

Visible-light-induced installation of oxyfluoroalkyl groups

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General Considerations

General Reagent Information

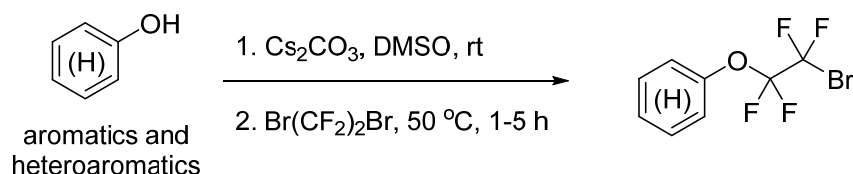
Anhydrous Solvents were purchased from Sigma-Aldrich, Alfa Aesar chemical company in Sure-Seal bottles and degassed by repeated sonication under light vacuum and replenishing the atmosphere with argon. Commercially available reagents including $[\text{Ru}(\text{Phen})_3]\text{Cl}_2$ were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI companies, Junsei or Combi-blocks. Flash column chromatography was performed using Merck silica gel 60 (70–230 mesh).

General Analytical Information

The (hetero)aryloxytetrafluoroethylated products were characterized by ^1H , ^{13}C , and ^{19}F NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^1H NMR, 151 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR) and Varian 300 MHz instrument (300 MHz for ^1H NMR). Copies of ^1H NMR and ^{13}C 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) and in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuteriochloroform (77.23 ppm), and all were obtained with ^1H decoupling. ^{19}F NMR spectra are reported in ppm, and all were taken composite pulse decoupling (CPD) mode. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Tensor 27 Bruker FT-IR spectrometer. Reactions were monitored by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector. Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.

Experimental Details

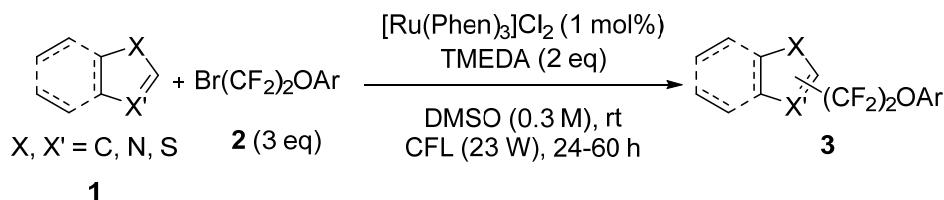
Preparation of (hetero)aryloxytetrafluoroethyl reagents



The aryloxyfluoroalkylation reagents were synthesized on 10 mmol scale following a reported procedure.^{S1}

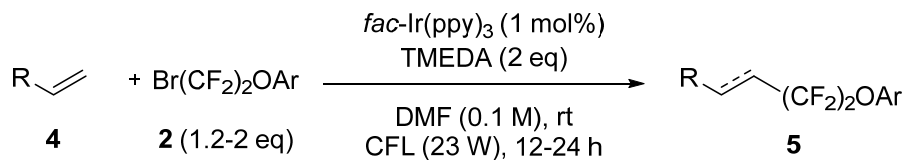
Ref. S1: J. Li, J. X. Qiao, D. Smith, B. -C. Chen, M. E. Salvati, J. Y. Roberge and B. N. Balasubramanian, *Tetrahedron Lett.*, 2007, **48**, 7516.

Aryloxytetrafluoroethylation of heteroaromatic alkenes



A flame-dried tube equipped with a magnetic stirring bar was charged with argon. The substrate (**1**: 0.3 mmol), $[\text{Ru}(\text{Phen})_3]\text{Cl}_2$ (0.003 mmol), TMEDA (0.6 mmol), and DMSO (1.0 mL) were added to the tube. Argon was bubbled through the reaction mixture for 5 min. Then, $\text{Br}(\text{CF}_2)_2\text{OAr}$ (**2**: 0.9 mmol) was added. The mixture was stirred at room temperature and irradiated with visible light using a 23 W CFL. The reaction progress was monitored by thin layer chromatography and gas chromatography. Upon completion of the reaction, the mixture was diluted with diethyl ether and washed with brine. The layers were separated, and the organic layer was dried with MgSO_4 , filtered, and concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding aryloxytetrafluoroethylated product.

Aryloxytetrafluoroethylation of alkenes



A flame-dried tube equipped with a magnetic stirring bar was charged with argon. The substrate (**4**: 0.3 mmol), $\text{fac-Ir}(\text{ppy})_3$ (0.003 mmol), TMEDA (0.6 mmol) and DMF (3.0 mL) were added to the tube. Argon was bubbled through the reaction mixture for 5 min. Then, $\text{Br}(\text{CF}_2)_2\text{OAr}$ (**2**: 0.36-0.6 mmol) was added. The mixture was stirred at room temperature and irradiated with visible light using a 23 W CFL. The reaction progress was monitored by thin layer chromatography and gas chromatography. Upon completion of the reaction, the mixture was diluted with diethyl ether and washed with brine. The layers were separated, and the organic layer was dried with MgSO_4 , filtered, and concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding aryloxytetrafluoroethylated product.

Optimization Studies of Alkenes

Table S1. Optimization Studies of Heteroaromatics^a

Reaction scheme: **1a** + **2a** (1.2 eq) $\xrightarrow[\text{solvent, rt, CFL (23 W), 24 h}]{\text{photocatalyst (1 mol%), base (2 eq)}}$ **3aa**

Entry	Photocatalyst (PC)	Base	Solvent (Conc.)	Variations	Yield (%) ^b
1	[Ru(Phen) ₃]Cl ₂	TMEDA	MeCN (0.2 M)		46
2	[Ru(bpy) ₃]Cl ₂	TMEDA	MeCN (0.2 M)		43
3	<i>fac</i> -Ir(ppy) ₃	TMEDA	MeCN (0.2 M)		31
4	<i>fac</i> -Ir(dFppy) ₃	TMEDA	MeCN (0.2 M)		28
5	Nile red	TMEDA	MeCN (0.2 M)		-
6	[Ru(Phen) ₃]Cl ₂	TMEDA	DMF (0.2 M)		67
7	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.2 M)		71
8	[Ru(Phen) ₃]Cl ₂	TMEDA	DCM (0.2 M)		18
9	[Ru(Phen) ₃]Cl ₂	TMEDA	MeOH (0.2 M)		trace
10	[Ru(Phen) ₃]Cl ₂	TMEDA	THF (0.2 M)		-
11	[Ru(Phen) ₃]Cl ₂	TMEDA	1,4-dioxane (0.2 M)		-
12	[Ru(Phen) ₃]Cl ₂	TMEDA	pyridine (0.2 M)		trace
13	[Ru(Phen) ₃]Cl ₂	TEA	DMSO (0.2 M)		58
14	[Ru(Phen) ₃]Cl ₂	DBU	DMSO (0.2 M)		24
15	[Ru(Phen) ₃]Cl ₂	DIPEA	DMSO (0.2 M)		65
16	[Ru(Phen) ₃]Cl ₂	2,6-lutidine	DMSO (0.2 M)		-
17	[Ru(Phen) ₃]Cl ₂	K ₂ CO ₃	DMSO (0.2 M)		trace
18	[Ru(Phen) ₃]Cl ₂	Cs ₂ CO ₃	DMSO (0.2 M)		trace
19	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.2 M)	no hv	trace
20	-	TMEDA	DMSO (0.2 M)		trace
21	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.2 M)	blue LEDs (21 W)	64
22	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.1 M)		70
23	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.3 M)		76
24	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.5 M)		58
25	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.3 M)	2 mol % PC	75
26	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.3 M)	0.5 mol % PC	60
27	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.3 M)	1 equiv TMEDA	62
28	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.3 M)	3 equiv TMEDA	76
29	[Ru(Phen) ₃]Cl ₂	TMEDA	DMSO (0.3 M)	2 equiv 2a	82
30	[Ru(Phen)₃]Cl₂	TMEDA	DMSO (0.3 M)	3 equiv 2a	87

^aReaction scale: **1a** (0.1 mmol); ^byield (%) was determined by GC spectroscopy using dodecane as internal standard.

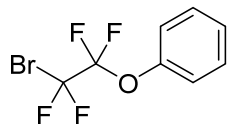
Table S2. Optimization Studies of Alkenes^a

Reaction scheme: **4a** + **2a** (1.2 eq) $\xrightarrow[\text{Solvent, rt, CFL (23 W), 12 h}]{\text{photocatalyst (1 mol%), base (2 eq)}}$ **5aa** + **5aa'**

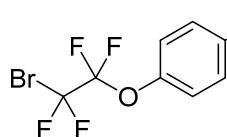
Entry	Photocatalyst	Base	Solvent (Conc.)	Variations	Yield (%) ^b	
					5aa	5aa'
1	[Ru(Phen) ₃]Cl ₂	TMEDA	DCM (0.2 M)		trace	-
2	[Ru(bpy) ₃]Cl ₂	TMEDA	DCM (0.2 M)		trace	-
3	<i>fac</i> -Ir(ppy) ₃	TMEDA	DCM (0.2 M)		55	9
4	<i>fac</i> -Ir(dFppy) ₃	TMEDA	DCM (0.2 M)		52	8
5	Nile red	TMEDA	DCM (0.2 M)		-	-
6	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.2 M)		75	8
7	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMSO (0.2 M)		26	9
8	<i>fac</i> -Ir(ppy) ₃	TMEDA	MeCN (0.2 M)		46	14
9	<i>fac</i> -Ir(ppy) ₃	TMEDA	MeOH (0.2 M)		14	3
10	<i>fac</i> -Ir(ppy) ₃	TMEDA	THF (0.2 M)		66	7
11	<i>fac</i> -Ir(ppy) ₃	TMEDA	1,4-dioxane (0.2 M)		51	14
12	<i>fac</i> -Ir(ppy) ₃	TMEDA	pyridine (0.2 M)		19	13
13	<i>fac</i> -Ir(ppy) ₃	TEA	DMF (0.2 M)		58	5
14	<i>fac</i> -Ir(ppy) ₃	DBU	DMF (0.2 M)		70	15
15	<i>fac</i> -Ir(ppy) ₃	DIPEA	DMF (0.2 M)		34	15
16	<i>fac</i> -Ir(ppy) ₃	2,6-Lutidine	DMF (0.2 M)		-	-
17	<i>fac</i> -Ir(ppy) ₃	K ₂ CO ₃	DMF (0.2 M)		66	15
18	<i>fac</i> -Ir(ppy) ₃	Cs ₂ CO ₃	DMF (0.2 M)		74	20
19	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.2 M)	no hv	-	-
20	-	TMEDA	DMF (0.2 M)		-	-
21	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.2 M)	blue LEDs (21 W)	69	11
22	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.02 M)		88	4
23	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.05 M)		89	6
24	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.1 M)		89	5
25	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.3 M)		63	12
26	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.1 M)	0.5 mol% <i>fac</i> -Ir(ppy) ₃	86	6
27	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.1 M)	2 mol% <i>fac</i> -Ir(ppy) ₃	75	9
28	<i>fac</i> -Ir(ppy) ₃	TMEDA	DMF (0.1 M)	2 equiv 2a	89	5

^aReaction scale: **4a** (0.1 mmol); ^bThe yield was determined by GC-Chromatography with dodecane as internal standard.

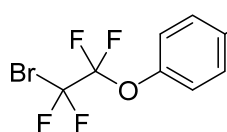
Analytic Data for Aryloxytetrafluoroethyl Reagents



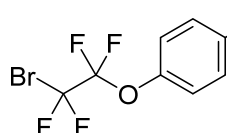
2a ((2-bromo-1,1,2,2-tetrafluoroethoxy)benzene): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.40 (dd, $J = 8.1, 7.4$ Hz, 2H), 7.30 (t, $J = 7.4$ Hz, 1H), 7.23 (d, $J = 8.1$ Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.8, 129.7, 126.7, 121.6 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -68.03, -85.89; **IR (neat)**: $\nu_{\text{max}} = 2361, 1492, 1194, 904, 725$ cm^{-1} ; $R_f = 0.70$ (hex:EtOAc = 4:1).



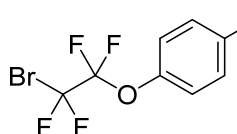
2b (4-(2-bromo-1,1,2,2-tetrafluoroethoxy)-1,1'-biphenyl): white solid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.61 (d, $J = 8.8$ Hz, 2H), 7.57 (d, $J = 8.1$ Hz, 2H), 7.46 (dd, $J = 8.1, 7.4$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.30 (d, $J = 8.8$ Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.1, 139.8, 128.9, 128.8, 128.4, 127.6, 127.1, 121.8 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -67.99, -85.87; **IR (neat)**: $\nu_{\text{max}} = 2973, 2361, 1488, 1328, 1200$ cm^{-1} ; $R_f = 0.75$ (hex:EtOAc = 4:1).



2c (1-(2-bromo-1,1,2,2-tetrafluoroethoxy)-4-methylbenzene): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.19 (d, $J = 8.6$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 146.5, 136.6, 130.2, 121.4, 20.8 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -67.96, -85.96; **IR (neat)**: $\nu_{\text{max}} = 2360, 1508, 1327, 1193, 929$ cm^{-1} ; $R_f = 0.72$ (hex:EtOAc = 4:1).



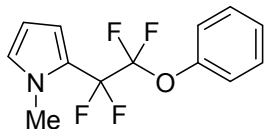
2d (1-(2-bromo-1,1,2,2-tetrafluoroethoxy)-4-methoxybenzene): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.15 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 3.81 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.1, 142.0, 122.8, 114.6, 55.6 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -67.93, -86.19; **IR (neat)**: $\nu_{\text{max}} = 2957, 2341, 1506, 1465, 1327, 1177, 929$ cm^{-1} ; $R_f = 0.60$ (hex:EtOAc = 4:1).



2e (4-(2-bromo-1,1,2,2-tetrafluoroethoxy)benzonitrile): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.8$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 151.9, 134.1, 122.0, 117.6, 110.9 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -68.39, -86.19;

IR (neat): ν_{\max} = 2973, 2235, 1604, 1328, 1250, 1202, 1093, 931 cm^{-1} ; R_f = 0.50 (hex:EtOAc = 4:1).

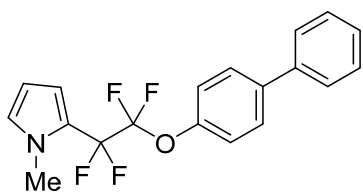
Analytic Data for Aryloxytetrafluoroethylated Compounds



3aa (1-methyl-2-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1*H*-pyrrole): yellow liquid;

^1H NMR (600 MHz, CDCl_3) δ 7.38 (dd, J = 7.9, 6.9 Hz, 2H), 7.27 (t, J = 6.9 Hz, 1H), 7.21 (d, J = 7.9 Hz, 2H), 6.74 (d, J = 2.7 Hz, 1H), 6.64 (d, J = 2.9 Hz, 1H), 6.16 (dd, J = 2.9, 2.7 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ

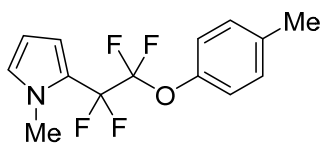
149.2, 132.7, 129.6, 127.1, 126.3, 121.6, 113.4, 107.4, 35.8 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl_3)** δ -85.62, -105.98; **IR (neat):** ν_{\max} = 2962, 1544, 1490, 1309, 1182, 1081, 1019, 951, 728 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{13}\text{H}_{11}\text{F}_4\text{NO}$ [M^+] 273.0777, found 273.0775; R_f = 0.55 (hex:EtOAc = 8:1).



3ab (2-(2-([1,1'-biphenyl]-4-yloxy)-1,1,2,2-tetrafluoroethyl)-1-methyl-1*H*-pyrrole): white solid; **^1H NMR (600 MHz, CDCl_3)** δ 7.59–7.55 (m, 4H), 7.45 (dd, J = 7.6, 7.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.26 (d, J =

7.9 Hz, 2H), 6.74 (d, J = 2.7 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 6.16 (dd, J = 3.0, 2.7 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ

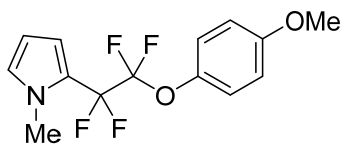
148.6, 140.0, 139.5, 131.4, 128.8, 128.2, 127.5, 127.1, 127.0, 121.8, 113.5, 107.4, 35.8 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl_3)** δ -85.61, -105.94; **IR (neat):** ν_{\max} = 2927, 1725, 1487, 1310, 1186, 1118, 952, 904, 759 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{19}\text{H}_{15}\text{F}_4\text{NO}$ [M^+] 349.1090, found 349.1091; R_f = 0.74 (hex:EtOAc = 4:1).



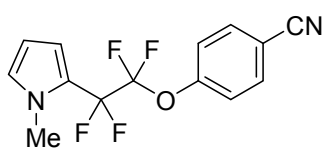
3ac (1-methyl-2-(1,1,2,2-tetrafluoro-2-(*p*-tolylloxy)ethyl)-1*H*-pyrrole):

colorless oil; **^1H NMR (600 MHz, CDCl_3)** δ 7.16 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 3.0 Hz, 1H), 6.62 (d, J = 3.7 Hz, 1H), 6.14

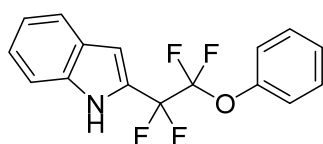
(dd, J = 3.7, 3.0 Hz, 1H), 3.79 (s, 3H), 2.34 (s, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ 146.9, 136.0, 134.1, 130.0, 127.1, 121.4, 113.4, 107.4, 35.8, 29.7 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl_3)** δ -85.68, -106.00; **IR (neat):** ν_{\max} = 2921, 1596, 1507, 1310, 1250, 1177, 1098, 953, 730 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{14}\text{H}_{13}\text{F}_4\text{NO}$ [M^+] 287.0933, found 287.0935; R_f = 0.55 (hex:EtOAc = 4:1)



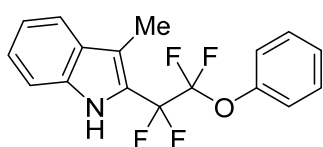
3ad (1-methyl-2-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)-1H-pyrrole): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.11 (d, $J = 9.1$ Hz, 2H), 6.86 (d, $J = 9.1$ Hz, 2H), 6.72 (d, $J = 3.0$ Hz, 1H), 6.61 (d, $J = 3.5$ Hz, 1H), 6.14 (dd, $J = 3.5, 3.0$ Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta = 157.7, 142.5, 140.7, 127.1, 122.9, 114.5, 113.4, 107.4, 55.6, 29.7$ (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) $\delta -85.85, -105.95$; **IR** (neat): $\nu_{\text{max}} = 2926, 1509, 1310, 1187, 1119, 904, 728, 650$ cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{14}\text{H}_{13}\text{F}_4\text{NO}_2$ $[\text{M}^+]$ 303.0882, found 303.0879; $R_f = 0.56$ (hex:EtOAc = 6:1).



3ae (4-(1,1,2,2-tetrafluoro-2-(1-methyl-1H-pyrrol-2-yl)ethoxy)benzonitrile): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.69 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 6.74 (d, $J = 2.9$ Hz, 1H), 6.59 (d, $J = 3.1$ Hz, 1H), 6.15 (d, $J = 3.1, 2.9$ Hz, 1H), 3.79 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.5, 133.9, 127.4, 121.9, 119.6, 117.8, 113.6, 110.2, 107.6, 35.8 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) $\delta -85.88, -105.86$; **IR** (neat): $\nu_{\text{max}} = 2233, 1605, 1504, 1309, 1173, 1123, 952, 903, 730$ cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{14}\text{H}_{10}\text{F}_4\text{N}_2\text{O}$ $[\text{M}^+]$ 298.0729, found 298.0730; $R_f = 0.52$ (hex:EtOAc = 4:1).

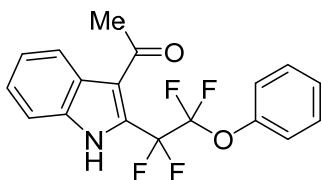


3ba (2-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1H-indole): yellow solid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.51 (s, 1H), 7.71 (d, $J = 8.1$ Hz, 1H), 7.46 (d, $J = 8.3$ Hz, 1H), 7.38–7.31 (m, 3H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.21–7.17 (m, 3H), 7.02 (s, 1H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 136.4, 129.6, 129.6, 126.9, 126.6, 125.9, 124.3, 121.9, 121.8, 120.8, 111.6, 105.4 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) $\delta -86.77, -117.06$; **IR** (neat): $\nu_{\text{max}} = 3477, 2927, 2340, 1590, 1491, 1298, 1188, 1022, 739$ cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{16}\text{H}_{11}\text{F}_4\text{NO}$ $[\text{M}^+]$ 309.0777, found 309.0778; $R_f = 0.67$ (hex:EtOAc = 4:1).



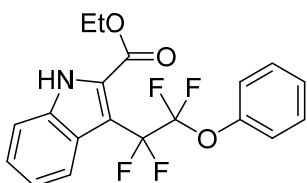
3ca (3-methyl-2-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1H-indole): yellow liquid; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.24 (s, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.35–7.27 (m, 3H), 7.25–7.14 (m, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 2.47 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.0, 135.6, 129.6, 128.5, 126.4, 124.3, 121.7, 120.0, 119.8, 117.9, 115.3, 111.4, 8.7 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 Hz, CDCl_3) $\delta -86.86, -111.55$; **IR** (neat):

ν_{\max} = 3479, 3063, 1590, 1491, 1304, 1186, 1025, 958, 737 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{17}\text{H}_{13}\text{F}_4\text{NO}$ $[\text{M}^+]$ 323.0933, found 323.0934; R_f = 0.52 (hex:EtOAc = 2:1).



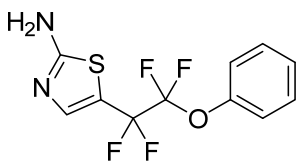
3da (1-(2-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1H-indol-3-yl)ethan-1-one): white solid; ^1H NMR (600 MHz, CDCl_3) δ 9.08 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.38–7.30(m, 4H), 7.26 (t, J = 6.9 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 2.71 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.1, 148.7, 134.7, 129.7, 126.7, 125.3, 125.1, 122.8, 122.5, 121.6, 119.9,

111.6, 31.5 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, CDCl_3) δ -85.81, -107.93; **IR** (neat): ν_{\max} = 3250, 2928, 1660, 1591, 1492, 1436, 1316, 1188, 1071, 740 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{18}\text{H}_{13}\text{F}_4\text{NO}_2$ $[\text{M}^+]$ 351.0882, found 351.0880; R_f = 0.30 (hex:EtOAc = 4:1).



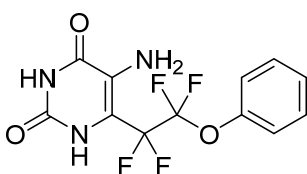
3ea (ethyl 3-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1H-indole-2-carboxylate): white solid; ^1H NMR (600 MHz, CDCl_3) δ 9.41 (s, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.31 (dd, J = 8.2, 7.7 Hz, 2H), 7.25 (dd, J = 8.4, 7.6 Hz, 1H), 7.20 (dd, J = 8.3, 7.6 Hz, 1H), 7.11 (d, J = 8.2 Hz, 2H), 4.45 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C

NMR (151 MHz, CDCl_3) δ 160.5, 149.5, 134.6, 132.5, 129.4, 126.6, 125.9, 125.8, 122.9, 122.2, 121.3, 111.8, 109.3, 61.9, 13.9 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, CDCl_3) δ -86.71, -104.62; **IR** (neat): ν_{\max} = 3324, 2990, 1683, 1591, 1492, 1334, 1187, 1064, 742 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{19}\text{H}_{15}\text{F}_4\text{NO}_3$ $[\text{M}^+]$ 381.0988, found 381.0990; R_f = 0.33 (hex:EtOAc = 4:1).



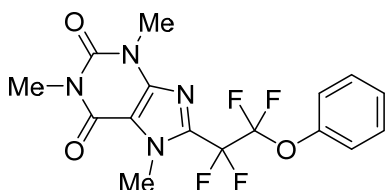
3fa (5-(1,1,2,2-tetrafluoro-2-phenoxyethyl)thiazol-2-amine): yellow liquid; ^1H NMR (600 MHz, CDCl_3) δ 7.47 (s, 1H), 7.37 (dd, J = 7.9, 7.5 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 5.23 (s, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.5, 156.6, 149.0, 141.7, 129.6, 126.4, 121.6, 109.9,

94.9; ^{19}F NMR (564 MHz, CDCl_3) δ -87.33, -103.62; **IR** (neat): ν_{\max} = 3156, 1607, 1552, 1492, 1284, 1190, 903, 724 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{11}\text{H}_8\text{F}_4\text{N}_2\text{OS}$ $[\text{M}^+]$ 292.0293, found 292.0296; R_f = 0.47 (hex:EtOAc = 1:1).



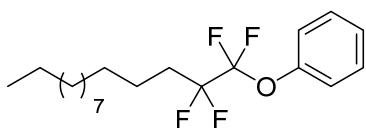
3ga (5-amino-6-(1,1,2,2-tetrafluoro-2-phenoxyethyl)pyrimidine-2,4(1H,3H)-dione): colorless liquid; ^1H NMR (600 MHz, CDCl_3) δ 8.70 (s, 1H), 7.61 (s,

1H), 7.39 (dd, $J = 8.0, 7.3$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 2H), 4.34 (s, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 160.1, 148.4, 148.0, 129.8, 126.9, 124.2, 121.4, 110.6 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, CDCl_3) δ -86.13, -119.18; IR (neat): $\nu_{\text{max}} = 3368, 3180, 3066, 2924, 1704, 1593, 1438, 1305, 1156, 957, 740$ cm^{-1} ; HRMS m/z (EI) calc. for $\text{C}_{12}\text{H}_9\text{F}_4\text{N}_3\text{O}_3$ [M^+] 319.0580, found 319.0578; $R_f = 0.44$ (hex:EtOAc = 1:1).



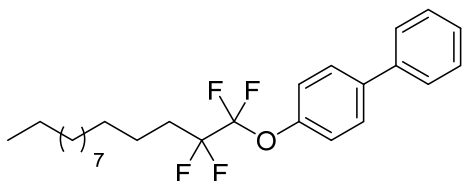
3ha (1,3,7-trimethyl-8-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-3,7-dihydro-1H-purine-2,6-dione): yellow solid; ^1H NMR (600 MHz, CDCl_3) δ 7.38 (dd, $J = 8.1, 7.4$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 8.1$ Hz, 2H), 4.24 (s, 3H), 3.62 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 155.5, 151.4, 148.6, 146.9, 139.5, 129.7, 126.8,

121.6, 109.8, 33.8, 29.9, 28.1 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, CDCl_3) δ -85.12, -111.97; IR (neat): $\nu_{\text{max}} = 2926, 1668, 1609, 1547, 1328, 1291, 1192, 994, 747$ cm^{-1} ; HRMS m/z (EI) calc. for $\text{C}_{16}\text{H}_{14}\text{F}_4\text{N}_4\text{O}_3$ [M^+] 386.1002, found 386.1004; $R_f = 0.43$ (hex:EtOAc = 1:1).



5aa ((1,1,2,2-tetrafluorotetradecyl)oxy)benzene): colorless liquid; ^1H NMR (600 MHz, CDCl_3) δ 7.38 (dd, $J = 8.2, 7.3$ Hz, 2H), 7.26 (t, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 8.2$ Hz, 2H), 2.12 (tt, $J_{\text{H-F}} = 9.8, J = 8.1$ Hz, 2H), 1.64 (tt, $J = 8.1, 7.5$ Hz, 2H), 1.45–1.21 (m, 18H), 0.89 (t, $J = 6.9$

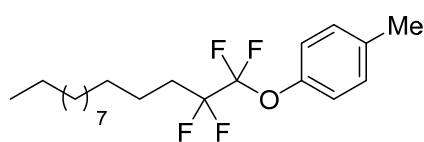
Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 149.2, 129.5, 126.2, 121.7, 31.9, 31.6, 31.1 (t, $J_{\text{C-F}} = 22.5$ Hz), 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 22.7, 20.5, 14.1 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, CDCl_3) δ -87.05, -117.71; IR (neat): $\nu_{\text{max}} = 2924, 2855, 1592, 1492, 1184, 1109, 806, 731$ cm^{-1} ; HRMS m/z (EI) calc. for $\text{C}_{20}\text{H}_{30}\text{F}_4\text{O}$ [M^+] 362.2233, found 362.2230; $R_f = 0.68$ (hex:EtOAc = 6:1).



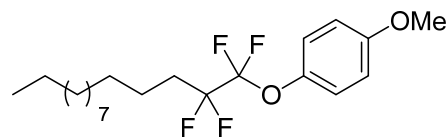
5ab (4-((1,1,2,2-tetrafluorotetradecyl)oxy)-1,1'-biphenyl): white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.59–7.55 (m, 4H), 7.45 (dd, $J = 8.6, 7.4$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.27 (d, $J = 8.6$ Hz, 2H), 2.13 (tt, $J_{\text{H-F}} = 18.27, J = 7.7$ Hz, 2H), 1.65 (tt, $J = 12.3, 7.7$ Hz, 2H), 1.43–1.26 (m, 18H), 0.89 (t, $J = 7.0$ Hz,

3H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.6, 140.0, 139.4, 128.8, 128.2, 127.5, 127.1, 121.9, 31.9, 31.1, 29.6, 29.6, 29.4, 29.4, 29.3, 29.2, 29.1, 22.7, 20.5, 14.1; ^{19}F NMR (564 MHz, CDCl_3) δ -87.93, -117.69;

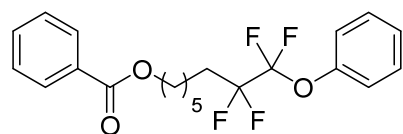
IR (neat): ν_{\max} = 2926, 1711, 1420, 1220, 1103, 903, 763, 529 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{26}\text{H}_{34}\text{F}_4\text{O}$ $[\text{M}^+]$ 438.2546, found 438.2548; R_f = 0.45 (hex).



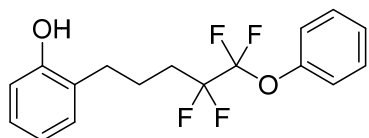
5ac (1-methyl-4-((1,1,2,2-tetrafluorotetradecyl)oxy)benzene): colorless liquid; **^1H NMR (600 MHz, CDCl_3)** δ 7.16 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H), 2.09 (tt, $J_{\text{H-F}}$ = 18.4, J = 8.3 Hz, 2H), 1.63 (tt, J = 8.3, 7.7 Hz, 2H), 1.27 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ 146.9, 135.9, 129.9, 121.5, 31.9, 31.1, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 22.7, 20.8, 20.5, 14.1 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl_3)** δ -88.01, -117.76; **IR (neat):** ν_{\max} = 2925, 2855, 1507, 1466, 1176, 1099, 1037, 906, 846, 731 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{21}\text{H}_{32}\text{F}_4\text{O}$ $[\text{M}^+]$ 376.2389, found 376.2387; R_f = 0.70 (hex:EtOAc = 6:1).



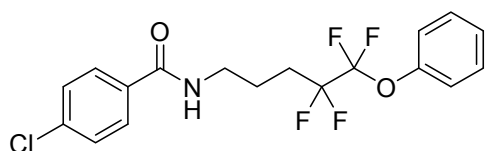
5ad (1-methoxy-4-((1,1,2,2-tetrafluorotetradecyl)oxy)benzene): colorless liquid; **^1H NMR (600 MHz, CDCl_3)** 7.12 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 2.11 (tt, $J_{\text{H-F}}$ = 18.4, J = 8.4 Hz, 2H), 1.63 (tt, J = 8.4, 8.0 Hz, 2H), 1.41–1.24 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ 165.4, 157.7, 122.9, 114.4, 55.6, 31.9, 31.1, 30.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 22.6, 20.5, 14.1 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl_3)** δ -88.19, -117.72; **IR (neat):** ν_{\max} = 2924, 2855, 1660, 1508, 1467, 1182, 1020, 904, 726 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{21}\text{H}_{32}\text{F}_4\text{O}_2$ $[\text{M}^+]$ 392.2338, found 392.2341; R_f = 0.68 (hex:EtOAc = 8:1).



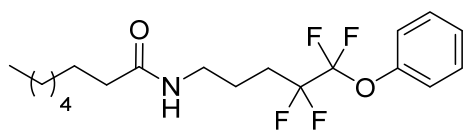
5ba (7,7,8,8-tetrafluoro-8-phenoxyoctyl benzoate): colorless liquid; **^1H NMR (600 MHz, CDCl_3)** δ 8.06 (d, J = 6.6 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.5, 6.6 Hz, 2H), 7.37 (dd, J = 8.0, 7.2 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 4.34 (t, J = 6.6 Hz, 2H), 2.15 (tt, $J_{\text{H-F}}$ = 18.2, J = 8.3 Hz, 2H), 1.81 (tt, J = 7.2, 6.6 Hz, 2H), 1.69 (tt, J = 8.3, 7.8 Hz, 2H), 1.55–1.47 (m, 4H); **^{13}C NMR (151 MHz, CDCl_3)** δ 166.6, 138.3, 136.3, 132.8, 130.4, 129.5, 128.3, 126.3, 121.7, 117.8, 117.0, 64.8, 31.0, 28.9, 28.5, 25.8, 20.5; **^{19}F NMR (564 MHz, CDCl_3)** δ -87.93, -117.75; **IR (neat):** ν_{\max} = 3324, 2990, 1683, 1591, 1335, 1259, 1187, 1064, 742 cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{21}\text{H}_{22}\text{F}_4\text{O}_3$ $[\text{M}^+]$ 398.1505, found 398.1503; R_f = 0.66 (hex:EtOAc = 4:1).



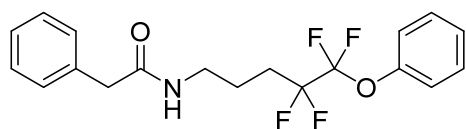
5ca (2-(4,4,5,5-tetrafluoro-5-phenoxy)pentyl)phenol) colorless liquid; **¹H NMR (600 MHz, CDCl₃)** δ 7.39 (dd, *J* = 8.2, 7.7 Hz, 2H), 7.28 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.92 (dd, *J* = 7.9, 7.2 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 4.87 (s, 1H), 2.76 (t, *J* = 7.9 Hz, 2H), 2.28–2.16 (m, 2H), 2.02 (tt, *J*_{H-F} = 15.7, *J* = 7.9 Hz, 2H); **¹³C NMR (151 MHz, CDCl₃)** δ 153.4, 149.2, 130.3, 129.6, 127.5, 126.3, 121.7, 120.9, 117.2, 115.3, 30.8 (t, *J*_{C-F} = 30.8 Hz), 29.5, 20.8 (carbon peaks of –C₂F₄– are omitted due to complicated C-F splitting); **¹⁹F NMR (564 MHz, CDCl₃)** δ –87.78, –117.32; **IR (neat):** *v*_{max} = 3324, 2990, 1683, 1492, 1335, 1187, 1117, 953, 743 cm⁻¹; **HRMS** *m/z* (EI) calc. for C₁₇H₁₆F₄O₂ [M⁺] 328.1086, found 328.1089; **R_f** = 0.50 (hex:EtOAc = 4:1).



