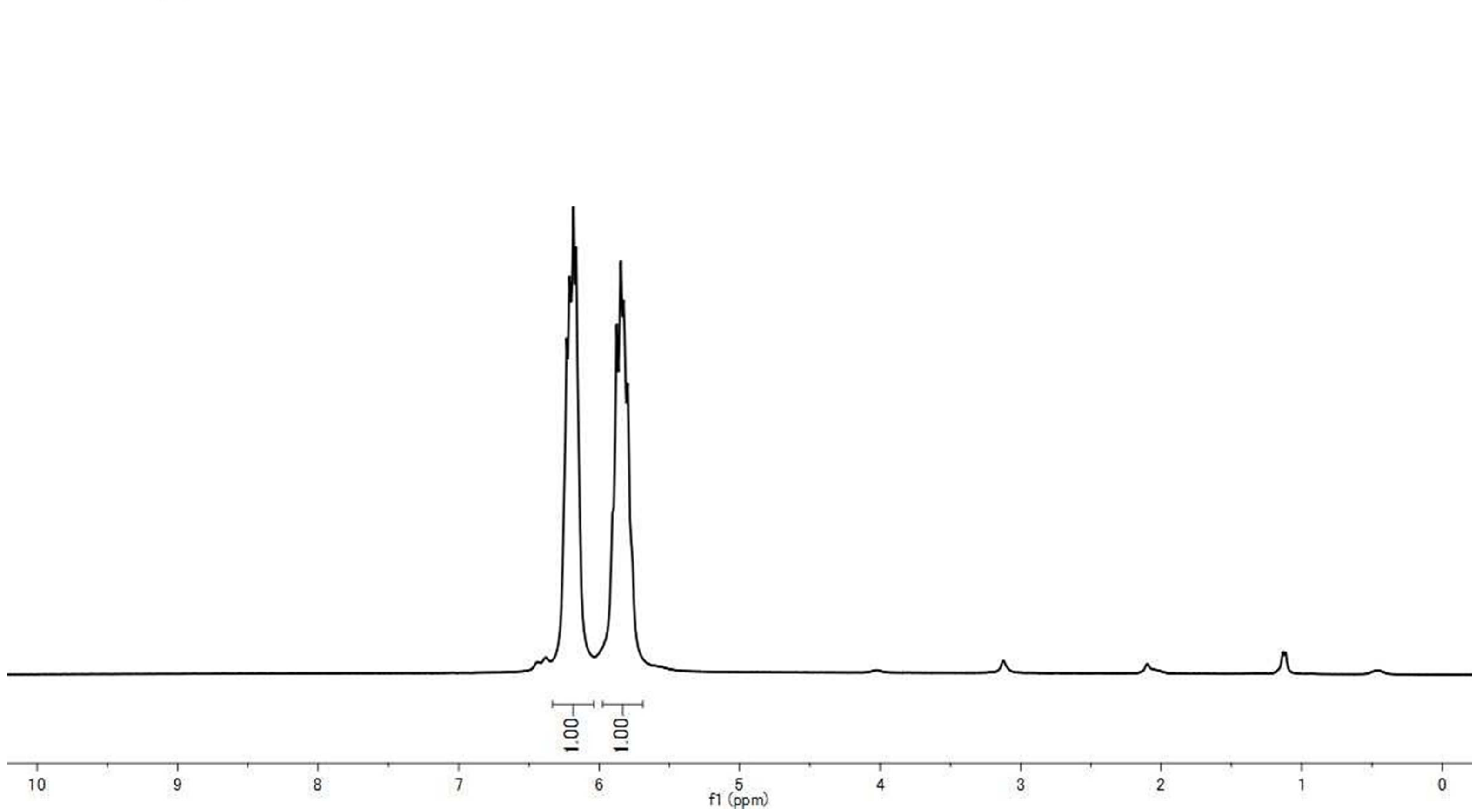
2



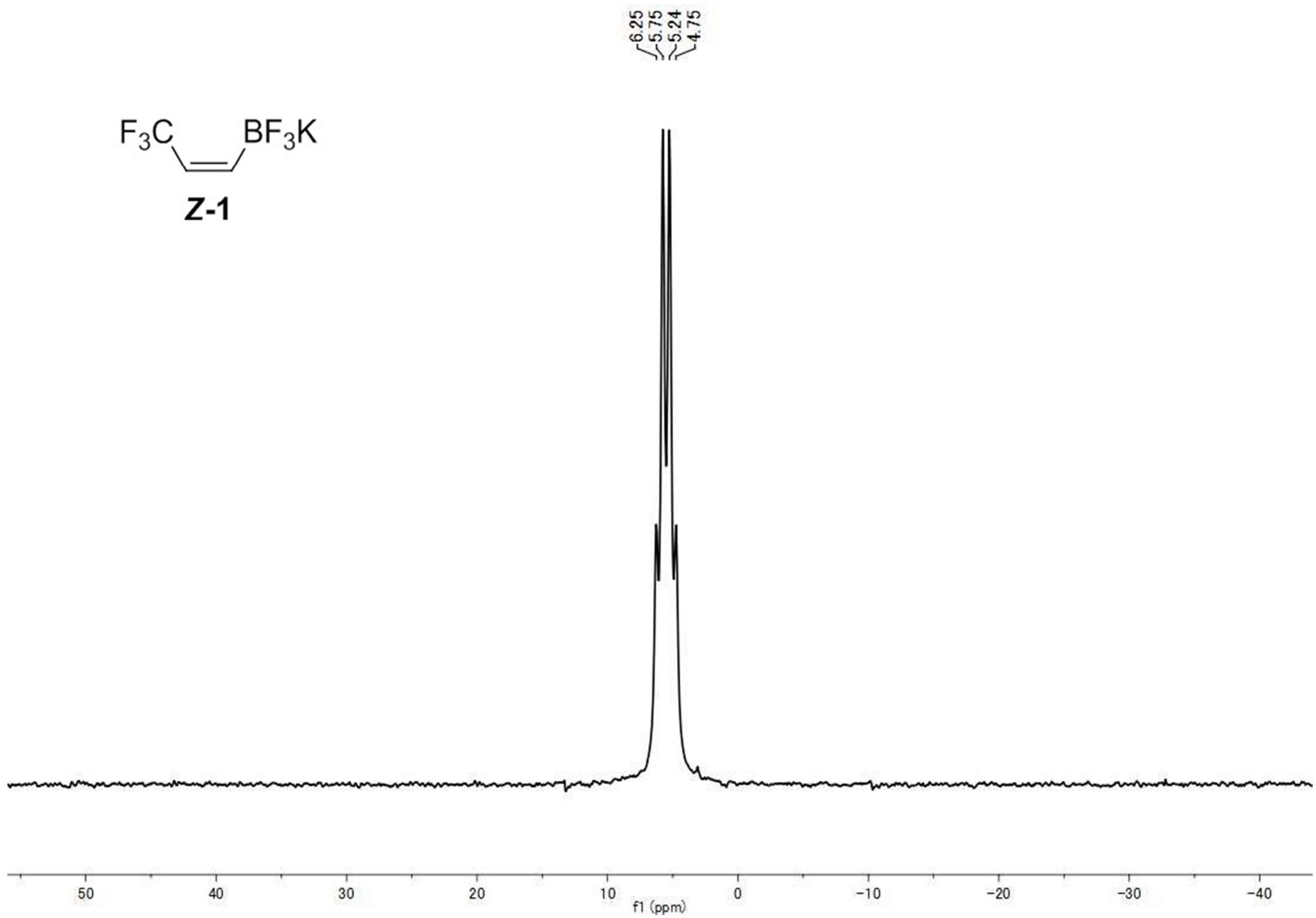
^{19}F NMR (376 MHz, CD_3CN) Potassium (3,3,3-trifluroprop-1-yn-1-yl)trifluoroborate (**2**)



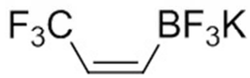
***Z*-1**



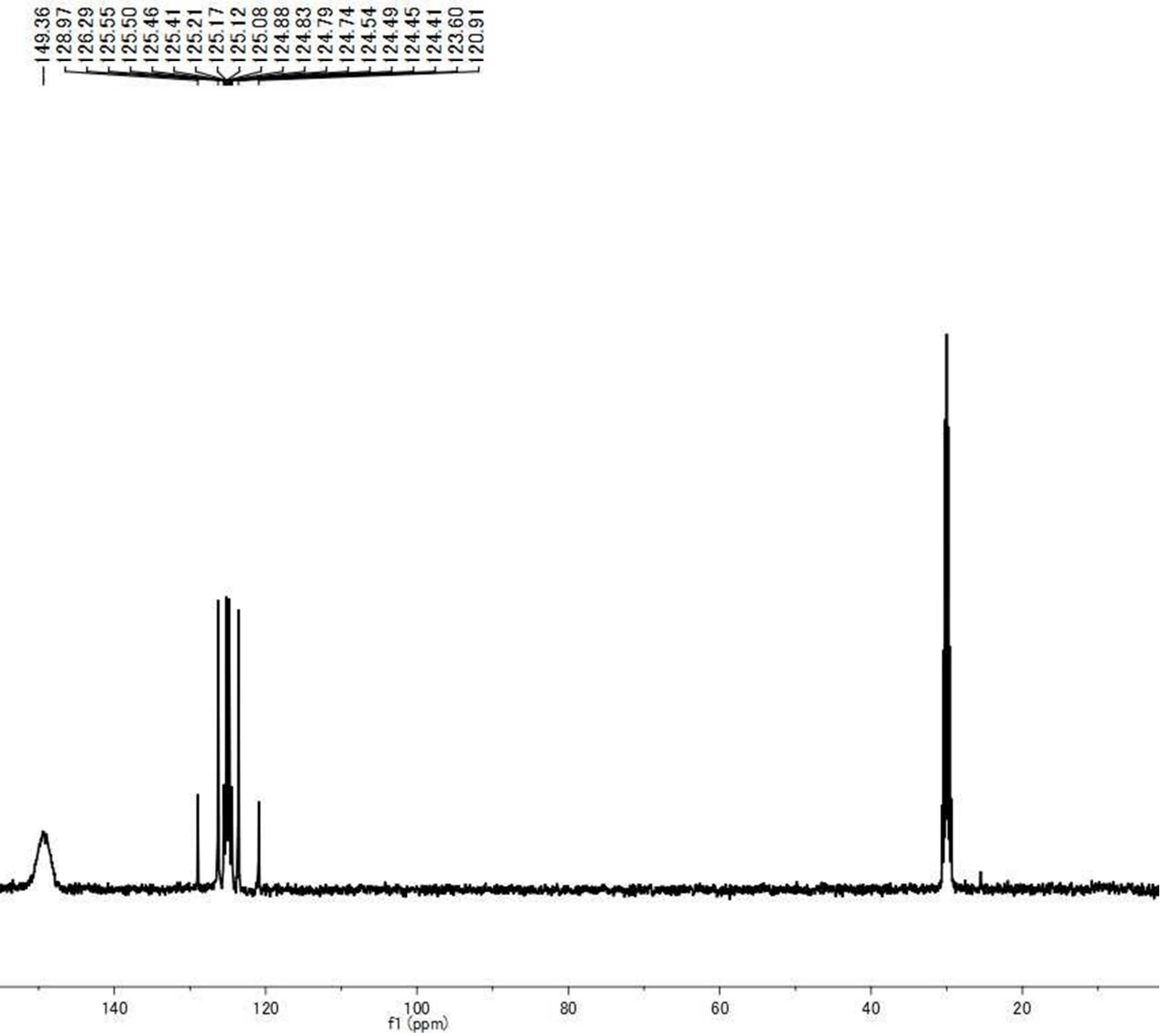
^{1}H NMR [400 MHz, $(CD_3)_2CO$] Potassium [(*Z*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***Z*-1**)



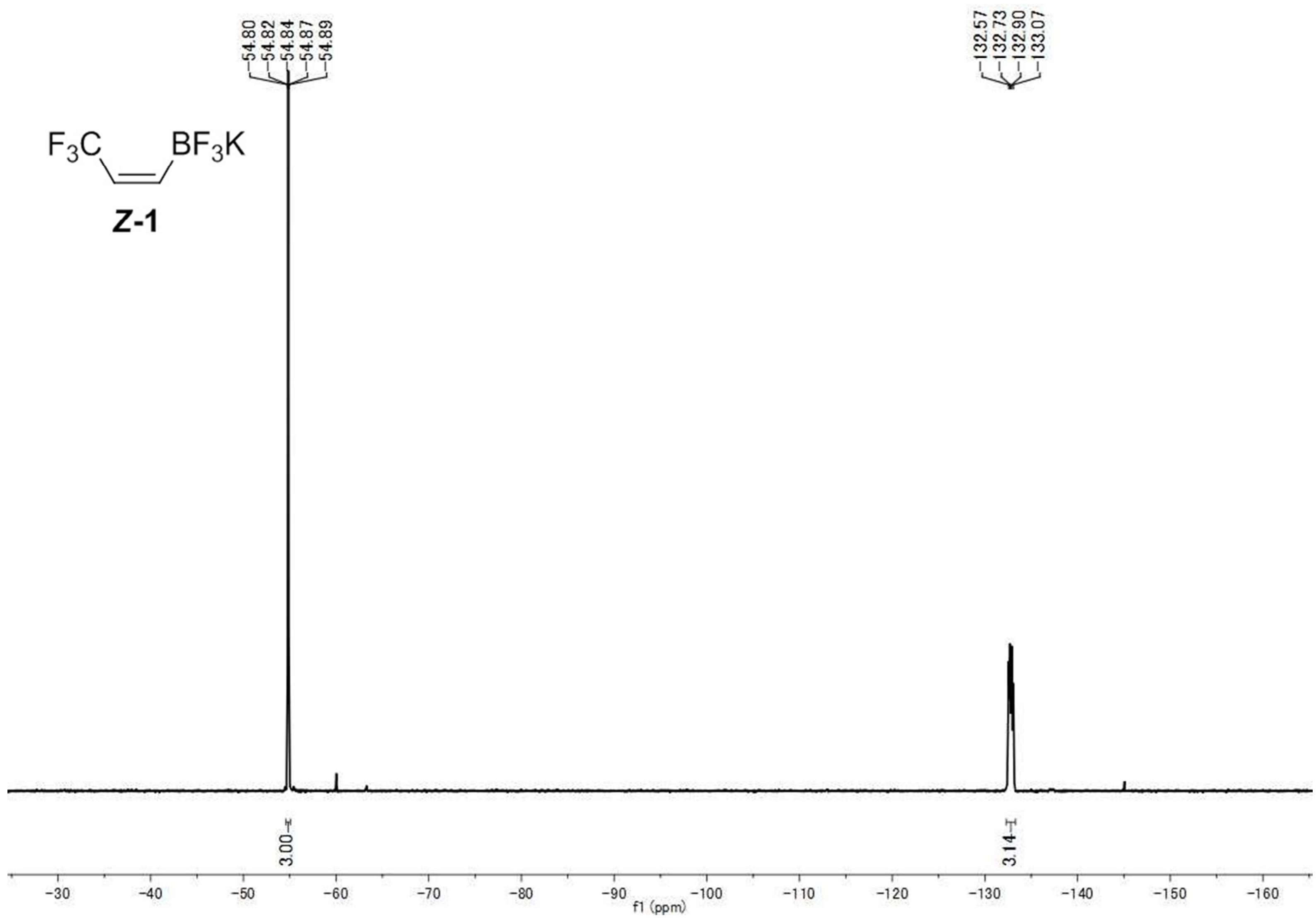
^{11}B NMR [96 MHz, $(CD_3)_2SO$] Potassium [(*Z*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***Z*-1**)