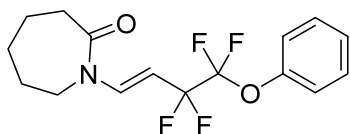
5da (4-chloro-*N*-(4,4,5,5-tetrafluoro-5-phenoxy)pentyl) benzamide) white solid; **¹H NMR (600 MHz, CDCl₃)** ; δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1, 7.7 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.40 (t, *J* = 6.0 Hz, 1H), 3.56 (td, *J* = 7.4, 6.0 Hz, 2H), 2.23 (tt, *J*_{H-F} = 17.9, *J* = 7.7 Hz, 2H), 1.98 (tt, *J* = 7.7, 7.4 Hz, 2H); **¹³C NMR (151 MHz, CDCl₃)** δ 166.7, 149.0, 137.8, 129.6, 128.8, 128.3, 126.4, 121.6, 123.4, 39.4, 28.6 (t, *J*_{C-F} = 22.7 Hz), 21.3 (carbon peaks of –C₂F₄– are omitted due to complicated C-F splitting); **¹⁹F NMR (564 MHz, CDCl₃)** δ –87.85, –117.37; **IR (neat):** *v*_{max} = 3324, 2990, 1683, 1591, 1492, 1335, 1259, 1187, 1117, 1014, 743 cm⁻¹; **HRMS** *m/z* (EI) calc. for C₁₈H₁₆ClF₄NO₂ [M⁺] 389.0806, found 389.0805; **R_f** = 0.27 (hex:EtOAc = 4:1).



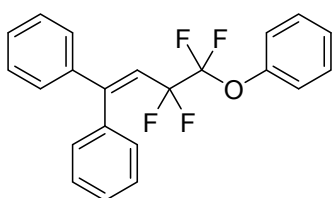
5ea (*N*-(4,4,5,5-tetrafluoro-5-phenoxy)pentyl)octanamide) yellow oil; **¹H NMR (600 MHz, CDCl₃)** δ 7.37 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 5.53 (s, 1H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.20–2.16 (m, 2H), 1.86 (tt, *J*_{H-F} = 14.9, *J* = 7.3 Hz, 2H), 1.61 (tt, *J* = 7.3, 6.8 Hz, 2H), 1.34–1.23 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); **¹³C NMR (151 MHz, CDCl₃)** δ 173.3, 129.6, 126.3, 121.7, 116.3, 38.6, 36.8, 31.6, 31.5, 29.2, 28.9, 28.5 (t, *J*_{C-F} = 22.7 Hz), 25.7, 22.6, 14.0 (carbon peaks of –C₂F₄– are omitted due to complicated C-F splitting); **¹⁹F NMR (564 MHz, CDCl₃)** δ –87.92, –117.51; **IR (neat):** *v*_{max} = 3293, 2927, 1644, 1550, 1492, 1189, 1115, 1004, 744 cm⁻¹; **HRMS** *m/z* (EI) calc. for C₁₉H₂₇F₄NO₂ [M⁺] 377.1978, found 377.1981; **R_f** = 0.60 (hex:EtOAc = 1:1).



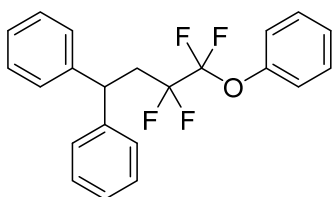
5fa (2-phenyl-*N*-(4,4,5,5-tetrafluoro-5-phenoxypropyl)acetamide): yellow oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.39–7.33 (m, 4H), 7.29 (t, $J = 7.2$ Hz, 1H), 7.27–7.24 (m, 3H), 7.18 (d, $J = 8.3$ Hz, 2H), 5.47 (t, $J = 6.5$, 1H), 3.59 (s, 2H), 3.32 (td, $J = 6.9, 6.5$ Hz, 2H), 2.09 (tt, $J_{\text{H-F}} = 18.3, J = 7.6$ Hz, 2H), 1.79 (tt, $J = 7.6, 6.9$ Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.2, 149.0, 134.7, 129.6, 129.4, 129.1, 127.4, 126.4, 121.6, 43.9, 38.8, 28.4, 21.2 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -87.95, -117.56; **IR** (neat): $\nu_{\text{max}} = 3324, 2990, 1683, 1591, 1541, 1492, 1334, 1258, 1187, 1064, 953, 742$ cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{19}\text{H}_{19}\text{F}_4\text{NO}_2$ [M^+] 369.1352, found 369.1349; $R_f = 0.40$ (hex:EtOAc = 2:1).



5ga ((*E*)-1-(3,3,4,4-tetrafluoro-4-phenoxybut-1-en-1-yl)azepan-2-one): colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.98 (d, $J = 14.5$ Hz, 1H), 7.37 (dd, $J = 7.9, 7.4$ Hz, 2H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 5.14 (dt, $J = 14.5, J_{\text{H-F}} = 11.5$ Hz, 1H), 3.62 (t, $J = 4.6$ Hz, 2H), 2.69 (t, $J = 5.3$ Hz, 2H), 1.80–1.71 (m, 6H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 174.6, 149.3, 134.4, 129.5, 126.2, 121.6, 96.3, 45.3, 37.0, 29.2, 27.1, 23.3 (carbon peaks of $-\text{C}_2\text{F}_4-$ are omitted due to complicated C-F splitting); $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -87.71, -110.79; **IR** (neat): $\nu_{\text{max}} = 2933, 1654, 1491, 1330, 1178, 1082, 969, 740$ cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{16}\text{H}_{17}\text{F}_4\text{O}_2$ [M^+] 331.1195, found 331.1193; $R_f = 0.40$ (hex:EtOAc = 4:1).

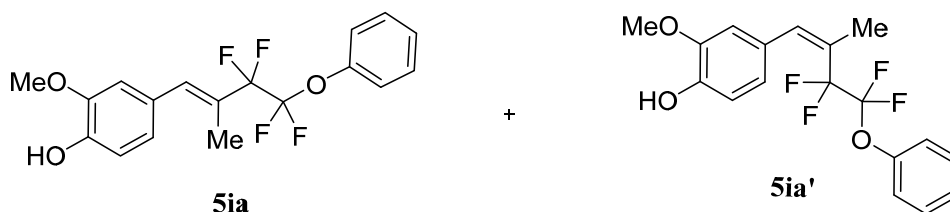


5ha ((3,3,4,4-tetrafluoro-4-phenoxybut-1-ene-1,1-diyl)dibenzene): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.40–7.20 (m, 13H), 7.21 (d, $J = 8.1$ Hz, 2H), 6.24 (t, $J = 14.4$ Hz, 1H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.1, 137.9, 129.6, 129.2, 129.1, 128.4, 128.0, 127.9, 127.7, 126.2, 121.6, 114.6; $^{19}\text{F NMR}$ (564 MHz, CDCl_3) δ -87.57, -107.30; **IR** (neat): $\nu_{\text{max}} = 3061, 2926, 1640, 1591, 1191, 1017, 730, 699$ cm^{-1} ; **HRMS** m/z (EI) calc. for $\text{C}_{22}\text{H}_{16}\text{F}_4\text{O}$ [M^+] 372.1137, found 372.1139; $R_f = 0.61$ (hex:EtOAc = 6:1).

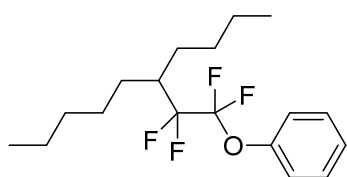


5ha' ((3,3,4,4-tetrafluoro-4-phenoxybutane-1,1-diyl)dibenzene): colorless liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.38–7.33 (m, 2H), 7.32–7.29 (m, 7H), 7.27–7.23 (m, 2H), 7.23–7.18 (m, 2H), 7.16 (d, $J = 7.6$ Hz, 2H), 4.52 (t, $J = 6.4$ Hz, 1H), 2.98 (td, $J_{\text{H-F}} = 18.0, J = 6.4$ Hz, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.0, 143.6, 129.5, 128.6, 127.6, 126.6, 126.3, 121.7, 44.0,

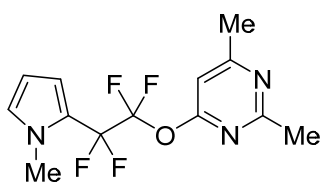
36.6(t, $J_{C-F} = 22.7$ Hz) (carbon peaks of $-C_2F_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -88.31, -116.22; IR (neat): $\nu_{max} = 3030, 1592, 1492, 1191, 1106, 907, 743, 700$ cm^{-1} ; HRMS m/z (EI) calc. for $C_{22}H_{18}F_4O$ $[M^+]$ 374.1294, found 374.1297; $R_f = 0.58$ (hex:EtOAc = 6:1).



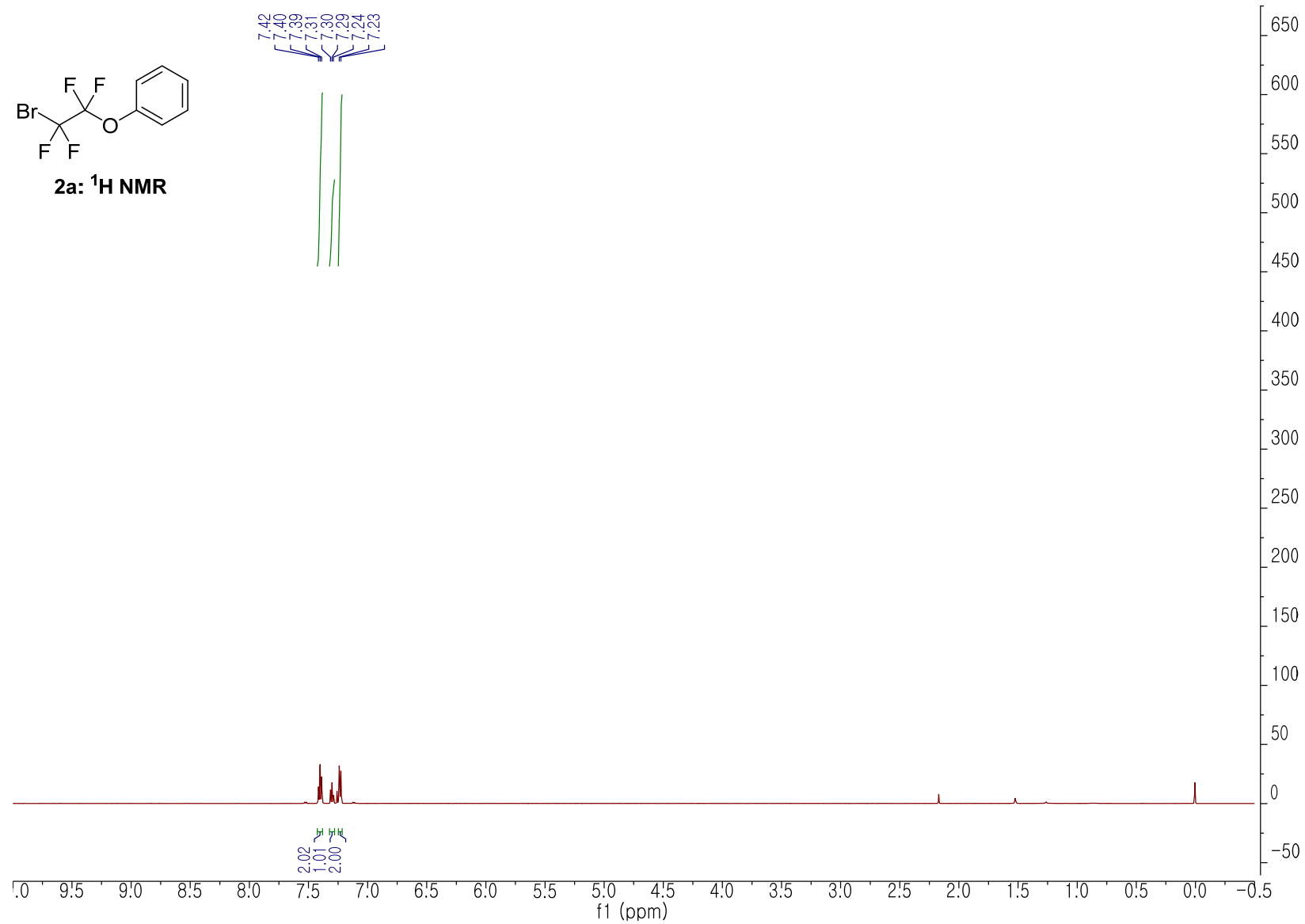
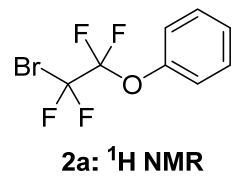
5ia ((E)-2-methoxy-4-(3,3,4,4-tetrafluoro-2-methyl-4-phenoxybut-1-en-1-yl)phenol) and **5ia'** ((Z)-2-methoxy-4-(3,3,4,4-tetrafluoro-2-methyl-4-phenoxybut-1-en-1-yl)phenol) colorless liquid; 1H NMR (600 MHz, $CDCl_3$) **5ia**: δ 7.37 (dd, $J = 8.2, 7.4$ Hz, 2H), 7.28–7.24 (m, 1H), 7.21 (d, $J = 8.2$ Hz, 2H), 6.99 (s, 1H), 6.94 (s, 1H), 6.89–6.85 (m, 2H), 5.69 (s, 1H), 3.92 (s, 3H), 2.11 (s, 3H); **5ia'**: δ 7.37 (dd, $J = 8.2, 7.4$ Hz, 2H), 7.28–7.24 (m, 1H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.94 (s, 1H), 6.91 (s, 1H), 6.84–6.80 (m, 2H), 5.59 (s, 1H), 3.83 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 145.0, 129.6, 129.5, 127.6, 126.3, 126.2, 122.9, 121.6, 121.6, 114.3, 113.6, 111.9, 111.1, 109.9, 109.9, 67.5, 56.5, 55.9, 29.7 (carbon peaks of $-C_2F_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) **5ia**: δ -84.69, -109.62; **5ia'**: δ -85.62, -115.60; IR (neat): $\nu_{max} = 3542, 2925, 2853, 1594, 1492, 1093, 978, 904, 730$ cm^{-1} ; HRMS m/z (EI) calc. for $C_{18}H_{16}F_4O_3$ $[M^+]$ 356.1036, found 356.1036; $R_f = 0.42$ (hex:EtOAc = 3:1).

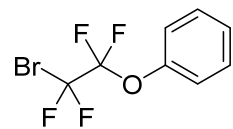


5ja (((3-butyl-1,1,2,2-tetrafluorooctyl)oxy)benzene) colorless liquid; 1H NMR (600 MHz, $CDCl_3$) ; δ 7.38 (dd, $J = 8.1, 7.4$ Hz, 2H), 7.26 (t, $J = 7.4$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 2H), 2.25–2.14 (m, 1H), 1.79–1.70 (m, 2H), 1.53–1.27 (m, 12H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.90 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 129.5, 126.2, 121.7, 67.1, 40.7, 32.0, 29.2, 27.0, 26.8, 26.7, 22.9, 22.5, 14.0 (carbon peaks of $-C_2F_4-$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -83.91, -116.79; IR (neat): $\nu_{max} = 2958, 1593, 1492, 1183, 1109, 1027, 741, 689$ cm^{-1} ; HRMS m/z (EI) calc. for $C_{18}H_{26}F_4O$ $[M^+]$ 334.1920, found 334.1924; $R_f = 0.66$ (hex).

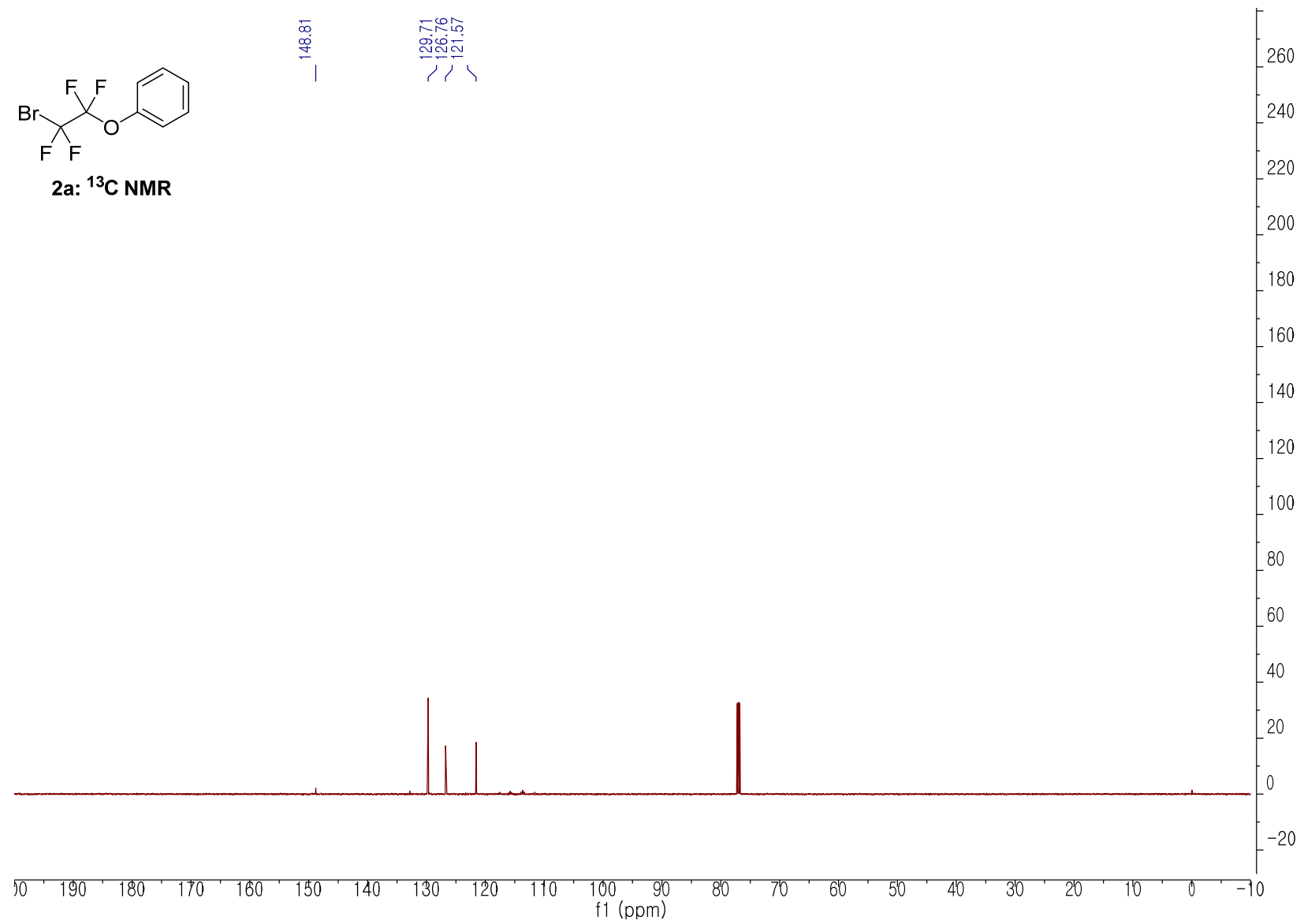


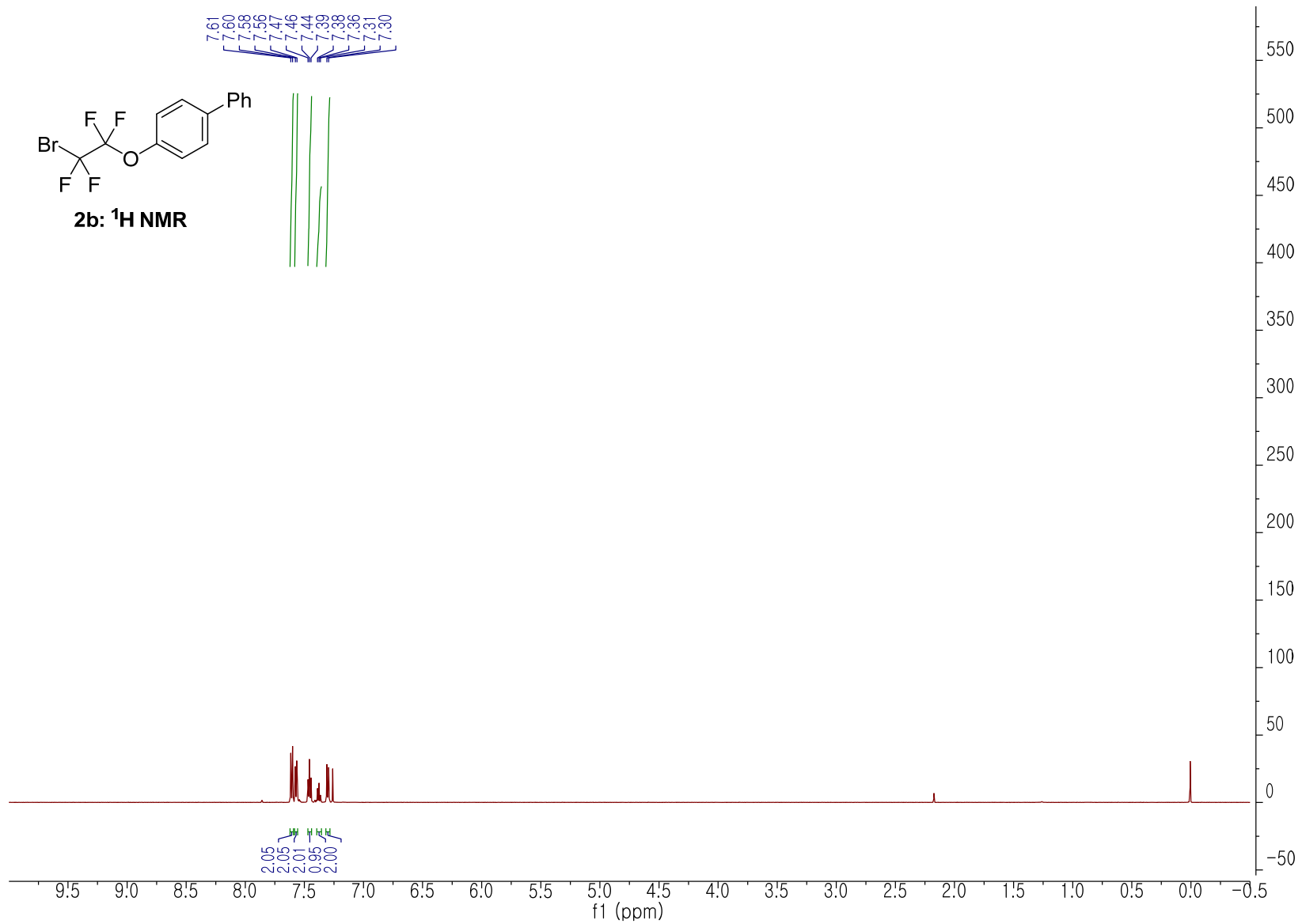
7 (2,4-dimethyl-6-(1,1,2,2-tetrafluoro-2-(1-methyl-1*H*-pyrrol-2-yl)ethoxy)pyrimidine): yellow oil; **¹H NMR (600 MHz, CDCl₃)** δ 6.72 (d, 1H), 6.70 (m, *J* = 2.9 Hz, 1H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.12 (dd, *J* = 3.2, 2.9 Hz, 1H), 3.80 (s, 3H), 2.65 (s, 3H), 2.50 (s, 3H); **¹³C NMR (151 MHz, CDCl₃)** δ 170.2, 168.5, 164.1, 127.3, 113.6, 107.5, 105.7, 35.8, 25.8, 24.1 (carbon peaks of -C₂F₄- are omitted due to complicated C-F splitting); **¹⁹F NMR (564 MHz, CDCl₃)** δ -87.25, -106.43; **IR (neat):** ν_{max} = 2929, 1593, 1566, 1437, 1358, 1154 1092, 956, 802, 733 cm⁻¹; **HRMS** m/z (EI) calc. for C₁₃H₁₃F₄N₃O [M⁺] 303.0995, found 303.0993; **R_f** = 0.40 (hex:EtOAc = 2:1)