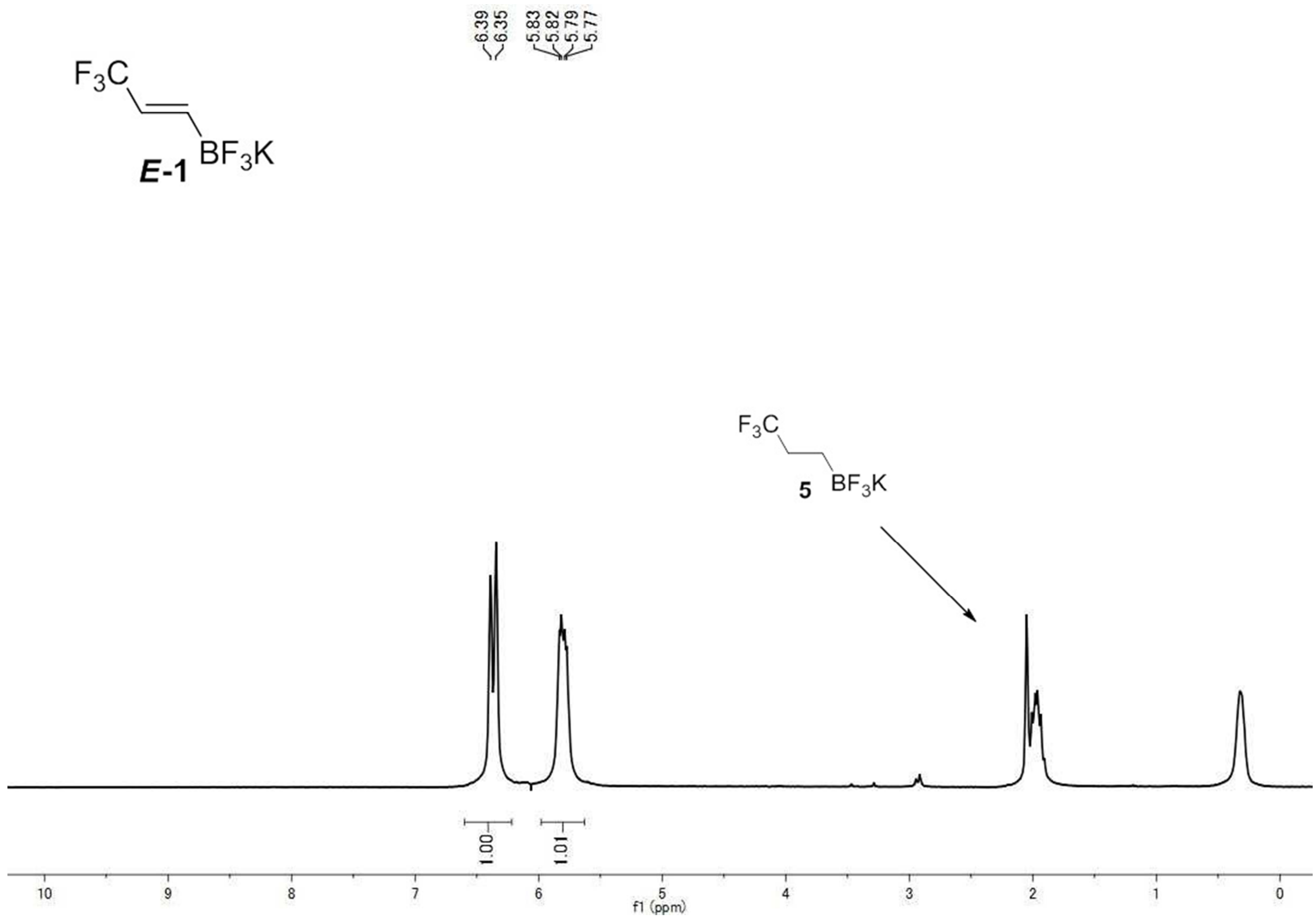
***Z*-1**



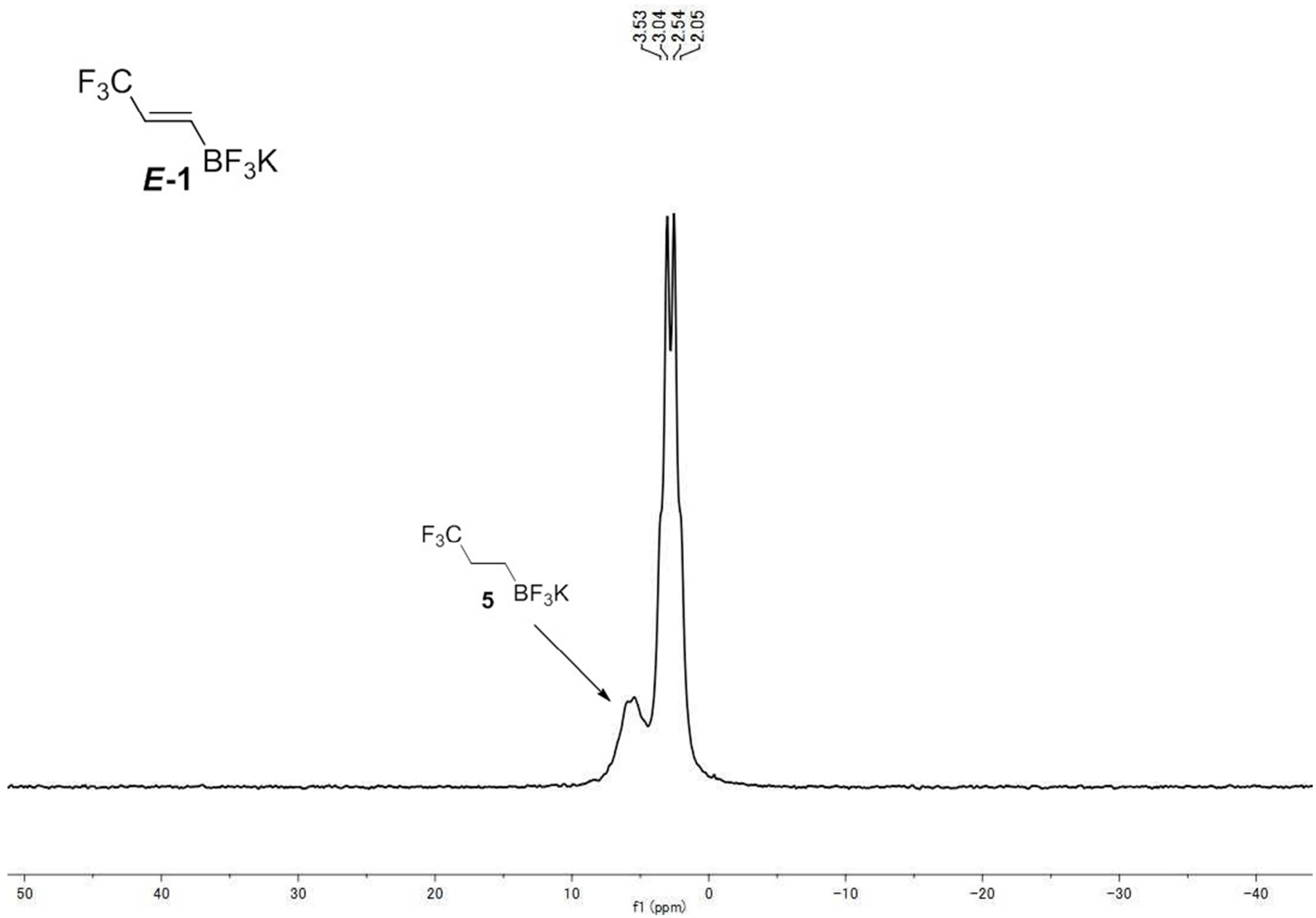
^{13}C NMR [101 MHz, $(CD_3)_2CO$] Potassium [(*Z*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***Z*-1**)



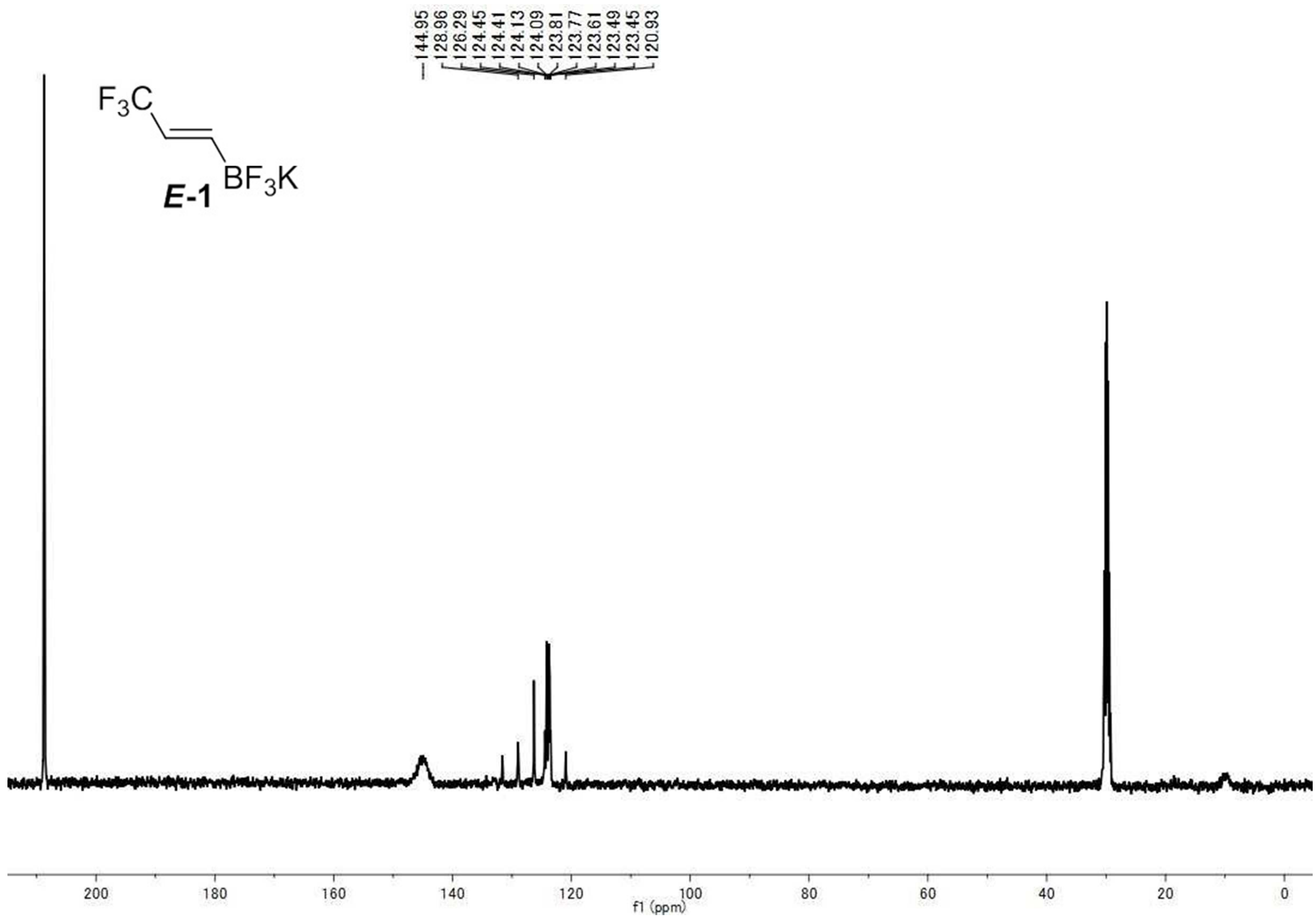
^{19}F NMR [282 MHz, $(CD_3)_2SO$] Potassium [(*Z*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***Z*-1**)



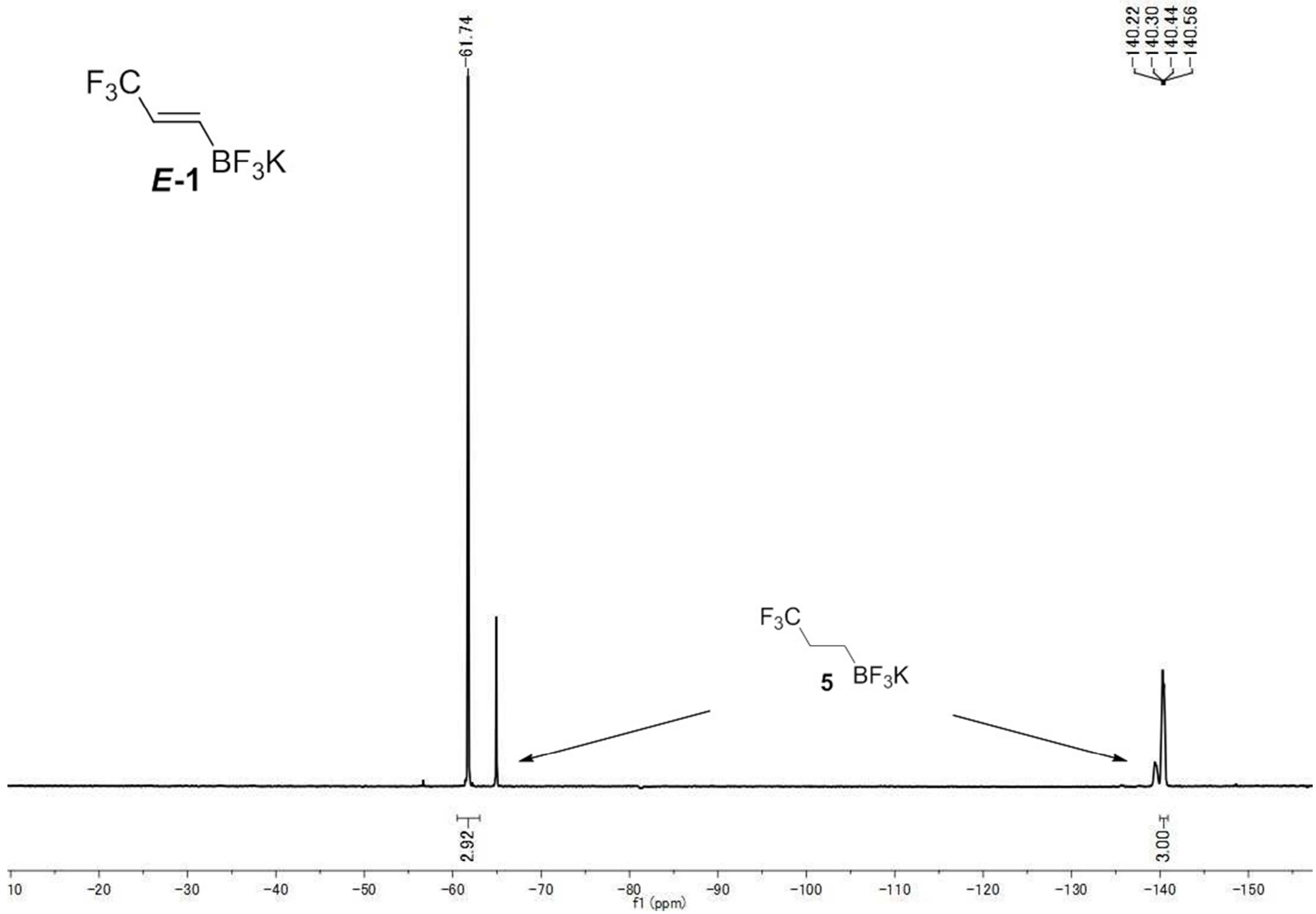
^{1}H NMR [400 MHz, $(CD_3)_2CO$] Potassium [(*E*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***E*-1**)



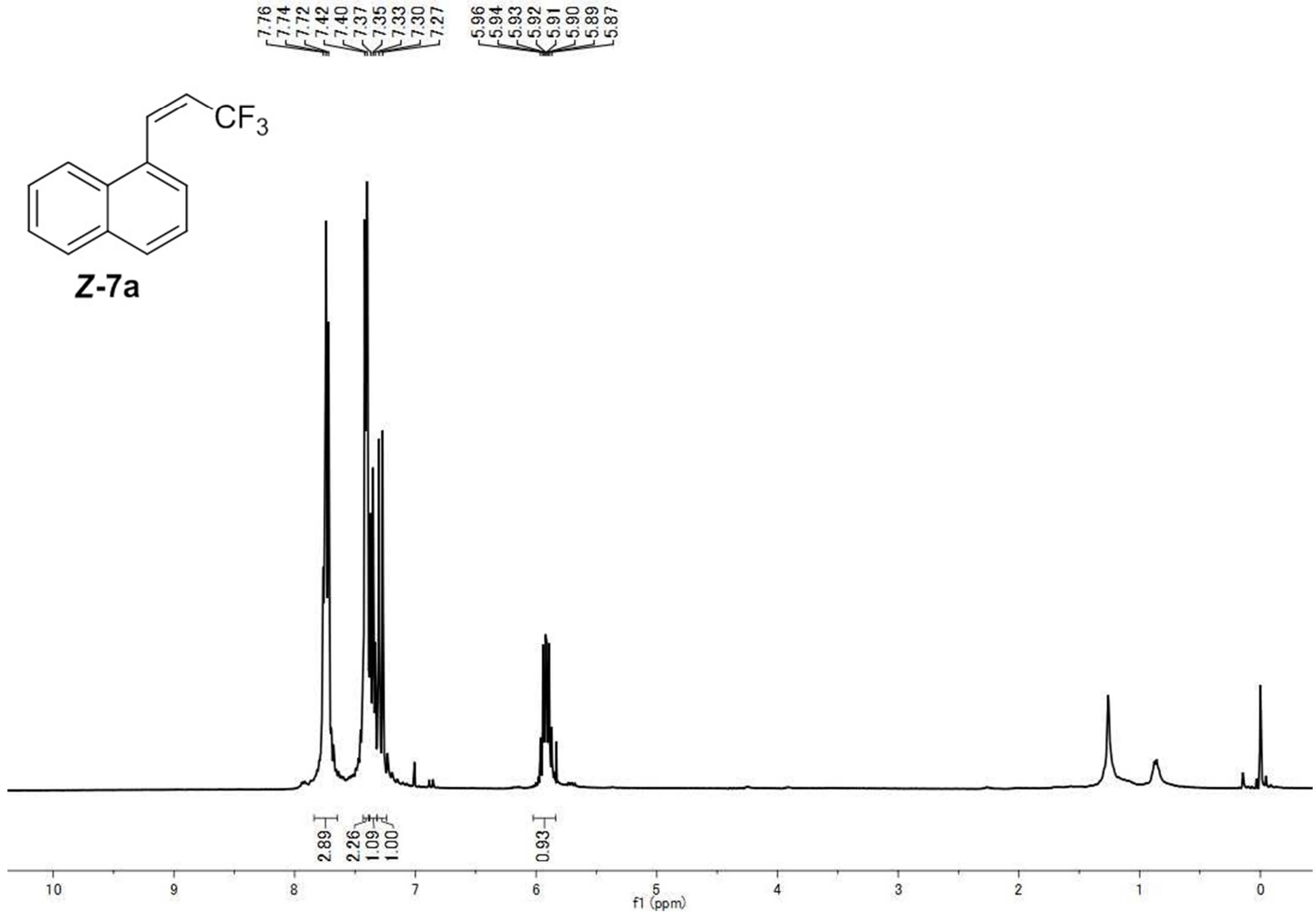
^{11}B NMR [96 MHz, $(CD_3)_2SO$] Potassium [(*E*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***E*-1**)



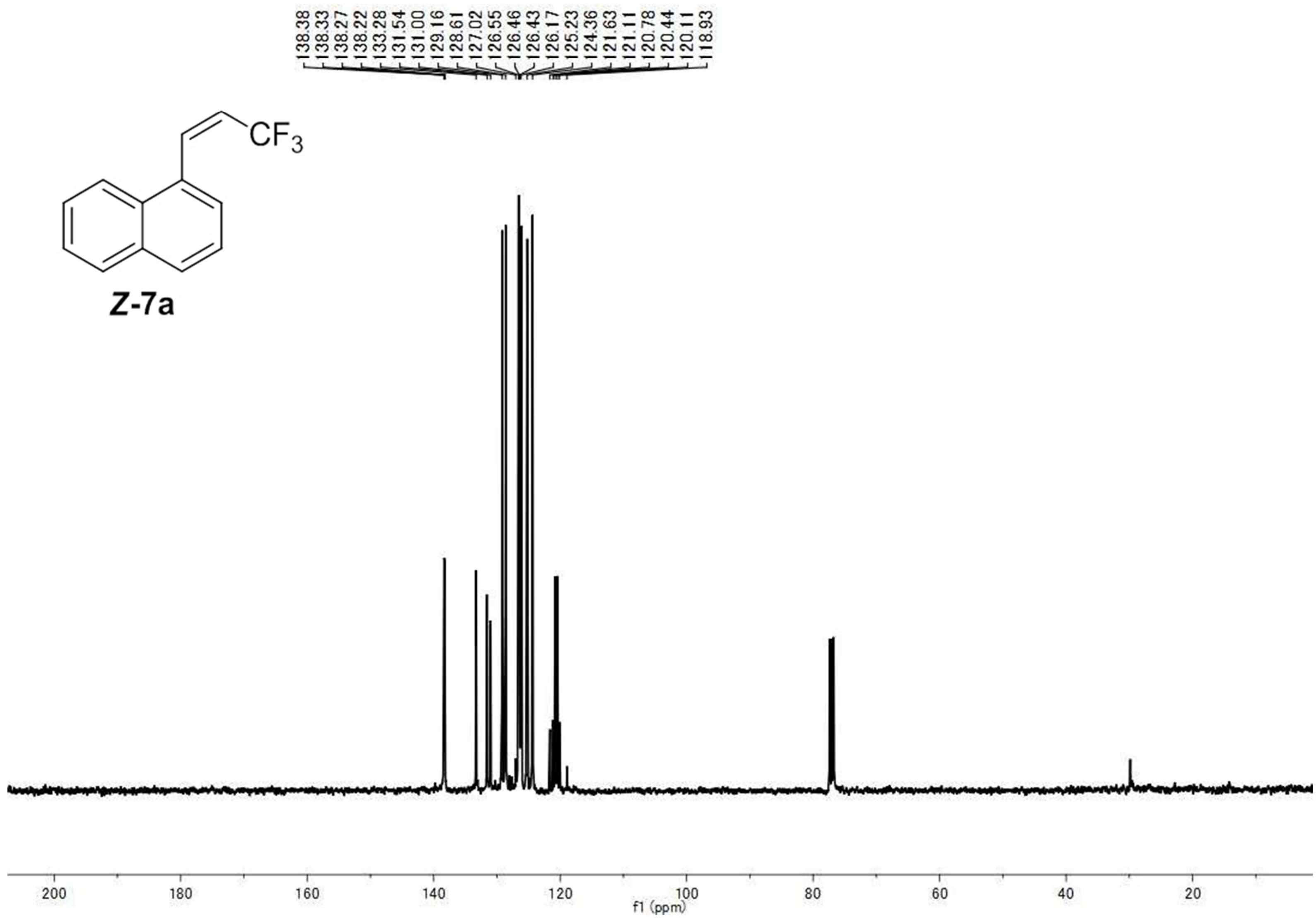
^{13}C NMR [101 MHz, $(CD_3)_2CO$] Potassium [(*E*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***E*-1**)