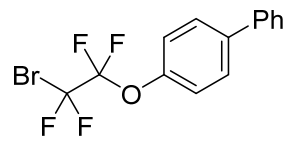




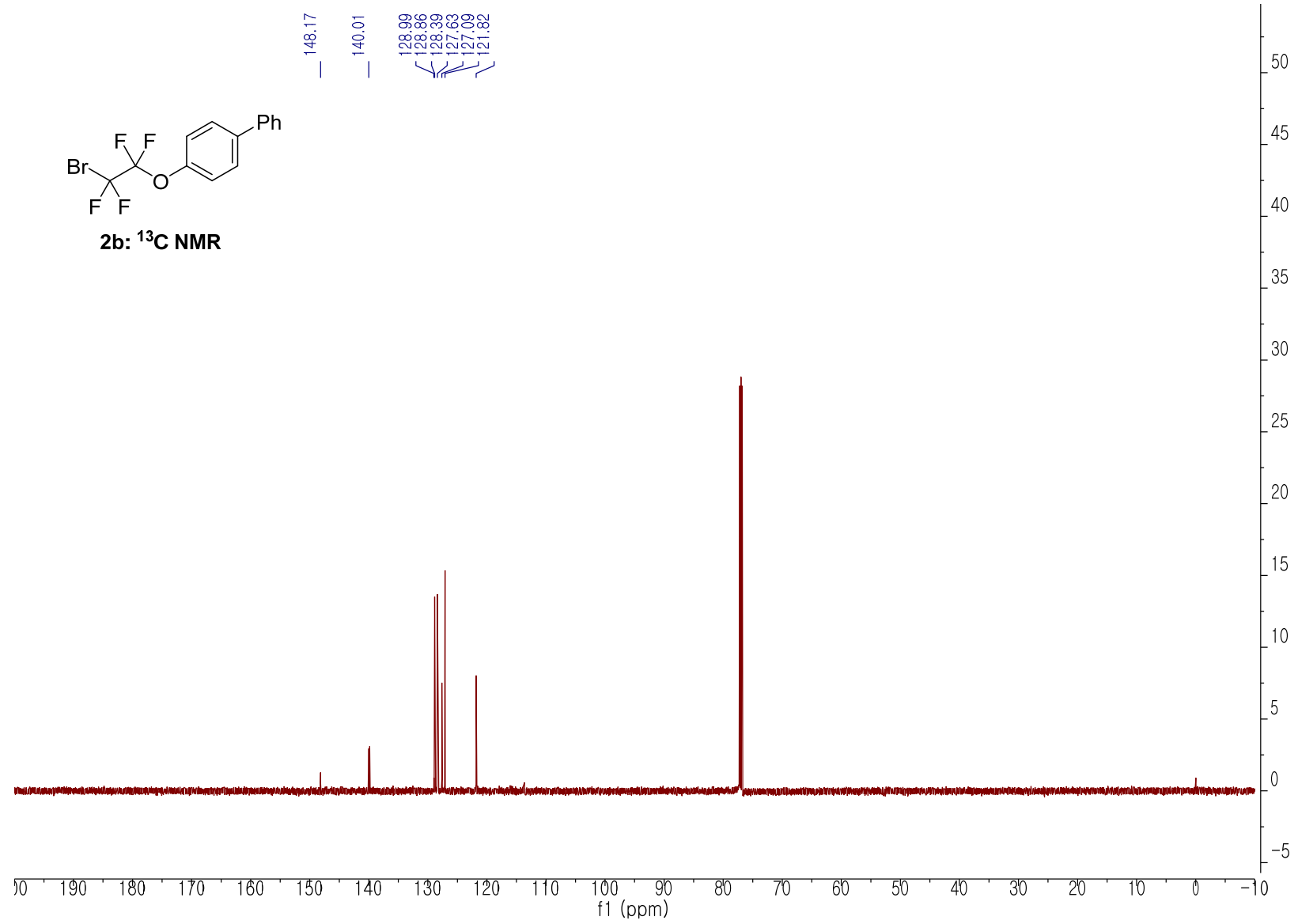
2a: ¹³C NMR

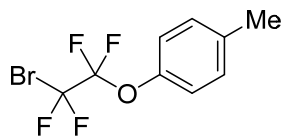




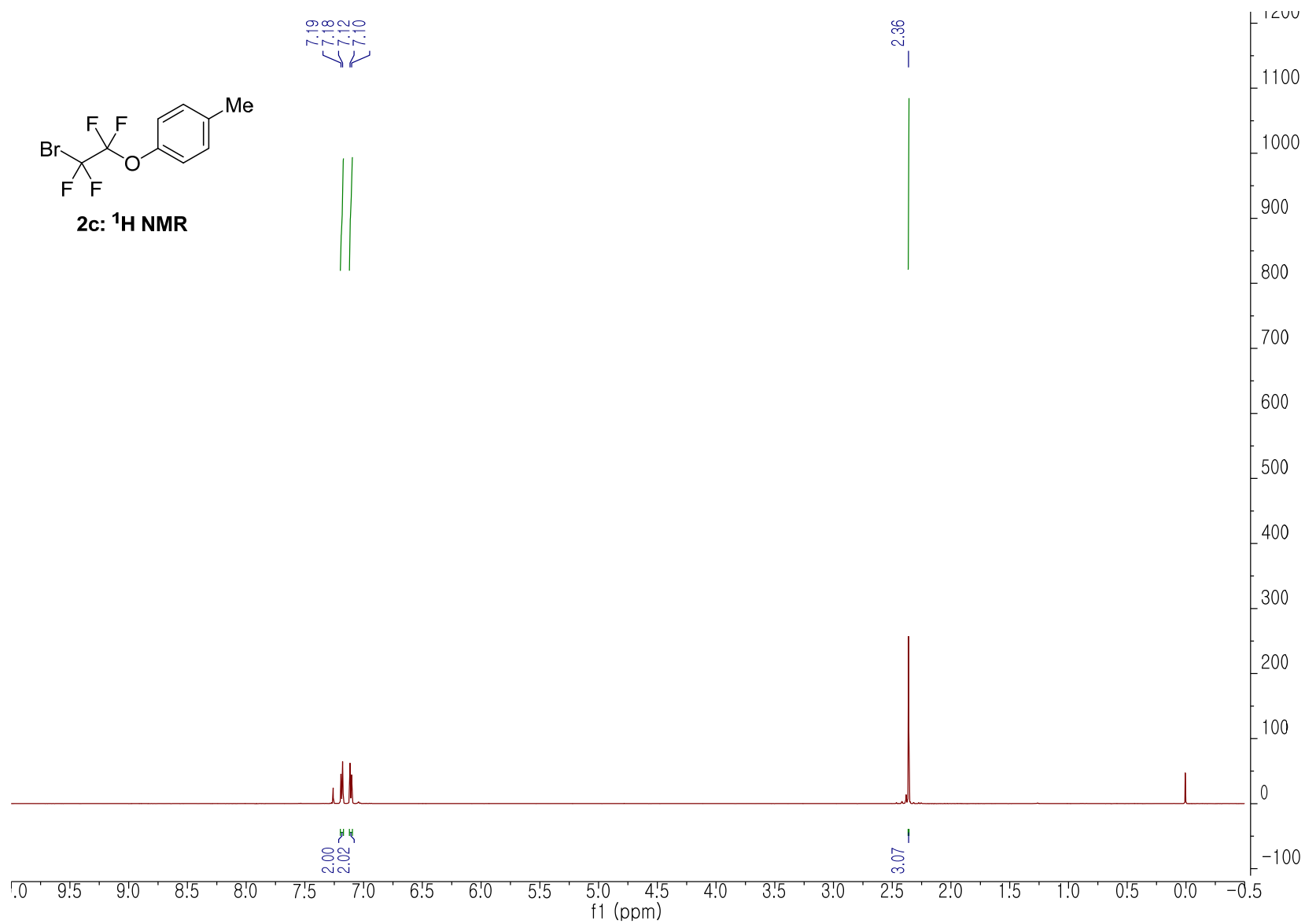


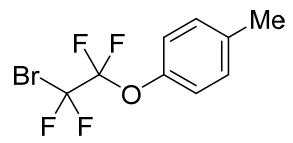
2b: ¹³C NMR



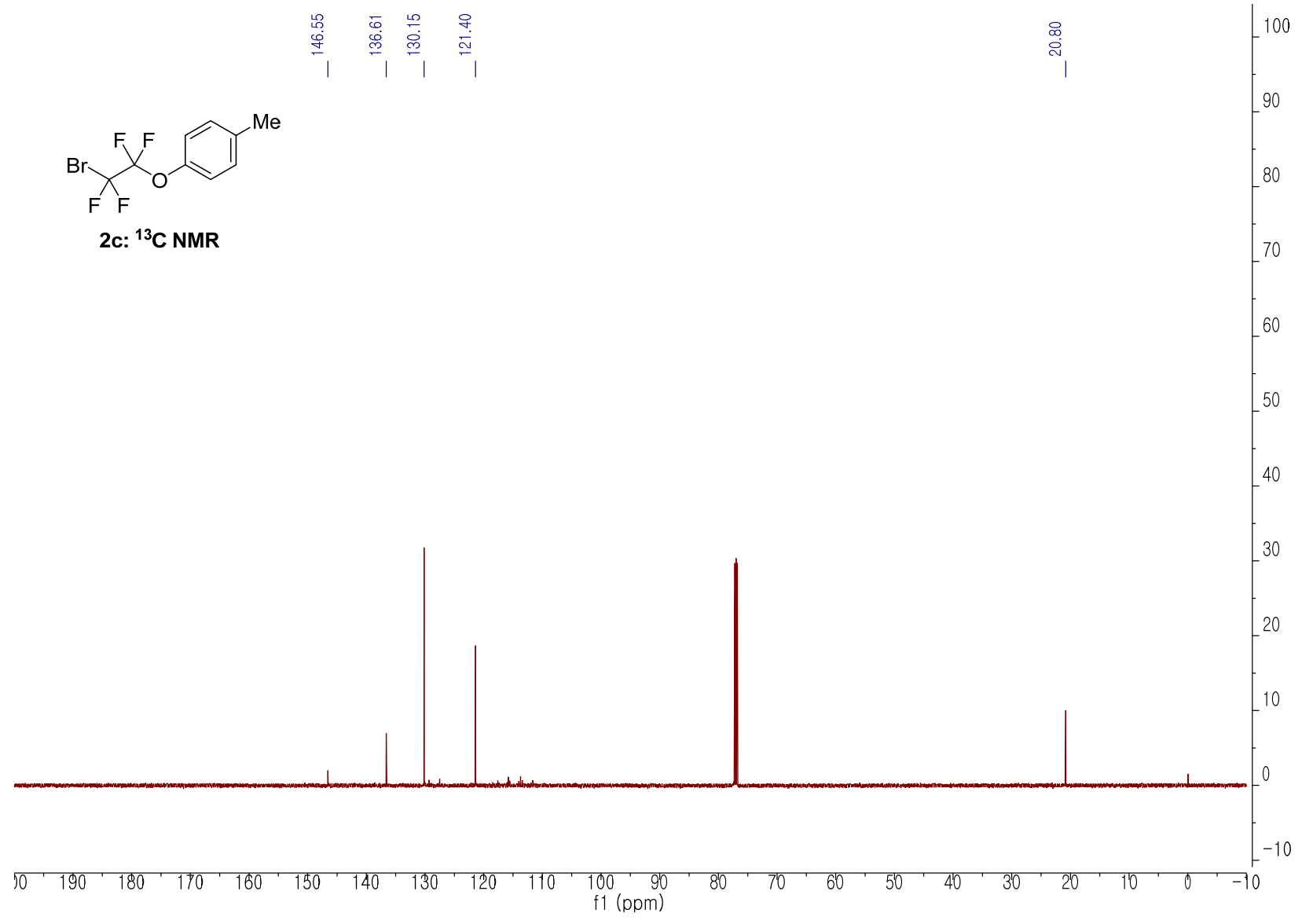


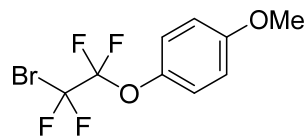
2c: ¹H NMR



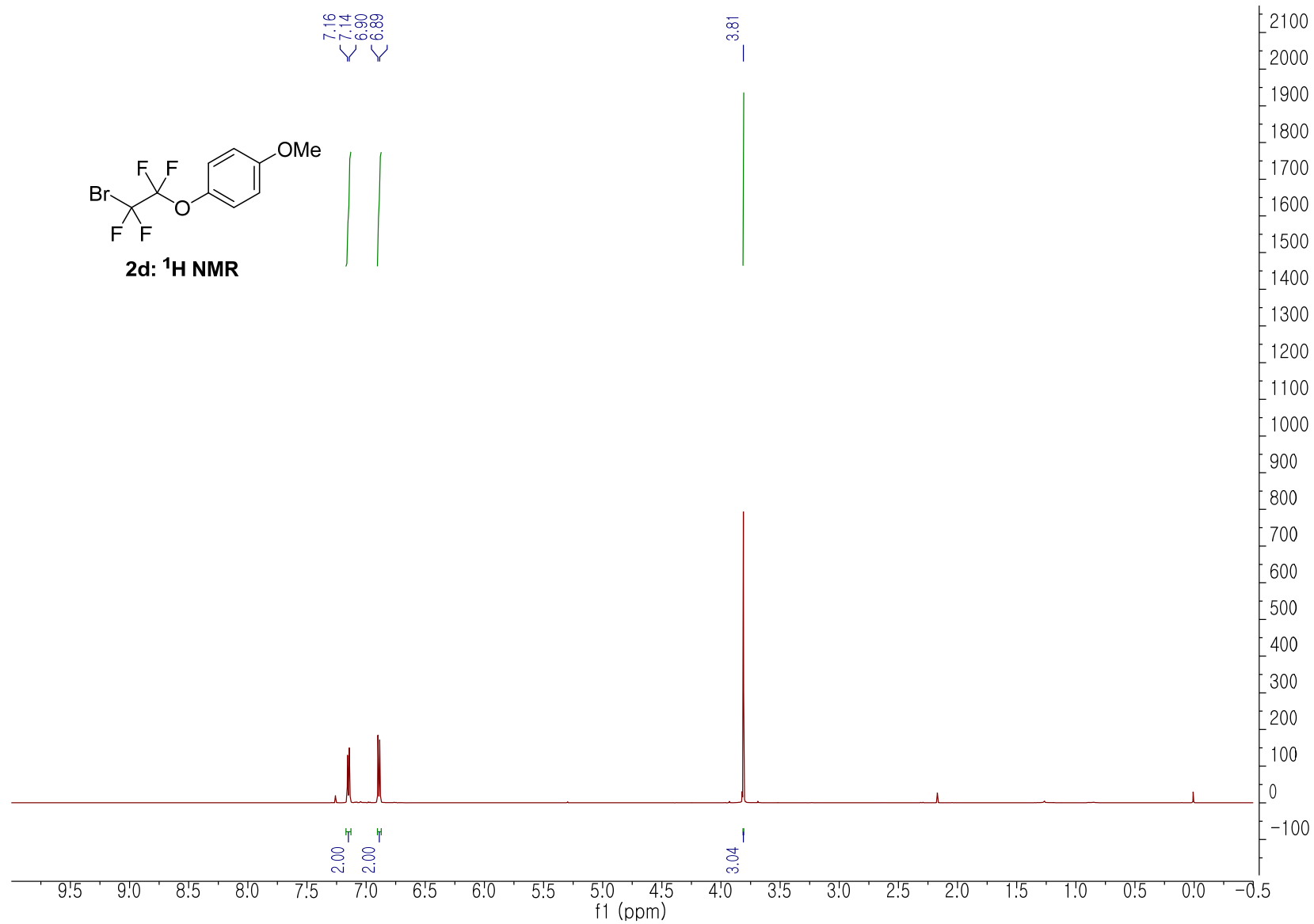


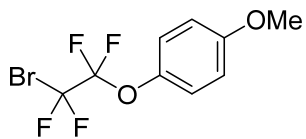
2c: ¹³C NMR



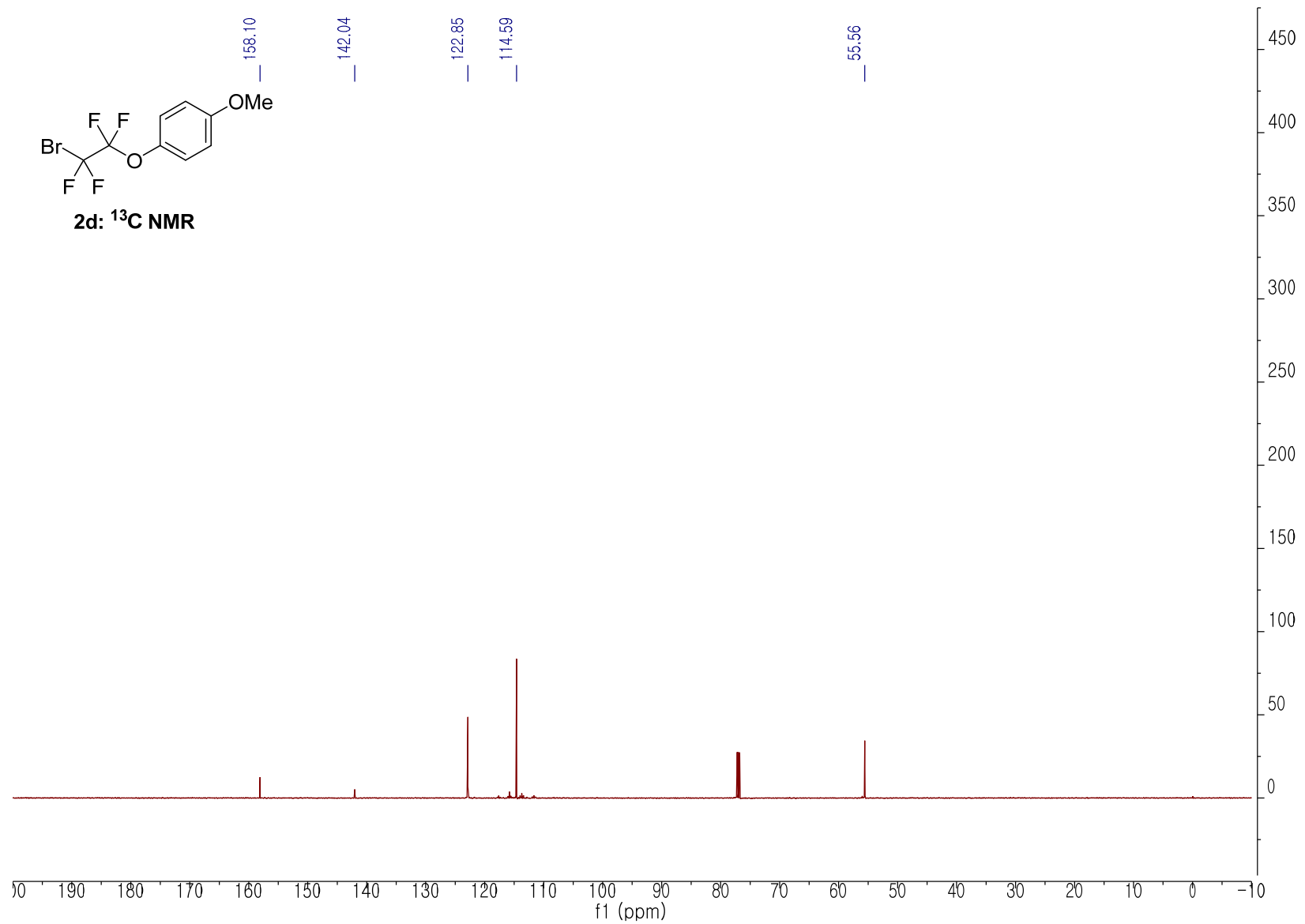


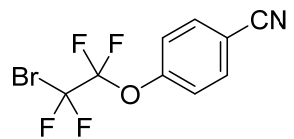
2d: ¹H NMR



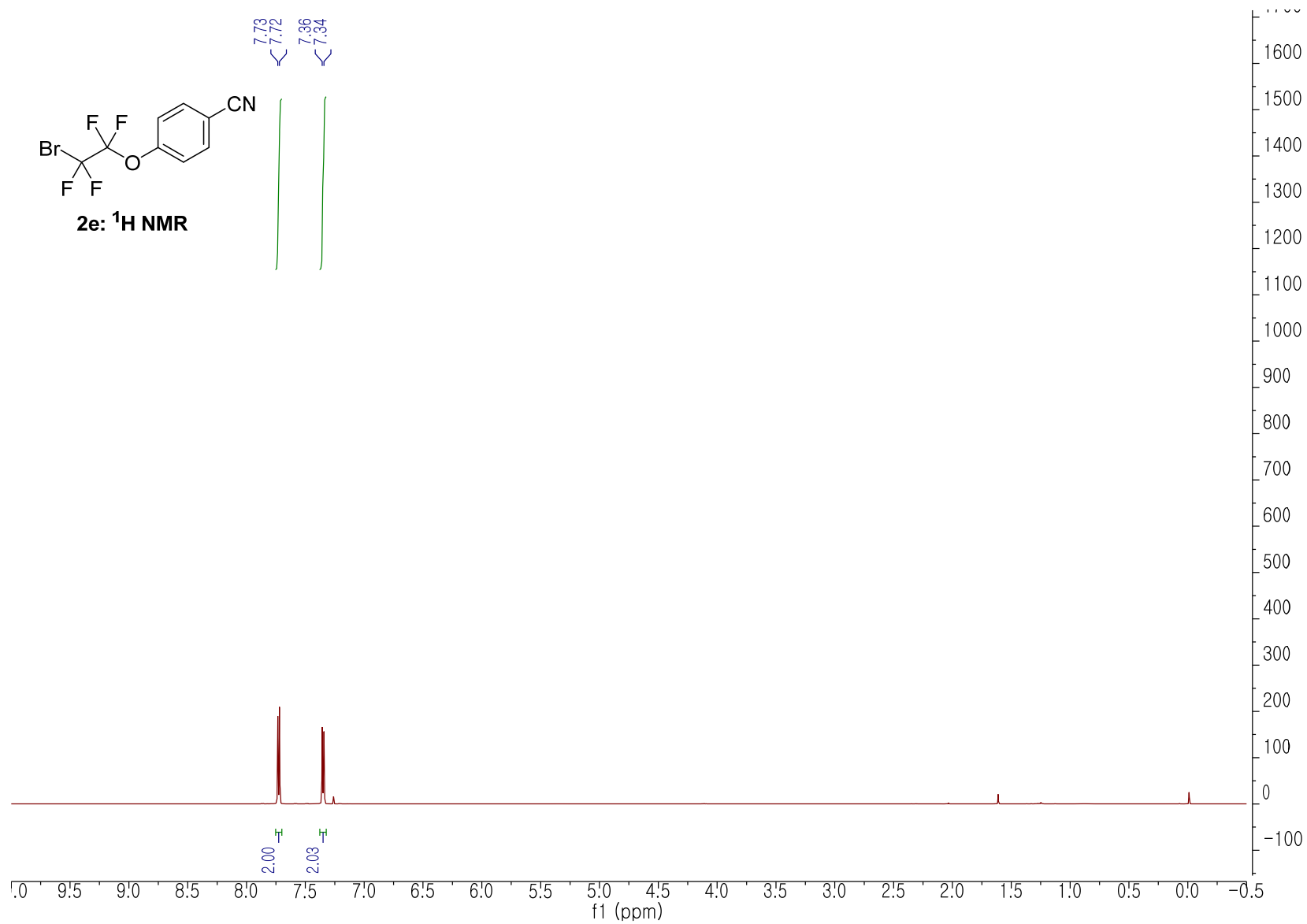


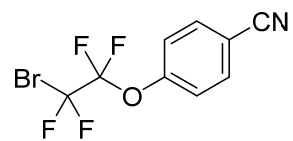
2d: ¹³C NMR



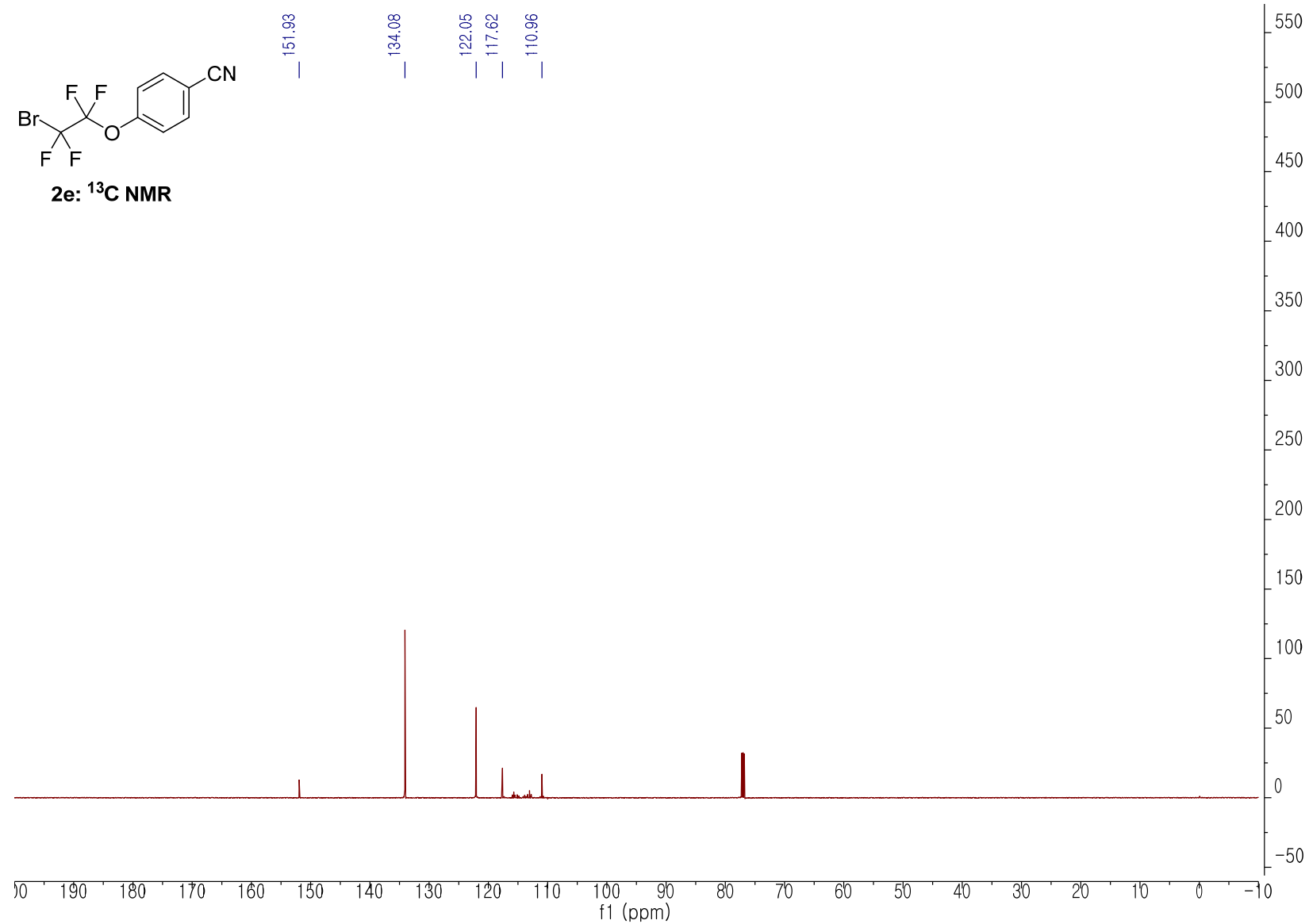


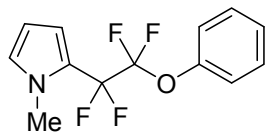
2e: ¹H NMR



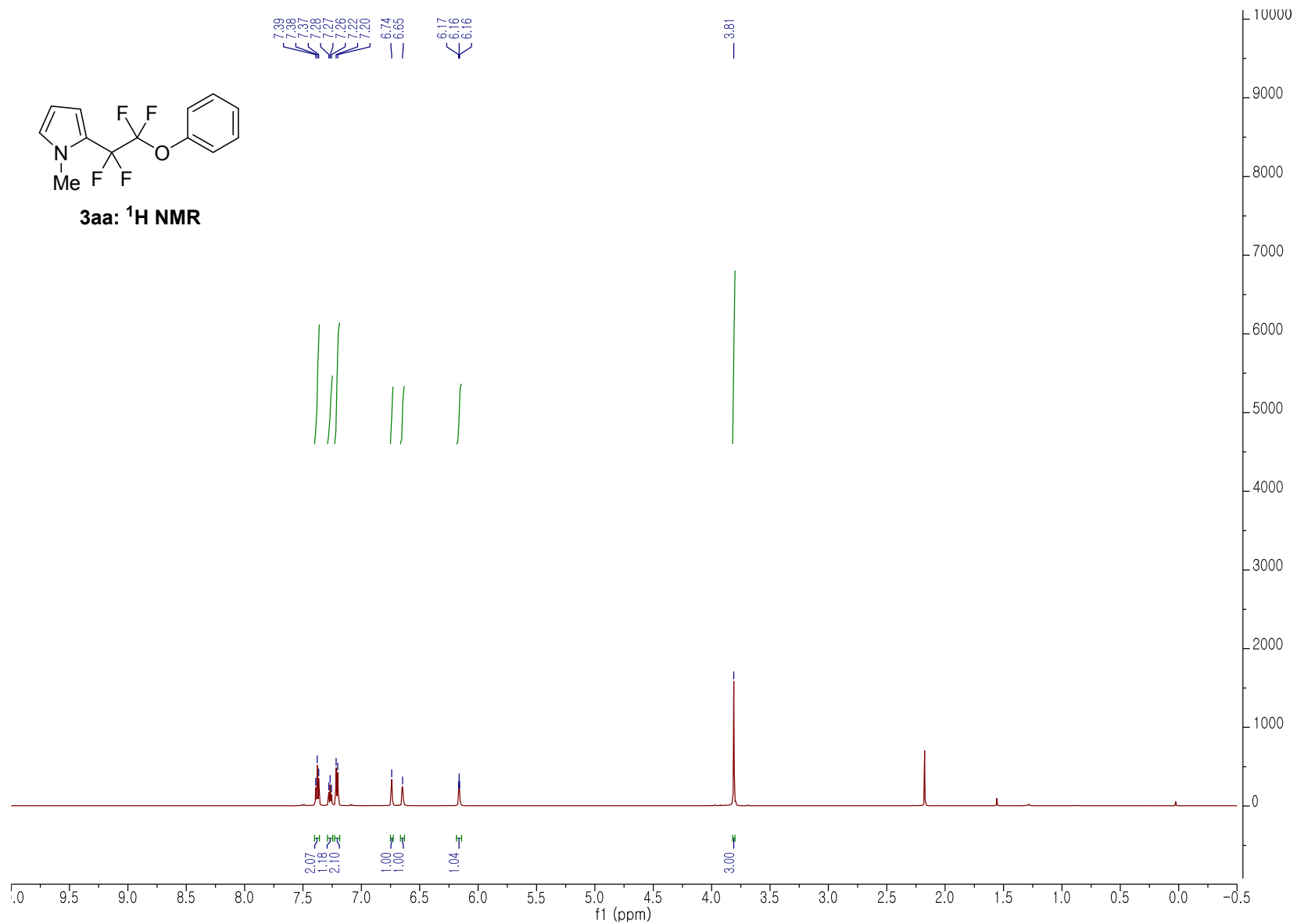


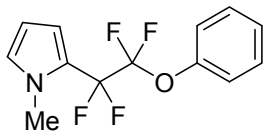
2e: ^{13}C NMR



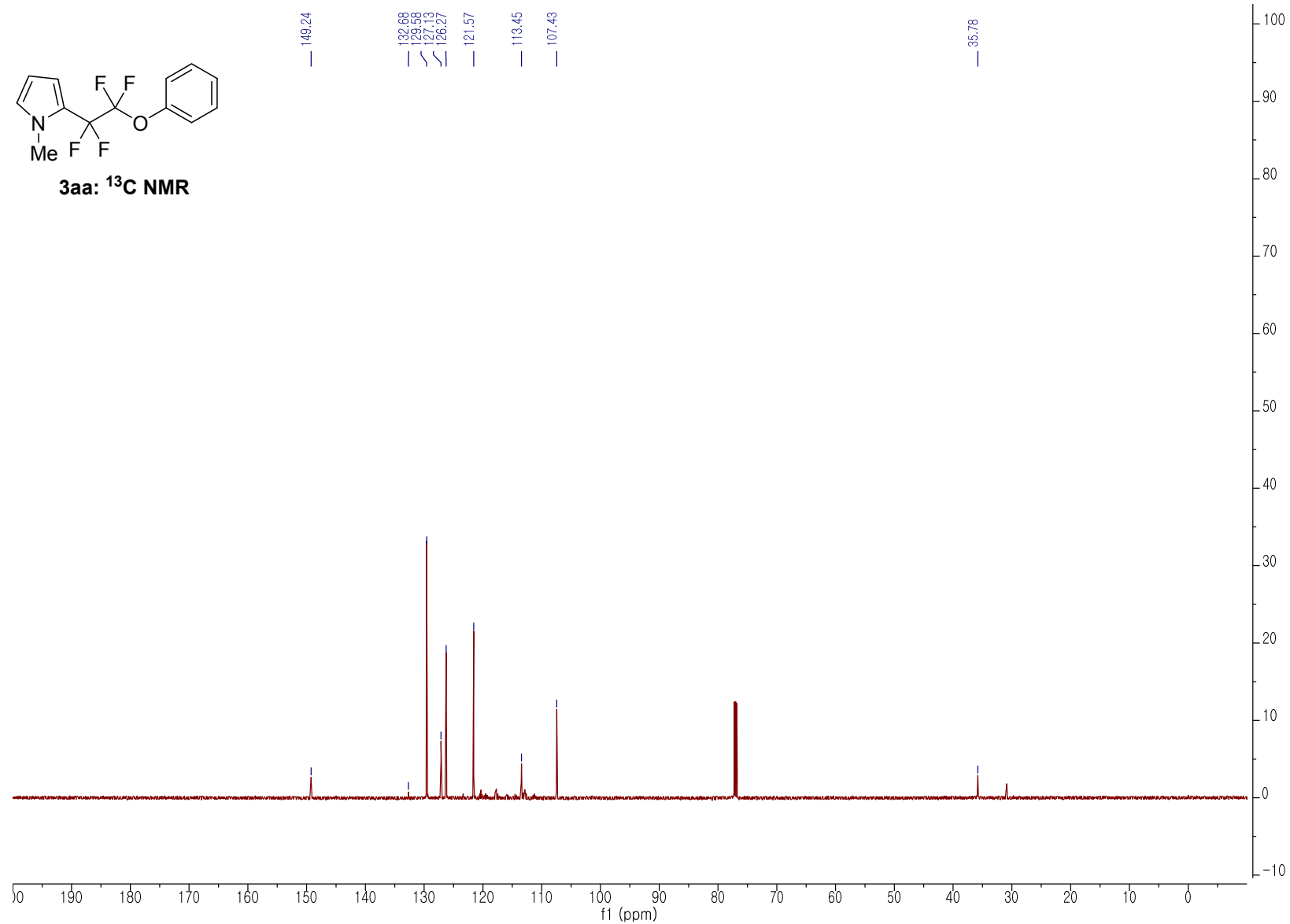


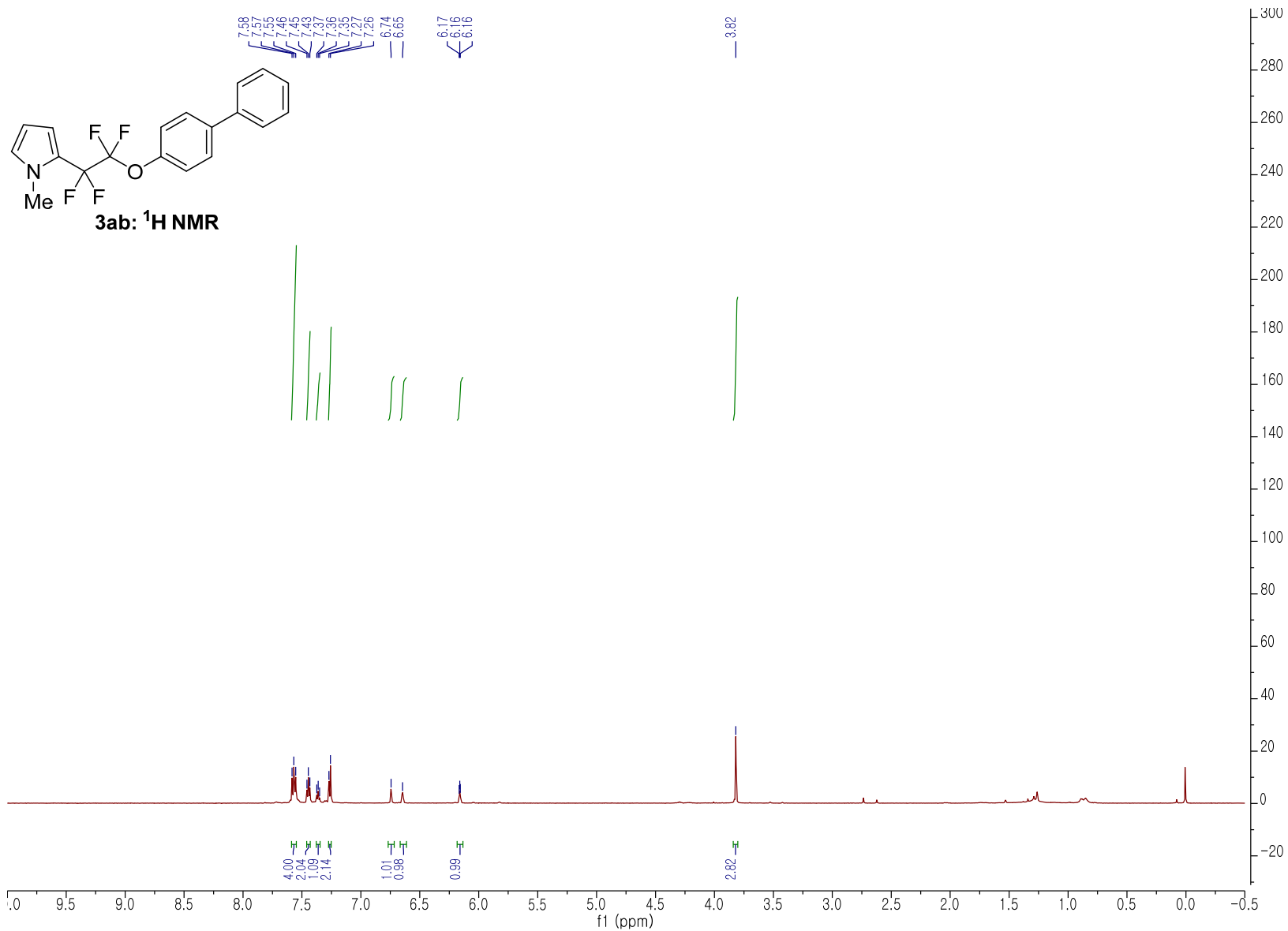
3aa: ¹H NMR

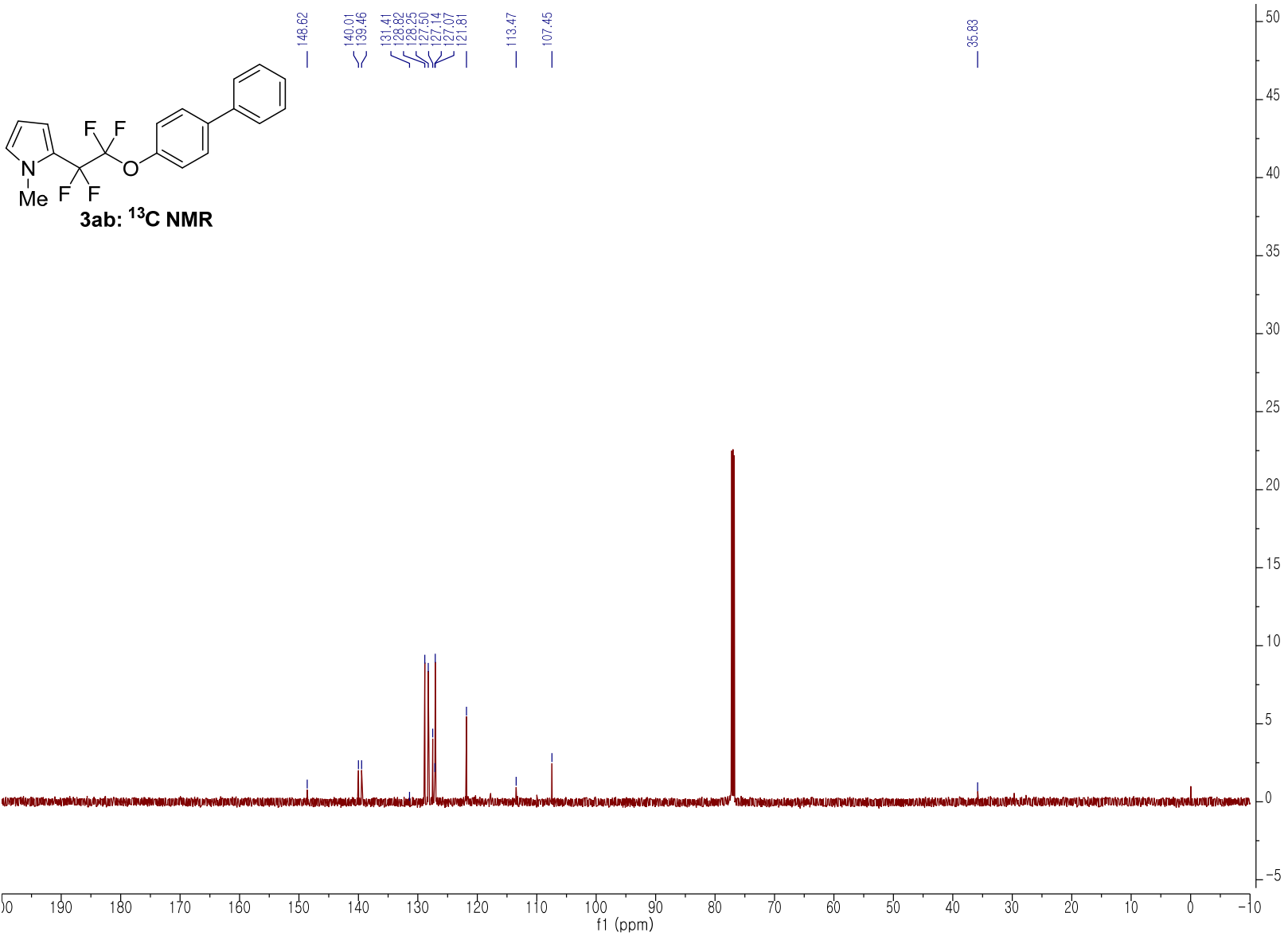


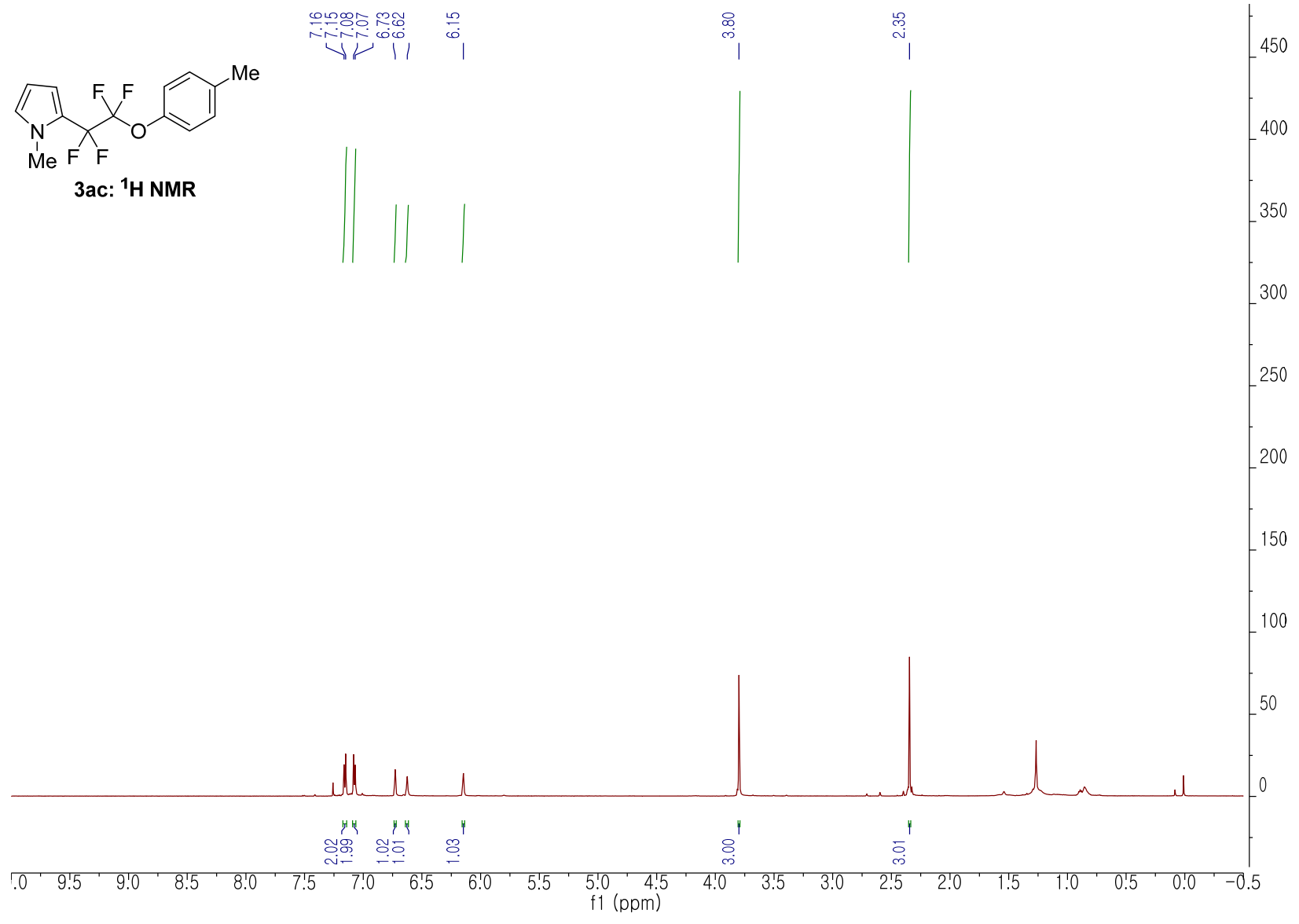
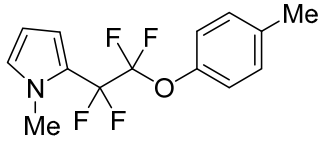


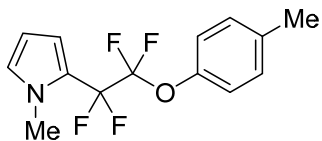
3aa: ¹³C NMR



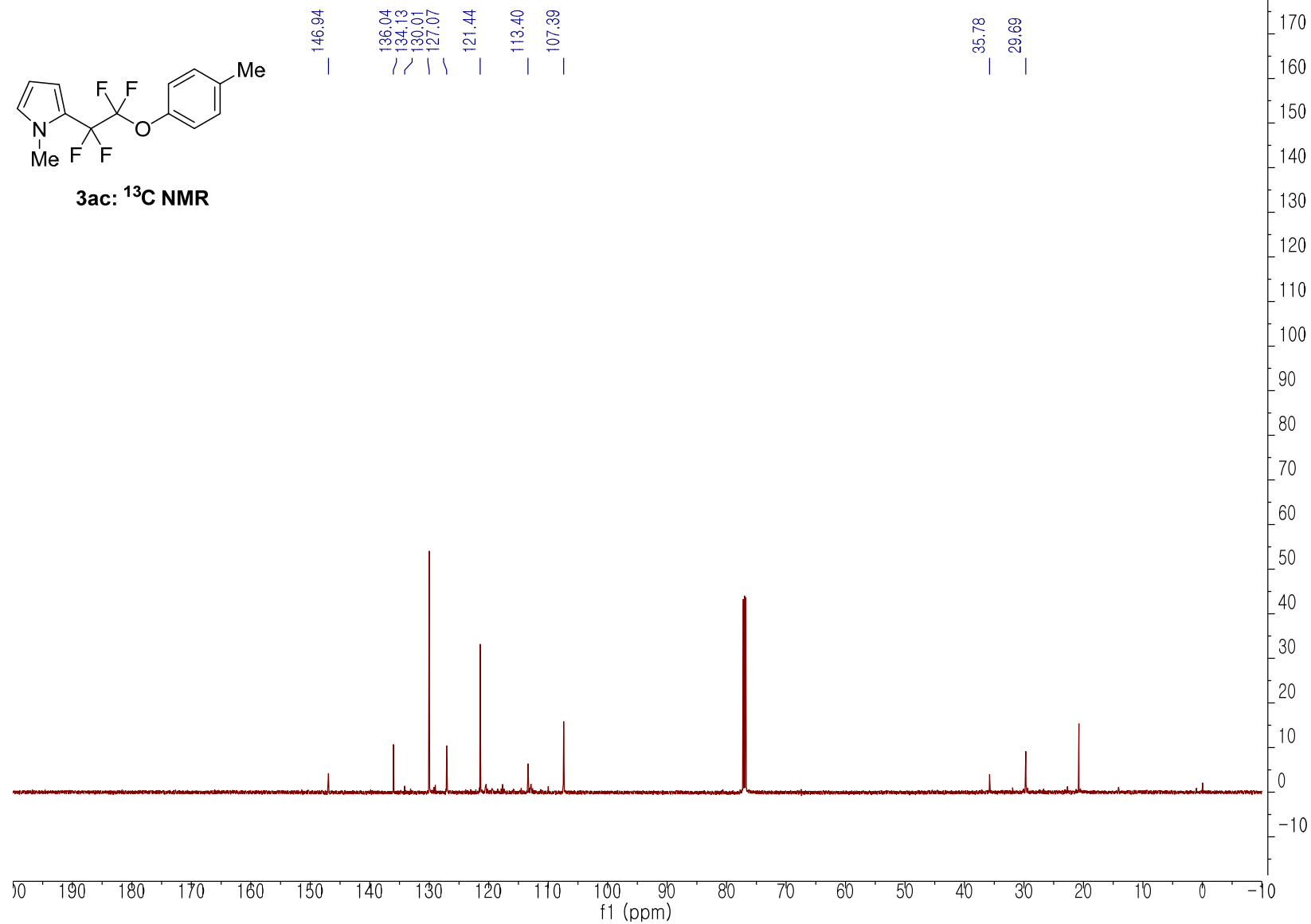


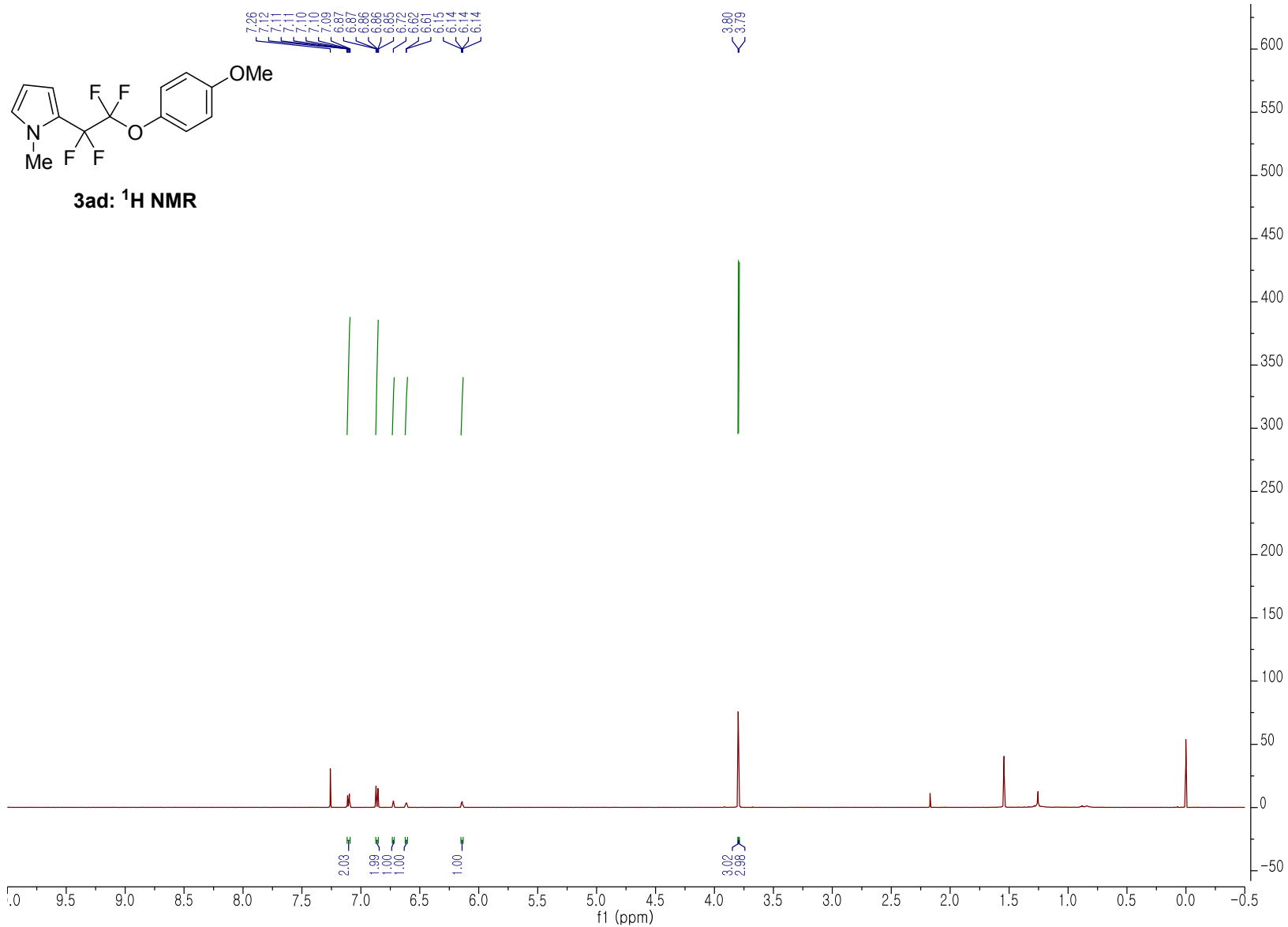


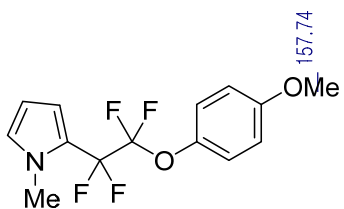




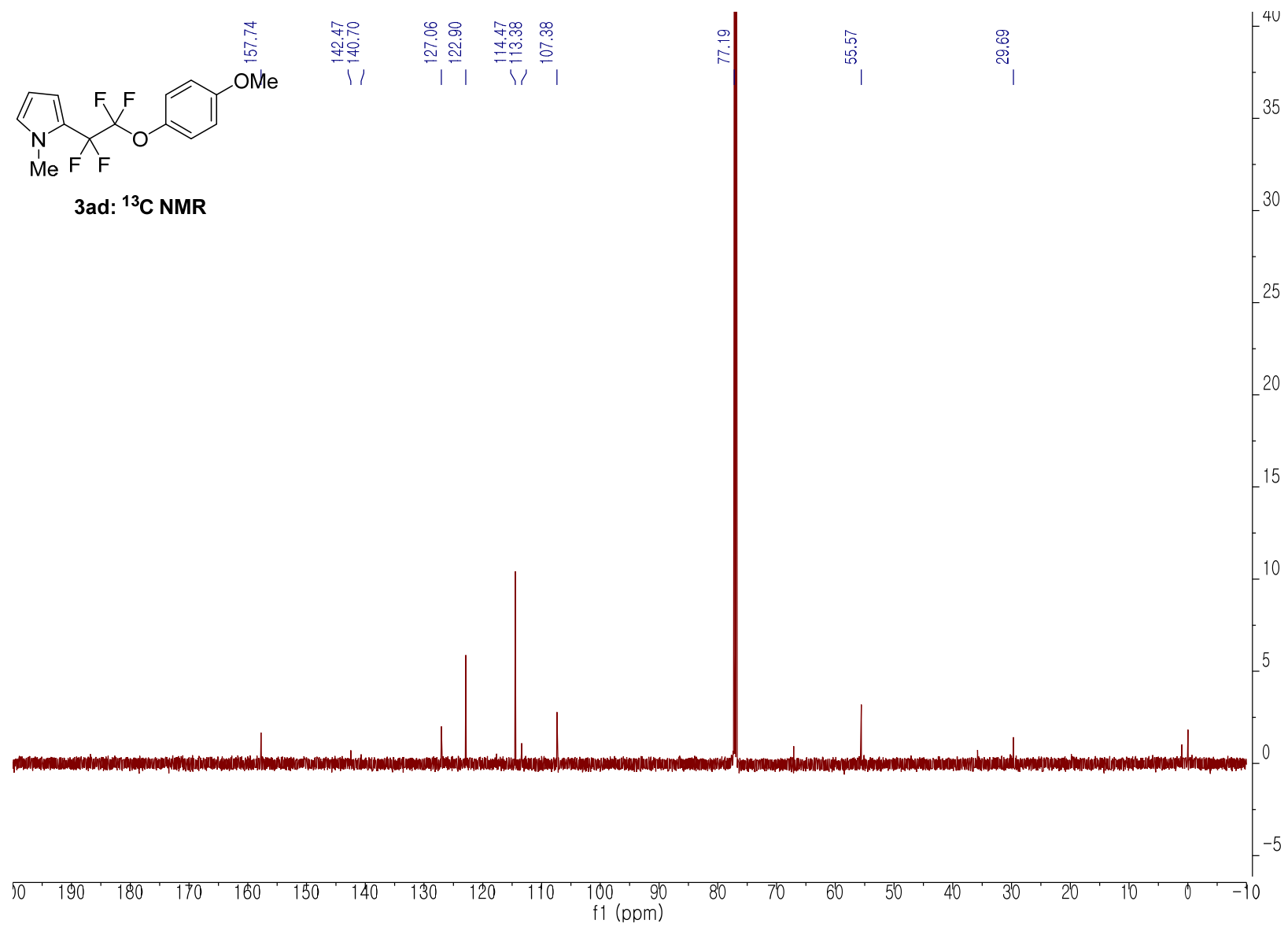
3ac: ¹³C NMR

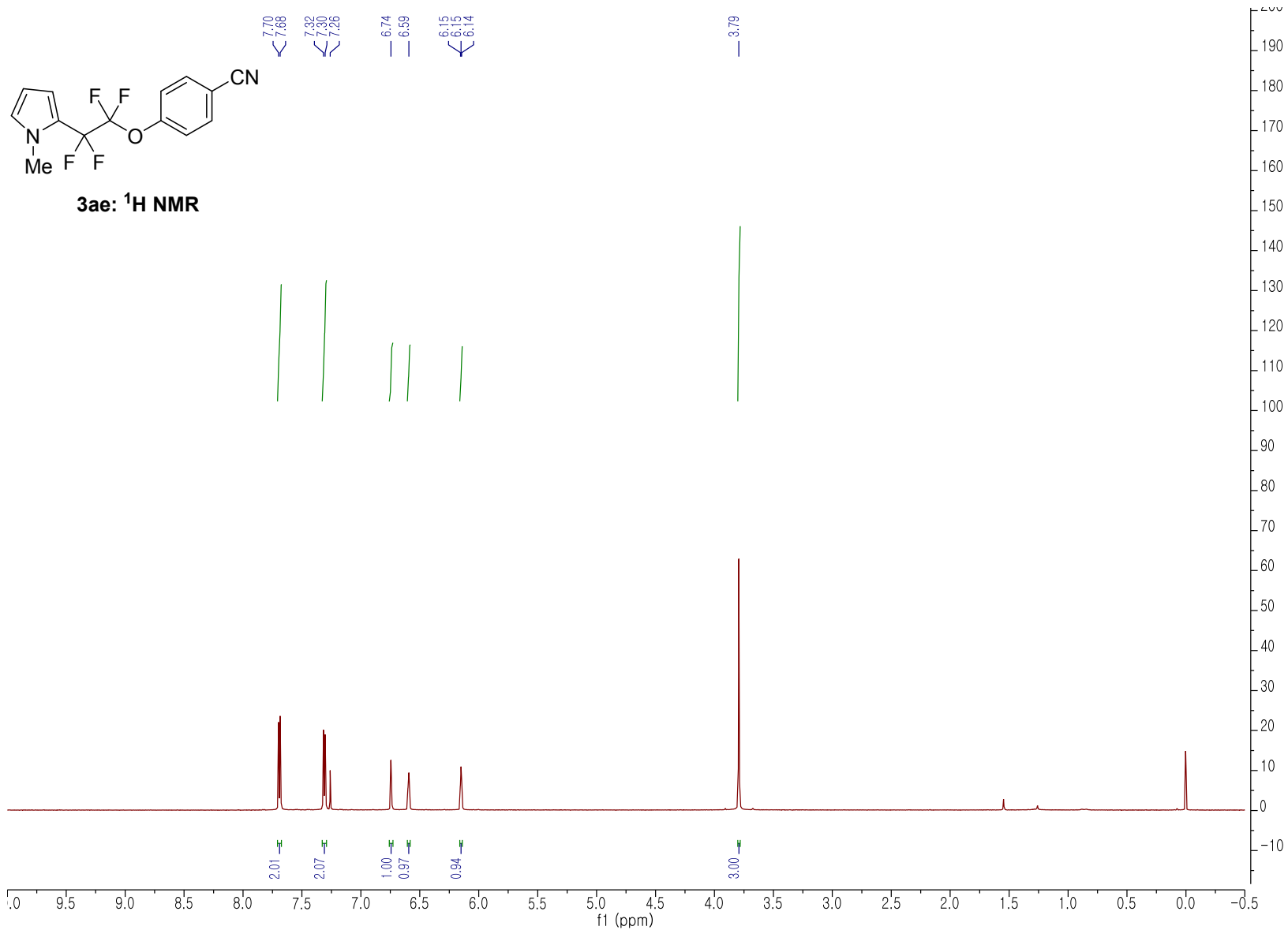


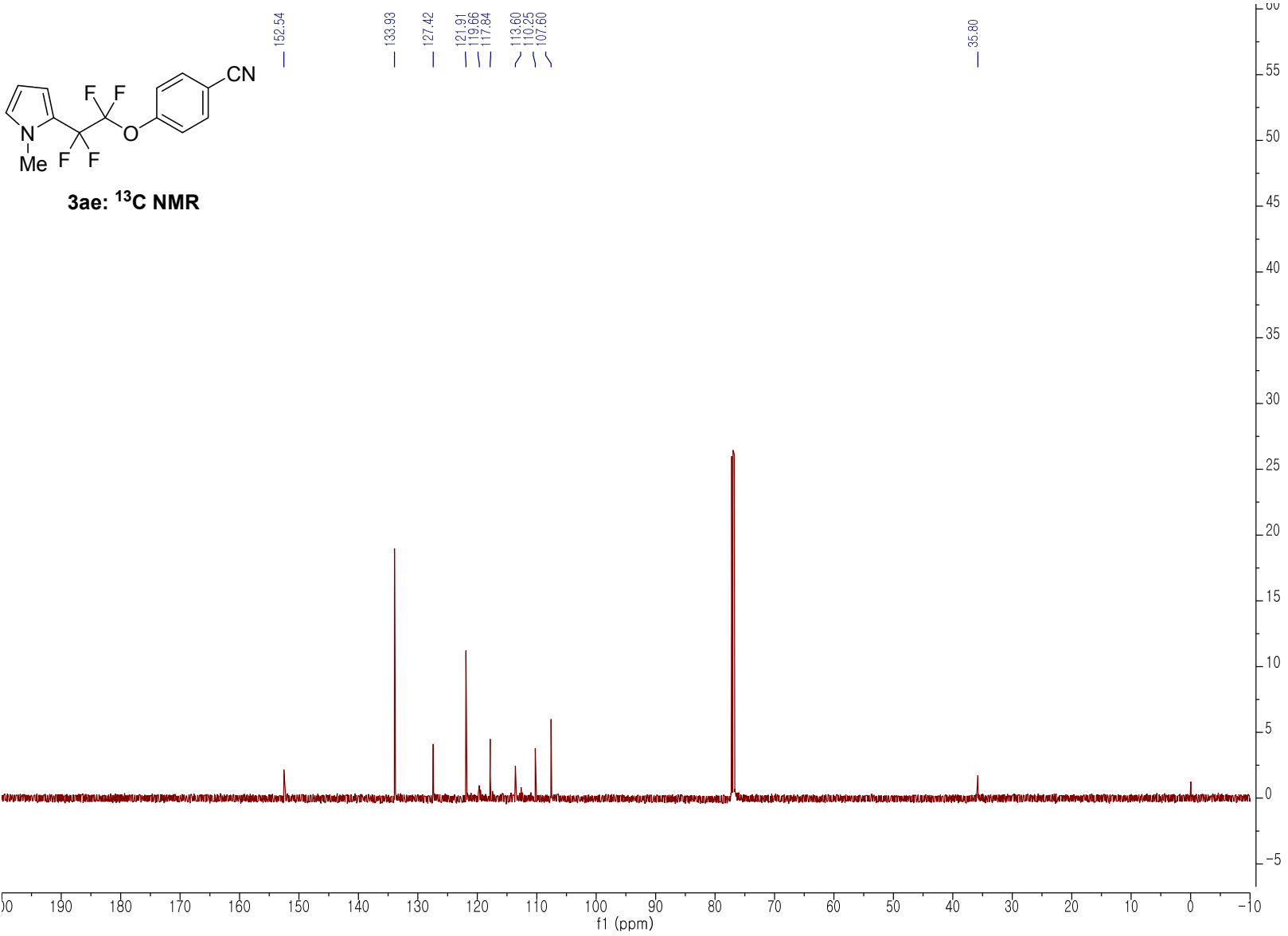


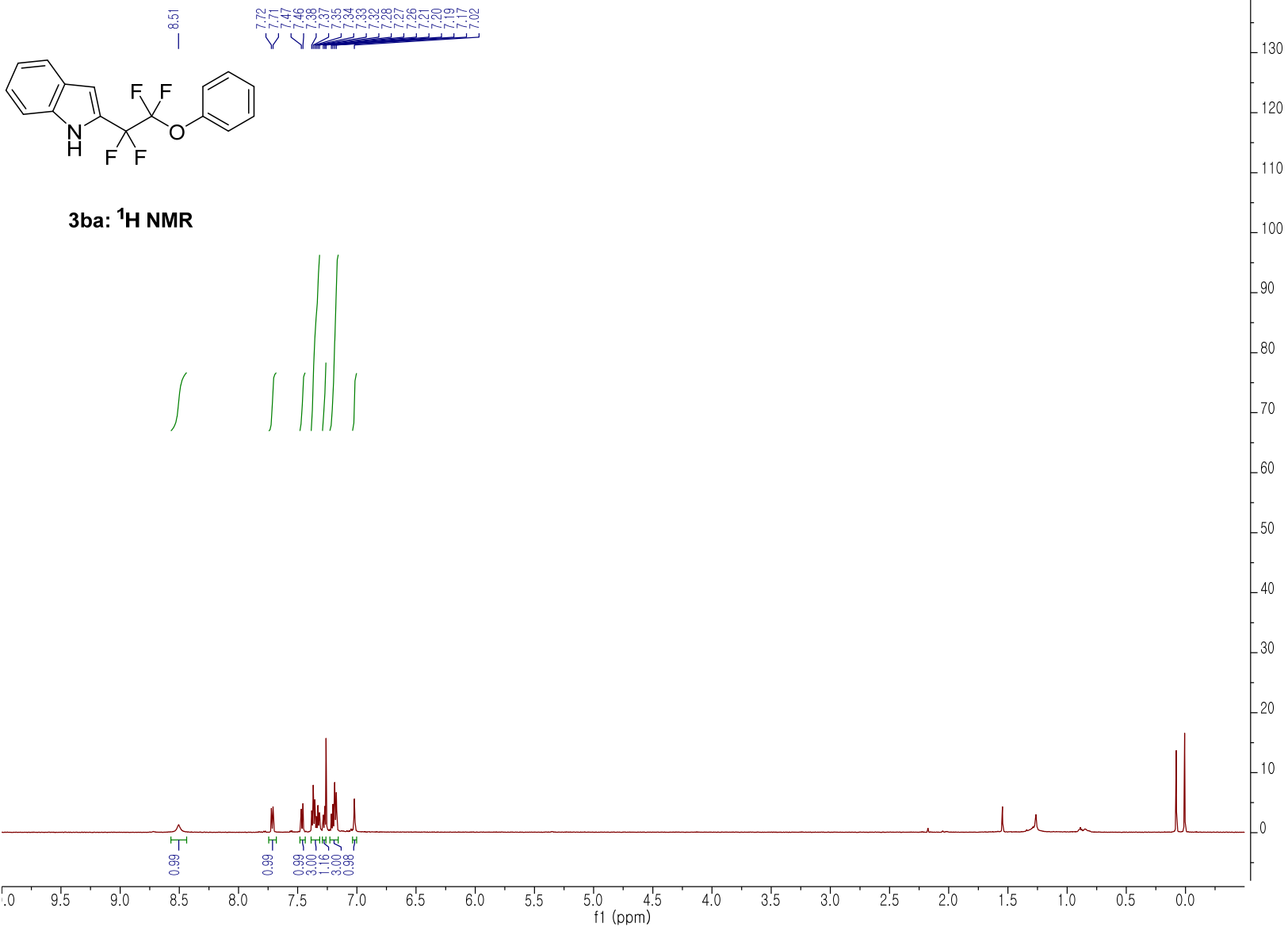


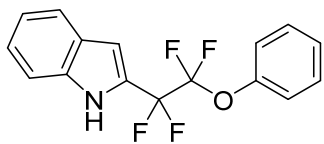
3ad: ^{13}C NMR



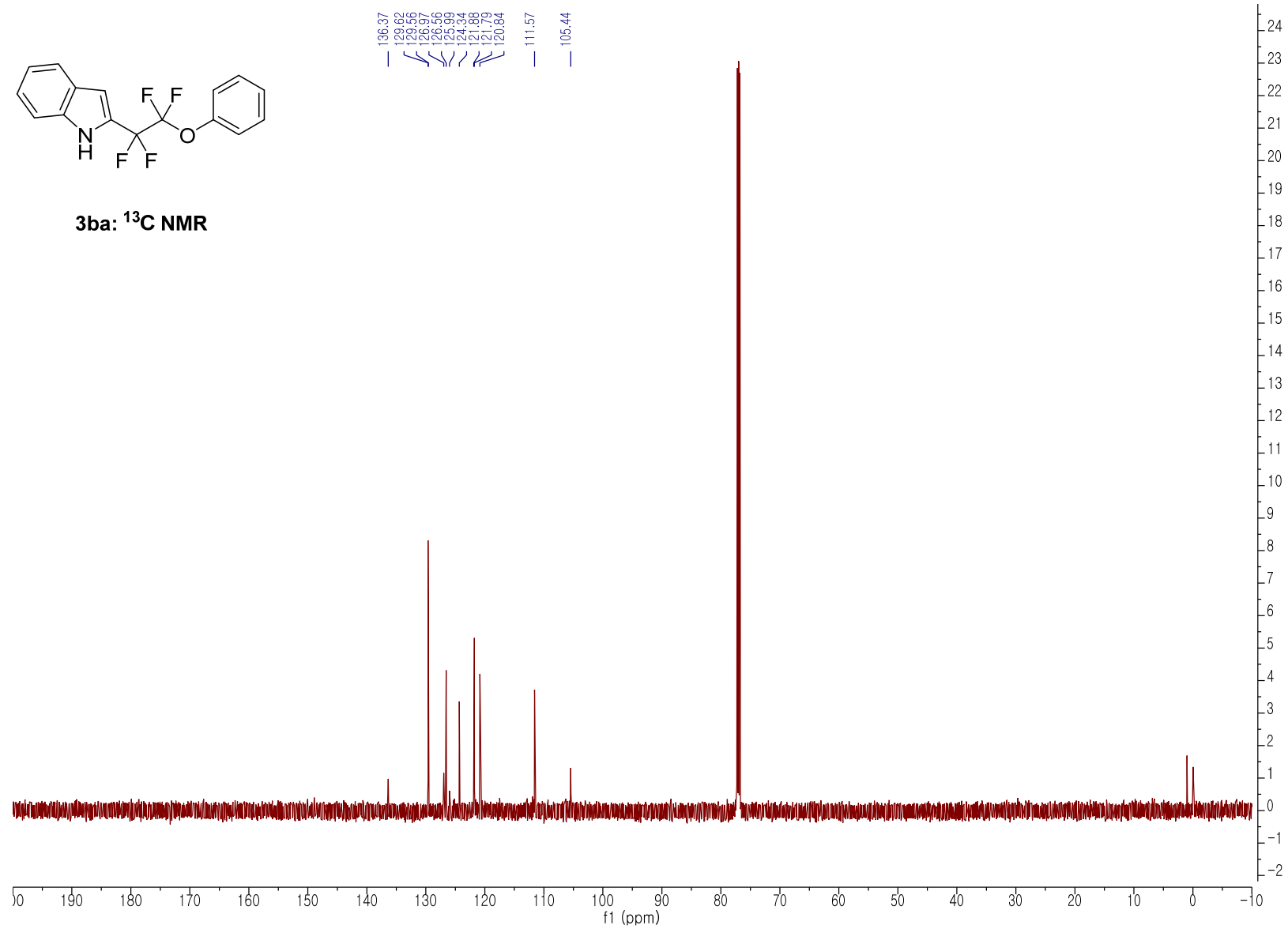


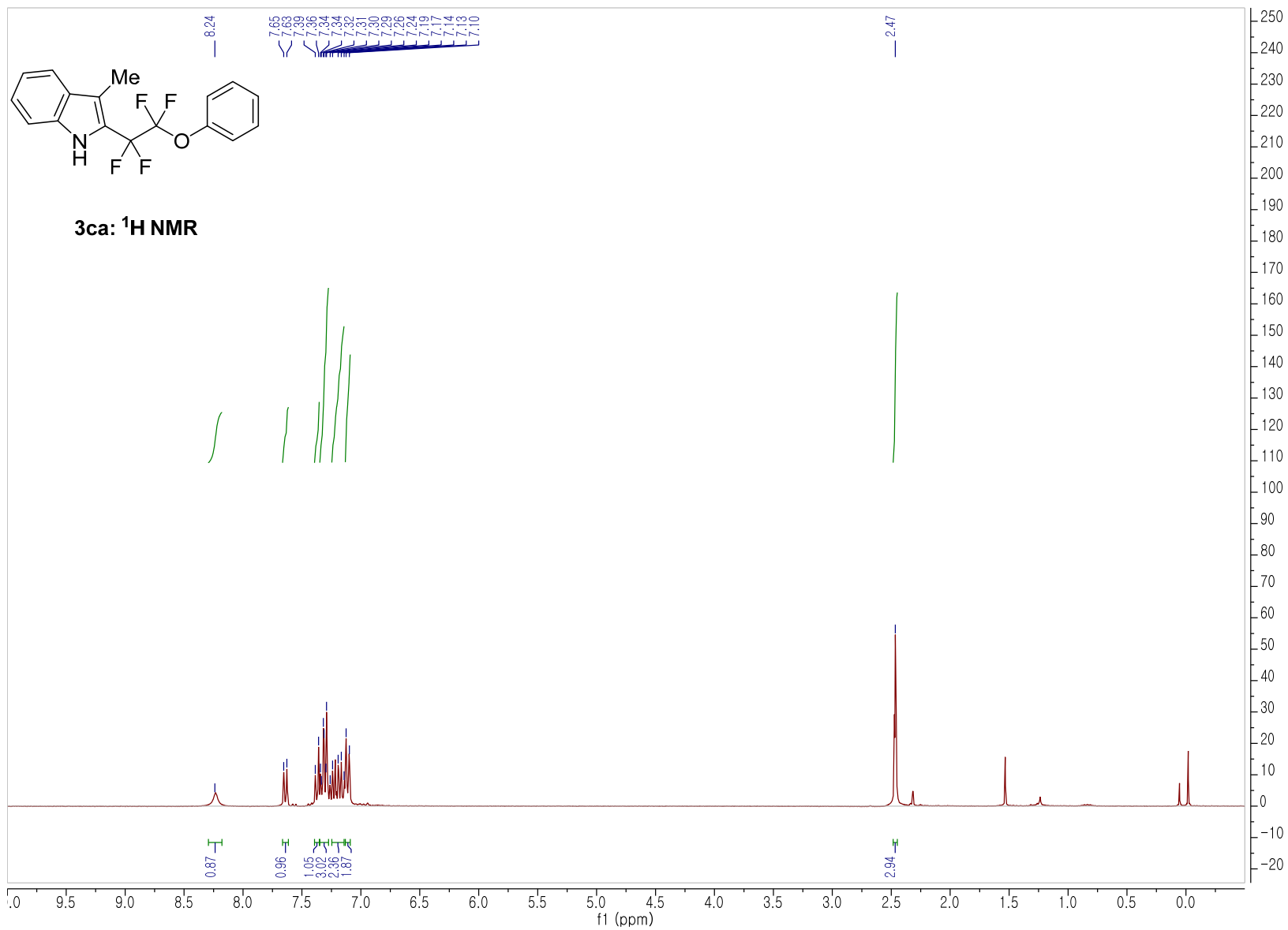


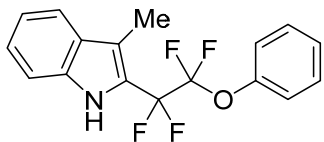




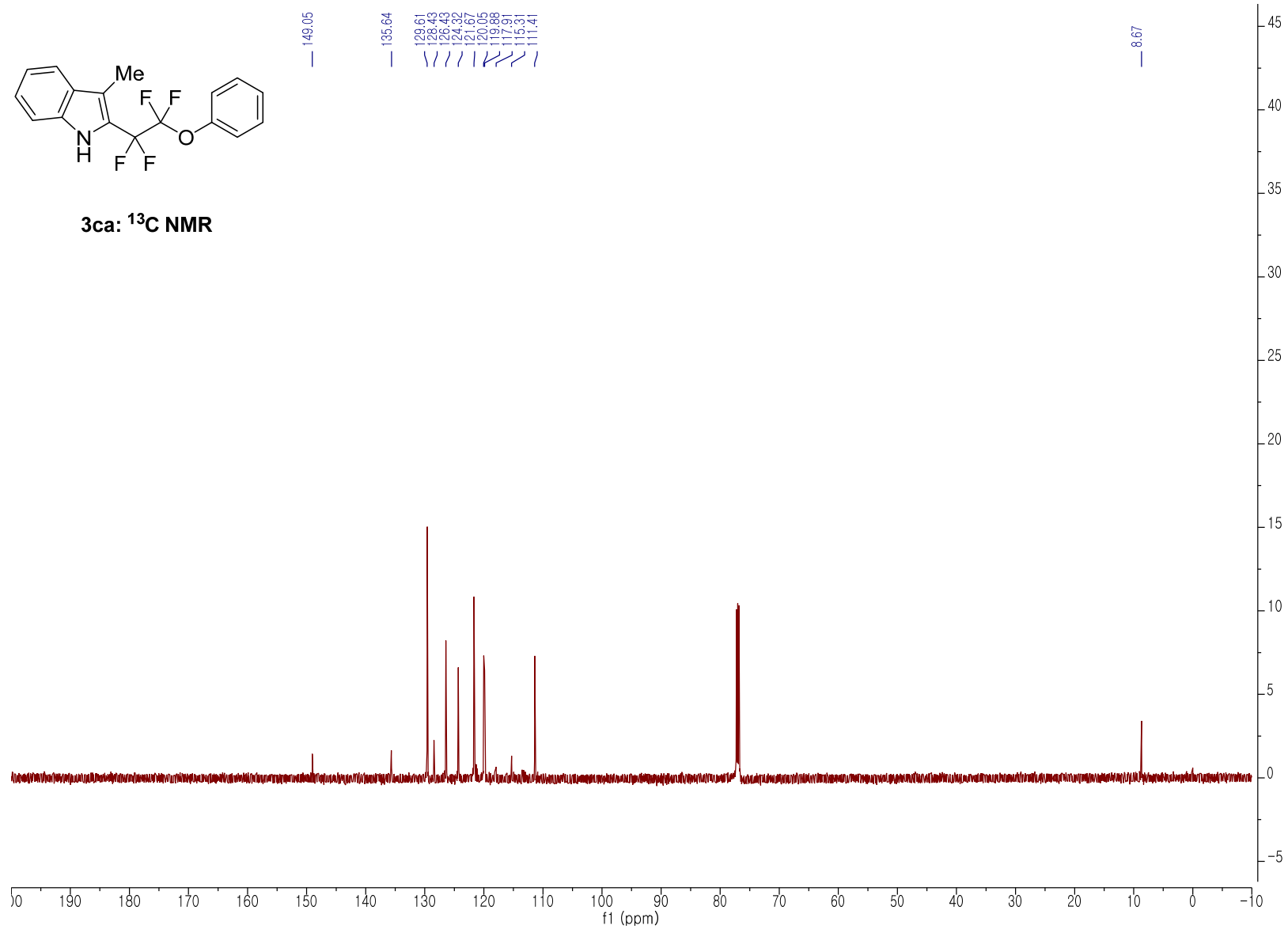
3ba: ^{13}C NMR

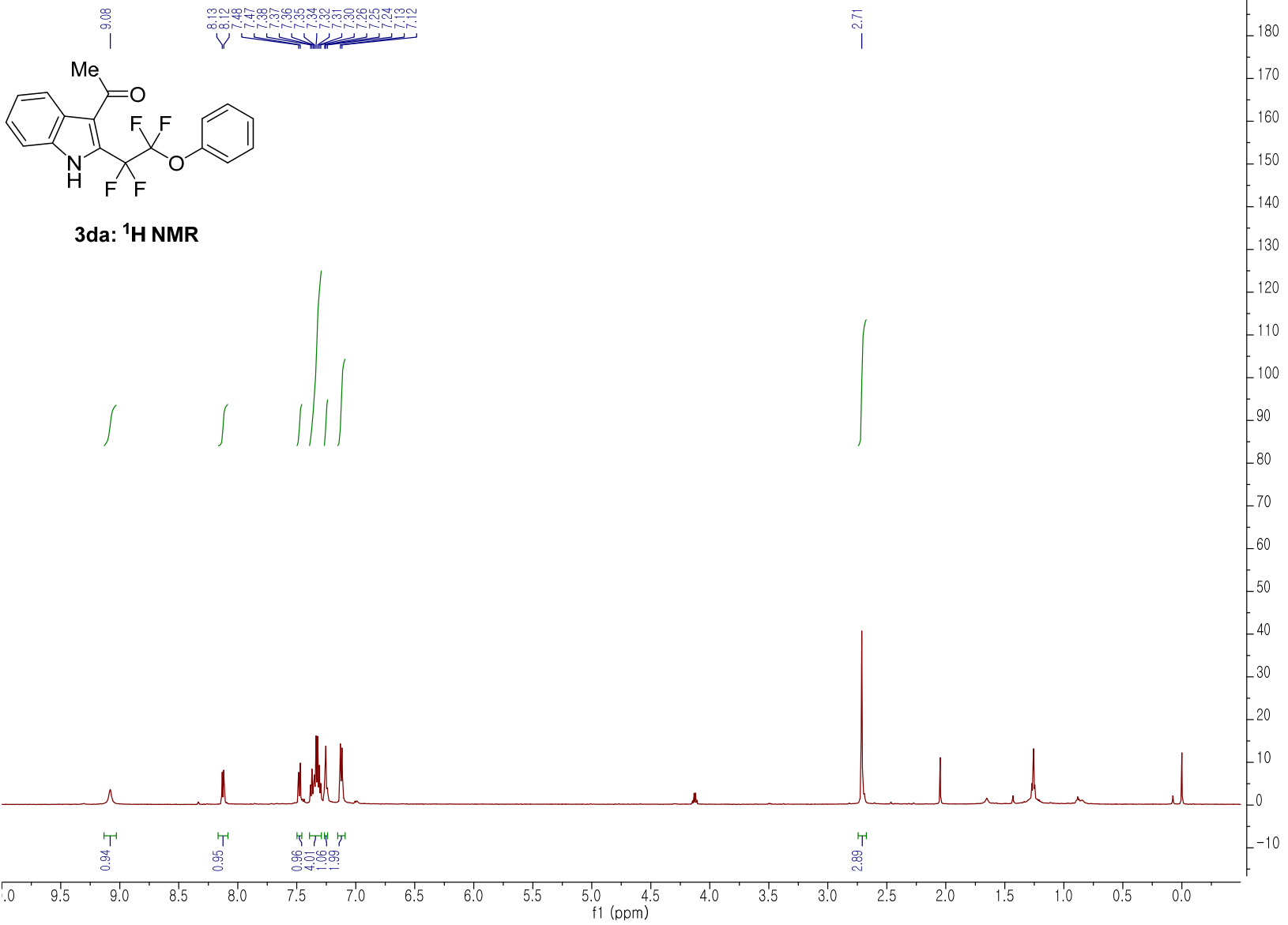


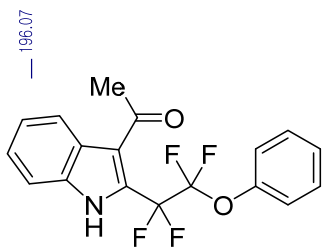