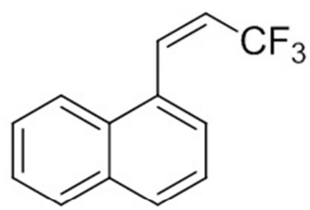
[19]F NMR [282 MHz, $(CD_3)_2SO$] Potassium [(*E*)-3,3,3-trifluoroprop-1-en-1-yl]trifuoroborate (***E*-1**)



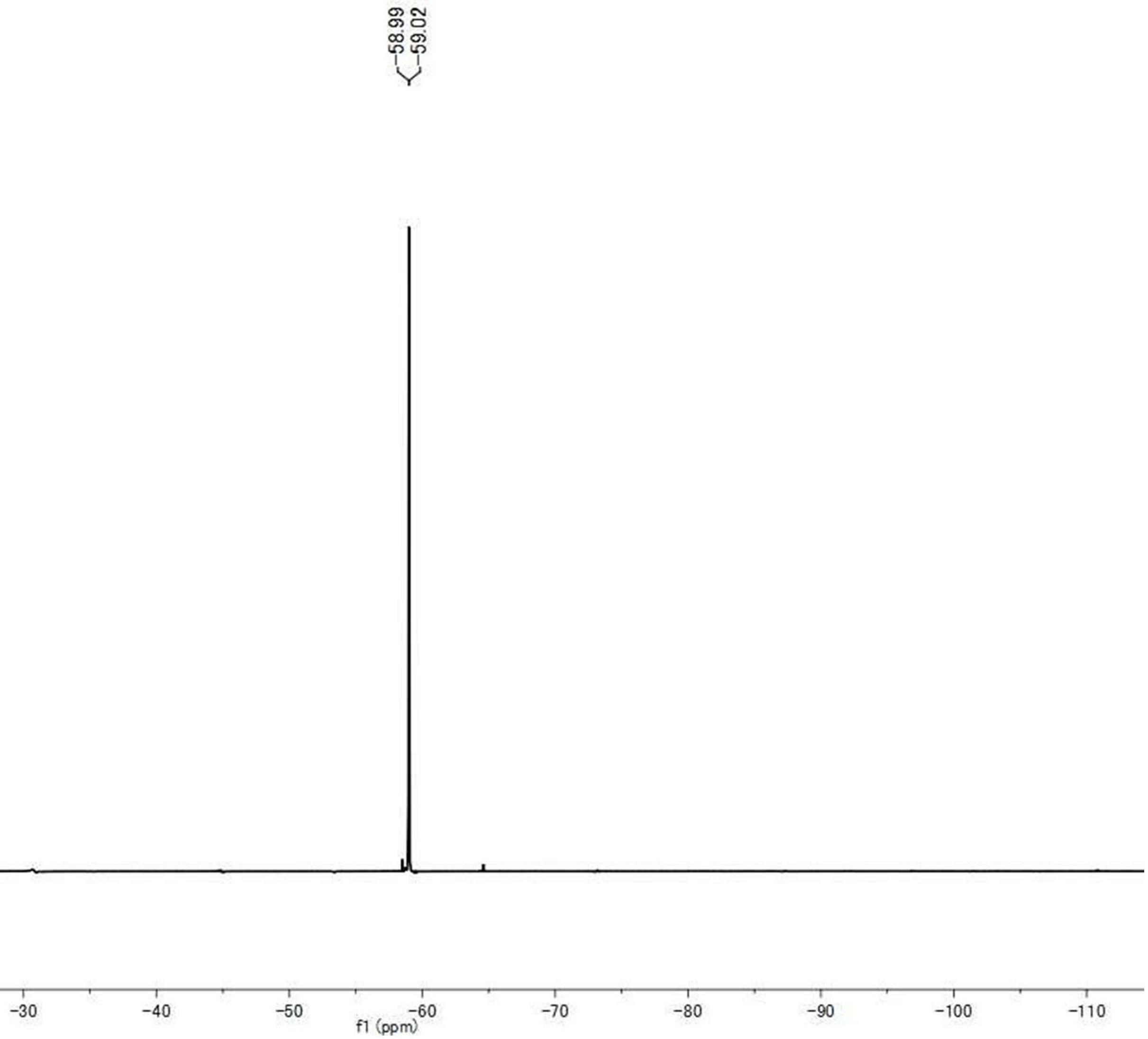
^{1}H NMR (400 MHz, $CDCl_3$) (*Z*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (***Z*-7a**)



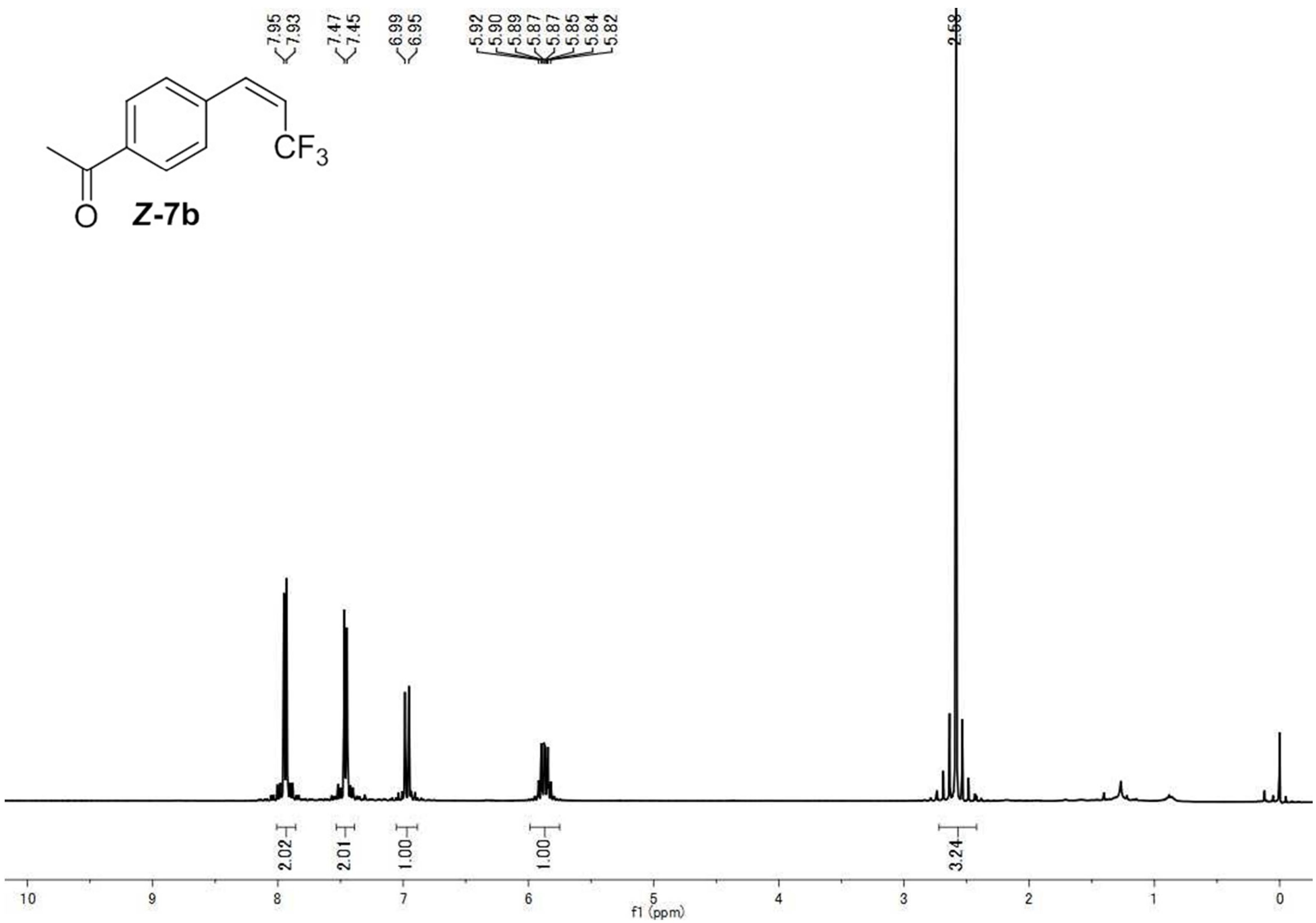
^{13}C NMR (101 MHz, $CDCl_3$) (*Z*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (***Z*-7a**)



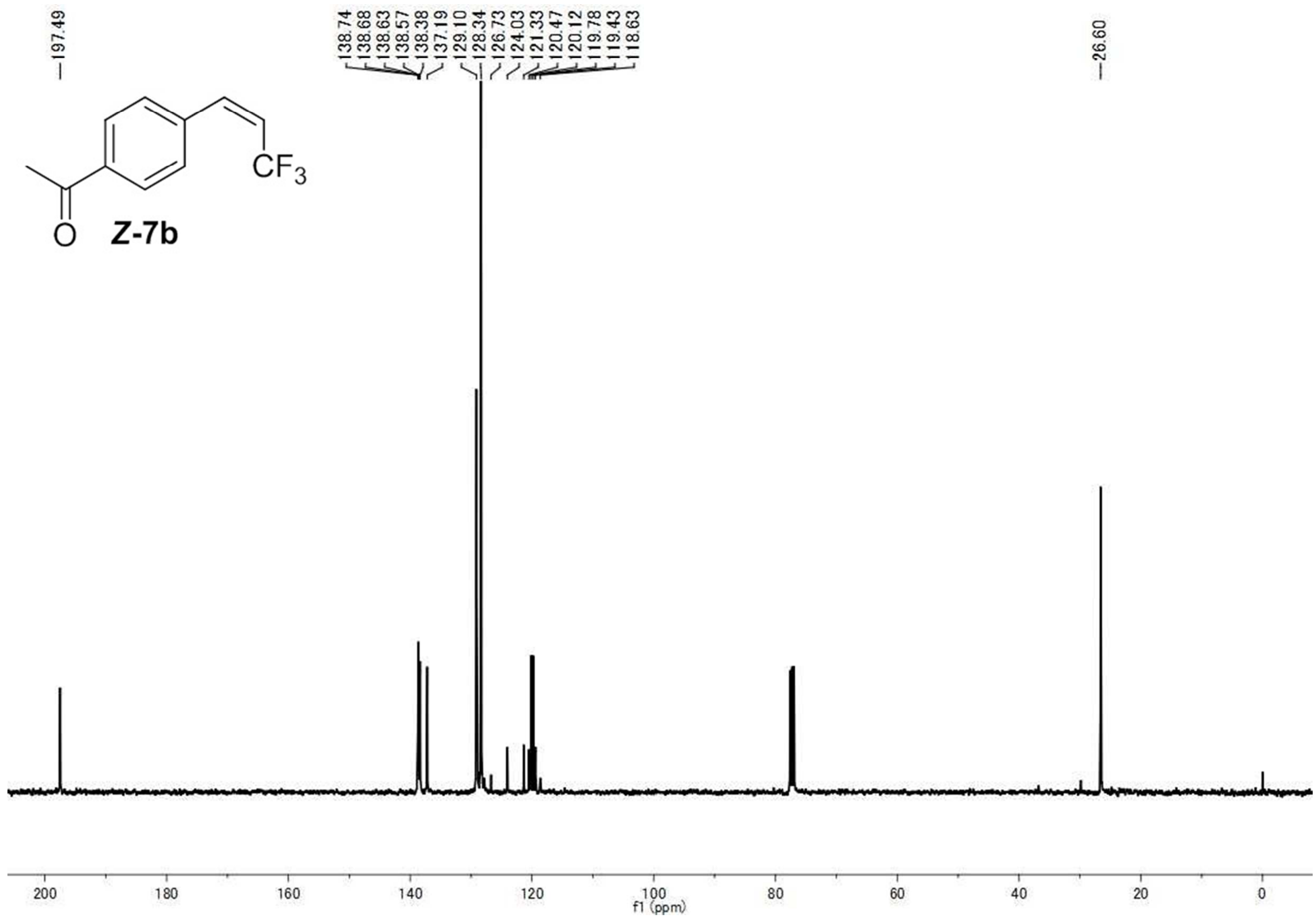
***Z*-7a**



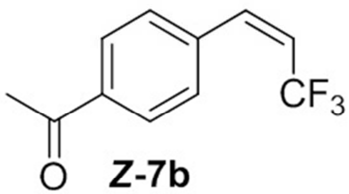
[19]F NMR (376 MHz, $CDCl_3$) (*Z*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (***Z*-7a**)



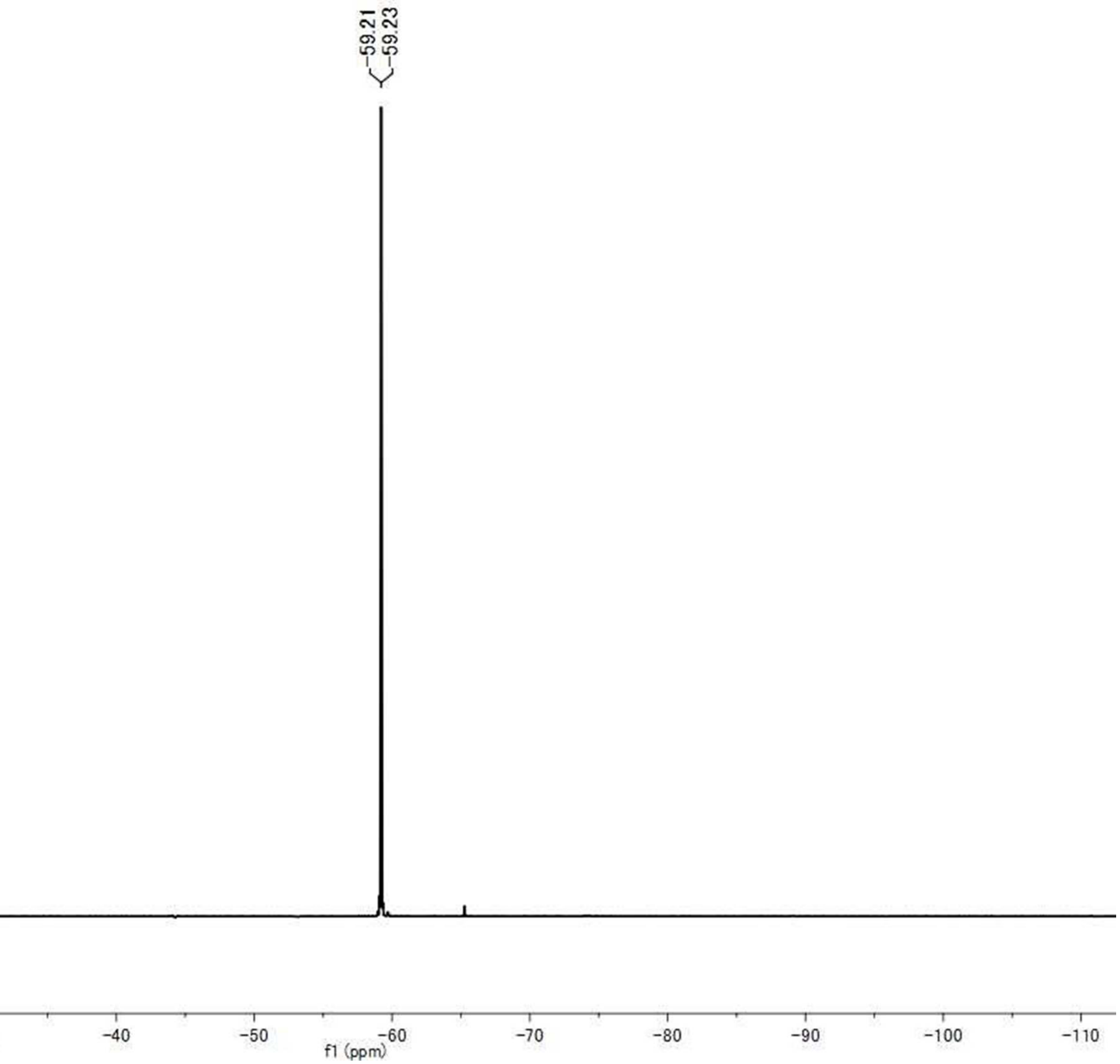
^{1}H NMR (400 MHz, $CDCl_3$) (*Z*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (***Z*-7b**)



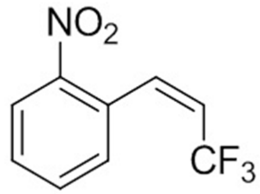
^{13}C NMR (101 MHz, $CDCl_3$) (*Z*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (***Z*-7b**)



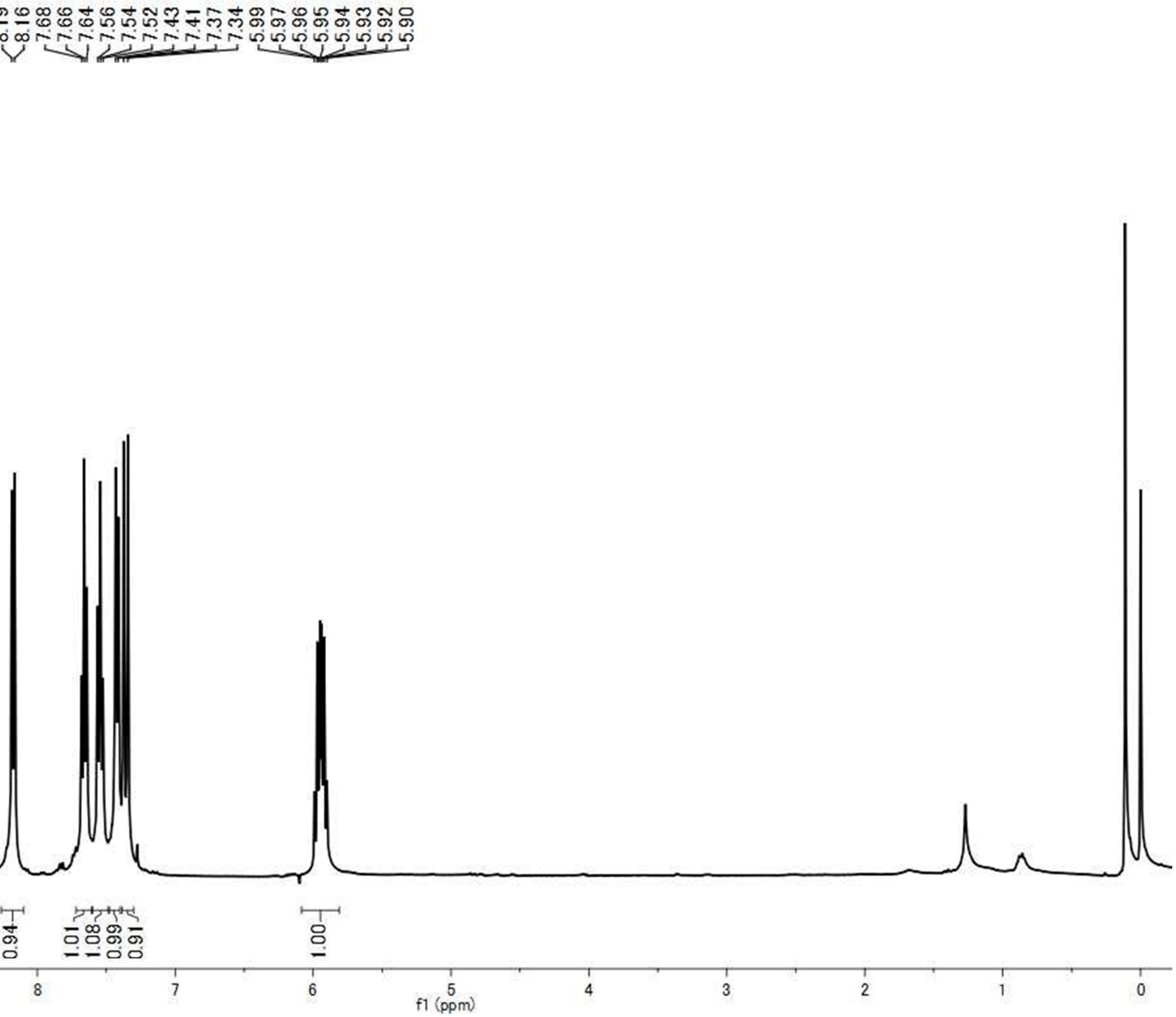
Z-7b



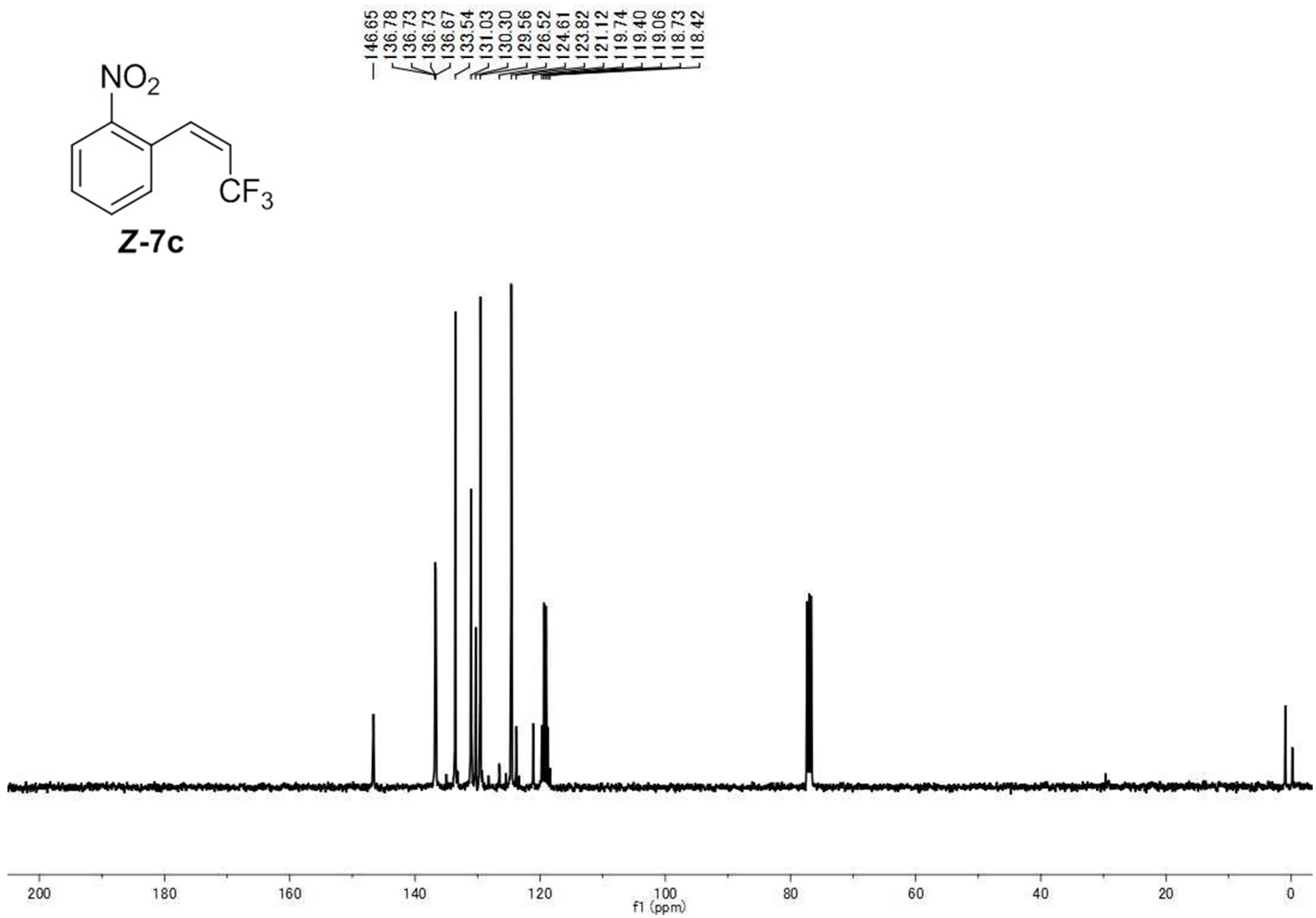
^{19}F NMR (376 MHz, $CDCl_3$) (*Z*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (***Z*-7b**)



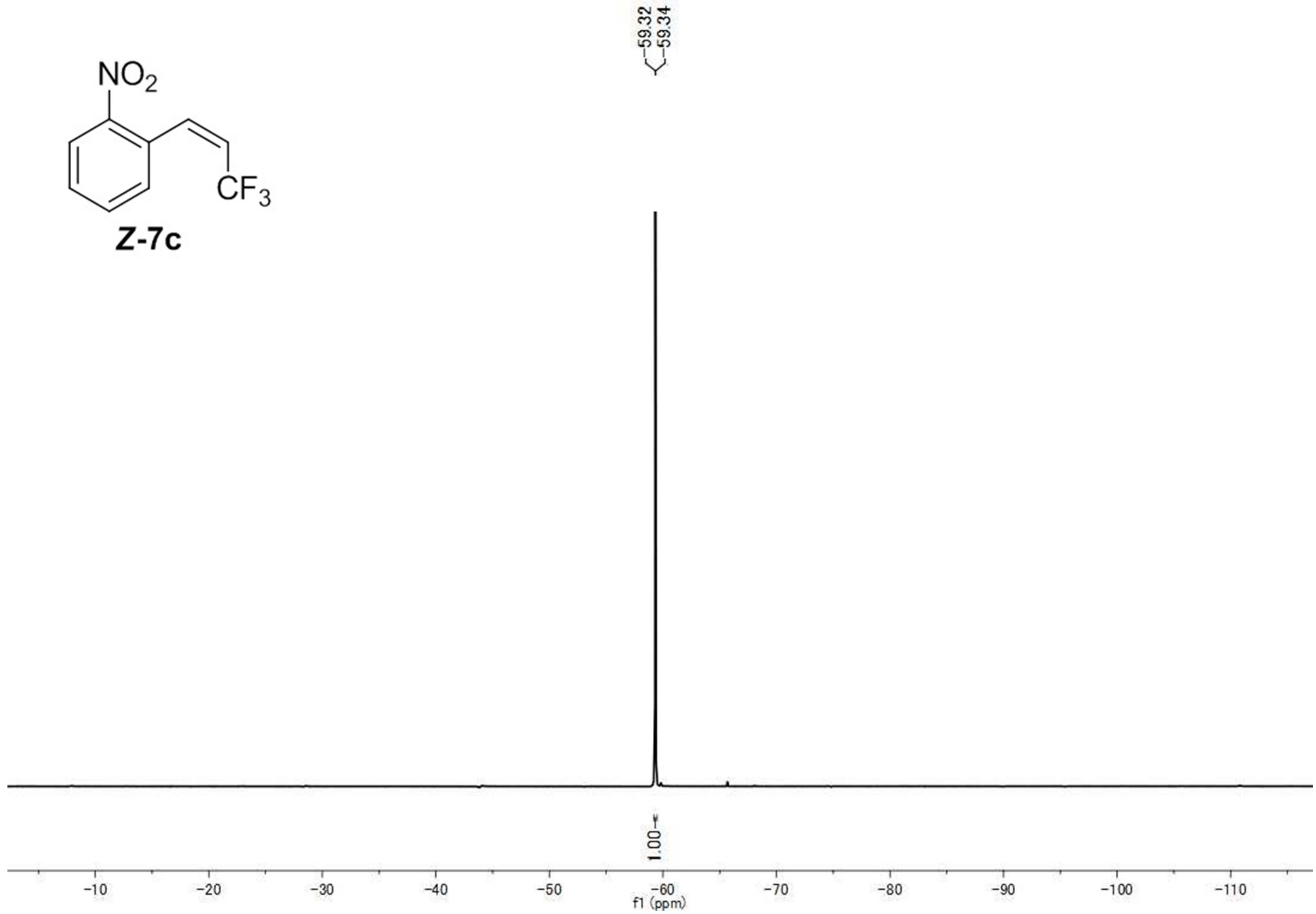
Z-7c



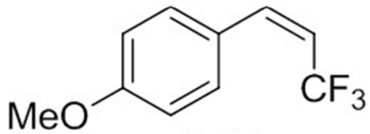
^{1}H NMR (400 MHz, $CDCl_3$) (Z)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***Z*-7c**)



^{13}C NMR (101 MHz, $CDCl_3$) (Z)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***Z*-7c**)

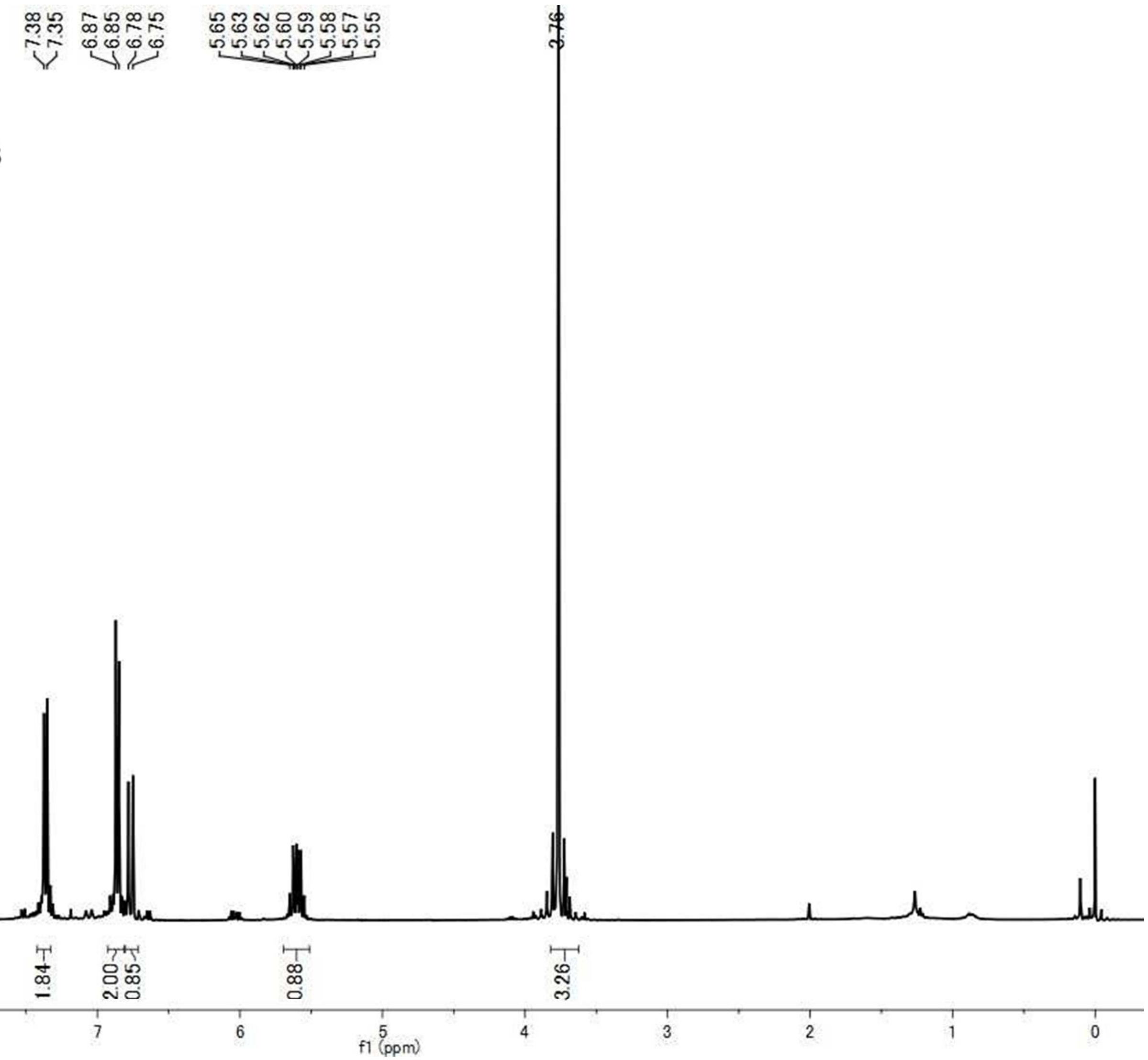


[19]F NMR (376 MHz, $CDCl_3$) (Z)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***Z*-7c**)