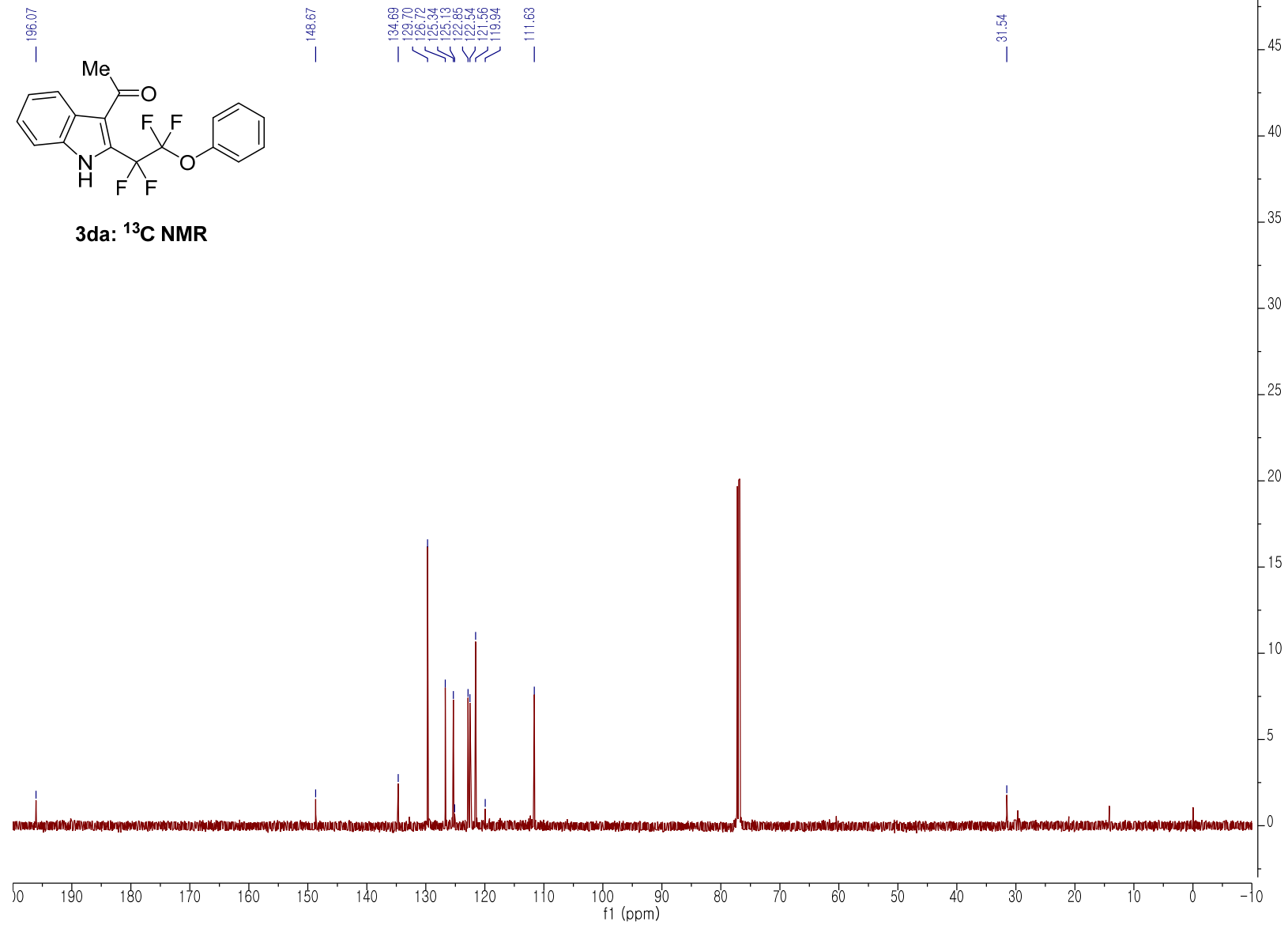
3ca: ^{13}C NMR

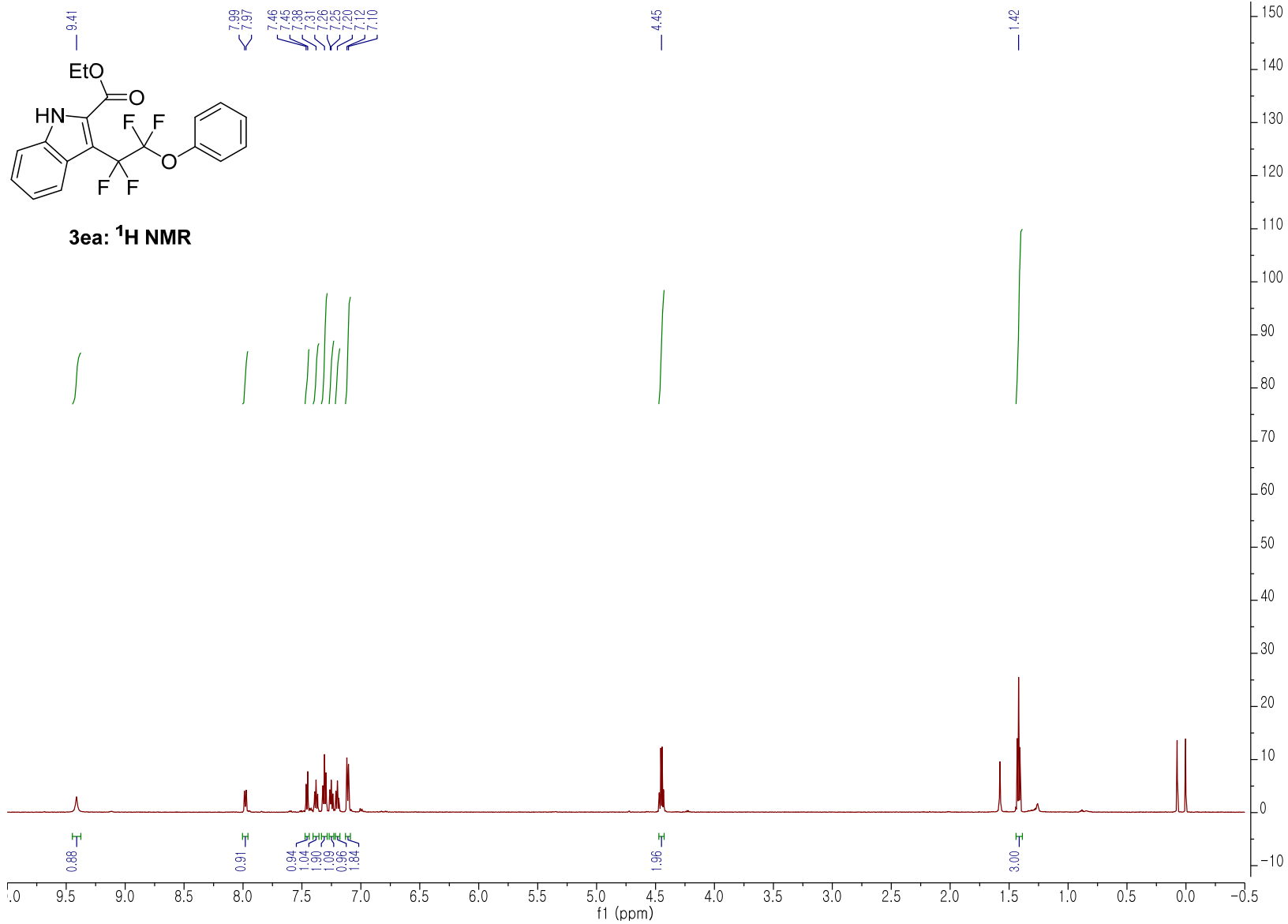


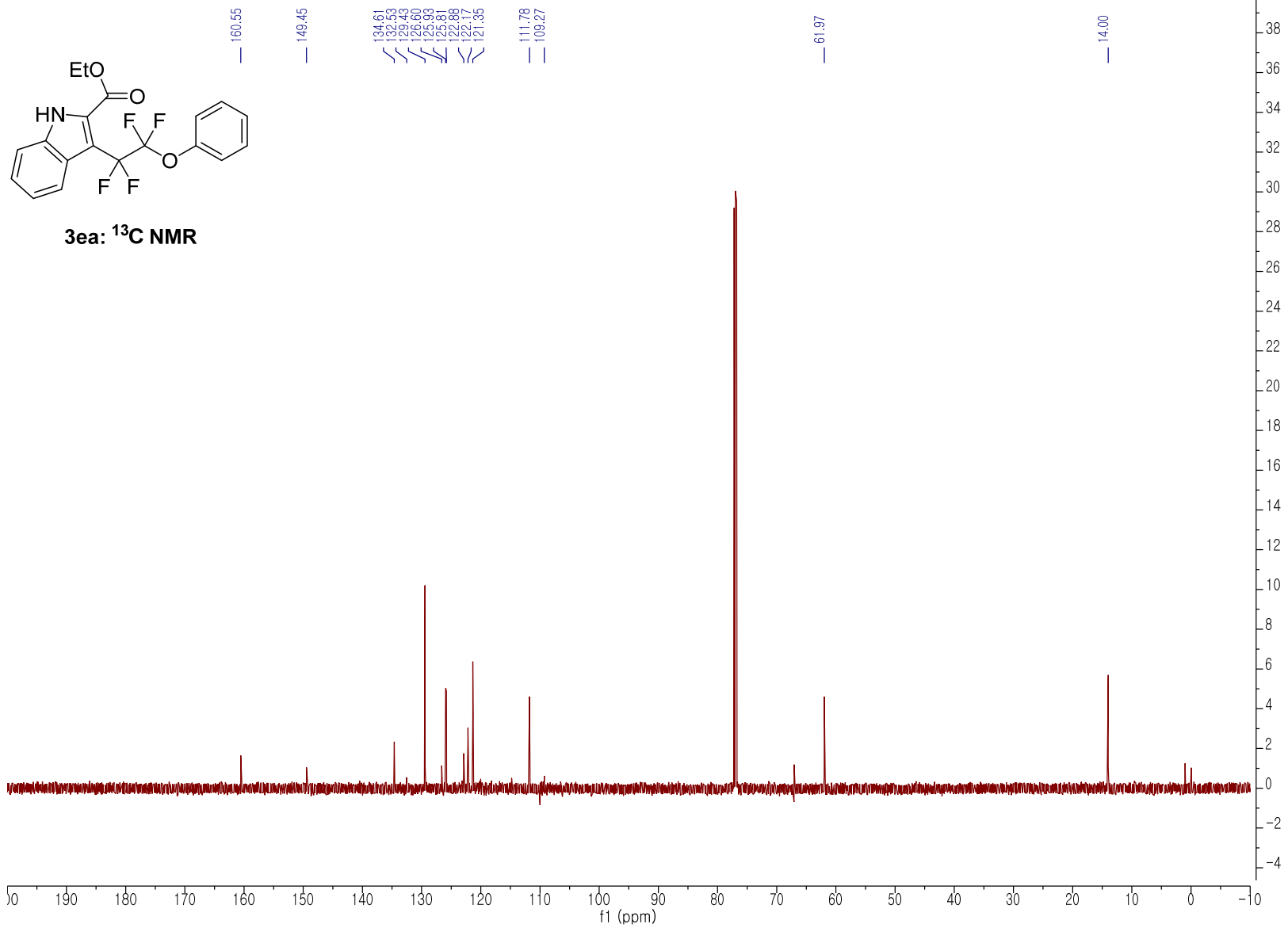


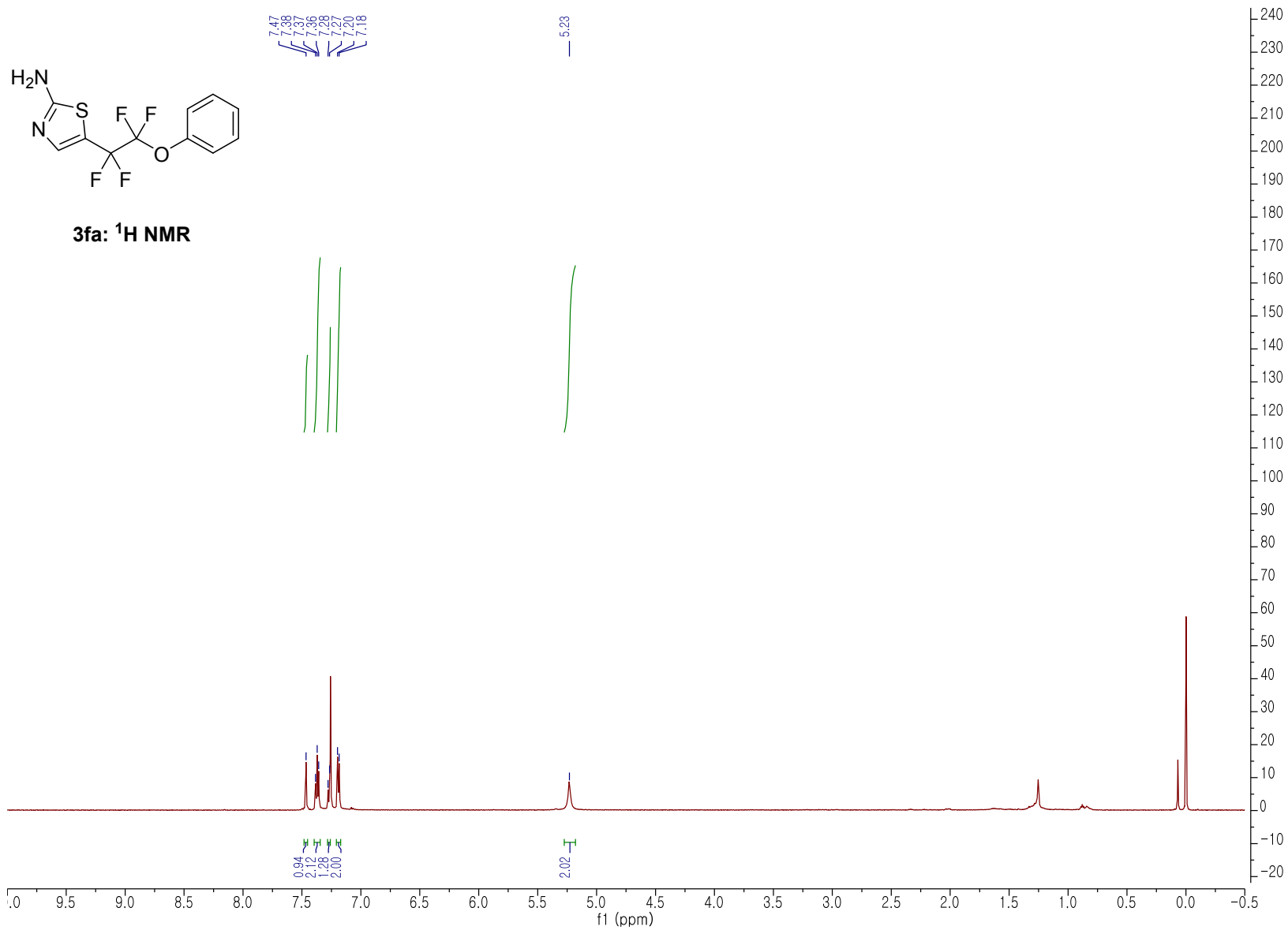


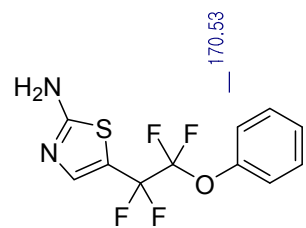
3da: ¹³C NMR



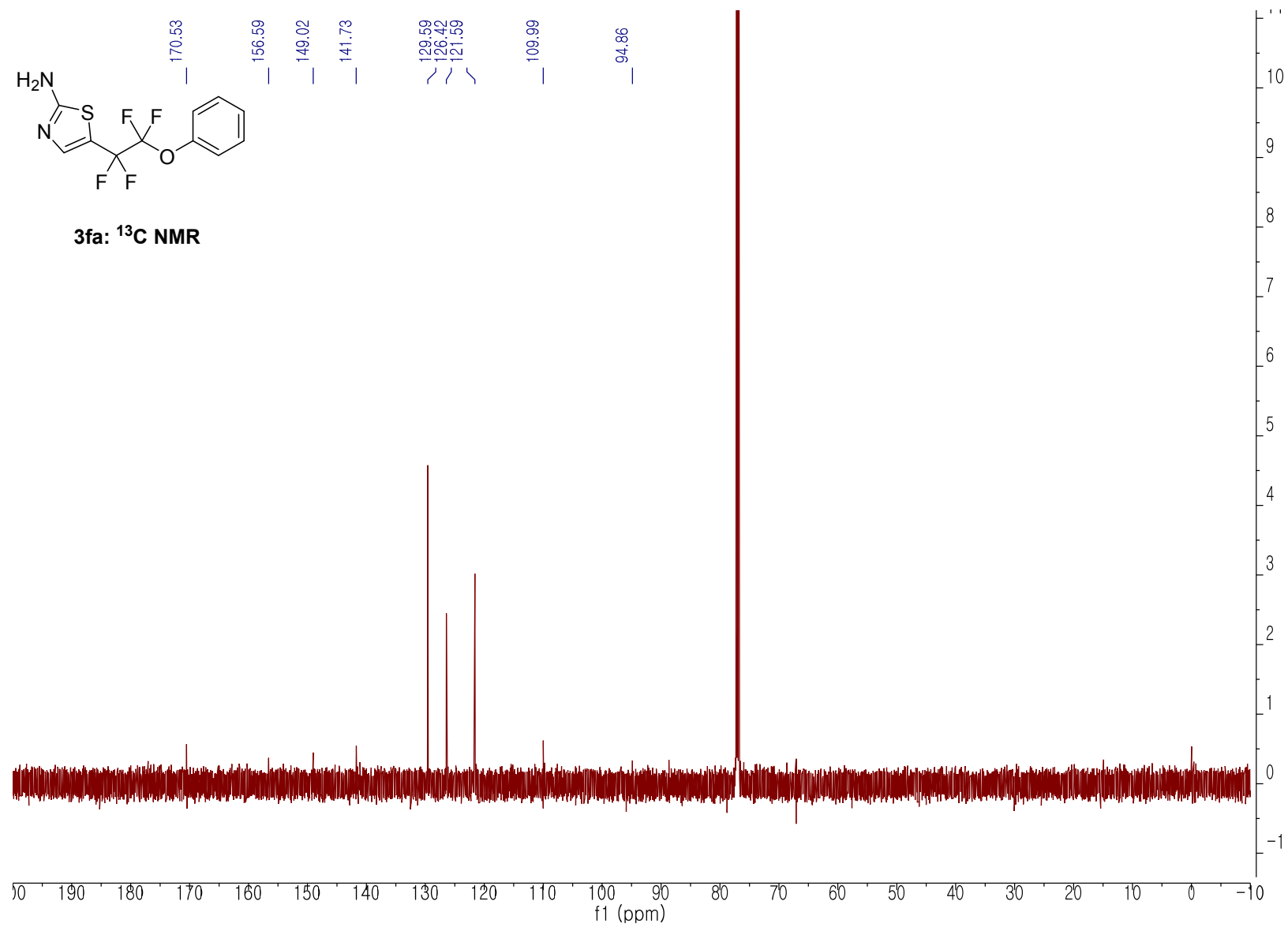


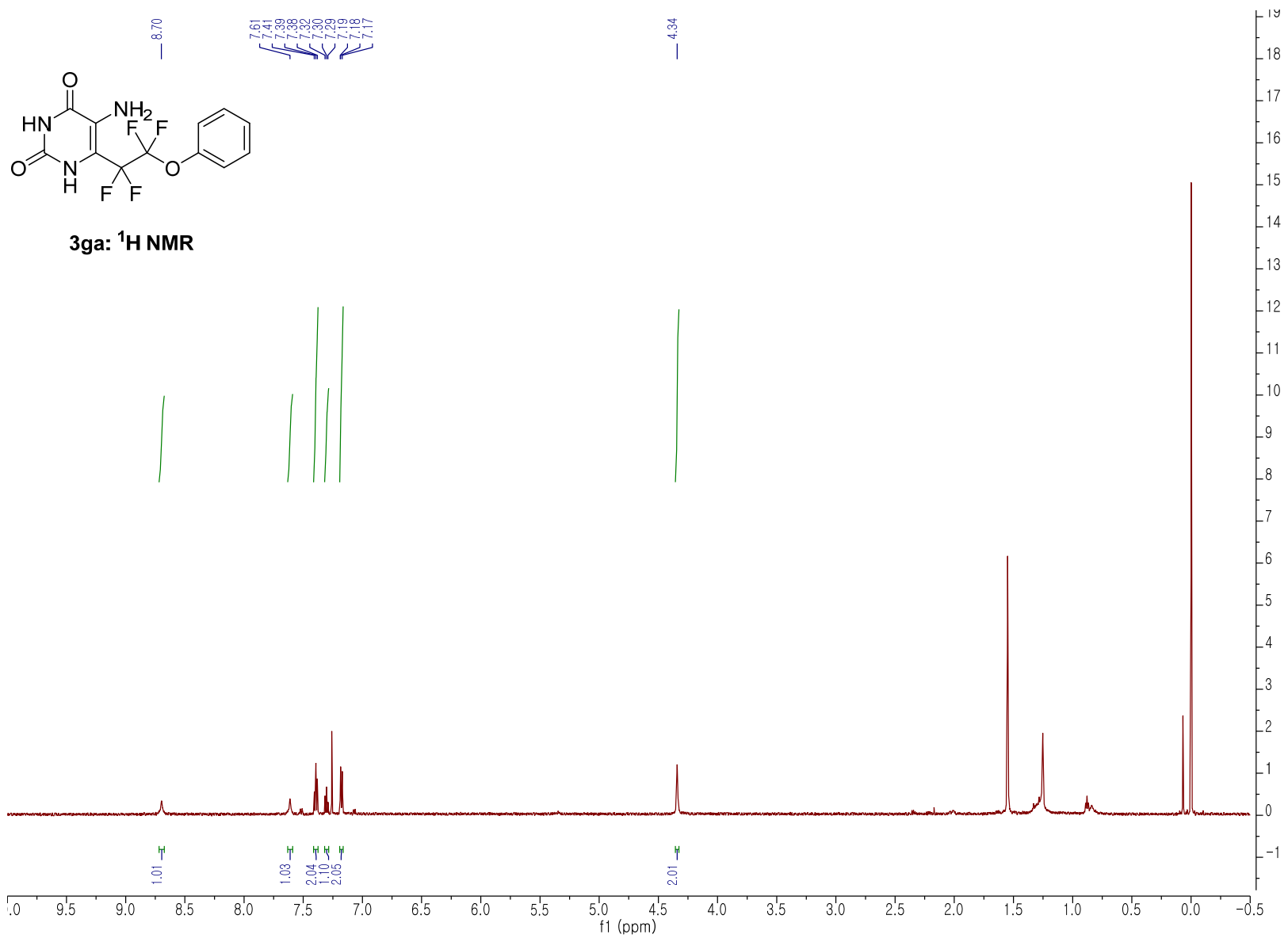


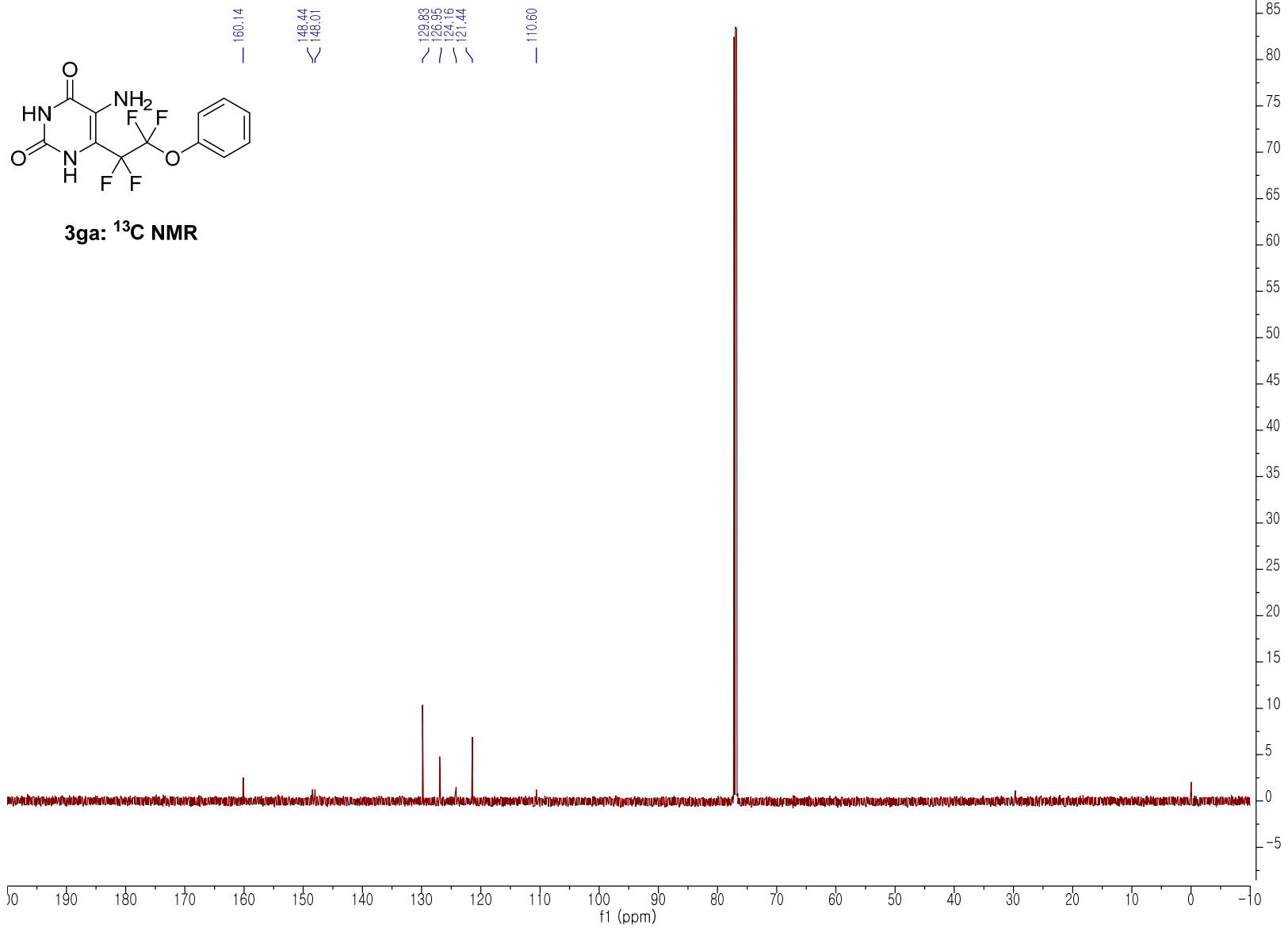


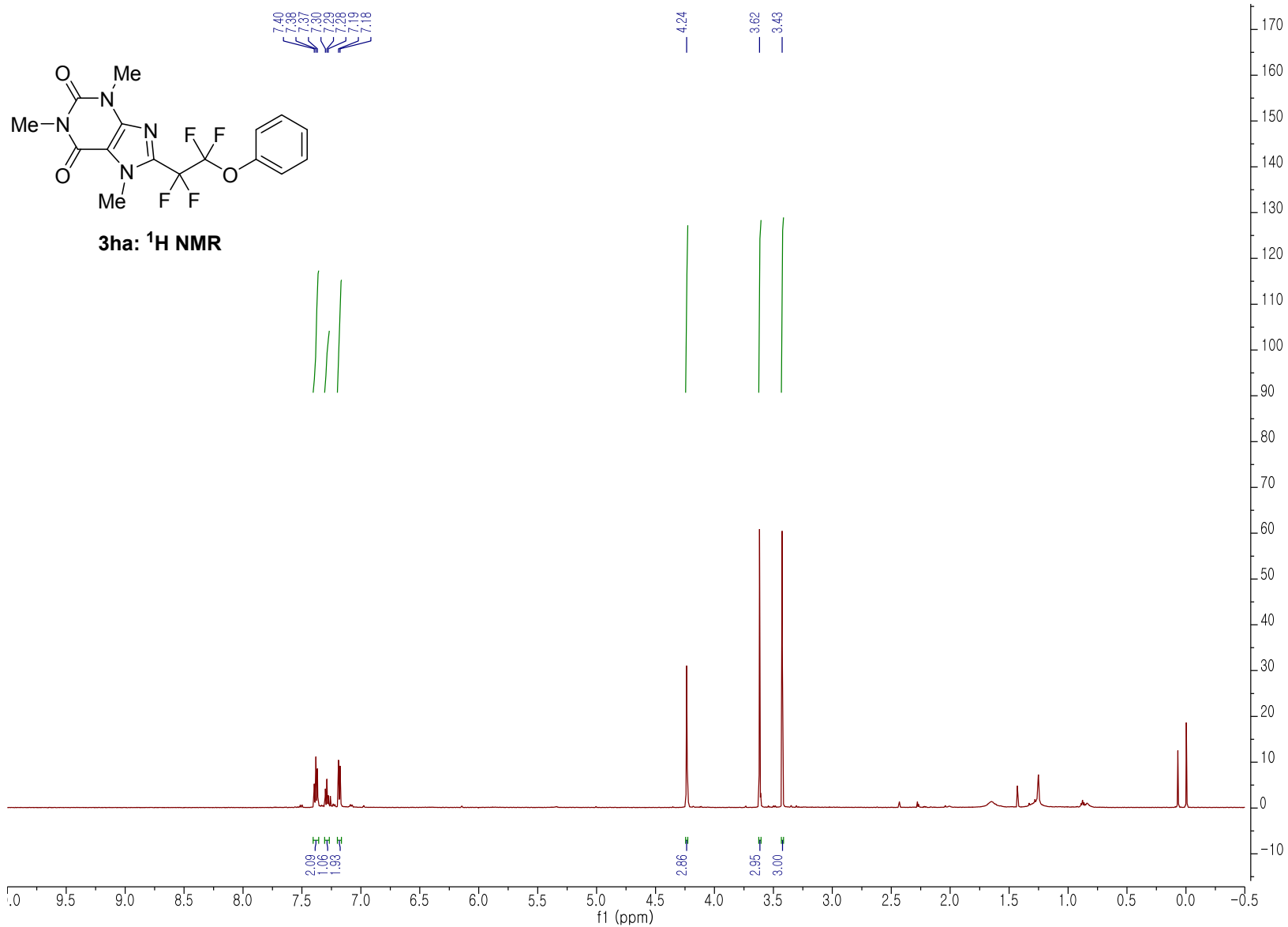


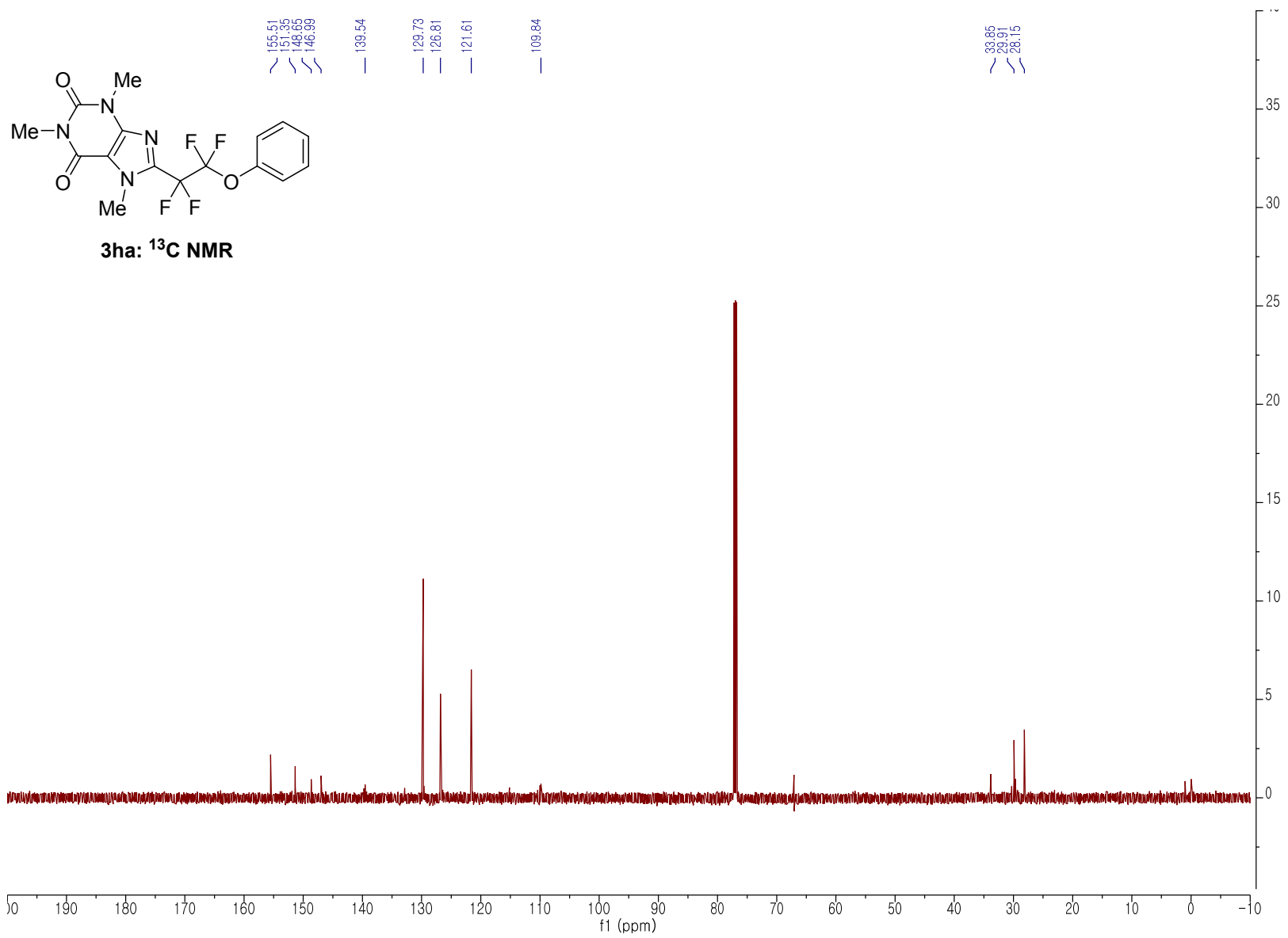
3fa: ^{13}C NMR

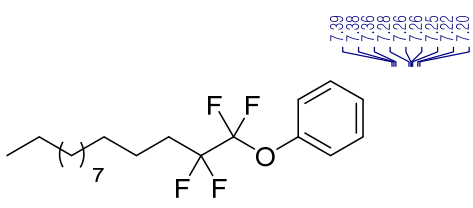




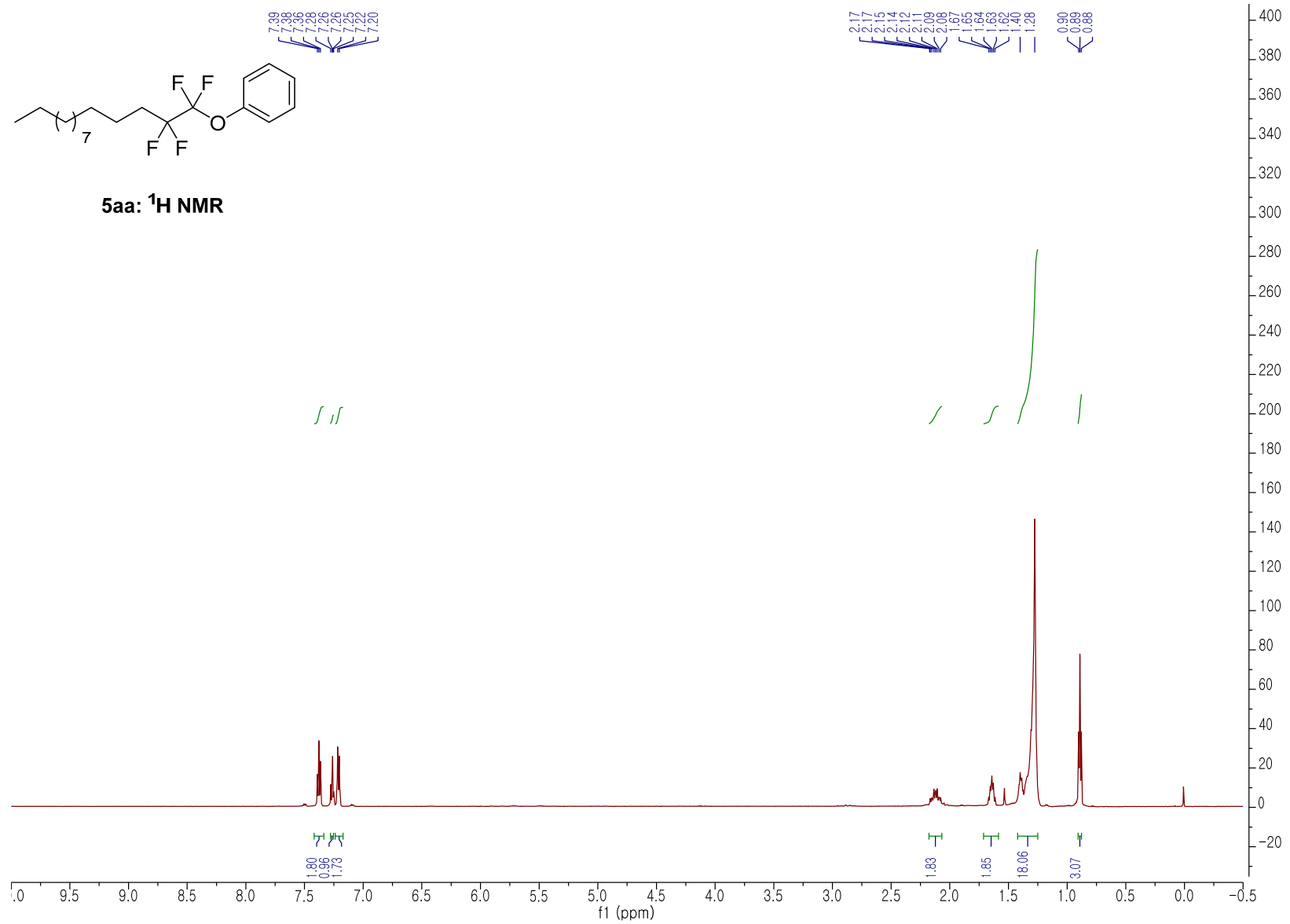


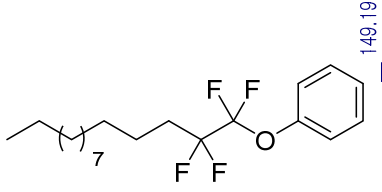




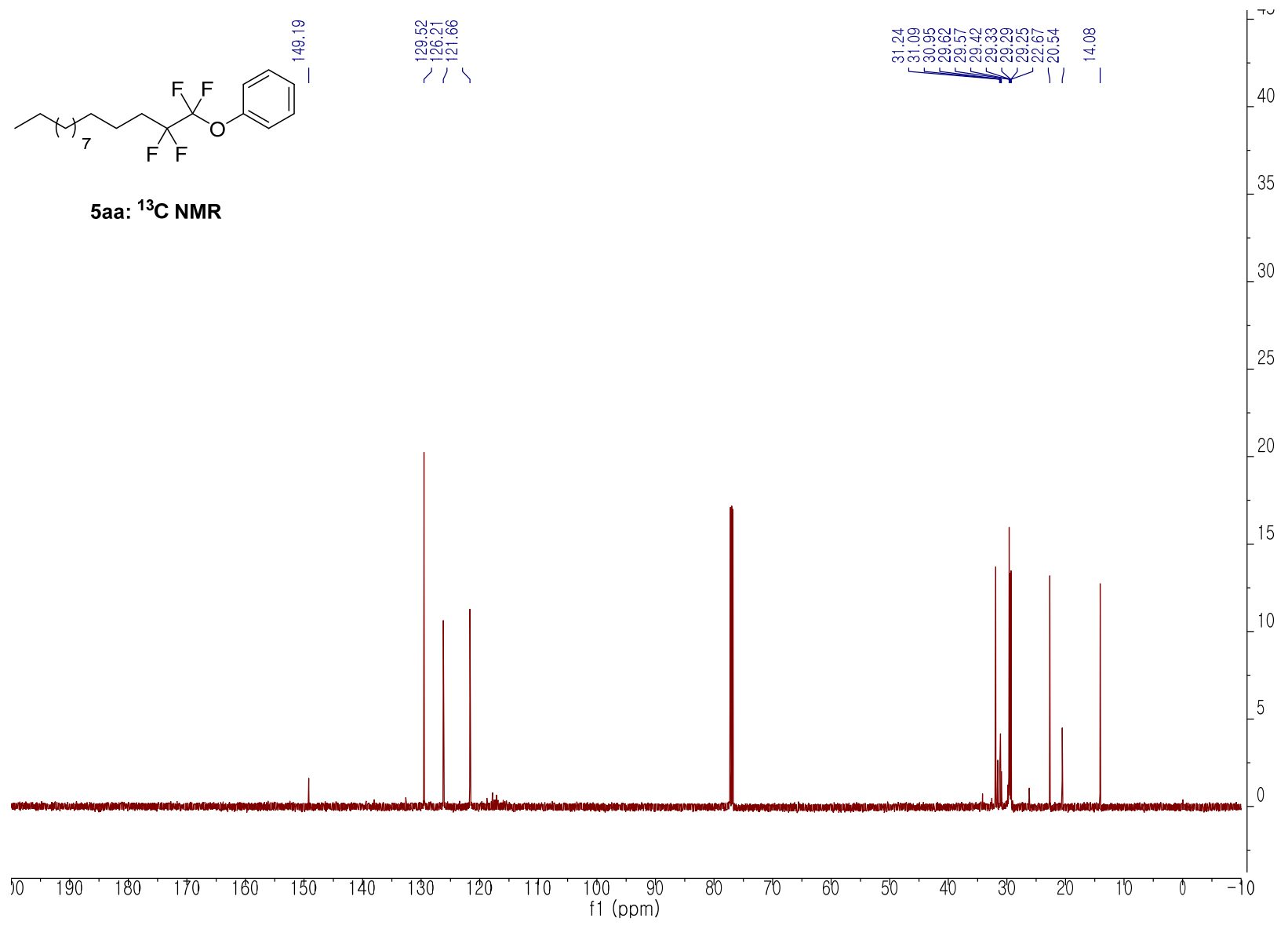


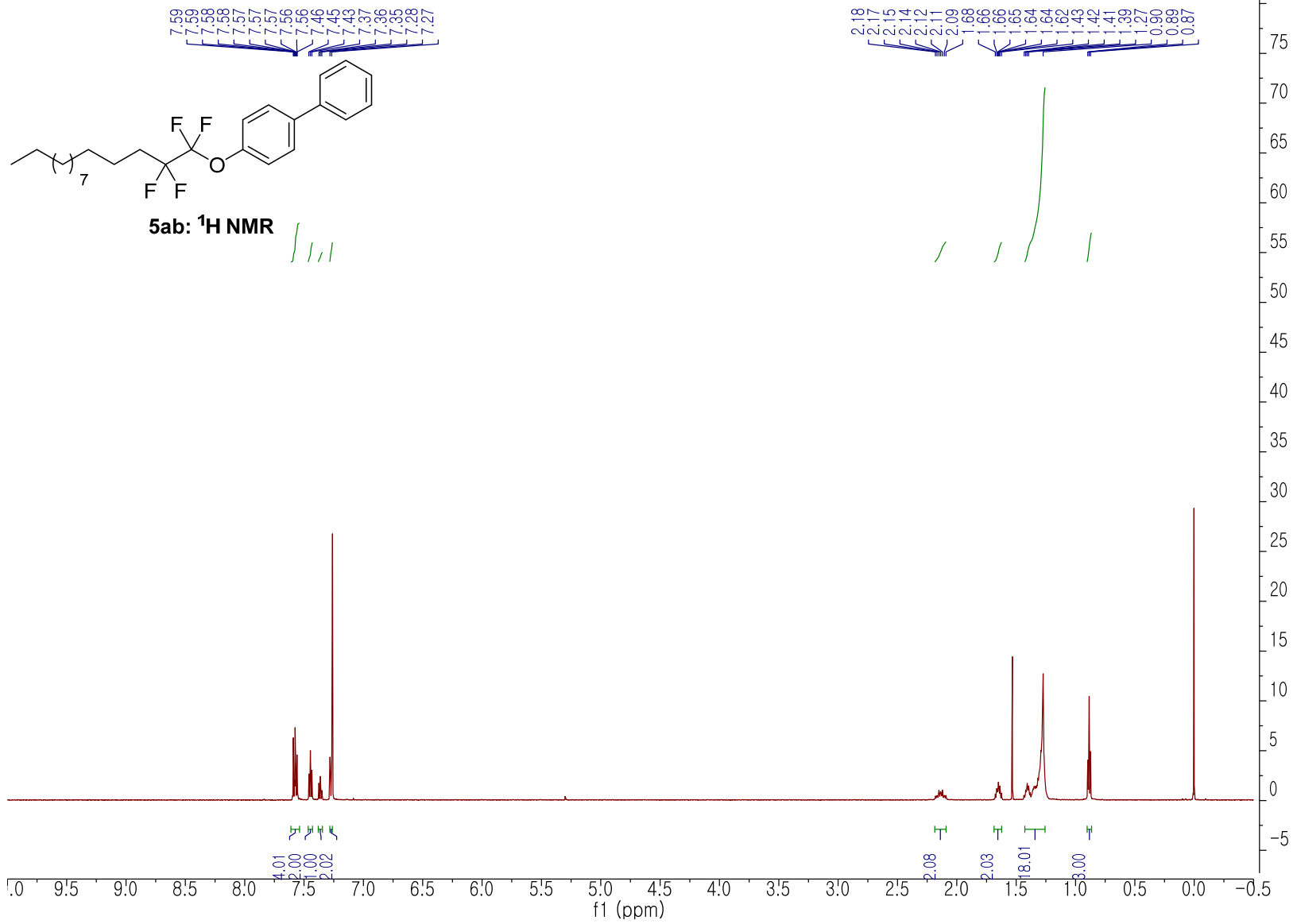