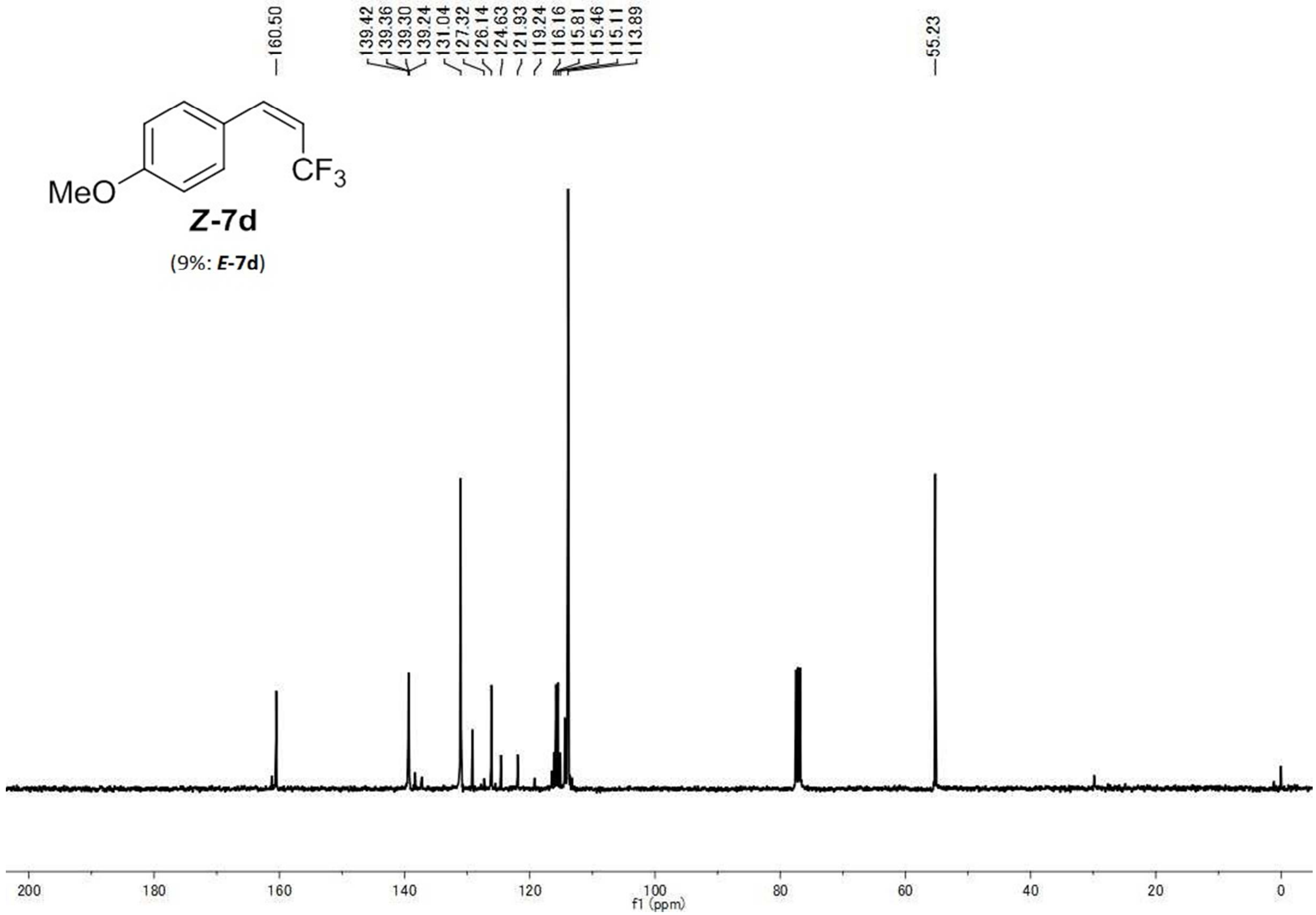


Z-7d

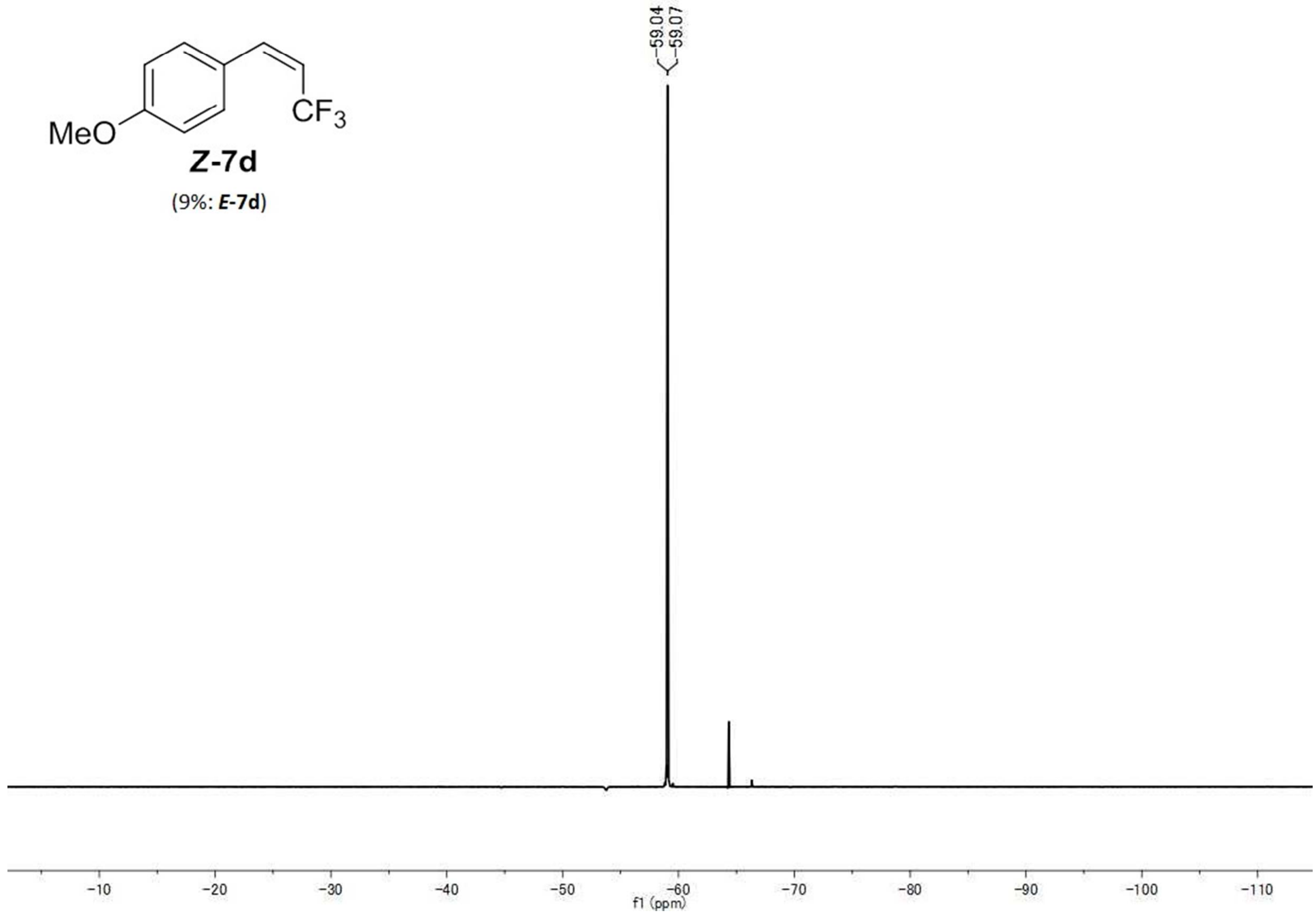
(9%: E-7d)



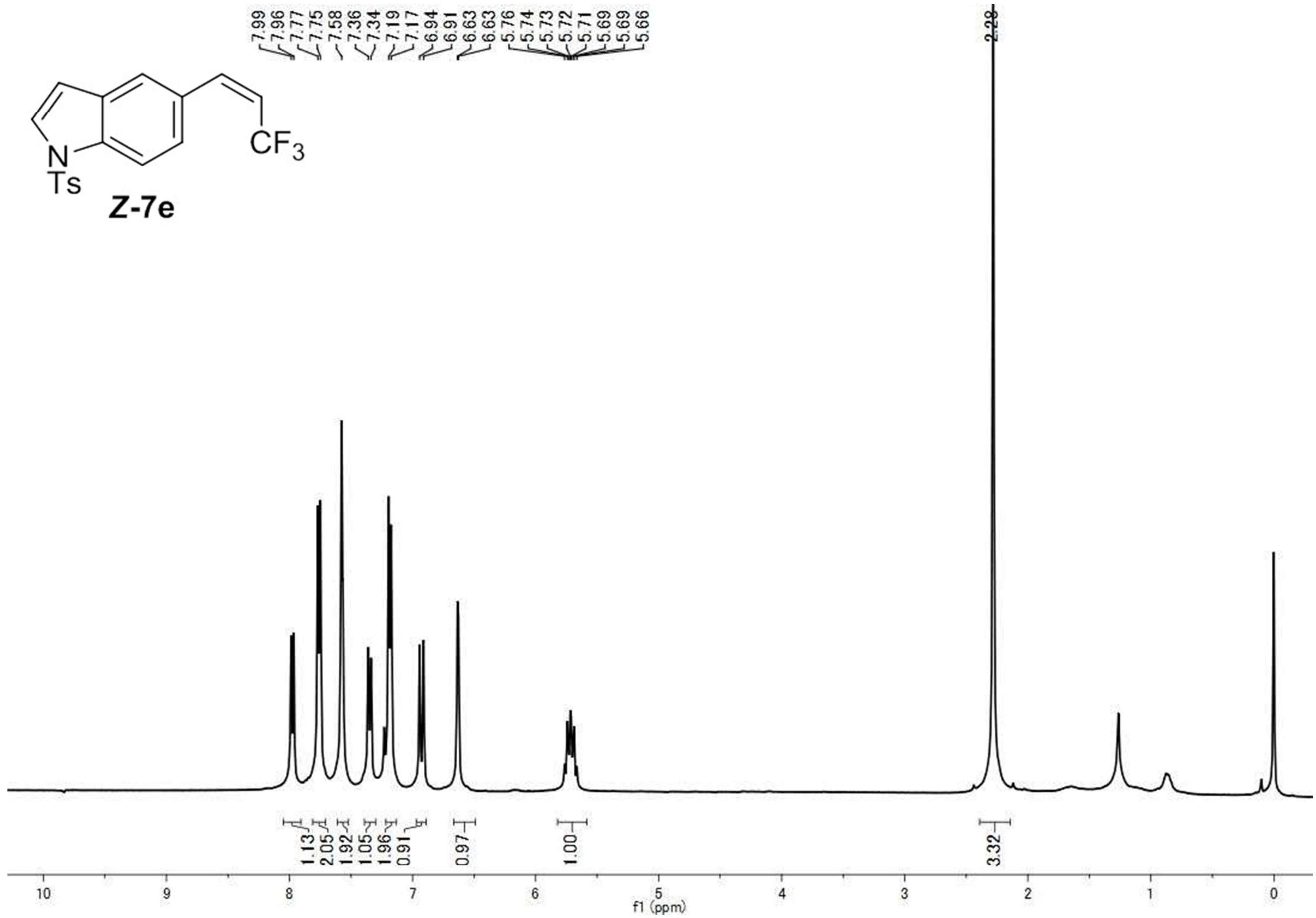
[1]H NMR (400 MHz, $CDCl_3$) (*Z*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***Z*-7d**)



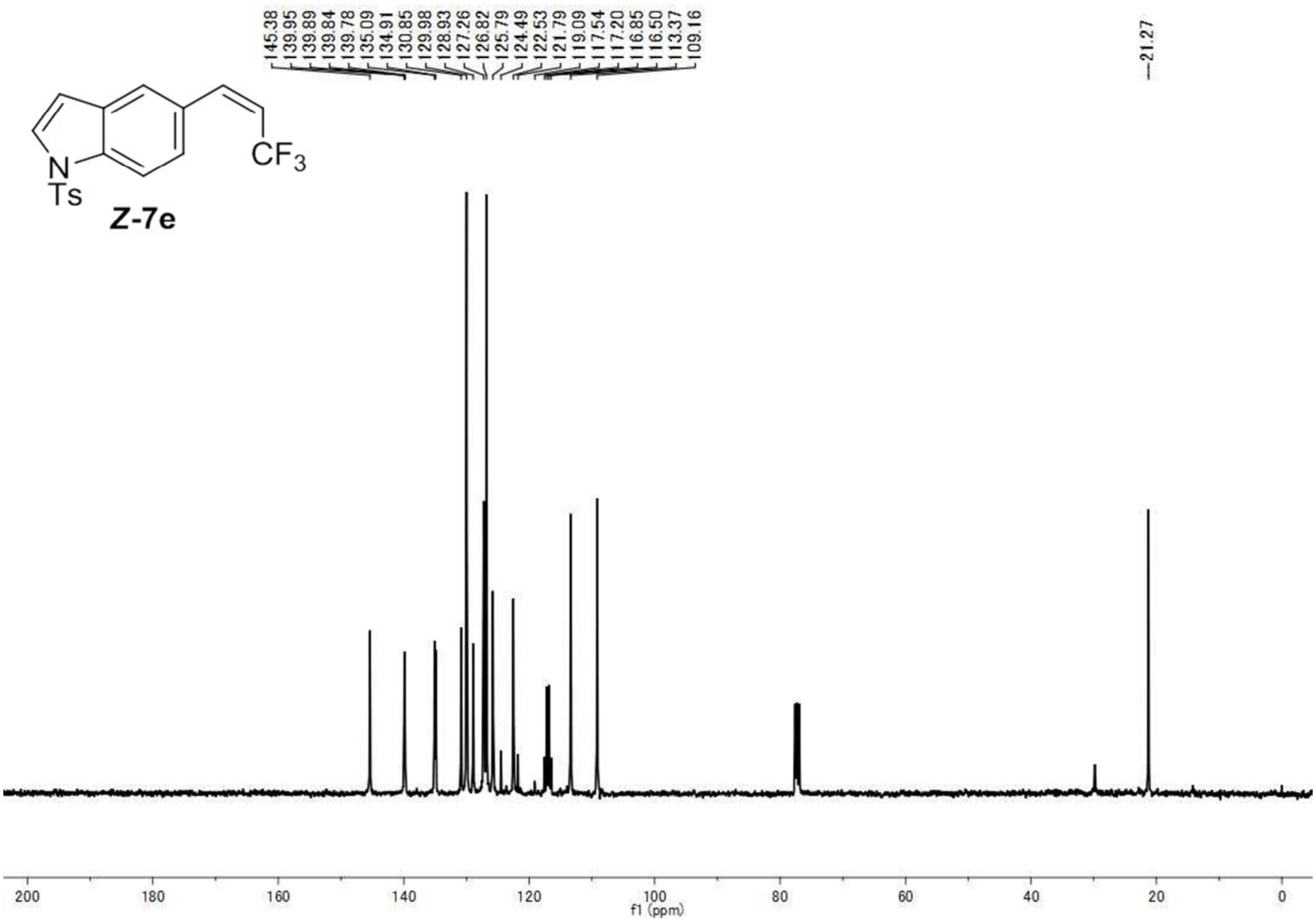
^{13}C NMR (101 MHz, $CDCl_3$) (*Z*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***Z*-7d**)



^{19}F NMR (376 MHz, $CDCl_3$) (*Z*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***Z*-7d**)

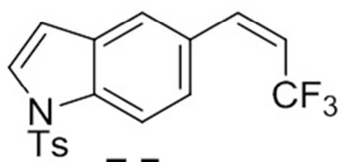


[1]H NMR (400 MHz, $CDCl_3$) (*Z*)-1-tosyl-5-(3,3,3-trifluoroprop-1-en-1-yl)-1H-indole (***Z*-7e**)

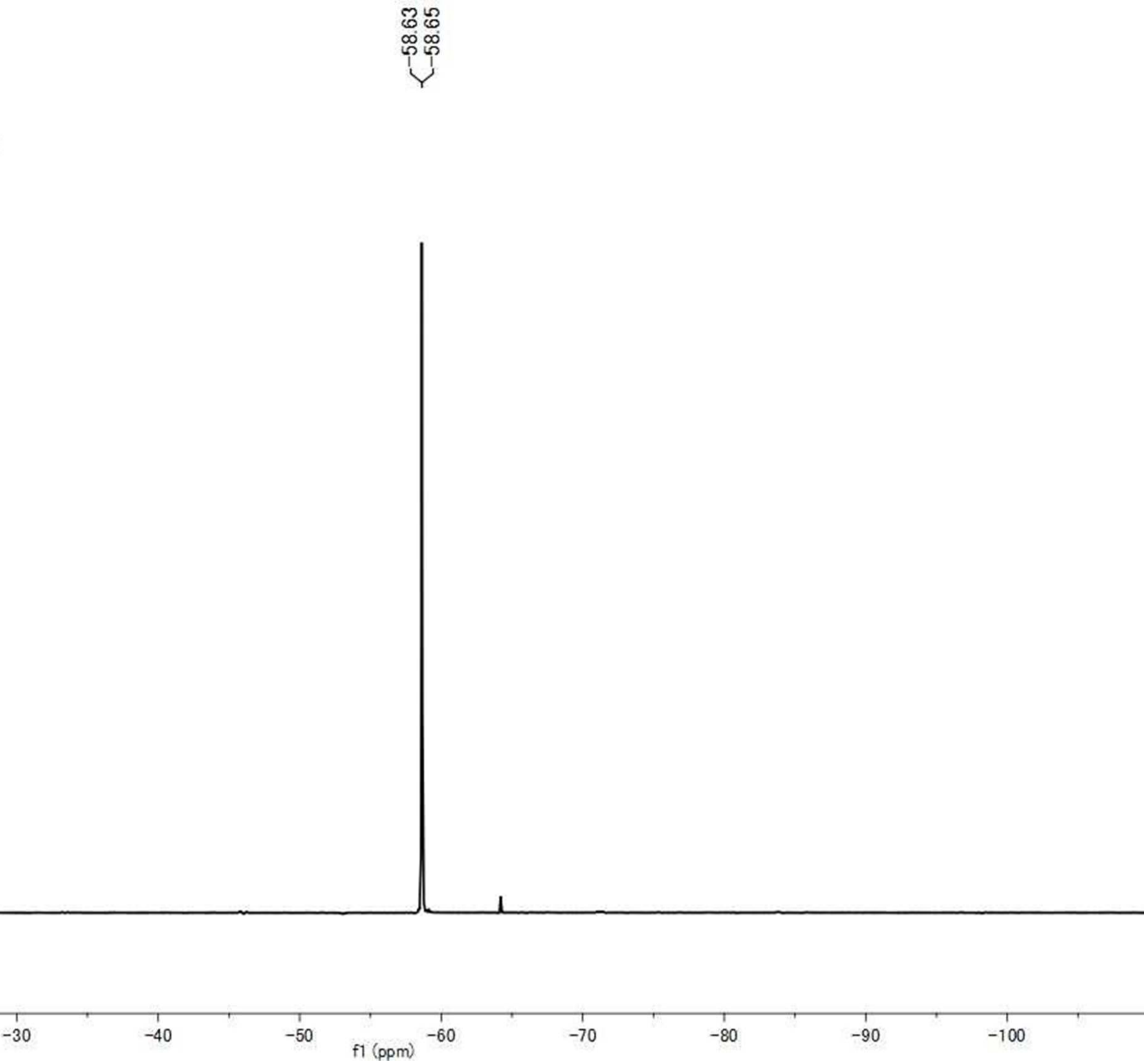


***Z*-7e**

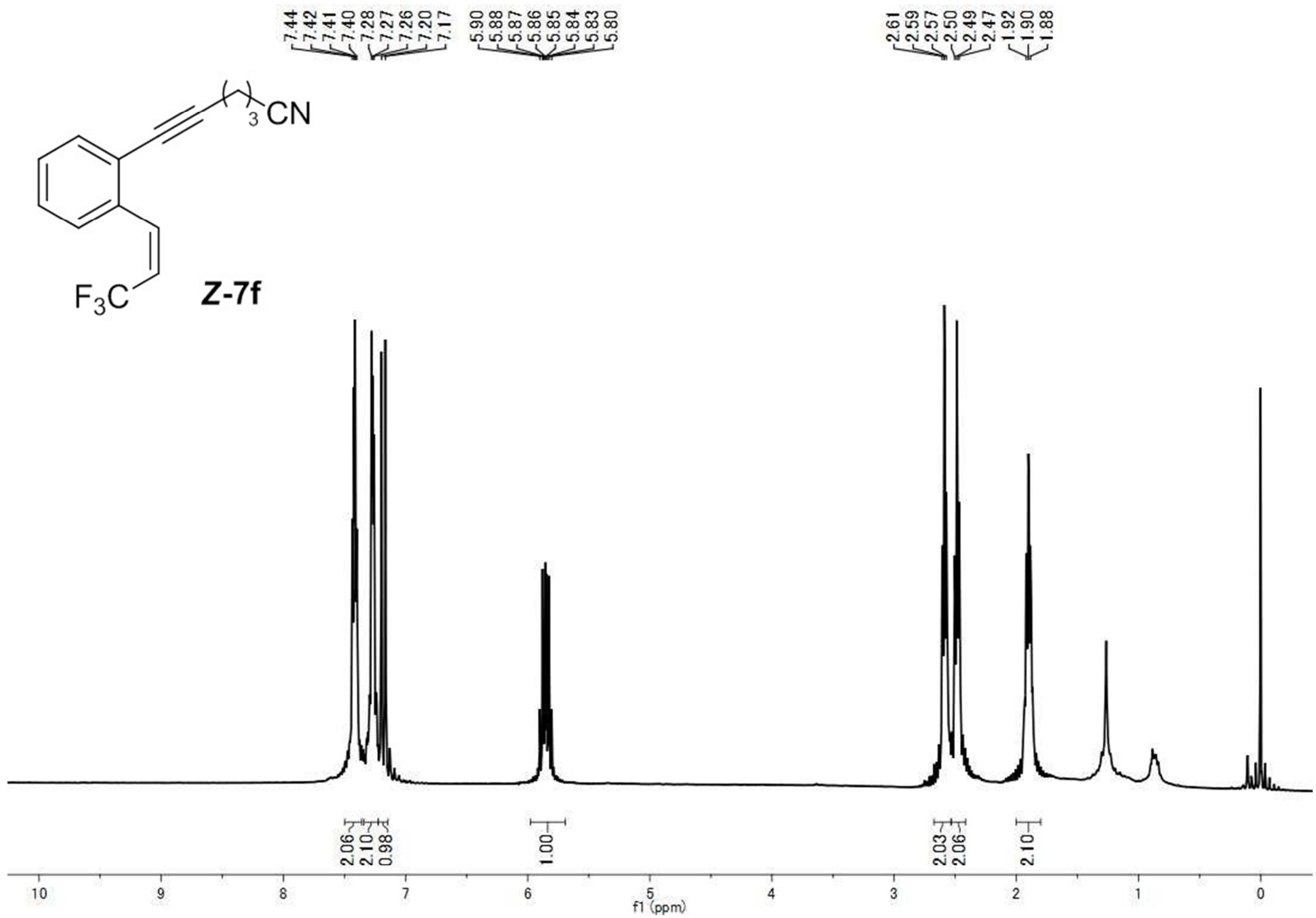
^{13}C NMR (101 MHz, $CDCl_3$) (*Z*)-1-tosyl-5-(3,3,3-trifluoroprop-1-en-1-yl)-1H-indole (***Z*-7e**)