5aa: ¹H NMR

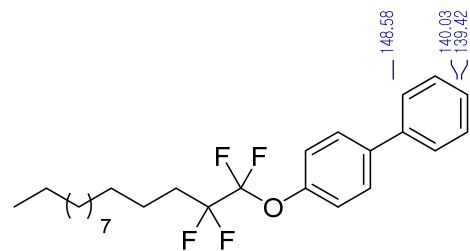




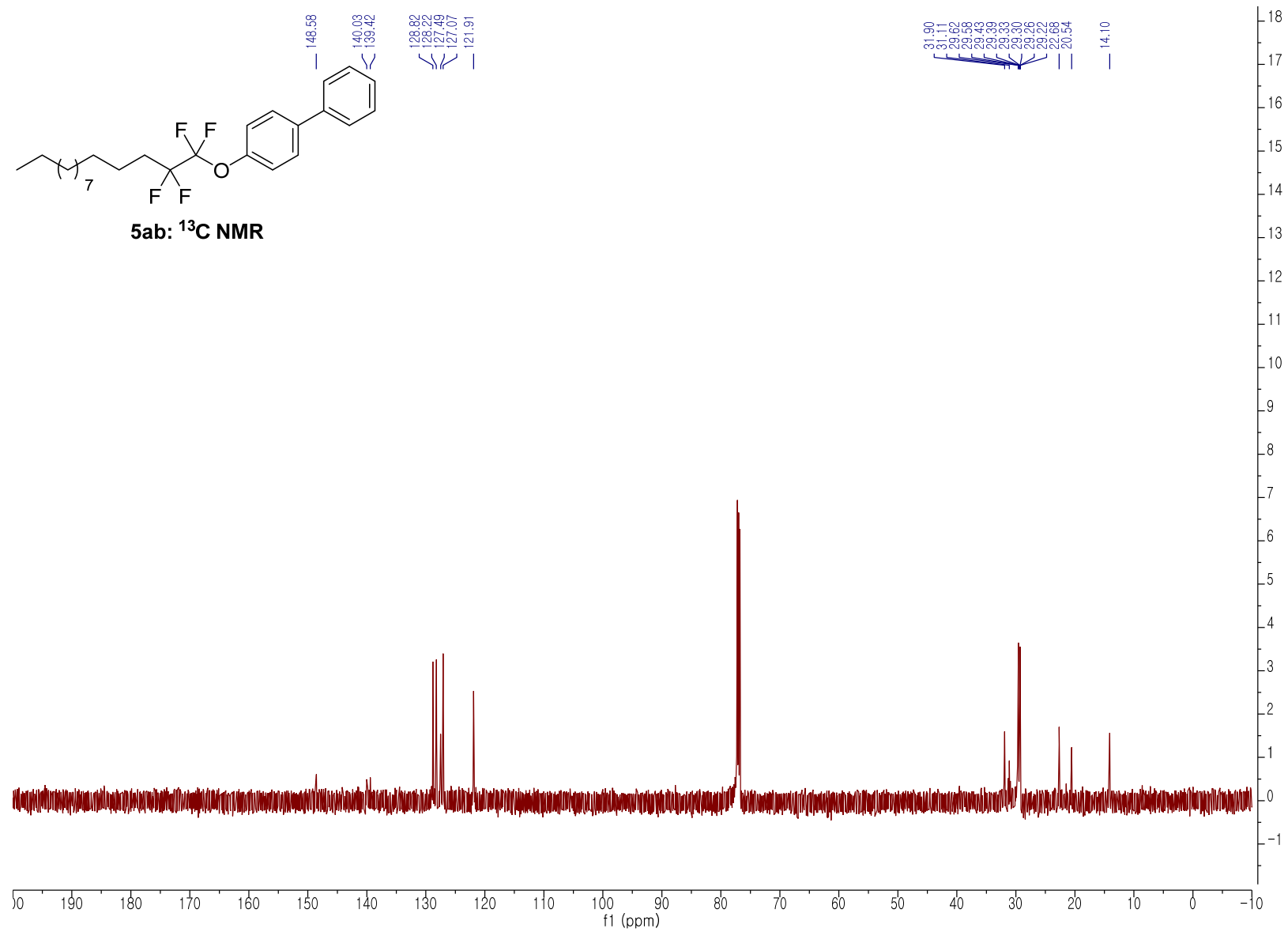
5aa: ¹³C NMR

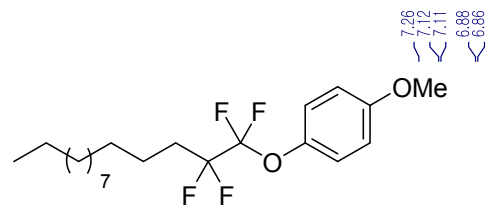




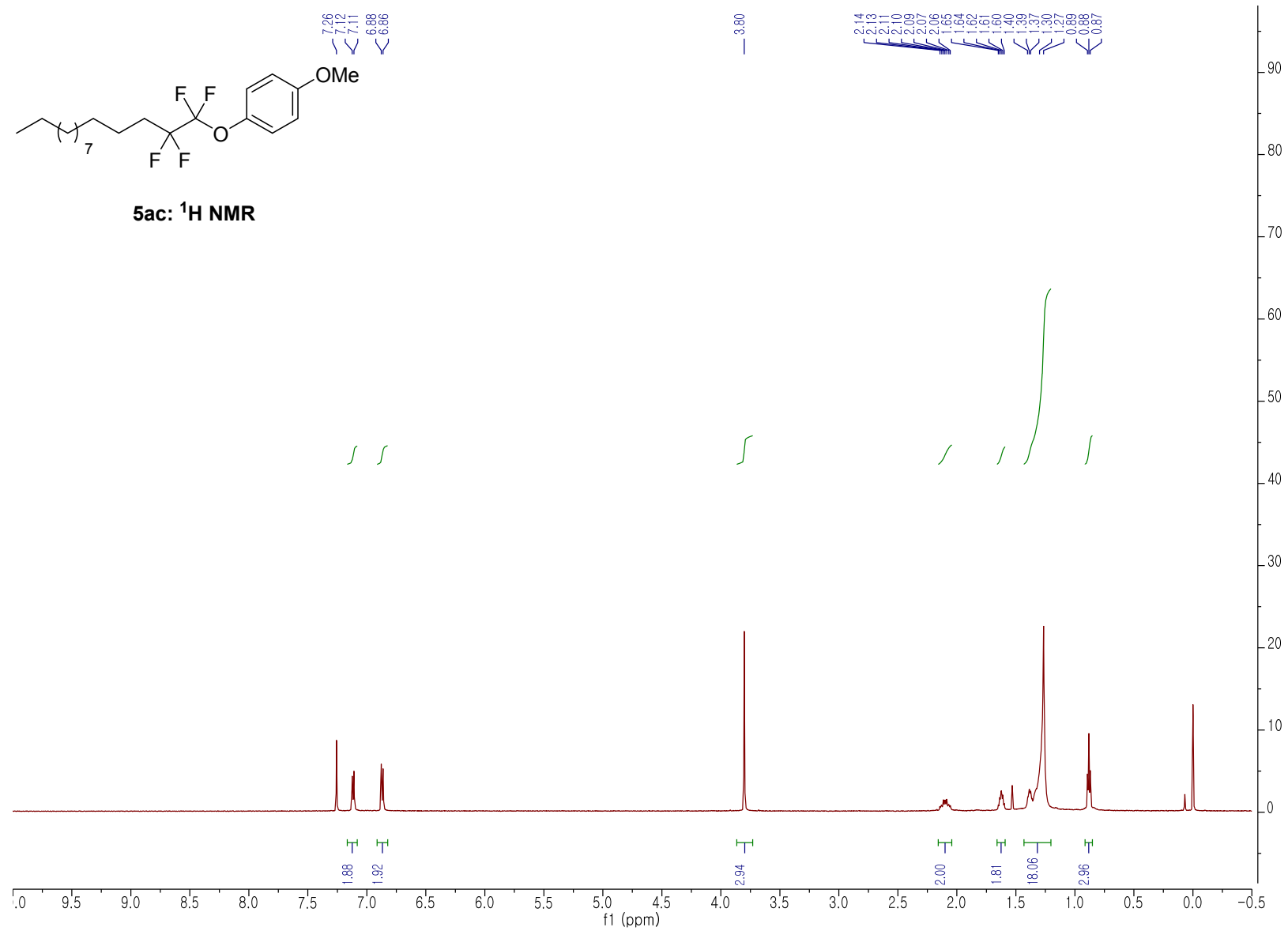


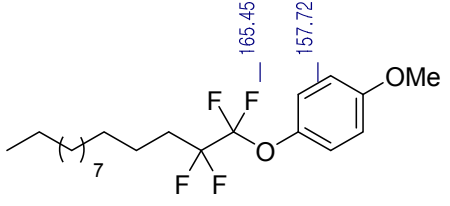
5ab: ^{13}C NMR



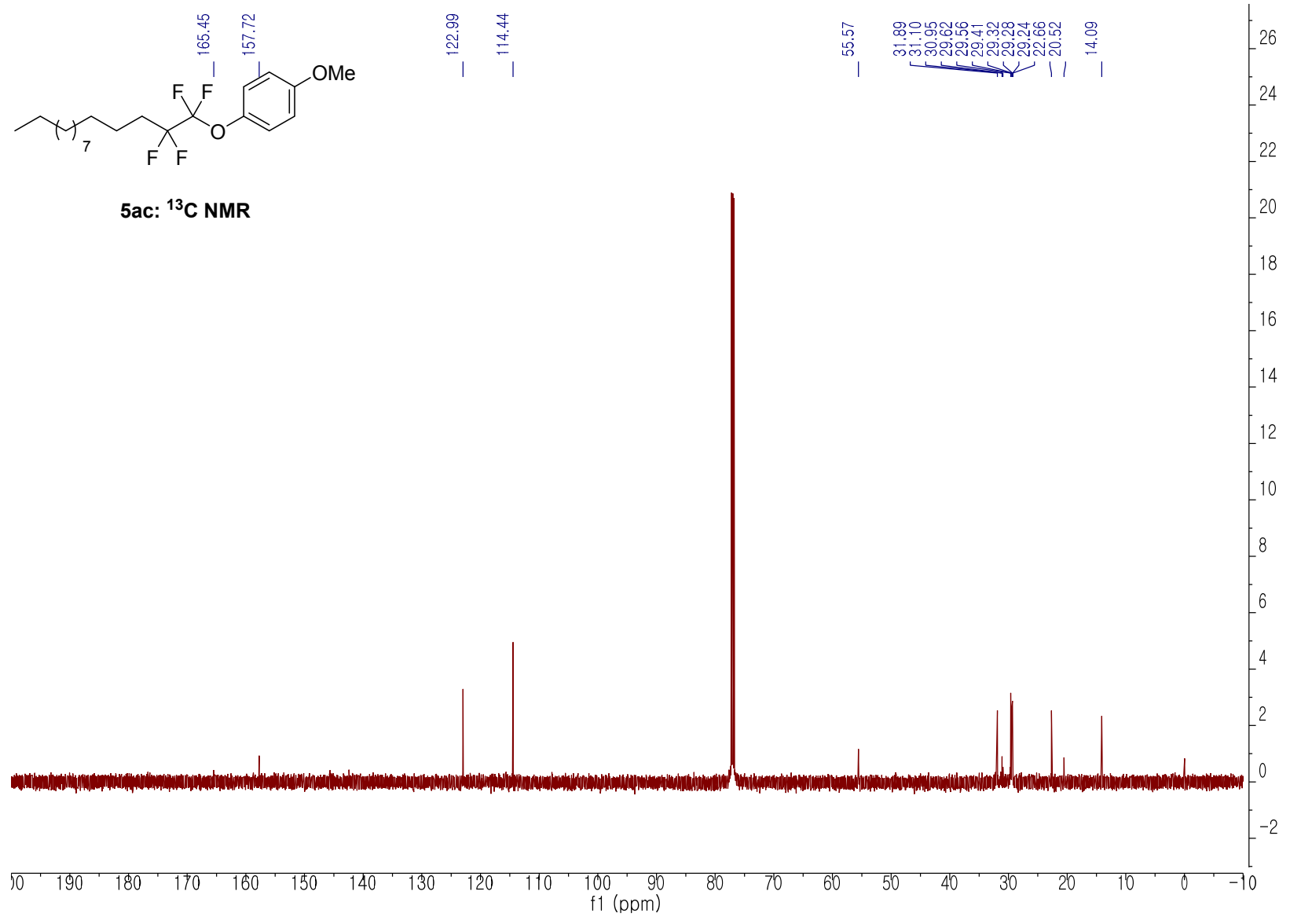


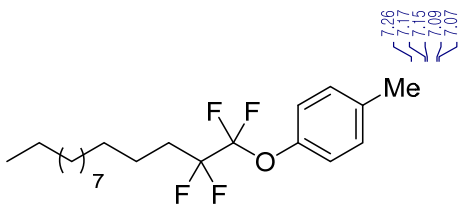
5ac: ¹H NMR



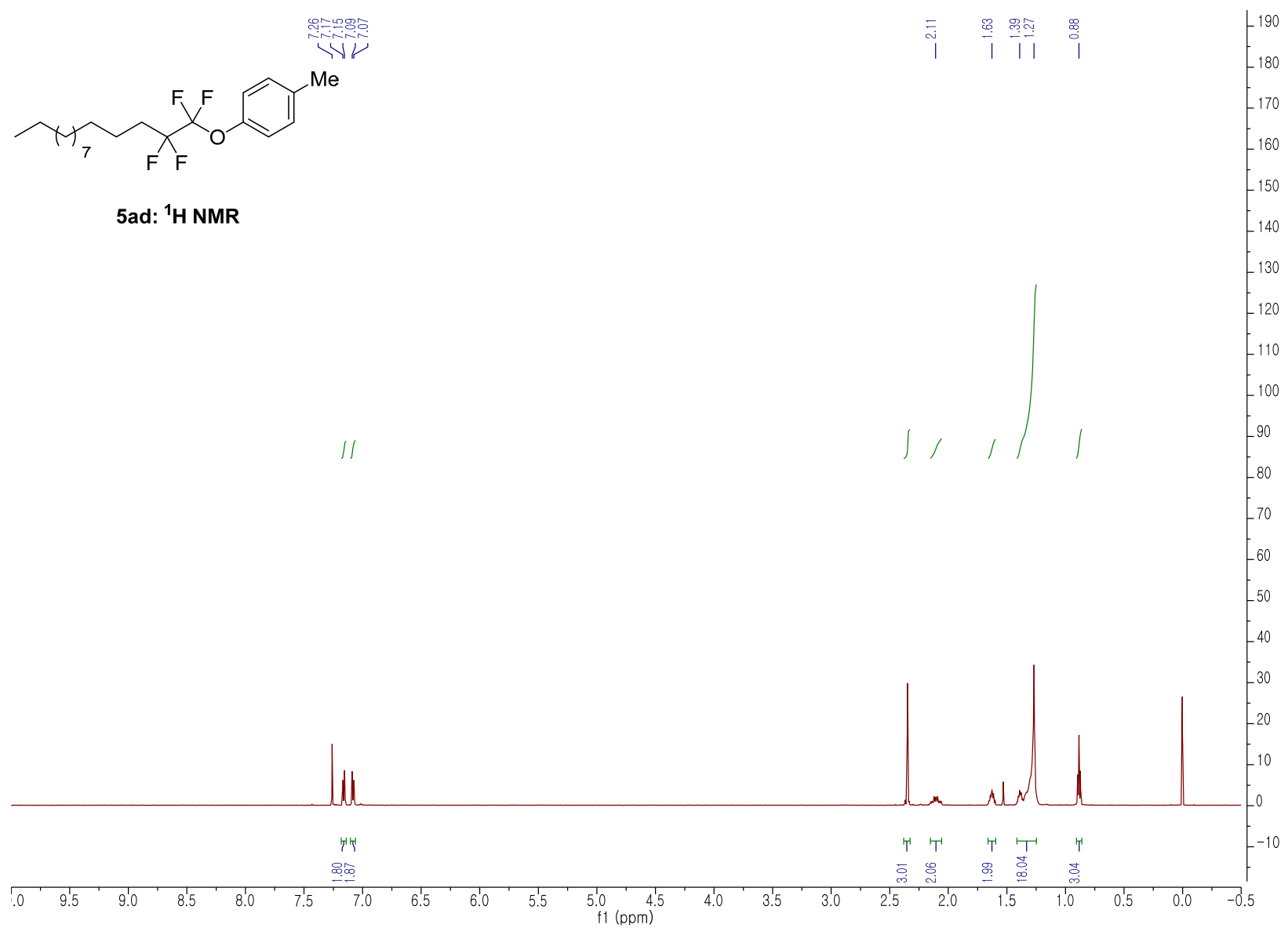


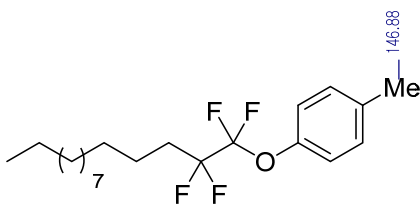
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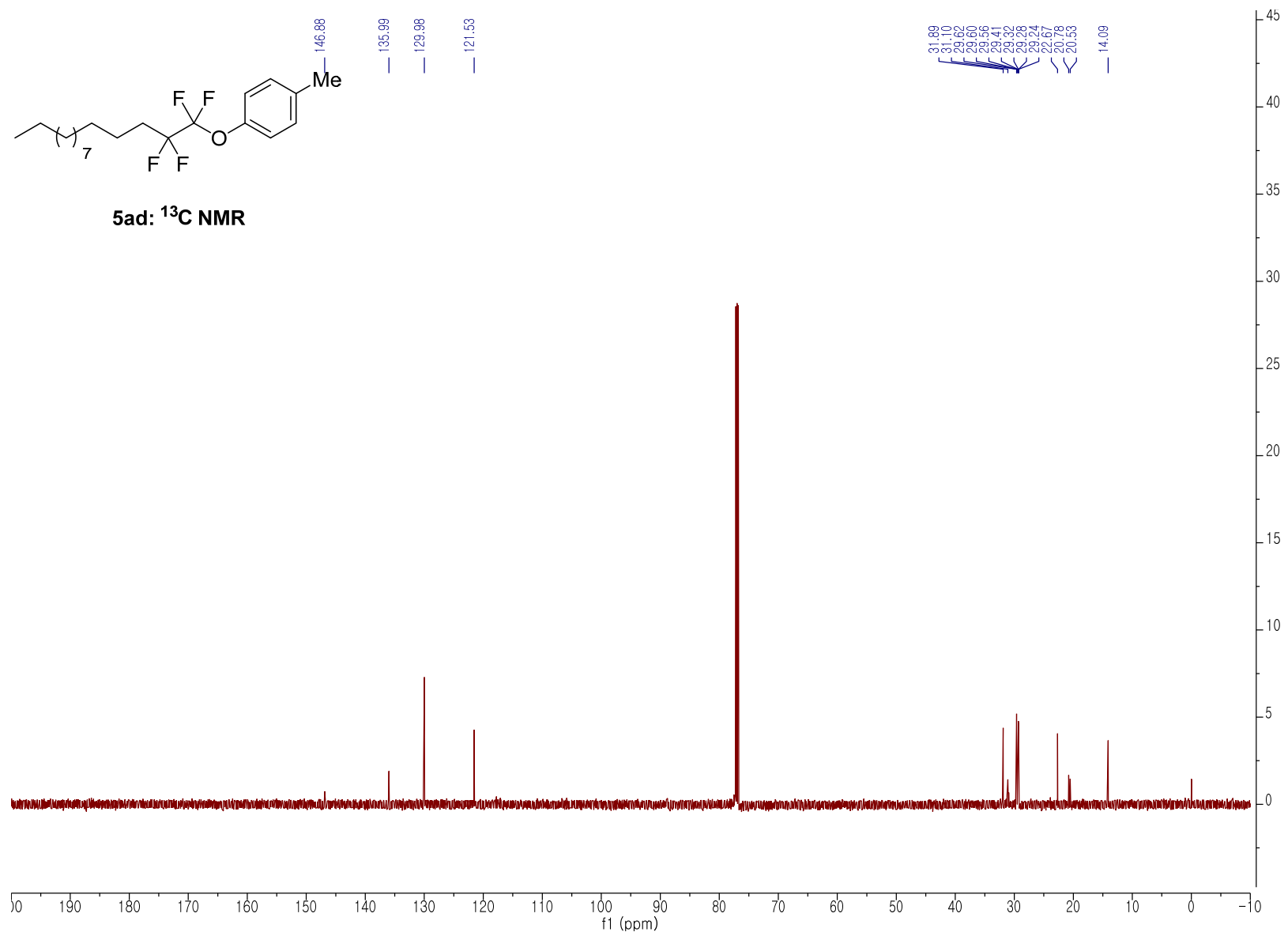


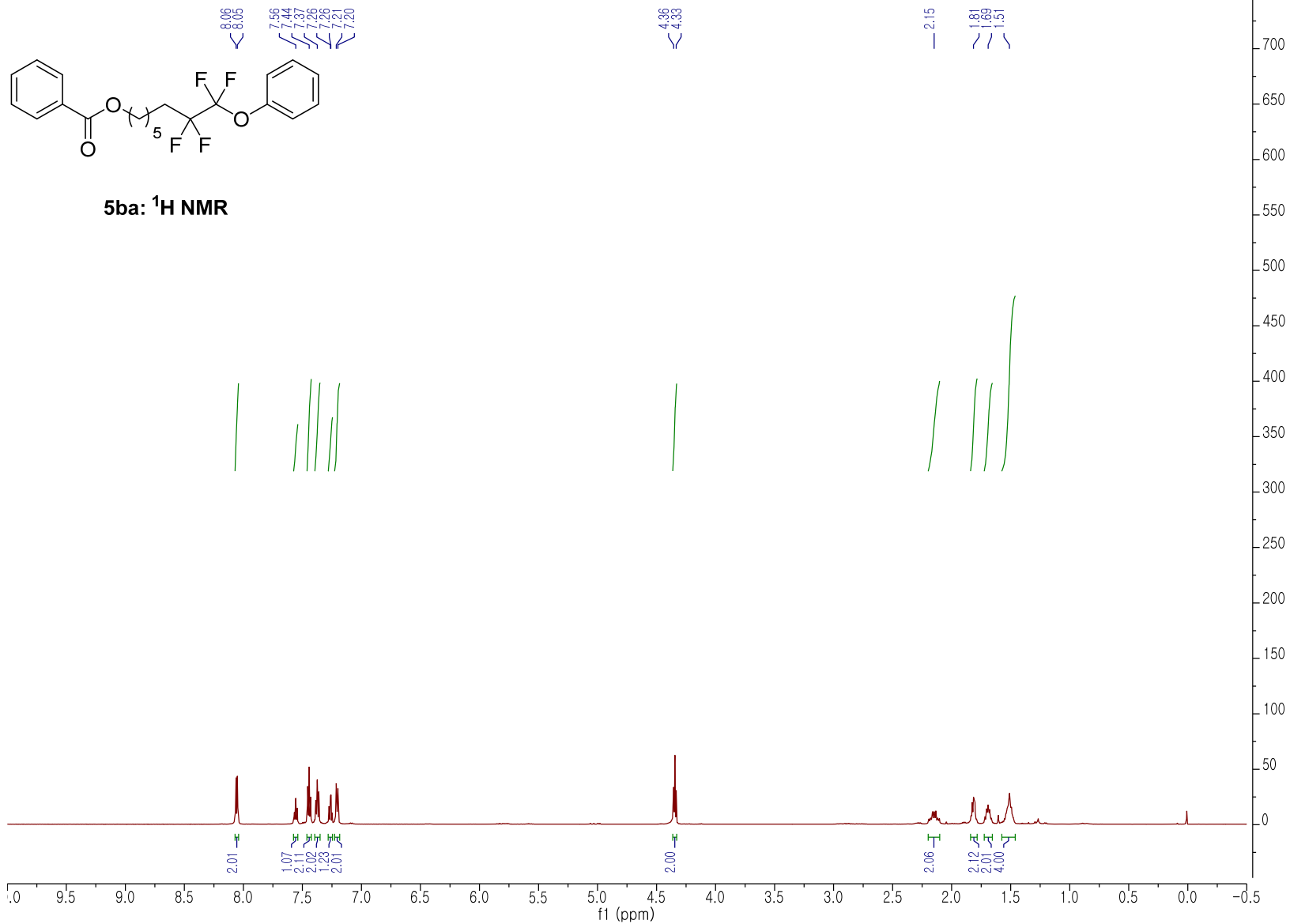
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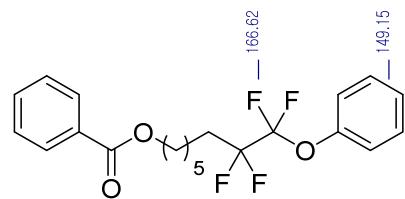