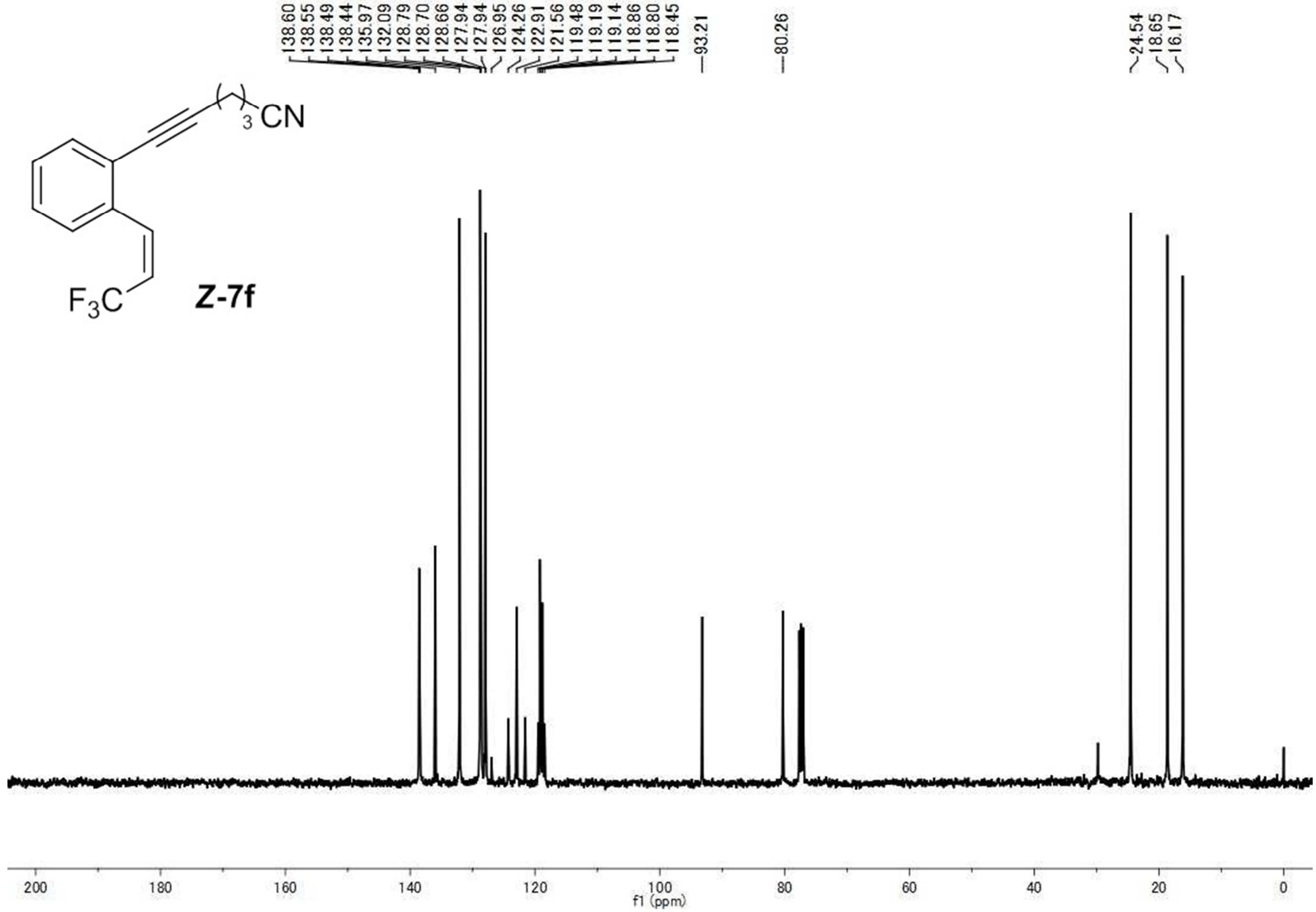
***Z*-7e**



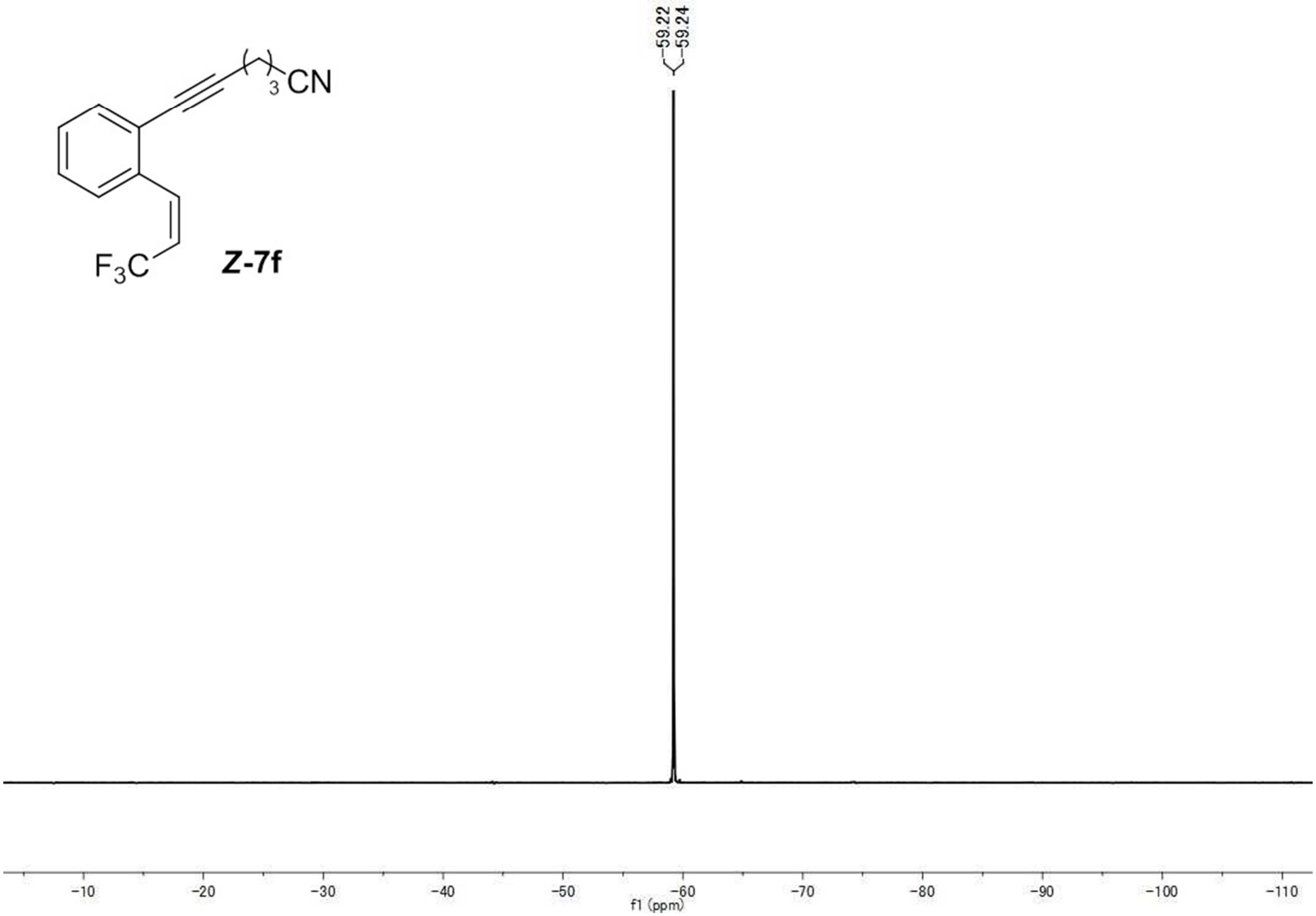
[19]F NMR (376 MHz, $CDCl_3$) (*Z*)-1-tosyl-5-(3,3,3-trifluoroprop-1-en-1-yl)-1H-indole (***Z*-7e**)



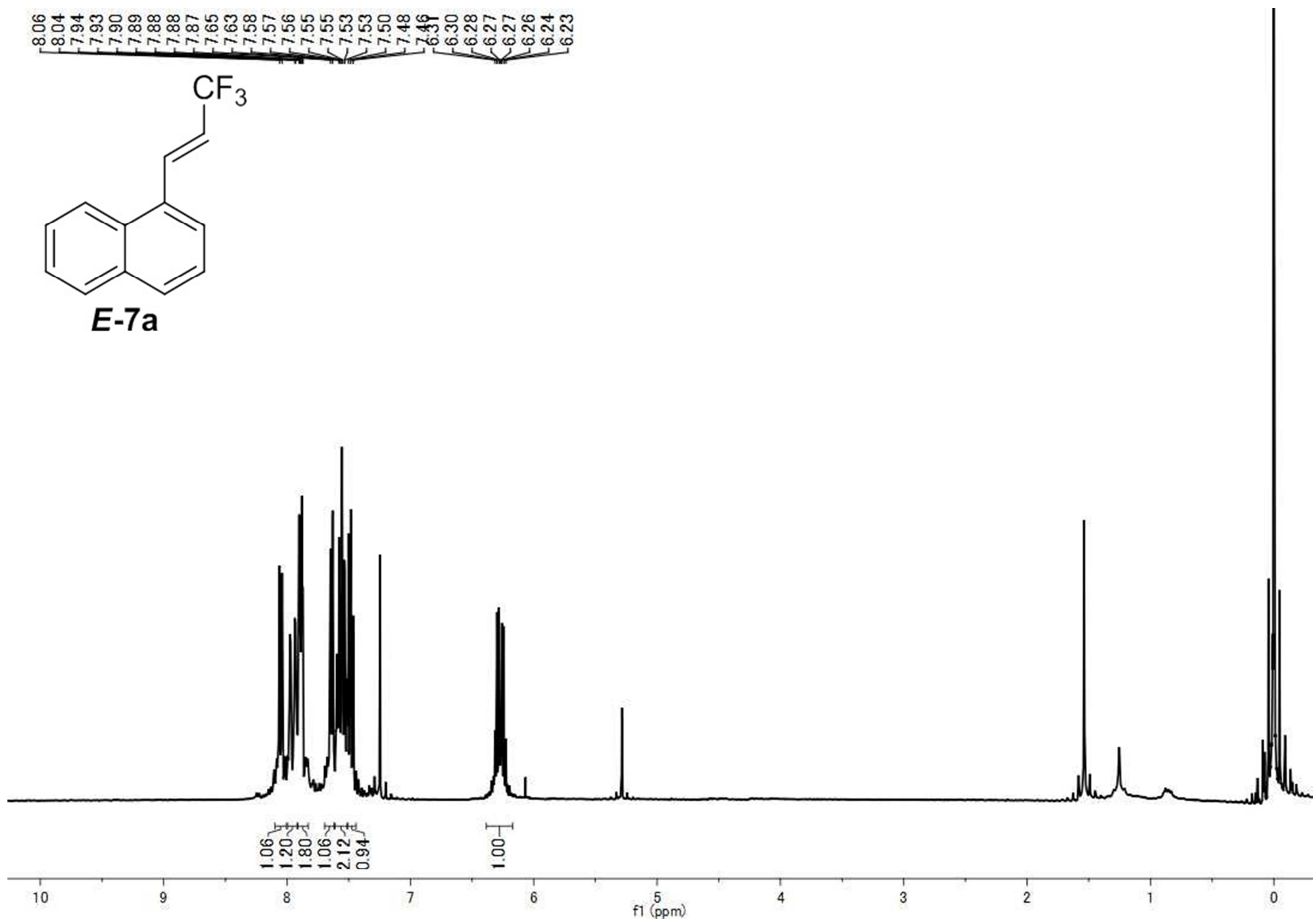
^{1}H NMR (400 MHz, $CDCl_3$) (*Z*)-6-(2-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)hex-5-ynenitrile (***Z*-7f**)



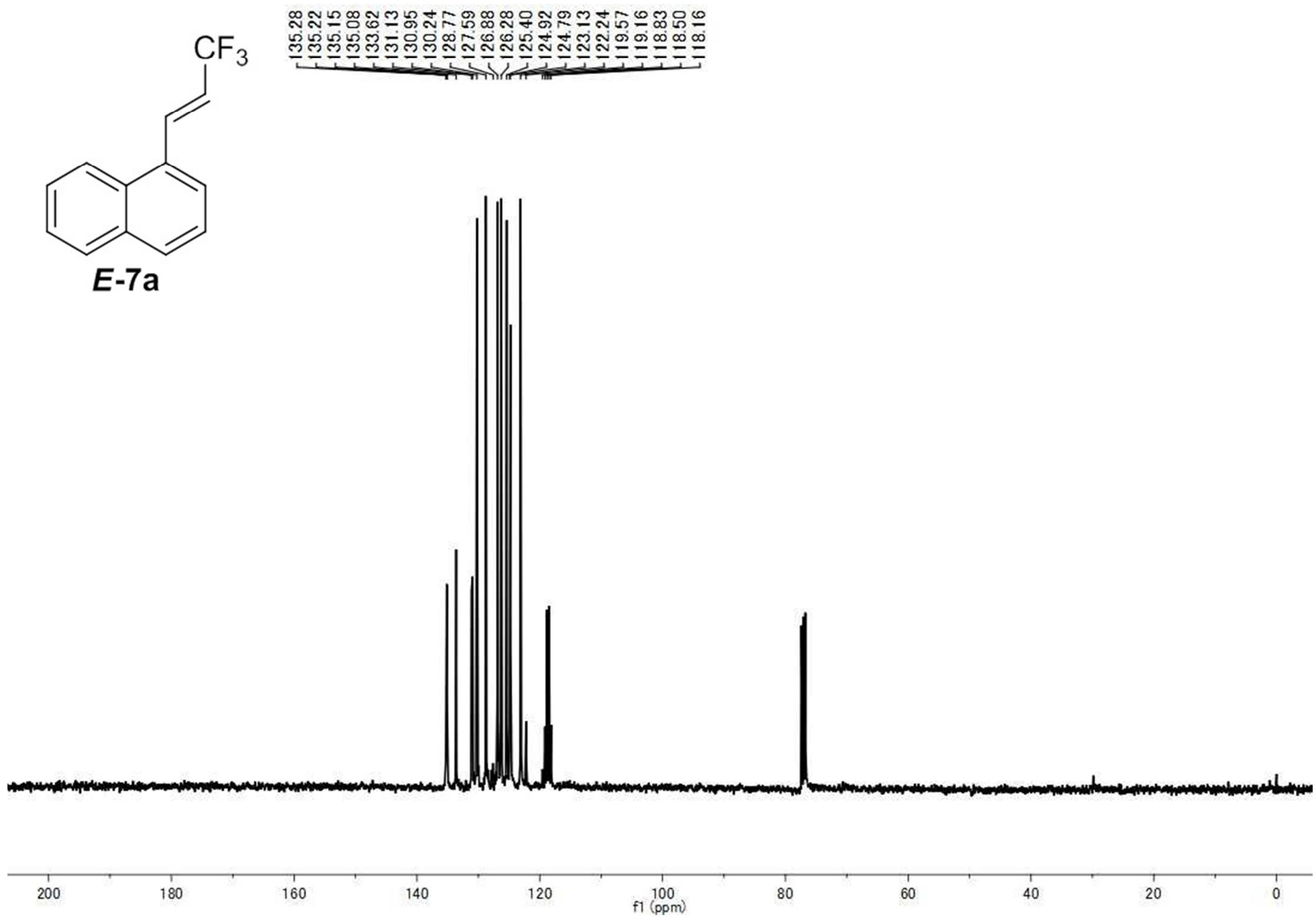
^{13}C NMR (101 MHz, $CDCl_3$) (*Z*)-6-(2-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)hex-5-ynenitrile (***Z*-7f**)



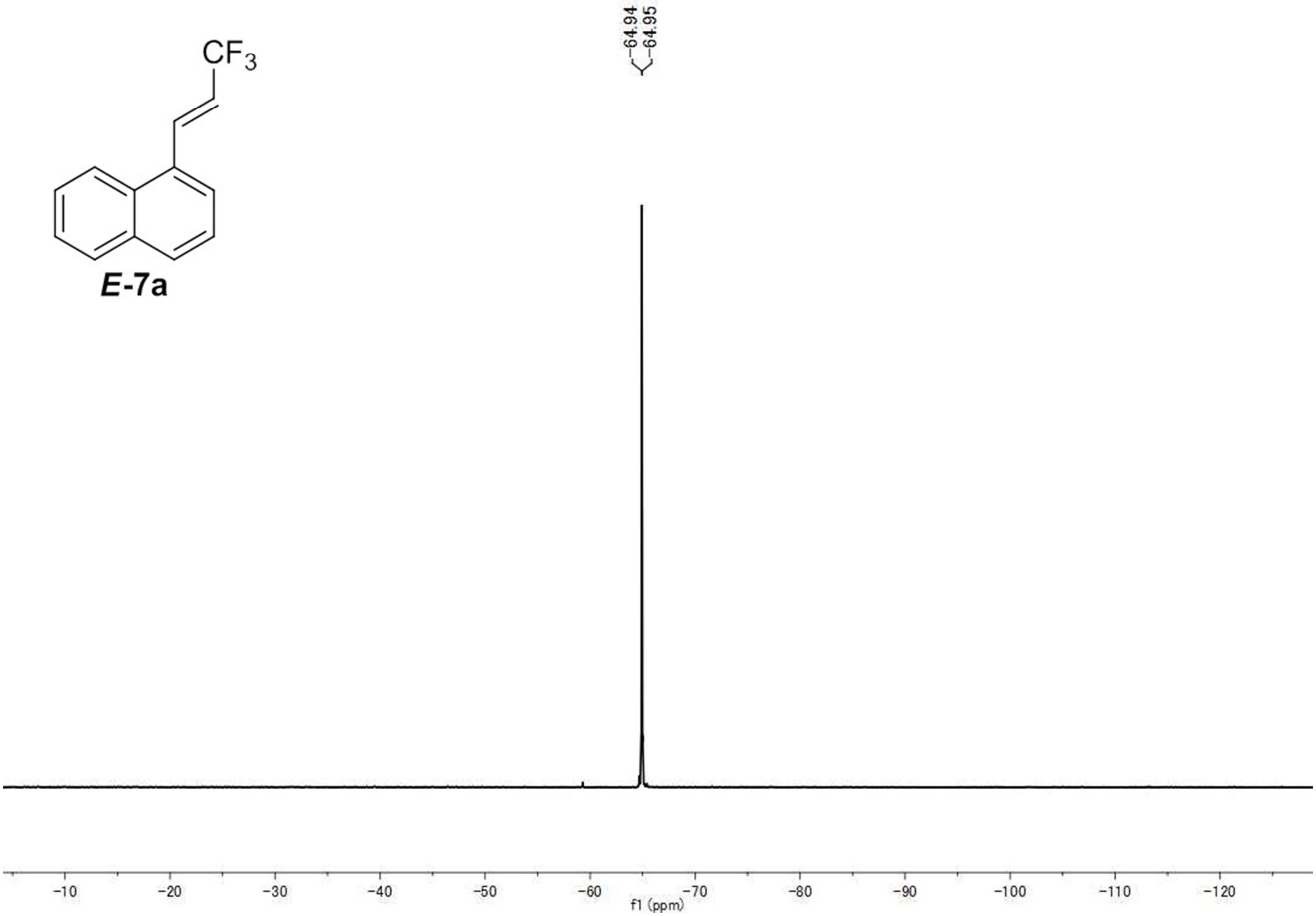
^{19}F NMR (376 MHz, $CDCl_3$) (*Z*)-6-(2-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)hex-5-ynenitrile (***Z*-7f**)