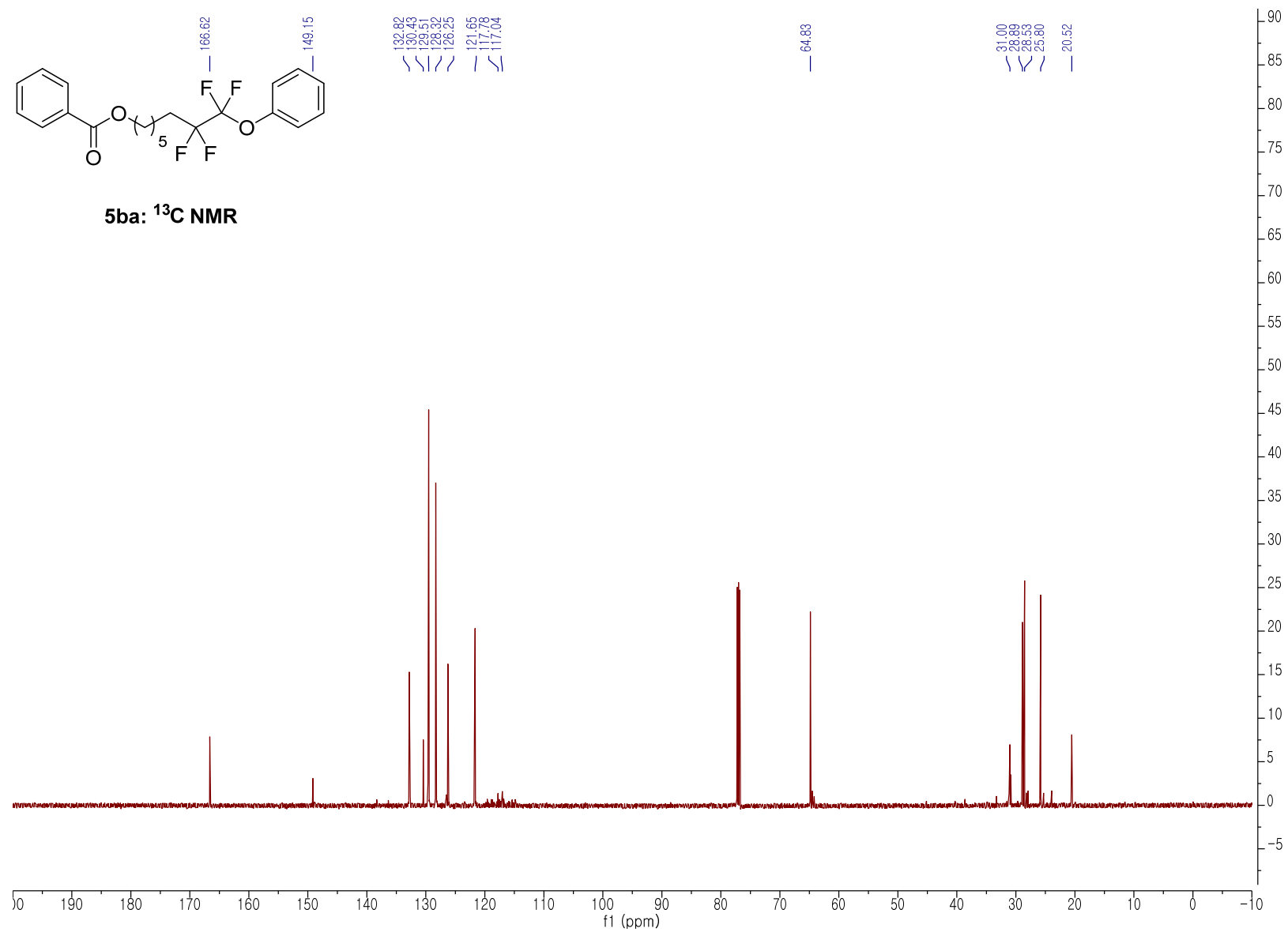
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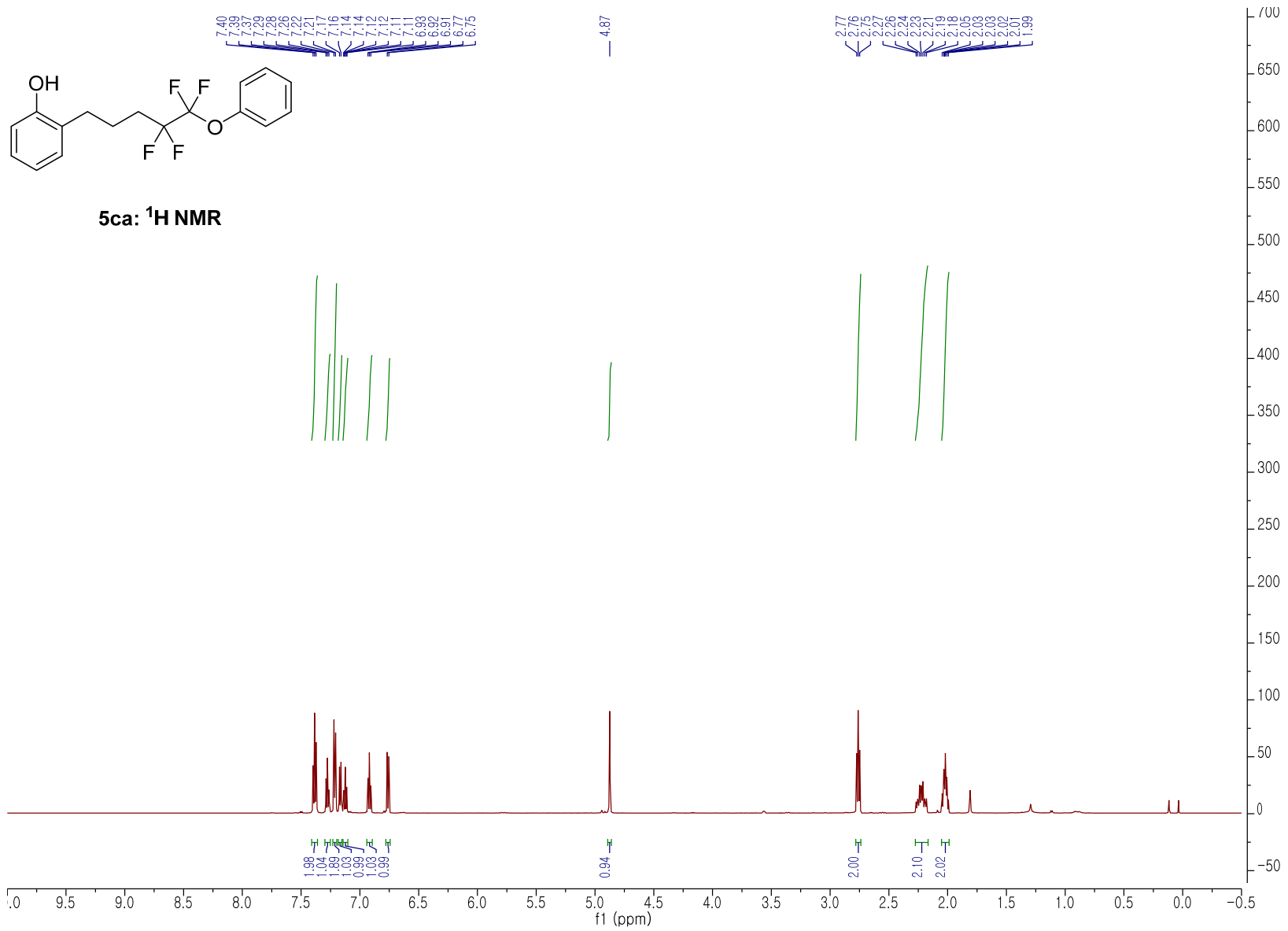


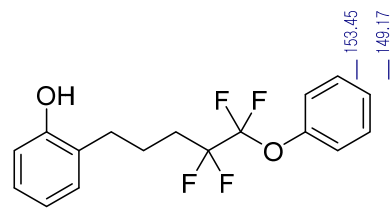




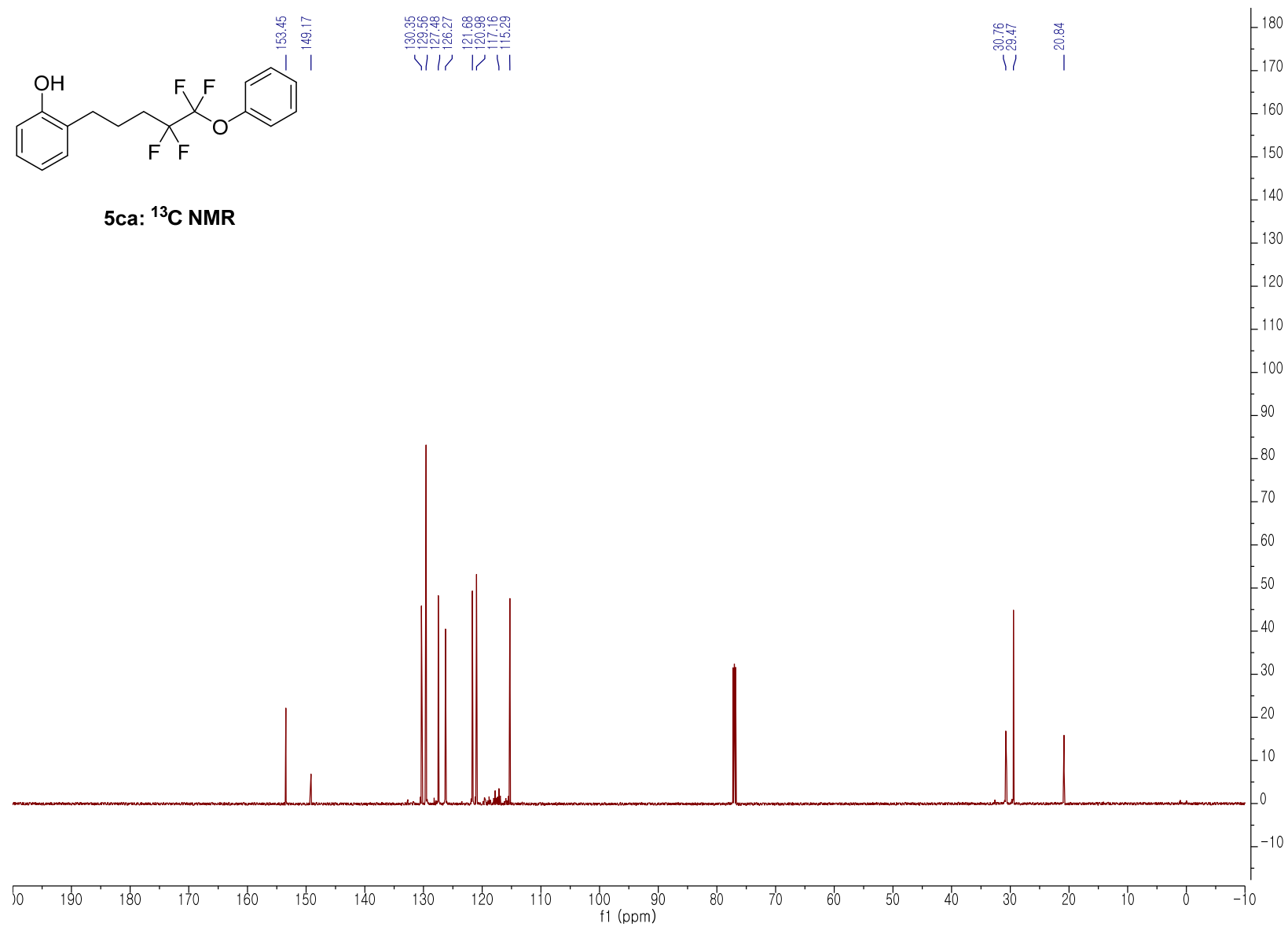
5ba: ^{13}C NMR

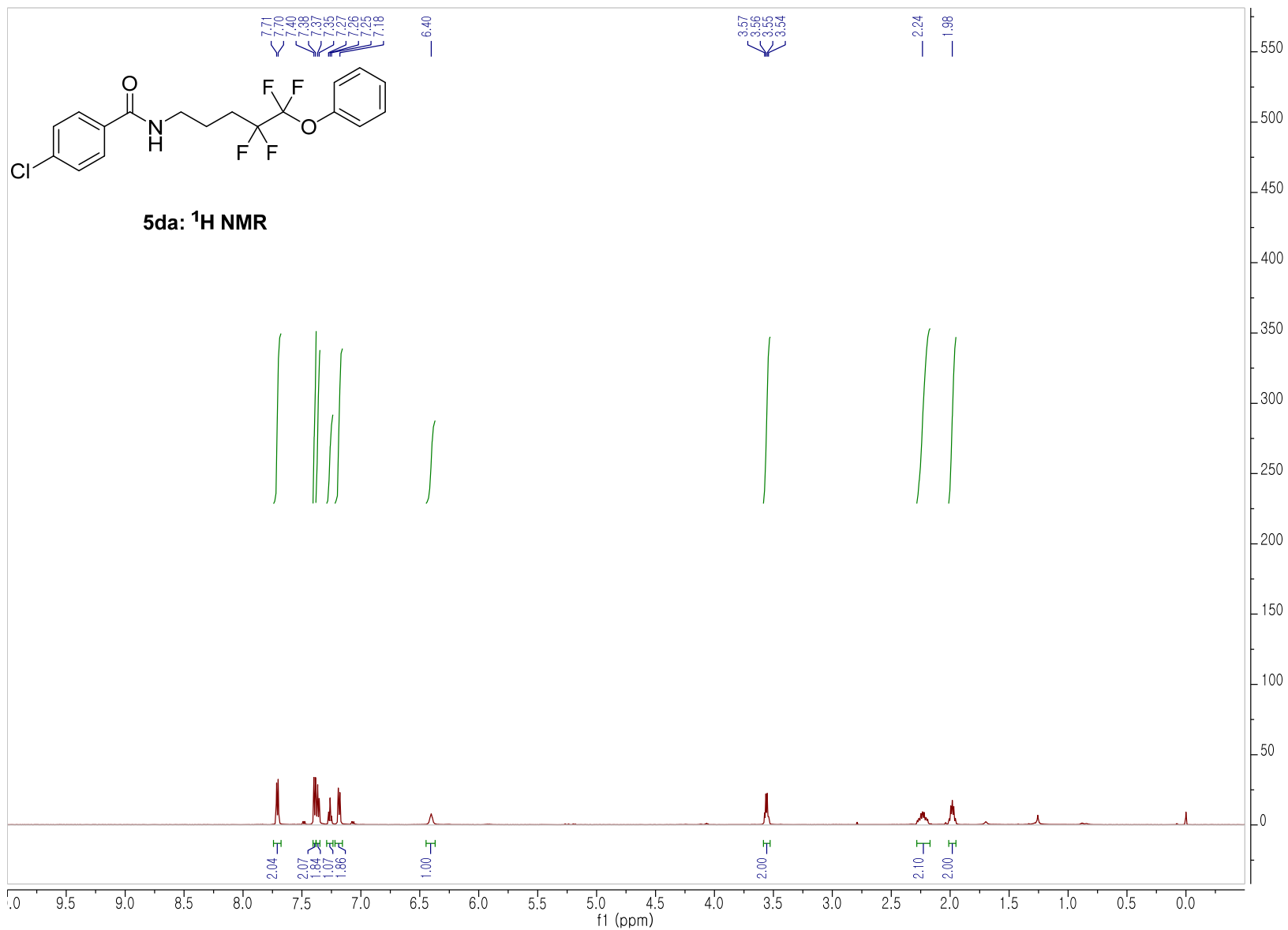


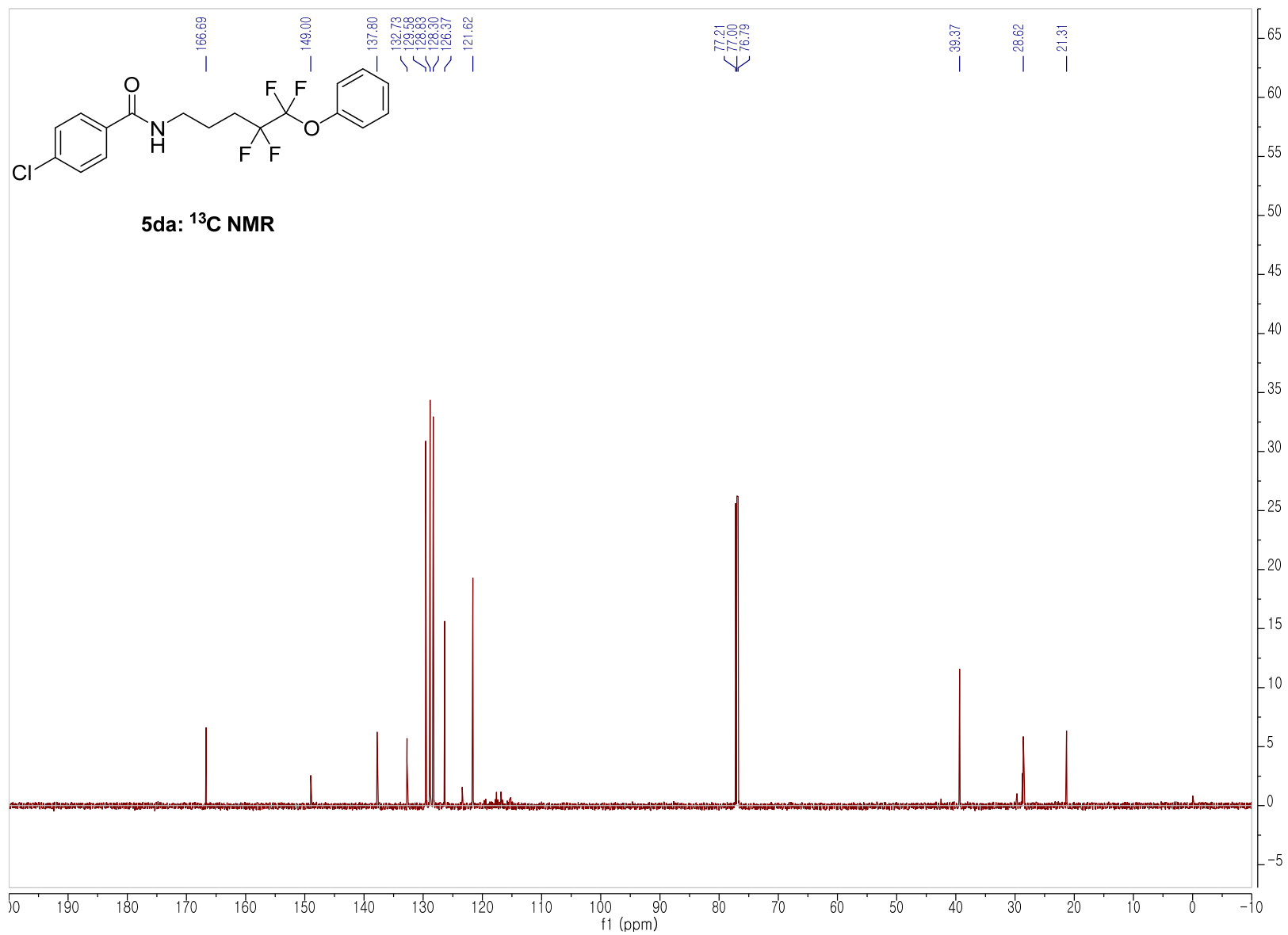


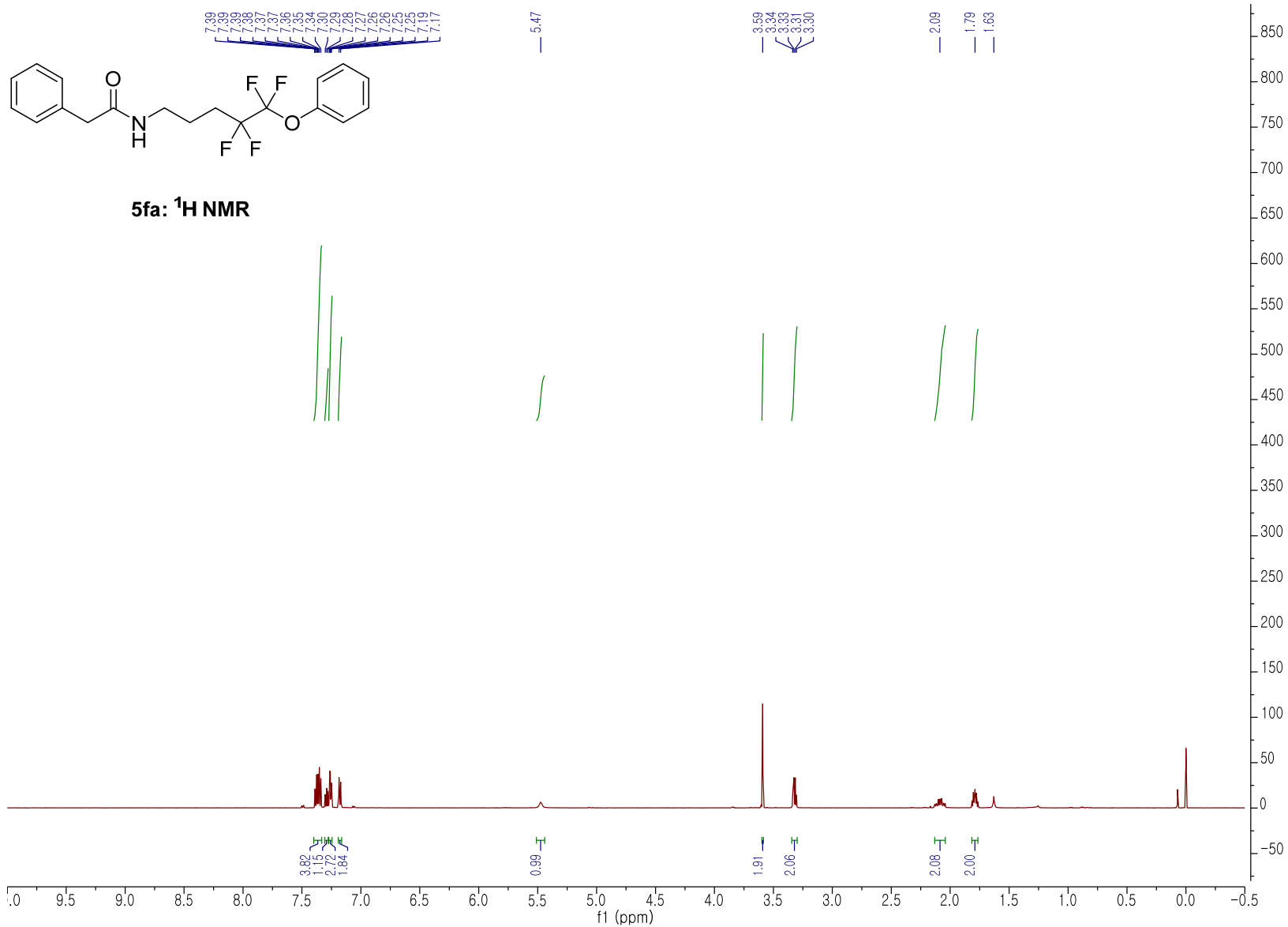


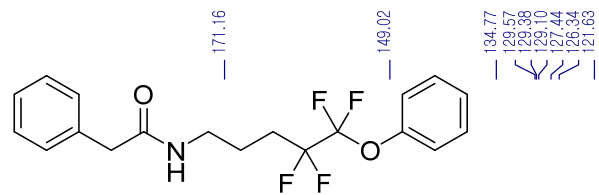
5ca: ^{13}C NMR



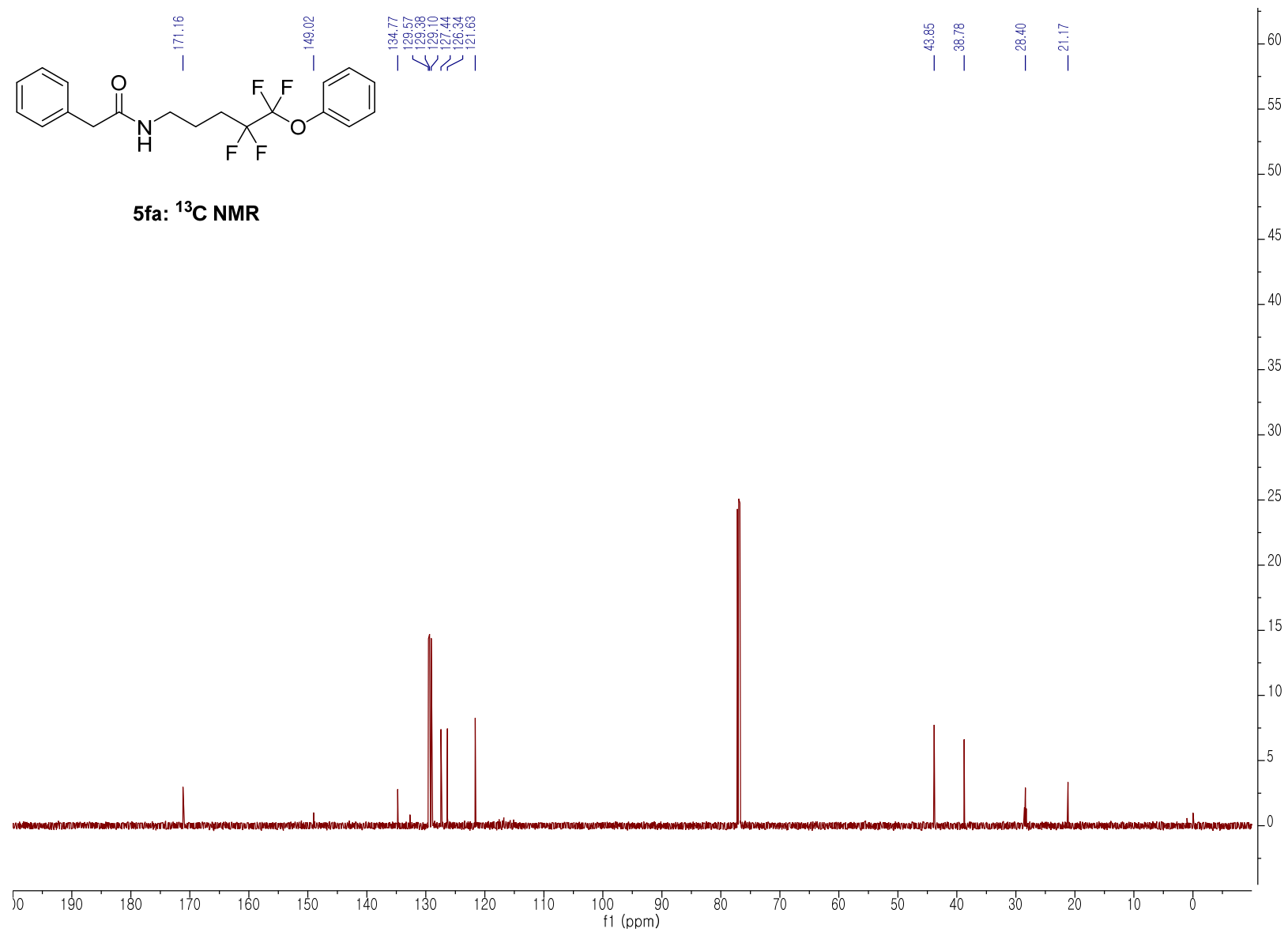


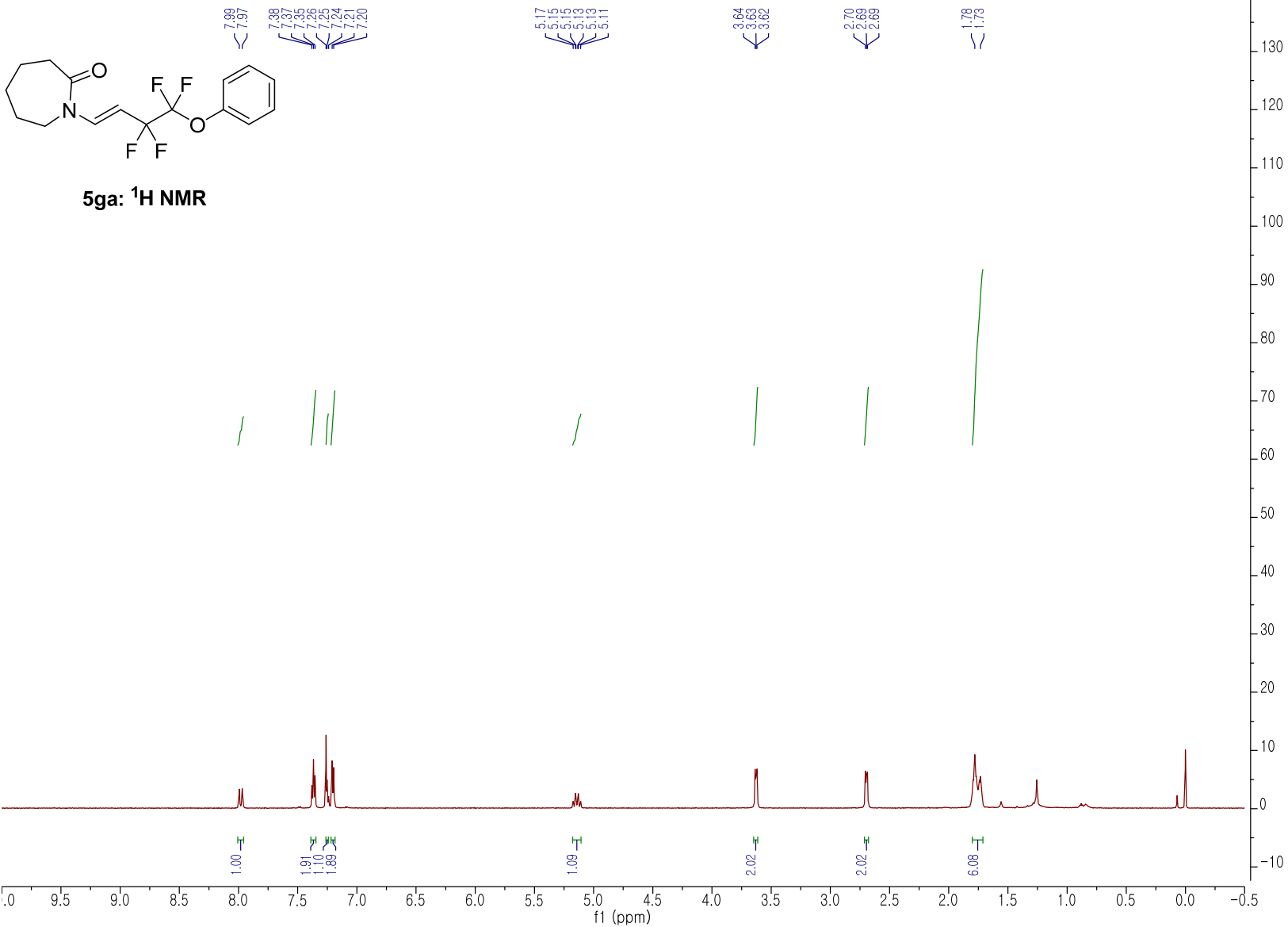


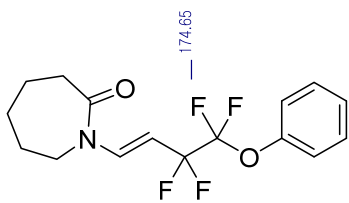




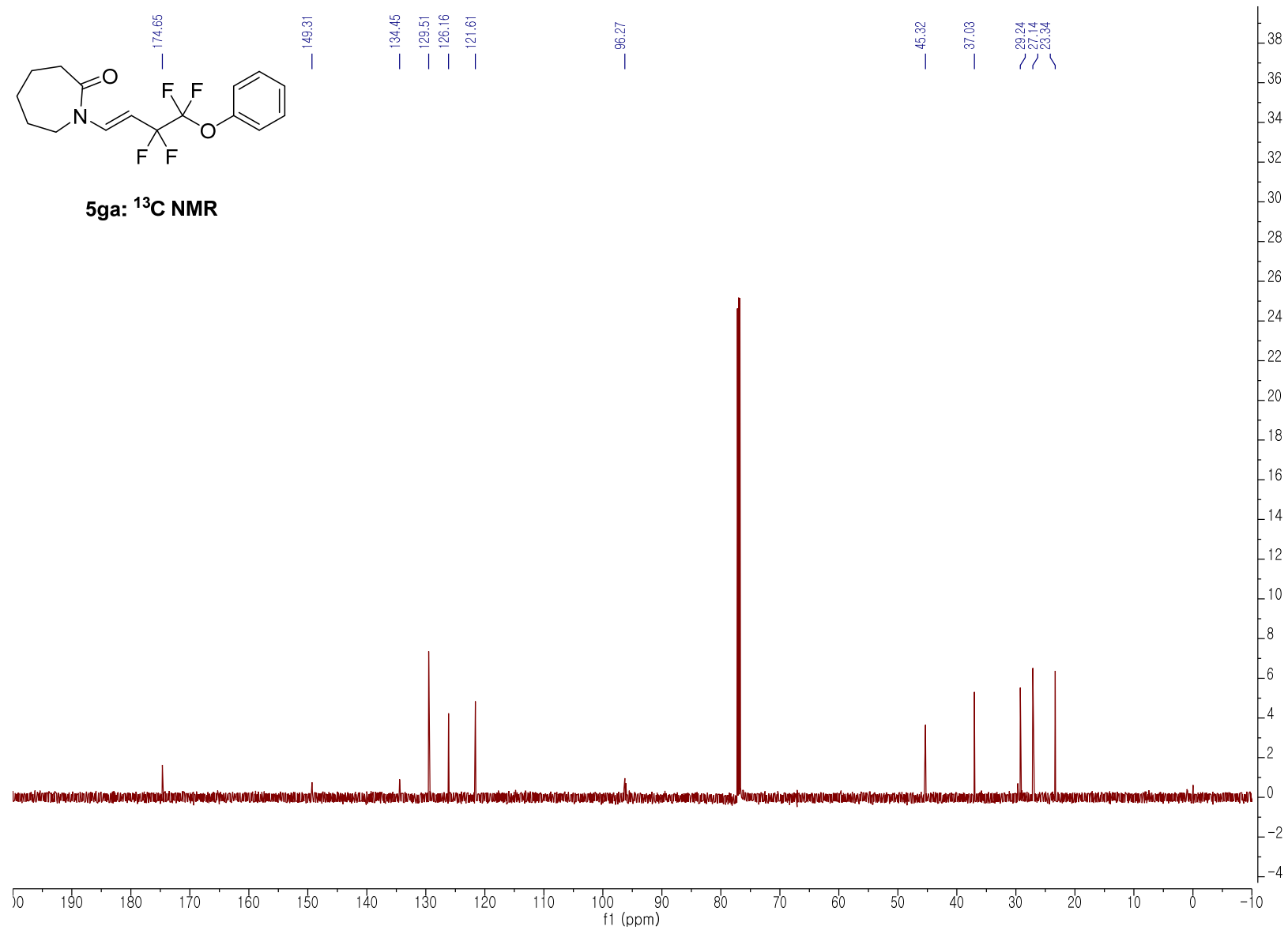
5fa: ¹³C NMR

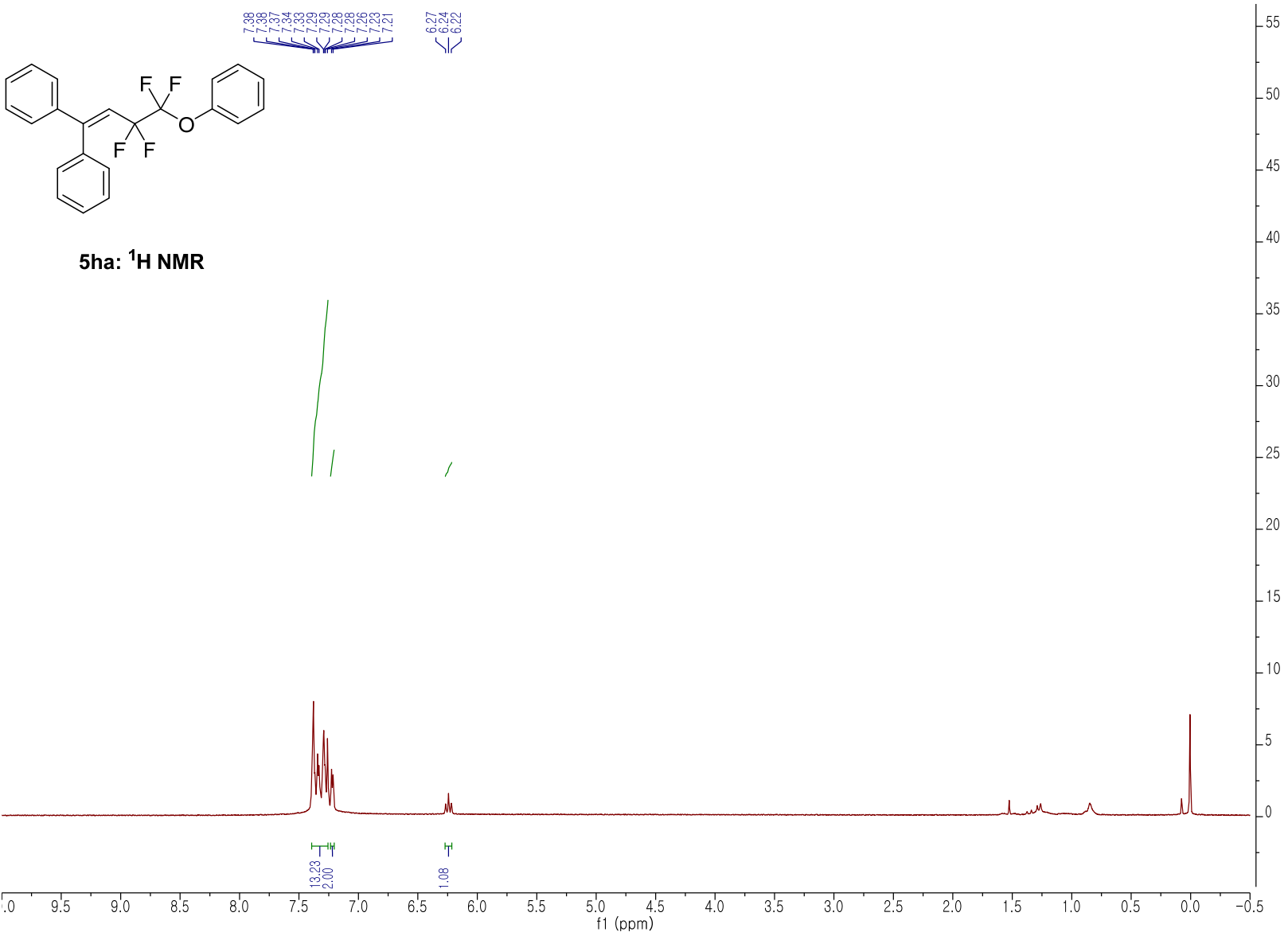


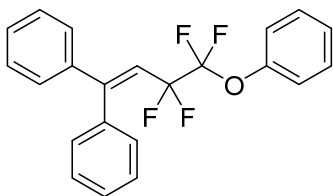




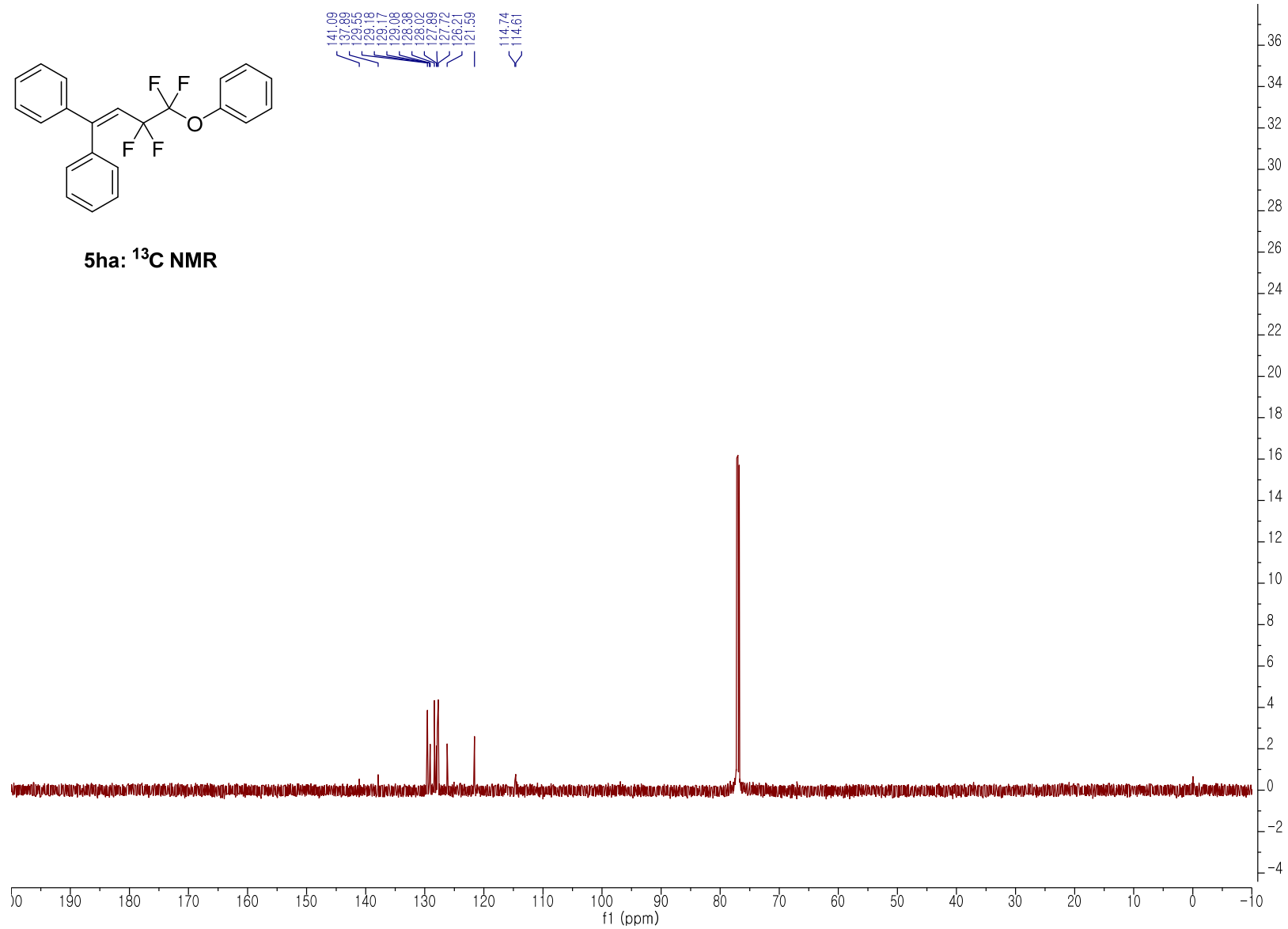
5ga: ^{13}C NMR

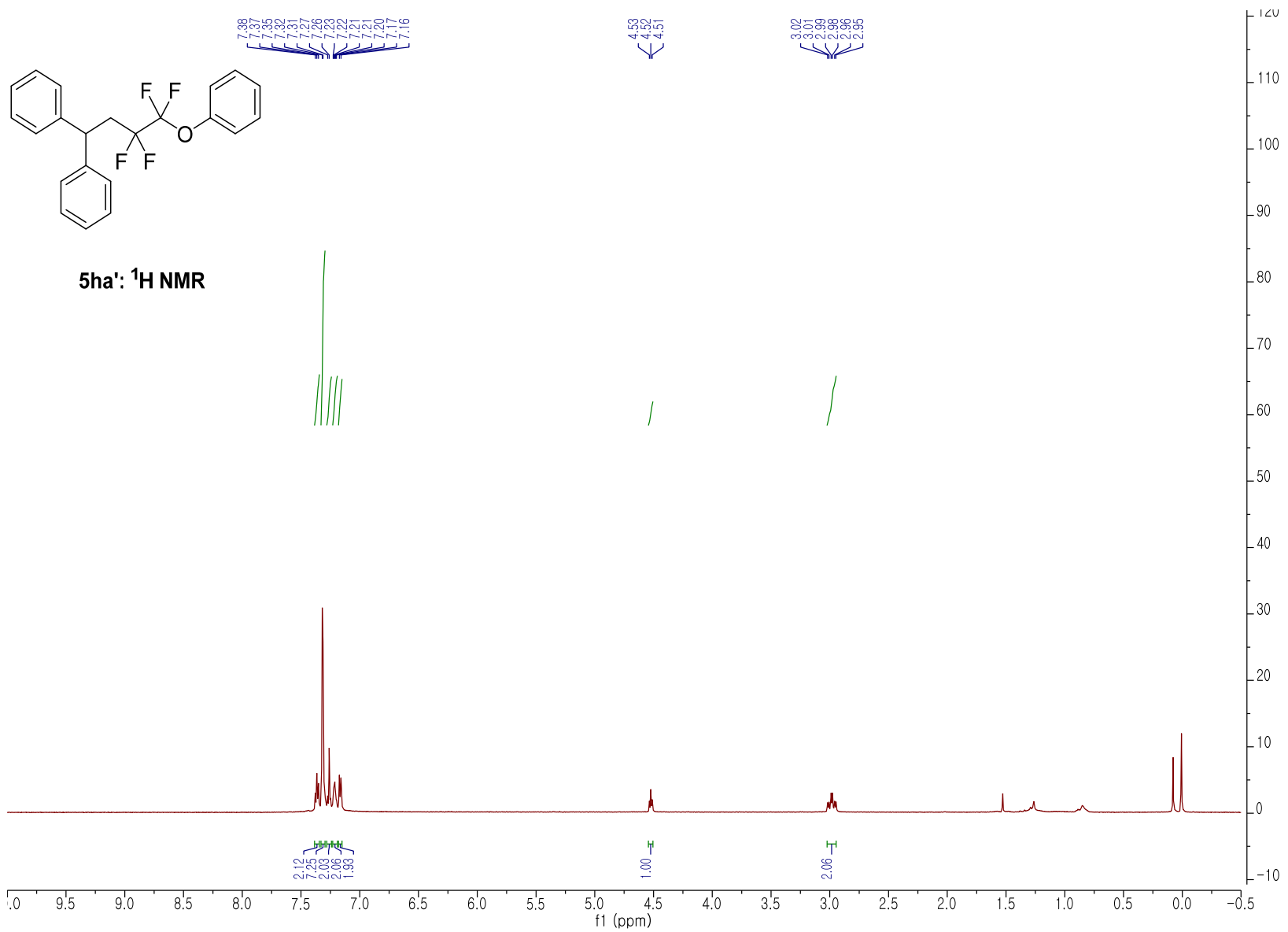




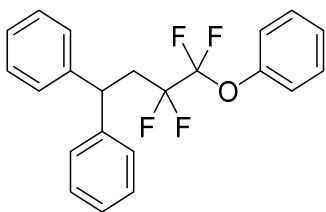


5ha: ¹³C NMR

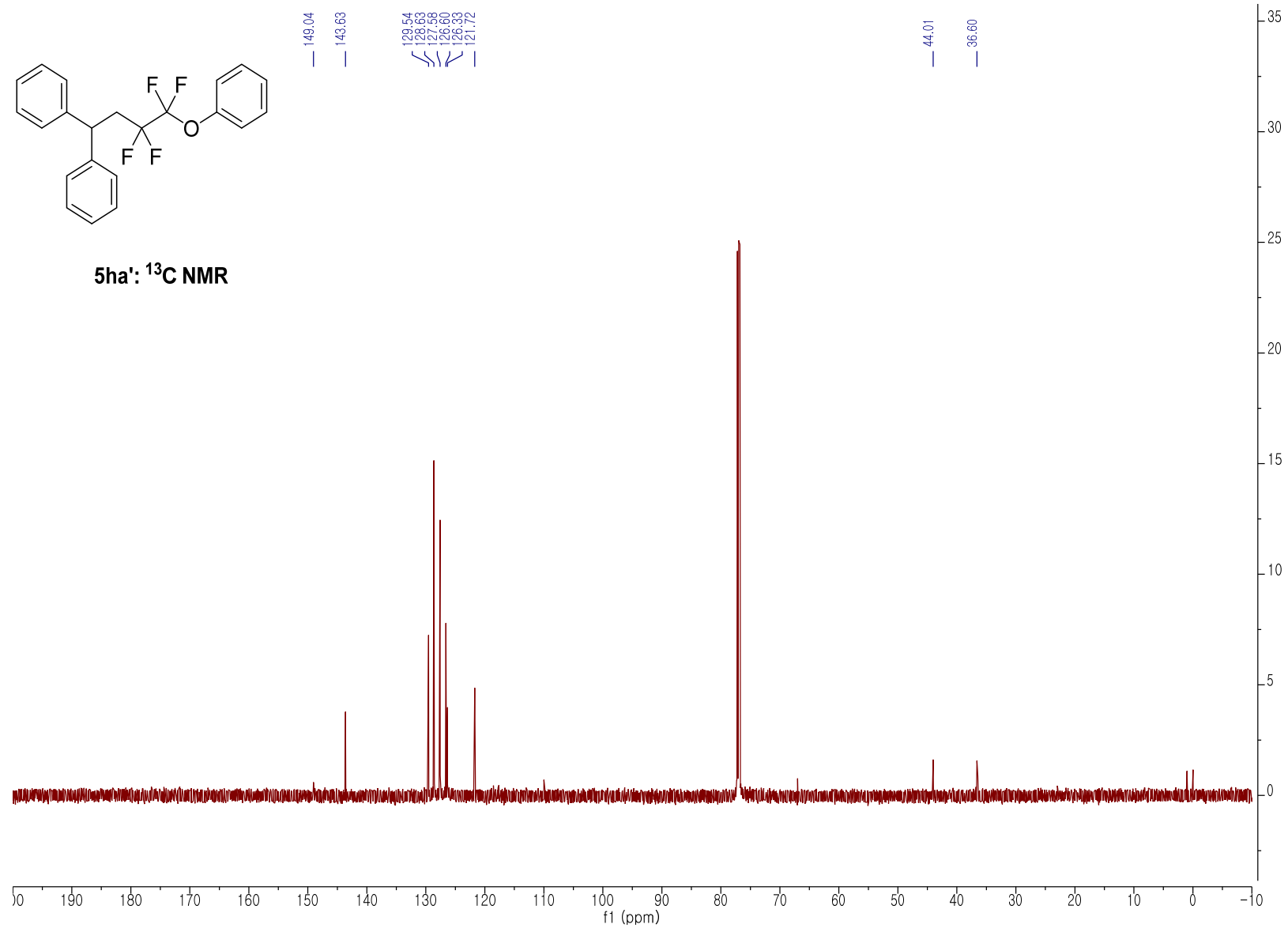


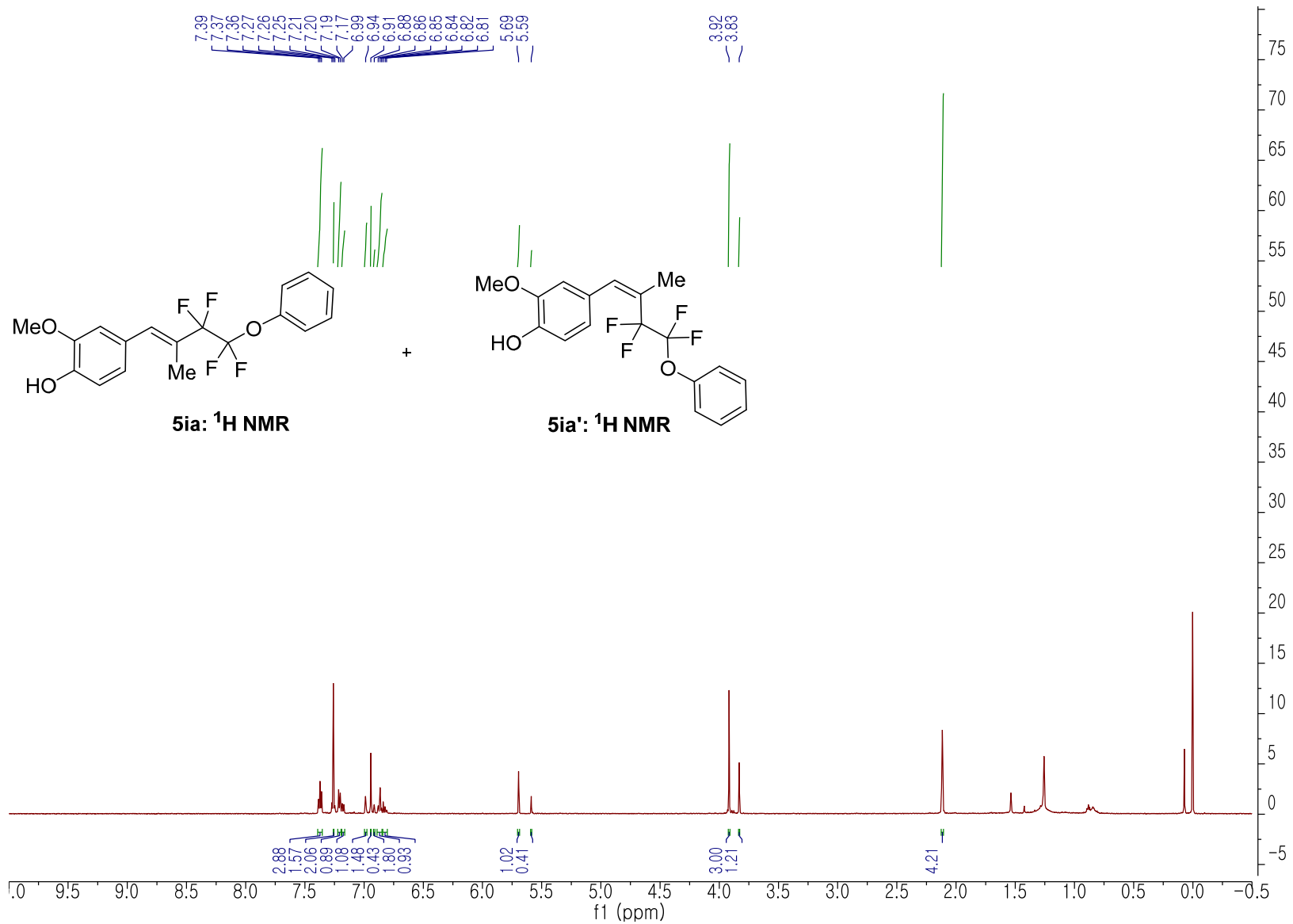


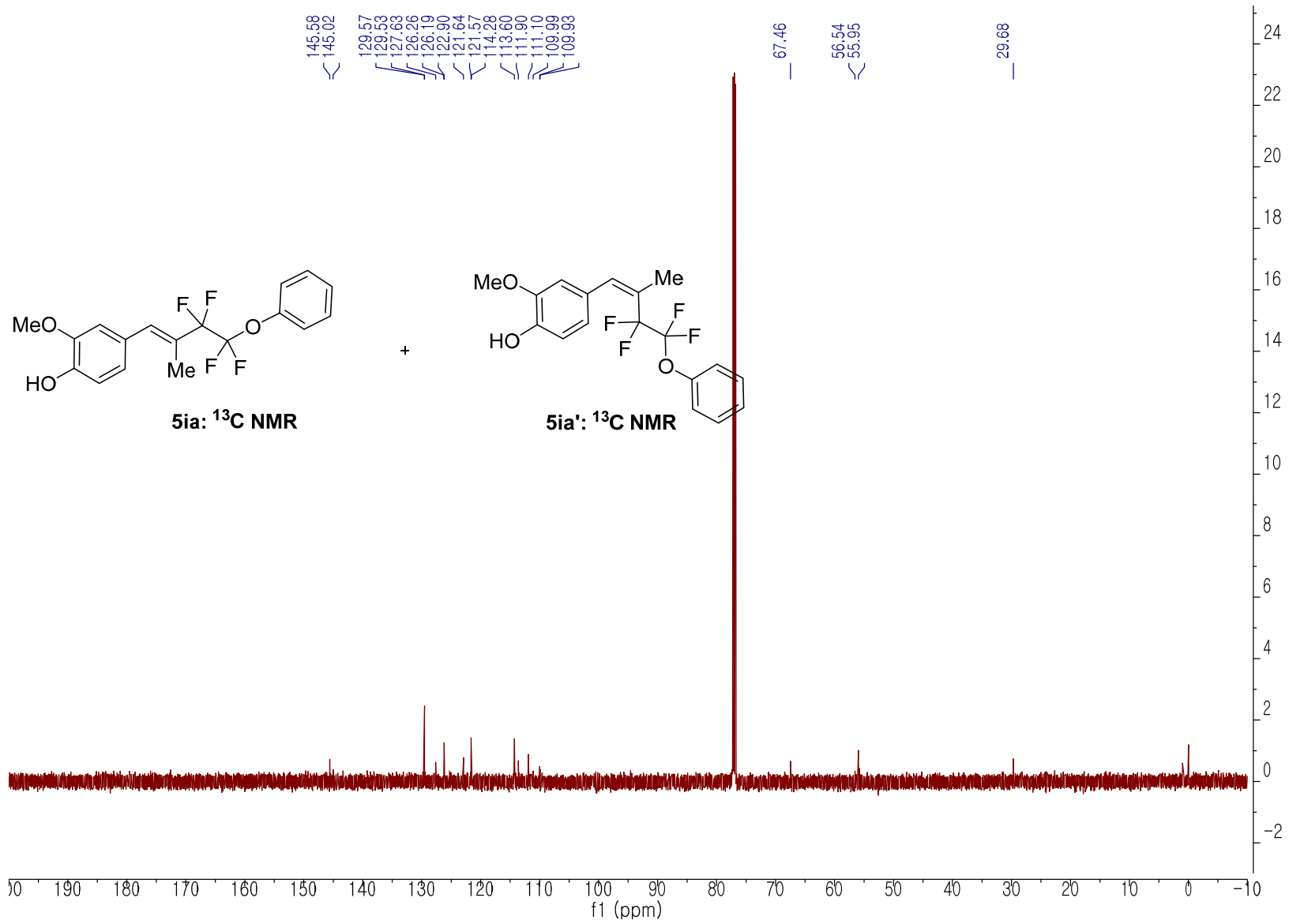
S-70

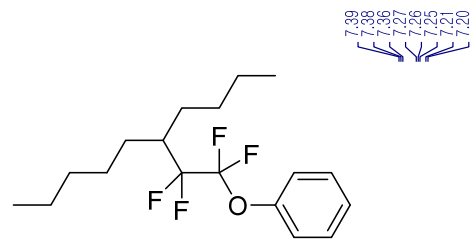


5ha: ¹³C NMR

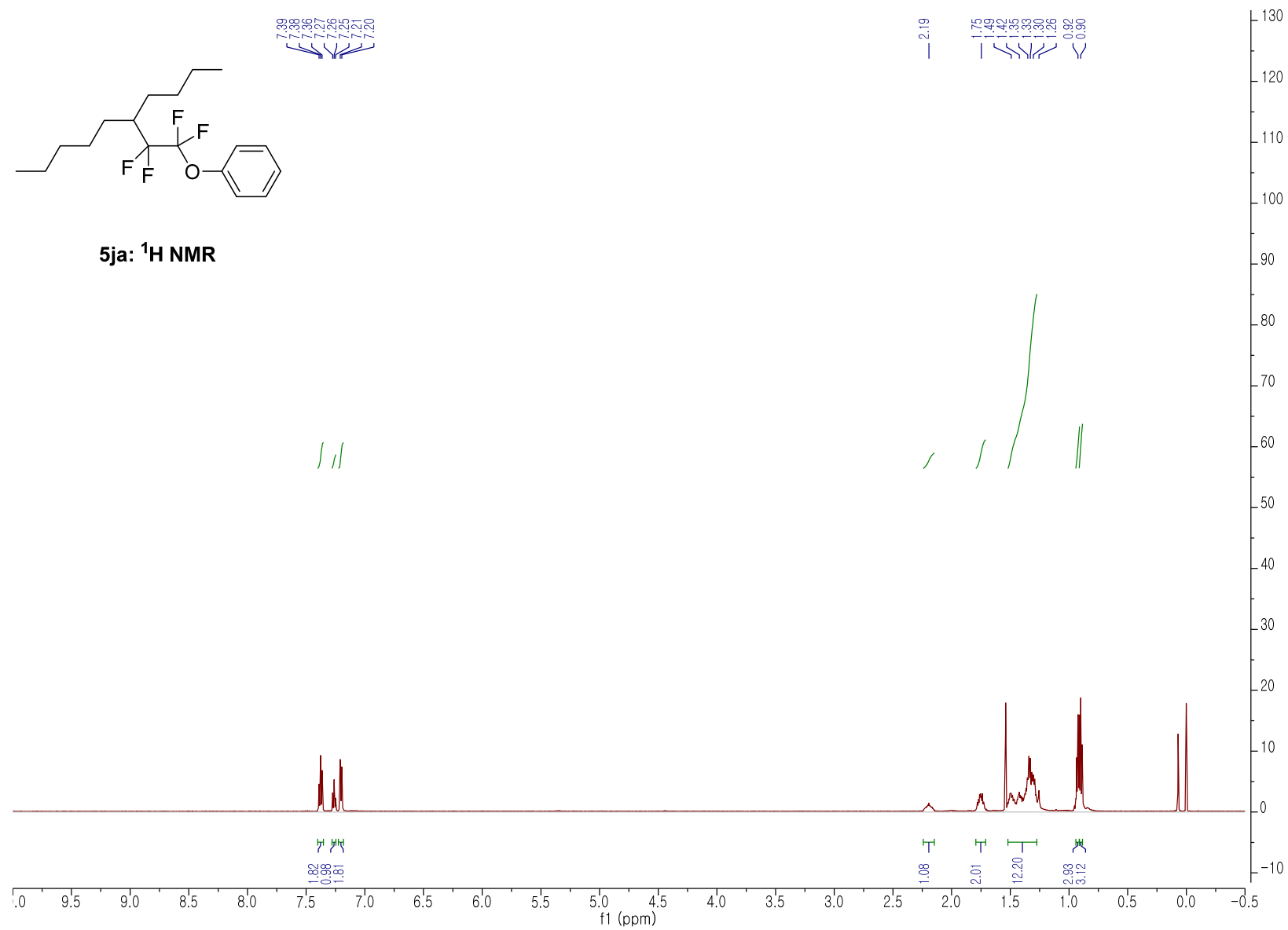


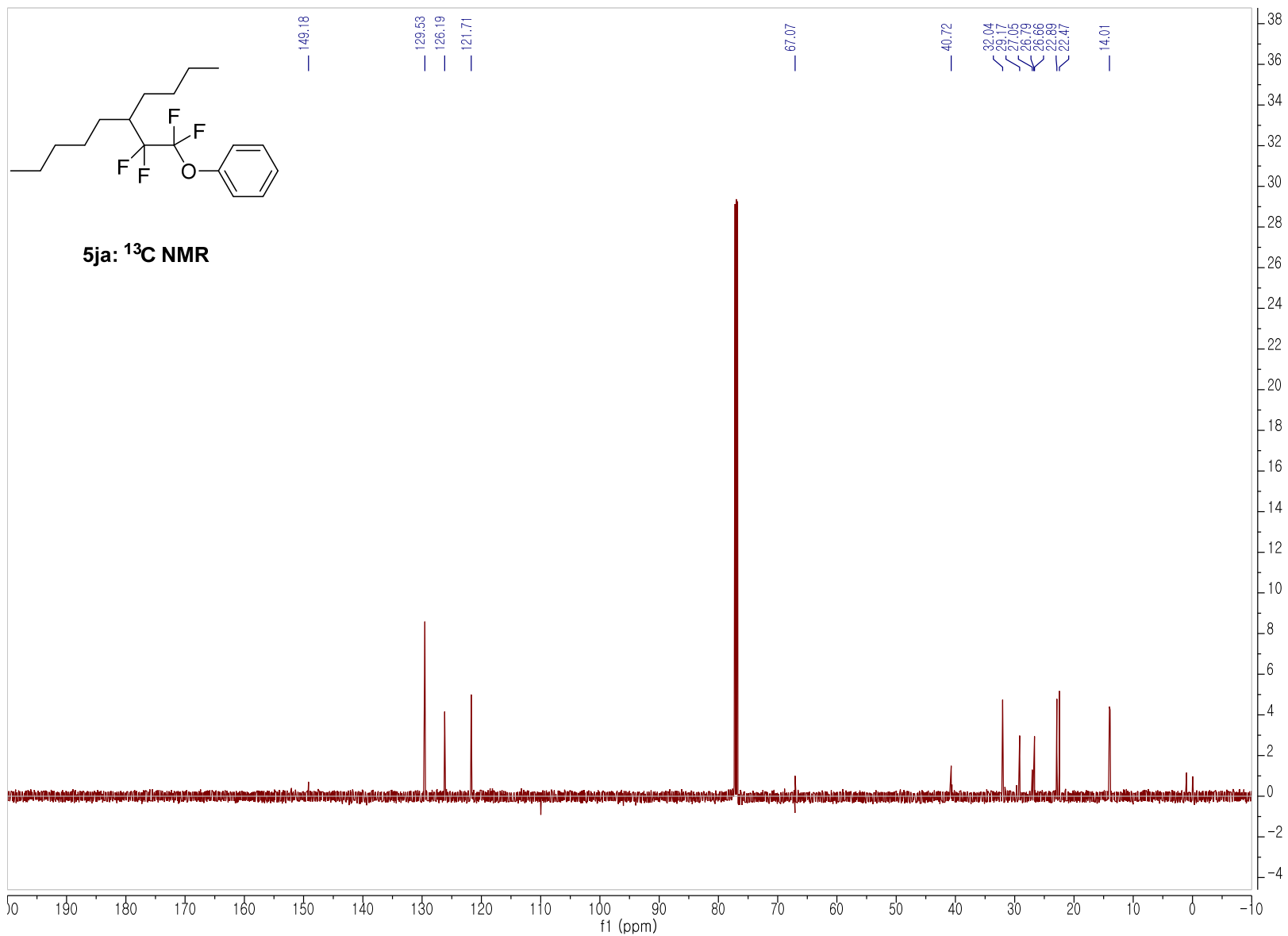


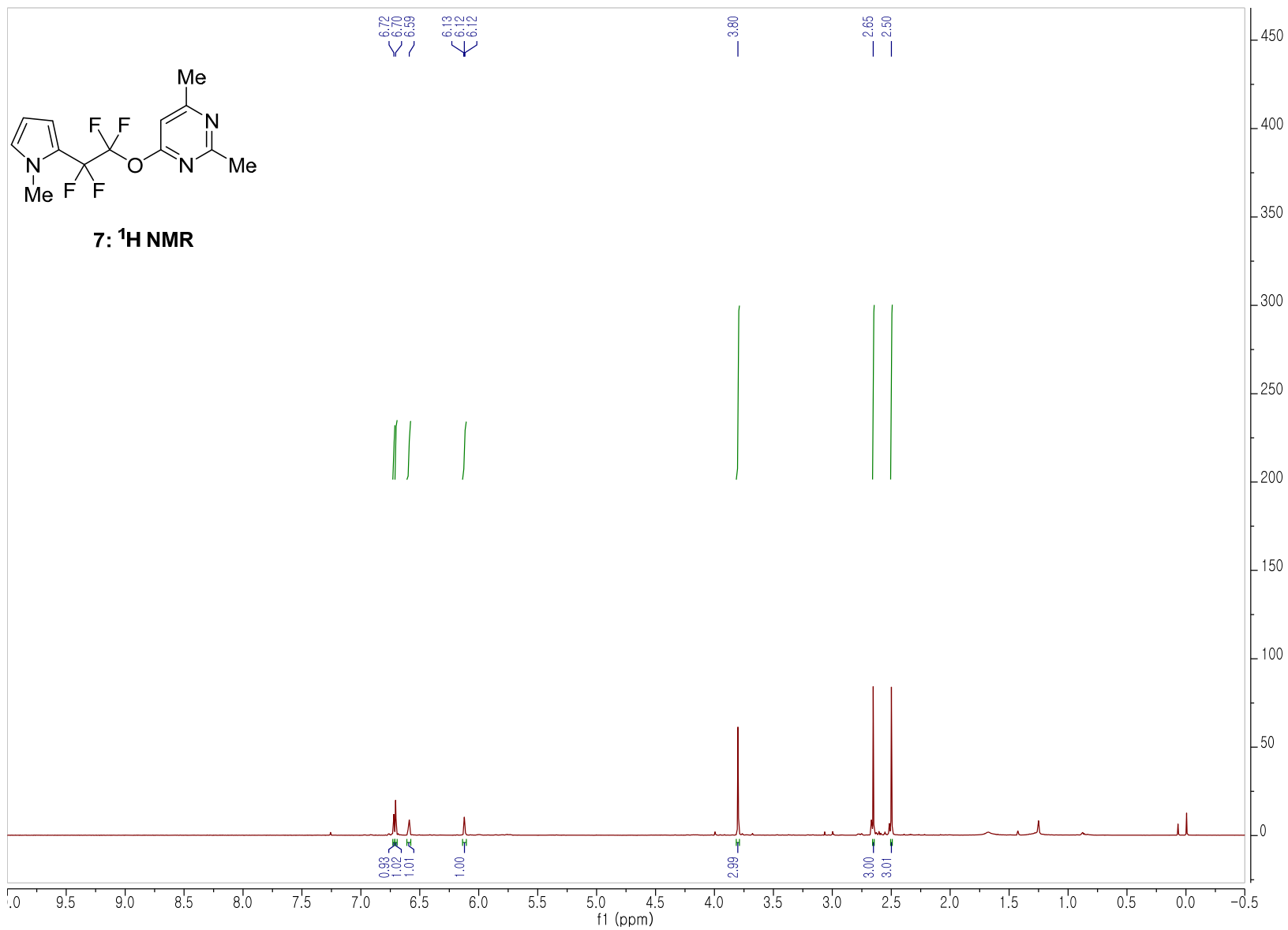


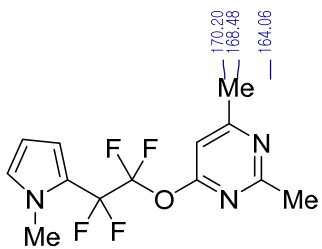


5ja: ^1H NMR









7: ¹³C NMR