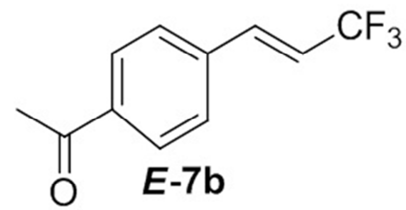
^{1}H NMR (400 MHz, $CDCl_3$) (*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (***E*-7a**)



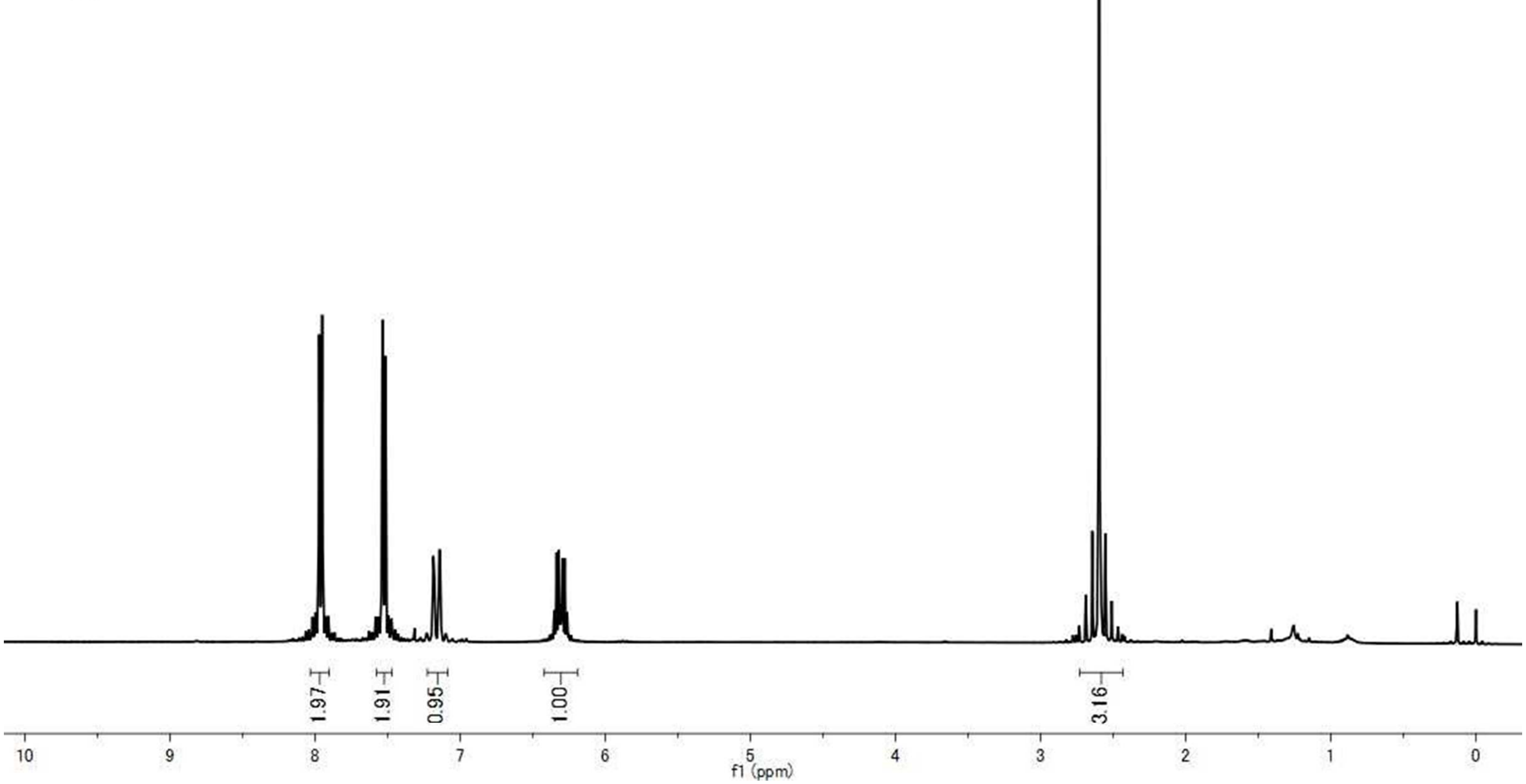
^{13}C NMR (101 MHz, $CDCl_3$) (*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (***E*-7a**)



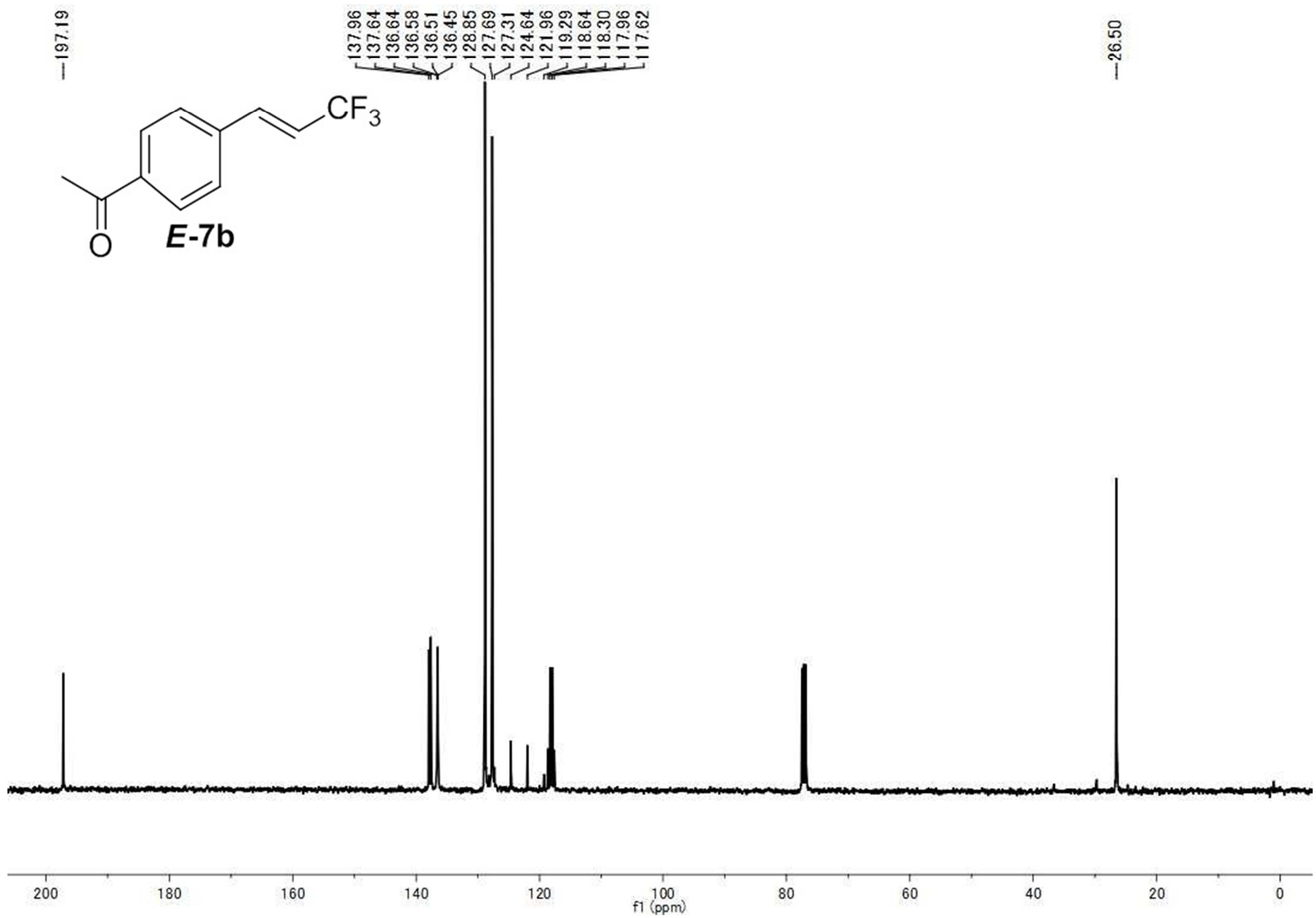
^{19}F NMR (376 MHz, $CDCl_3$) (*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (***E*-7a**)



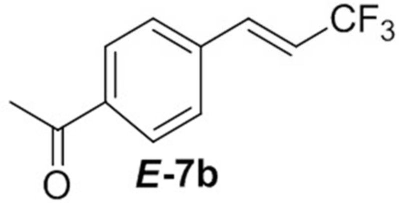
***E*-7b**



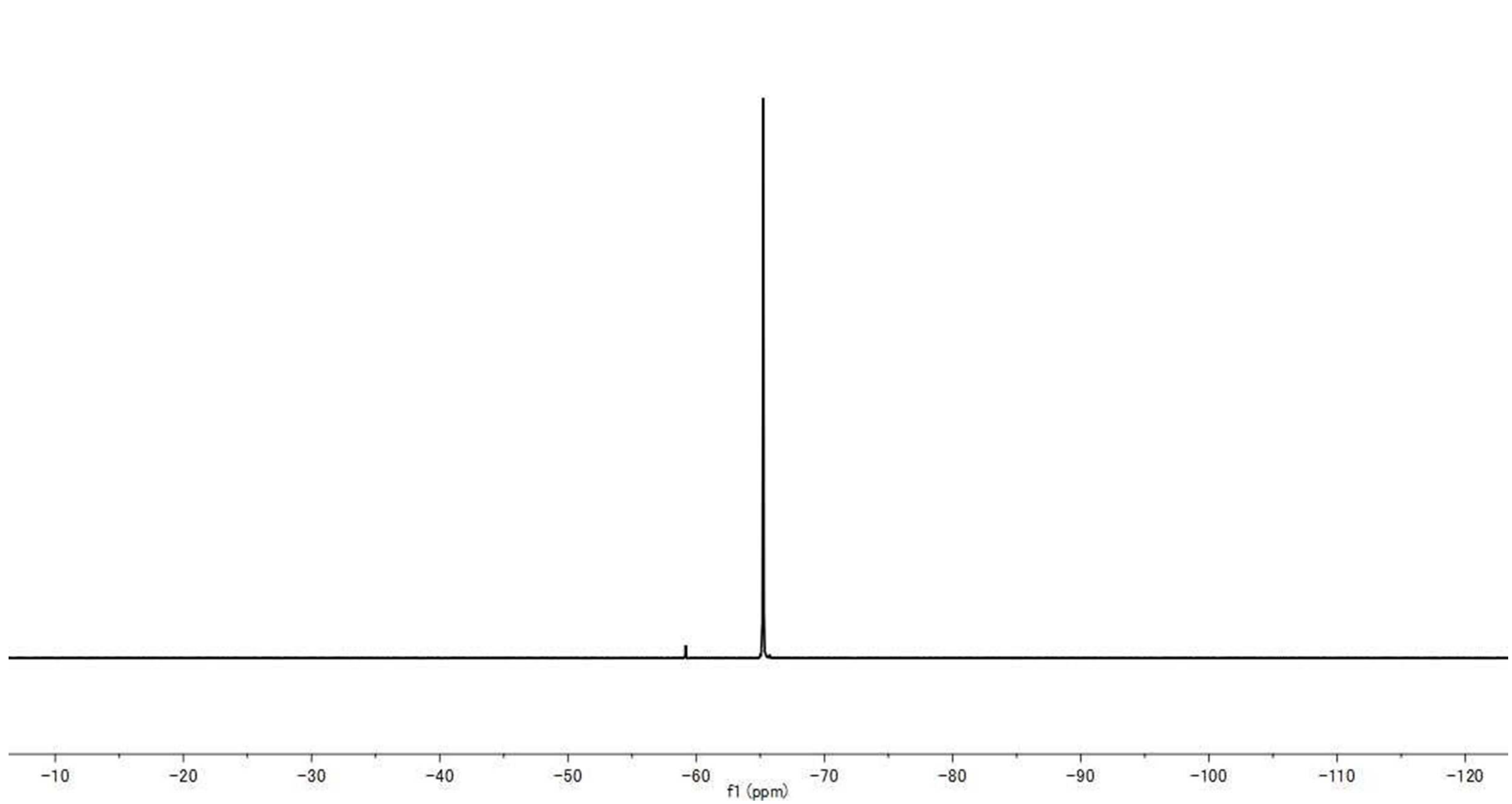
[1]H NMR (400 MHz, $CDCl_3$) (*E*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (***E*-7b**)



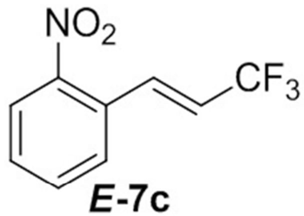
^{13}C NMR (101 MHz, $CDCl_3$) (*E*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (***E*-7b**)

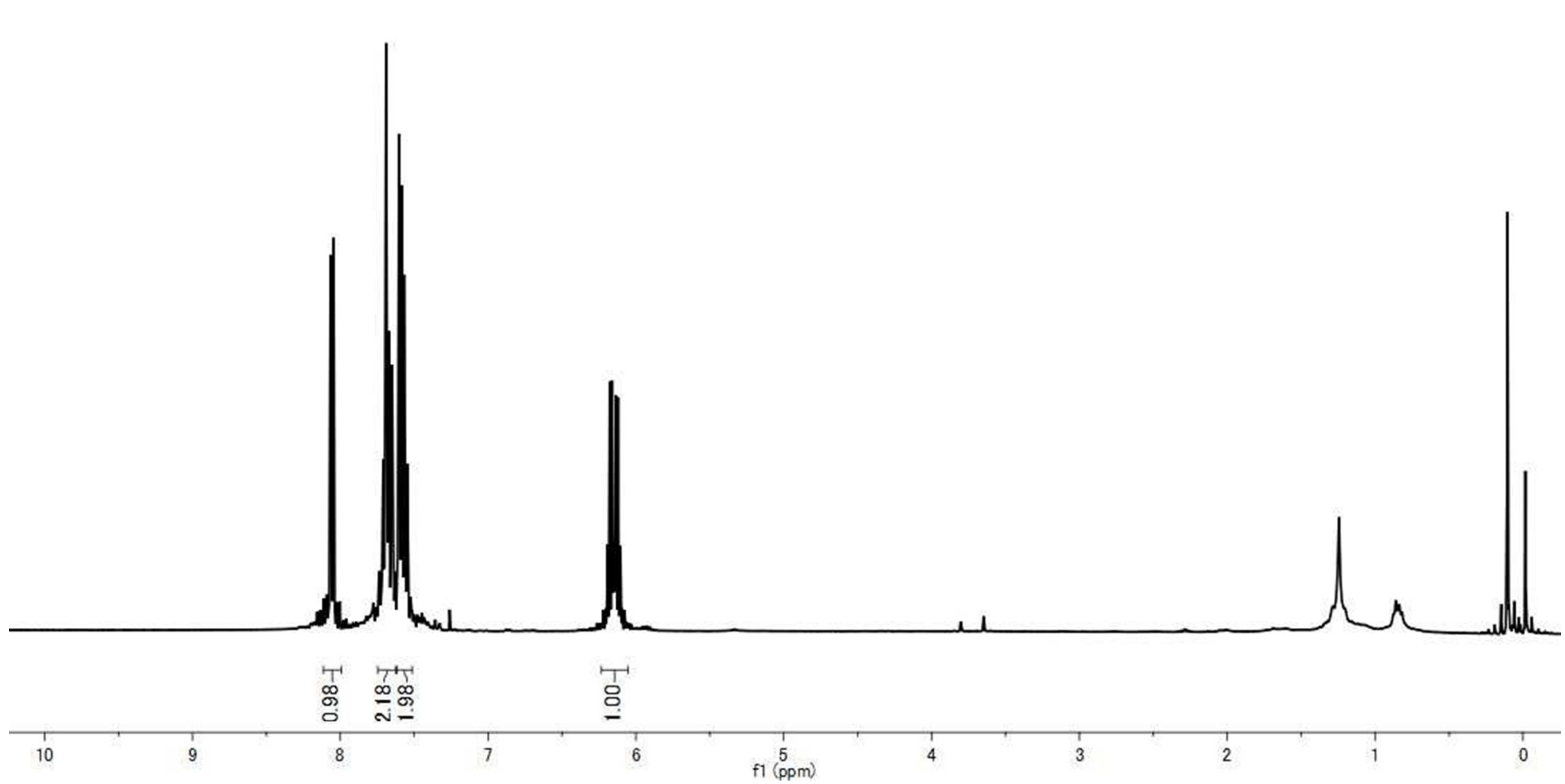


***E*-7b**

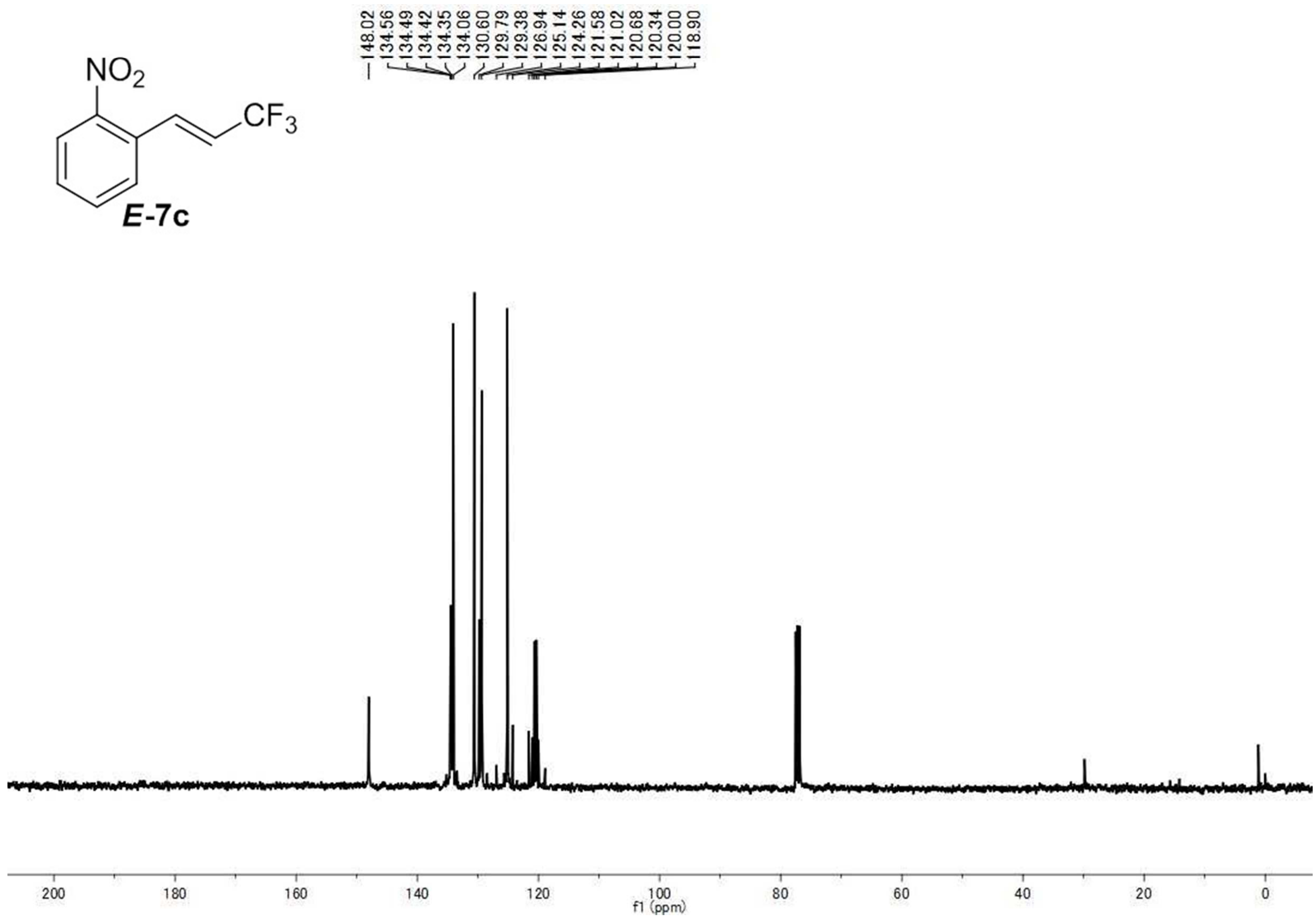


[19]F NMR (376 MHz, $CDCl_3$) (*E*)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethanone (***E*-7b**)

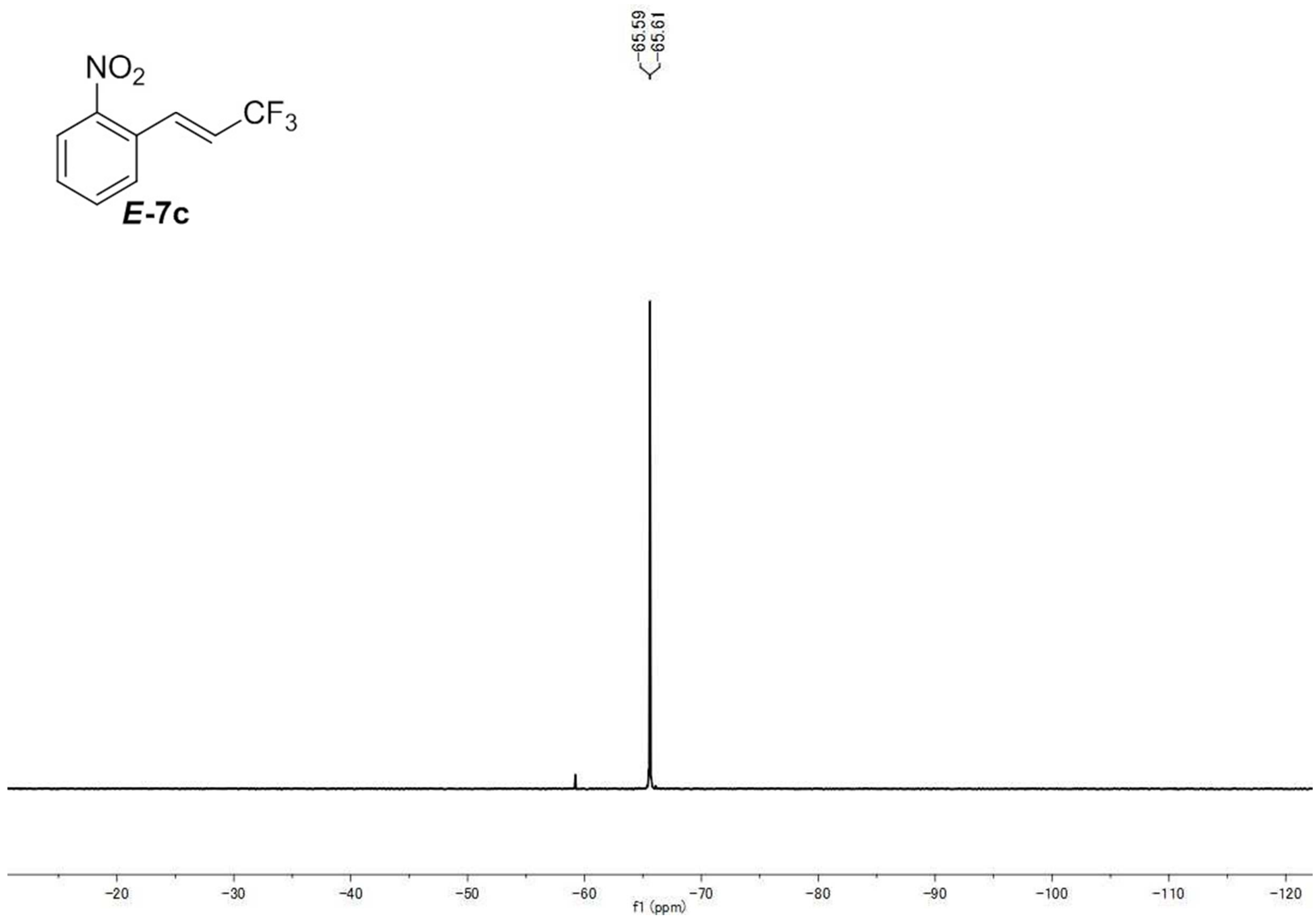




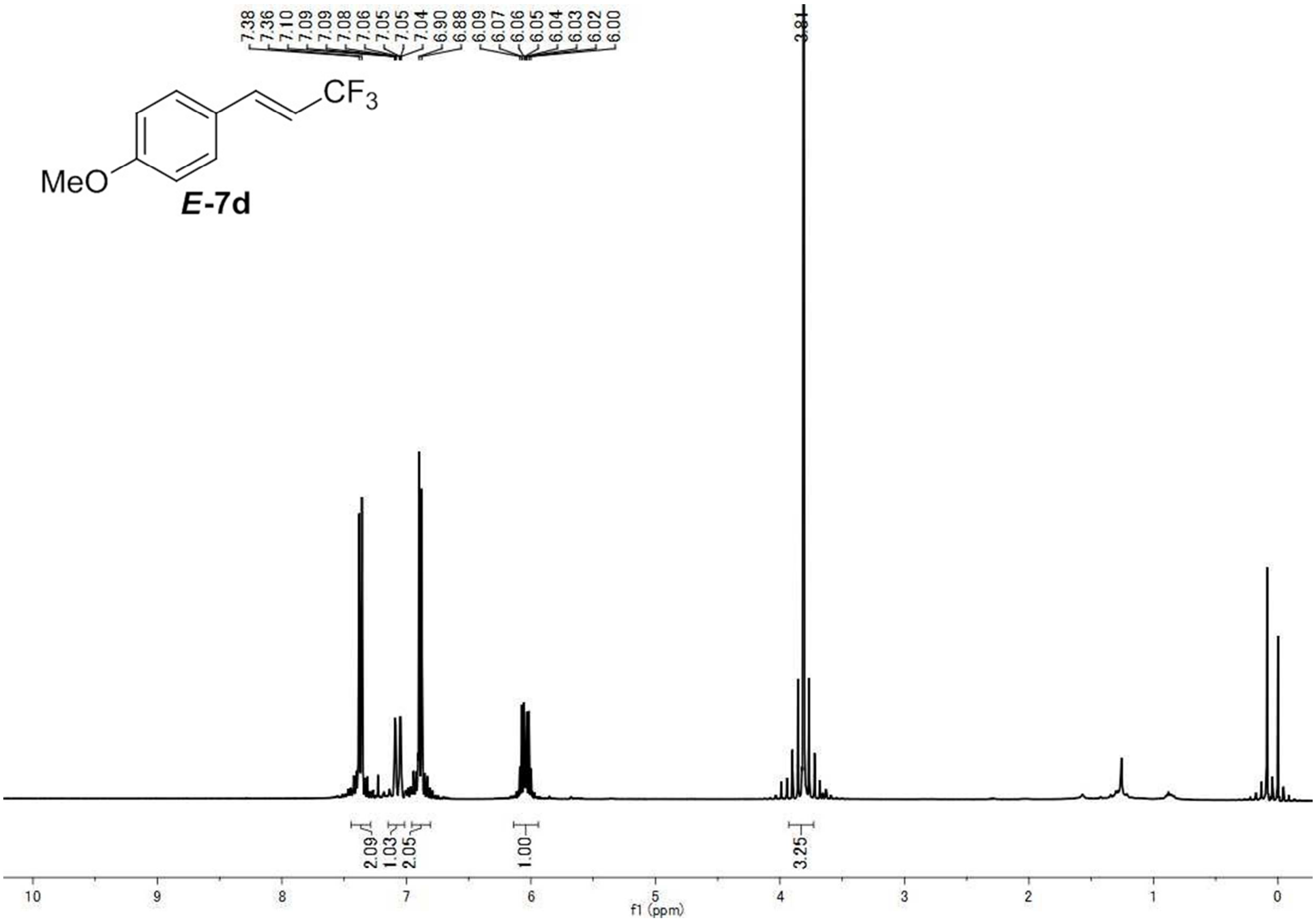
^{1}H NMR (400 MHz, $CDCl_3$) (*E*)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***E*-7c**)



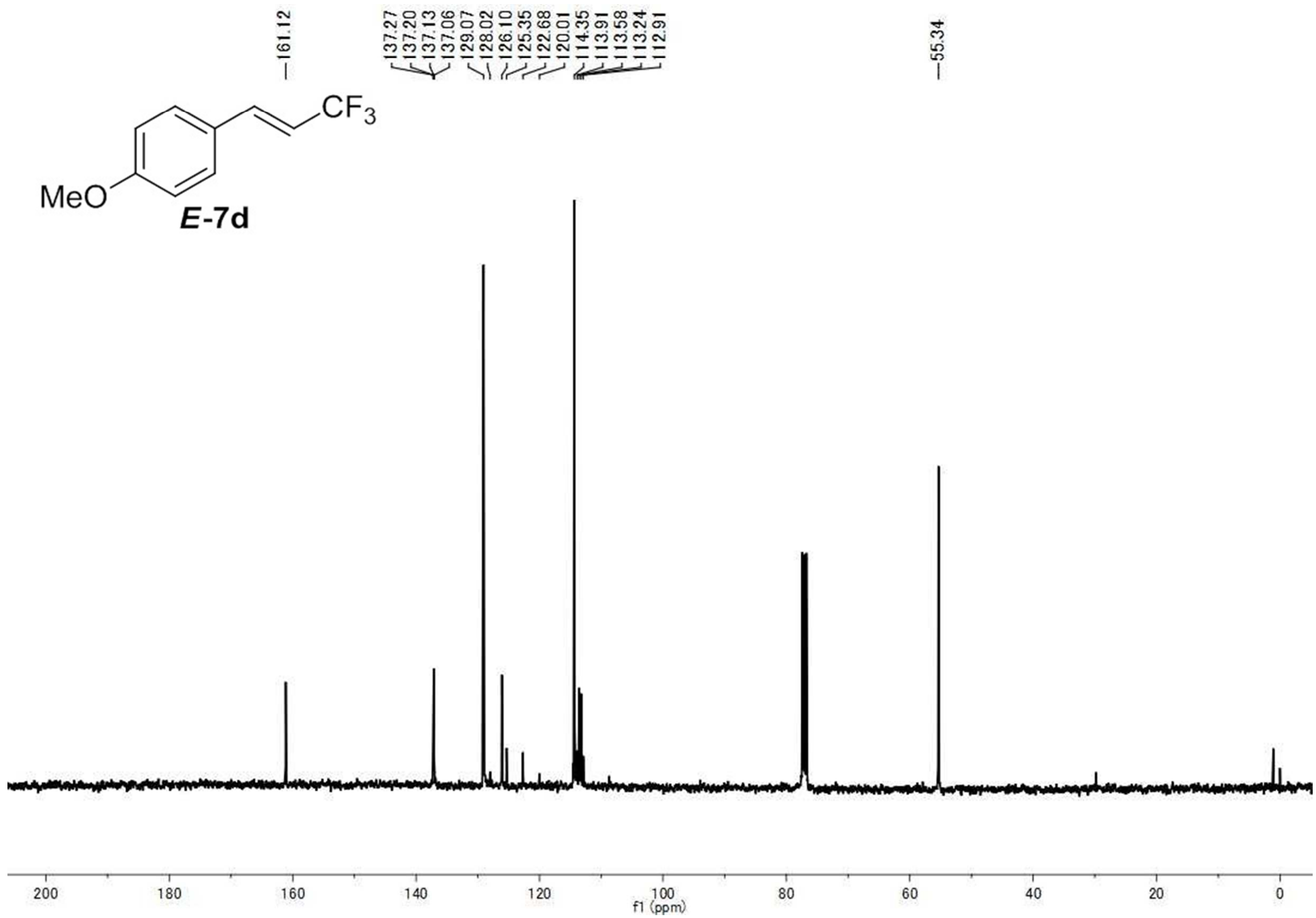
^{13}C NMR (101 MHz, $CDCl_3$) (*E*)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***E*-7c**)



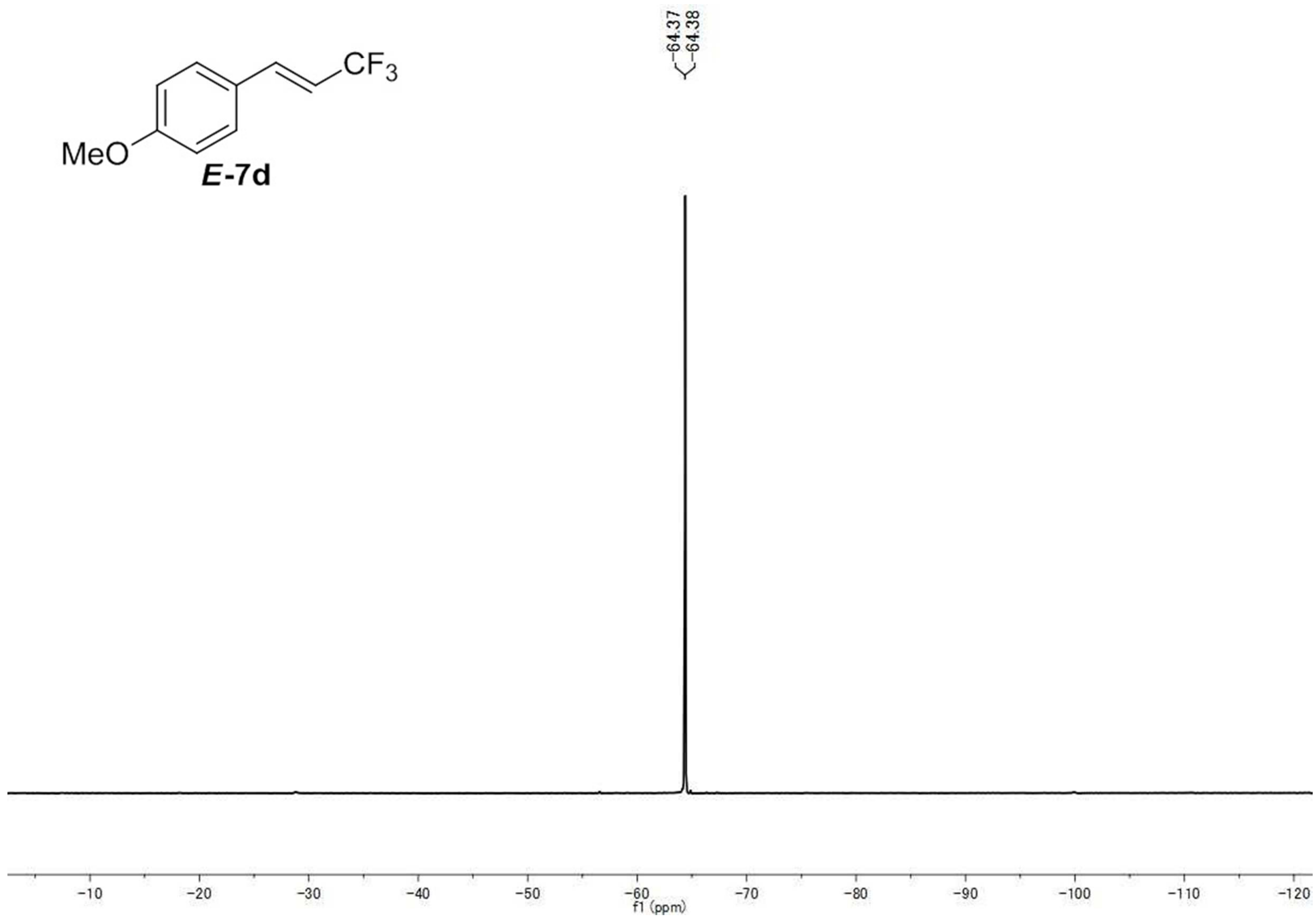
^{19}F NMR (376 MHz, $CDCl_3$) (*E*)-1-nitro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***E*-7c**)



[1]H NMR (400 MHz, $CDCl_3$) (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***E*-7d**)



^{13}C NMR (101 MHz, $CDCl_3$) (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***E*-7d**)



^{19}F NMR (376 MHz, $CDCl_3$) (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (***E*-7d**)

References

1) Fresneda, P. M.; Molina, P.; Bleda, J. A. *Tetrahedron* 2001, *57*, 2355.
2) Guilarte, V.; Fernández-Rodríguez, M. A.; García-García, P.; Hernando, E.; Sanz, R. *Org. Lett.* 2011, *13*, 5100.