Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-Catalyzed Arylstannylation of Arynes in Sequence

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1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{19}F, 470 MHz; ^{119}Sn, 186 MHz; ^{31}P, 202 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.16) as an internal standard, and hexafluorobenzene (^{19}F, δ = -163.6), tetramethytin (^{119}Sn, δ = 0) or H_3PO_4 (^{31}P, δ = 0) as an external standard (solvent: $CDCl_3$). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, m = multiplet), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GL Science), 30 m × 0.25 mm, film 0.25 μm; Flow rate: 1.89 mL/min; Injector temperature: 250 °C; Oven temperature: 100 °C to 250 °C at 20 °C/min, hold at 250 °C for 10 min; FID temperature: 250 °C). High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer or a JEOL JMS-T100GCV spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Column chromatography was carried out using Merck Kieselgel 60. All arylstannylated products were purified by column chromatography using 10% w/w anhydrous potassium carbonate-silica as a stationary phase.[1] All microwave reactions (Biotage, Initiator+) were conducted in a sealed tube, and the reaction temperature was maintained by an external infrared sensor. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieves 3Å. Commercial grade 18-crown-6 and CuCl were purified according to a literature procedures,[2] and stored under an argon atmosphere.

Abbreviations

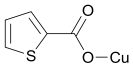
Å: Angstrom

equiv: Equivalent

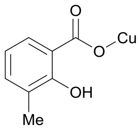
aq.: Aqueous

Mp: Melting point

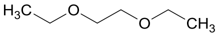
CuTC: Copper(I) 2-thiophenecarboxylate



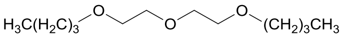
CuMS: Copper(I) 3-methylsalicylate



DEE: 1,2-Diethoxyethane



$C_{12}H_{26}O_3$: Diethylene glycol dibutyl ether



THF: Tetrahydrofuran

DME: 1,2-Dimethoxyethane

diglyme: Diethylene glycol dimethyl ether

DCM: Dichloromethane

DMF: *N*,*N*-Dimethylformamide

2. GC calibration curves

Table S1. Data for the GC Calibration Curve (1a)

Entry	GC Area		x	Amount of Substance (mmol)		y
	1a	**$C_{12}H_{26}O_3$**		**1a**	**$C_{12}H_{26}O_3$**	
1	7154332	3851566	1.8575125	0.05	0.05	1.00
2	8639158	9304781	0.9284644	0.05	0.10	0.50
3	7570432	12338071	0.6135831	0.05	0.15	0.33

x = (GC area of **1a**)/(GC area of $C_{12}H_{26}O_3$)

y = (amount of substance of **1a**)/(amount of substance of $C_{12}H_{26}O_3$)

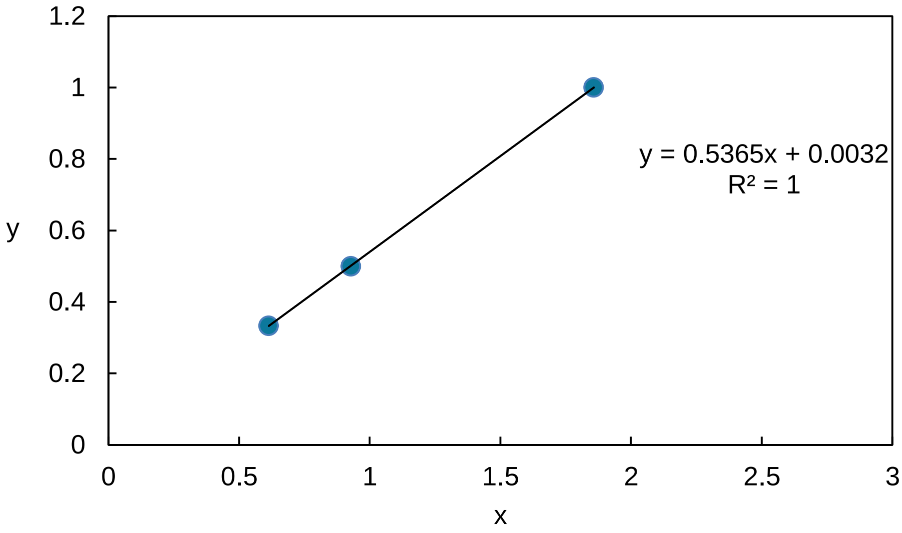
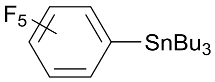


Figure S1. GC Calibration Curve for Decision of the Yield (1a)



1a

Table S2. Data for the GC Calibration Curve (2a)

Entry	GC Area		x	Amount of Substance (mmol)		y
	2a	$C_{12}H_{26}O_3$		**2a**	$C_{12}H_{26}O_3$	
1	4866420	6166143	0.7892162	0.05	0.05	1.00
2	3248633	7832454	0.4147657	0.05	0.10	0.50
3	3169155	11069768	0.2862892	0.05	0.15	0.33

x = (GC area of **2a**)/(GC area of $C_{12}H_{26}O_3$)

y = (amount of substance of **2a**)/(amount of substance of $C_{12}H_{26}O_3$)

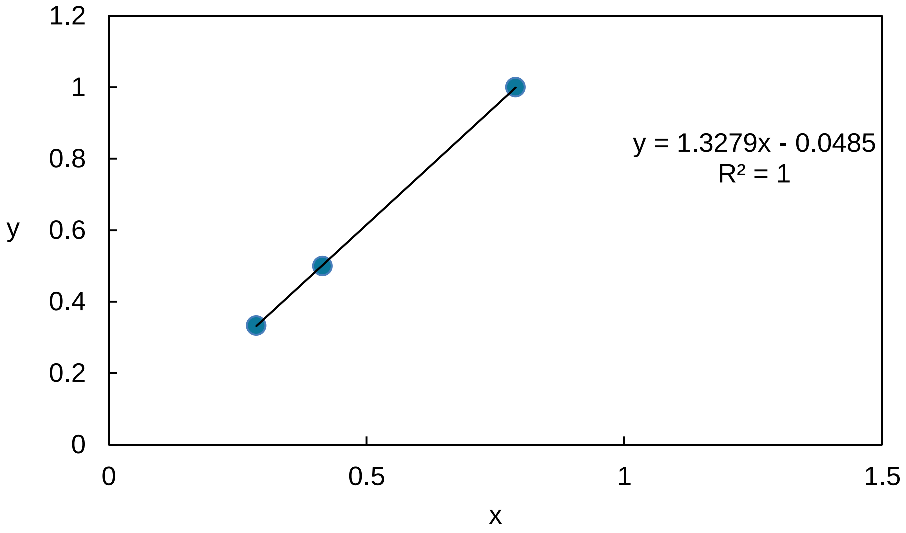
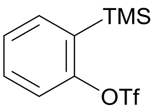


Figure S2. GC Calibration Curve for Decision of the Yield (2a)



2a

Table S3. Data for the GC Calibration Curve (3aa)

Entry	GC Area		x	Amount of Substance (mmol)		y
	3aa	**$C_{12}H_{26}O_3$**		**3aa**	**$C_{12}H_{26}O_3$**	
1	6256758	2550646	2.4530092	0.03	0.03	1.00
2	5725552	4711439	1.2152449	0.03	0.06	0.50
3	5807025	7132070	0.8142131	0.03	0.09	0.33

x = (GC area of **3aa**)/(GC area of $C_{12}H_{26}O_3$)

y = (amount of substance of **3aa**)/(amount of substance of $C_{12}H_{26}O_3$)

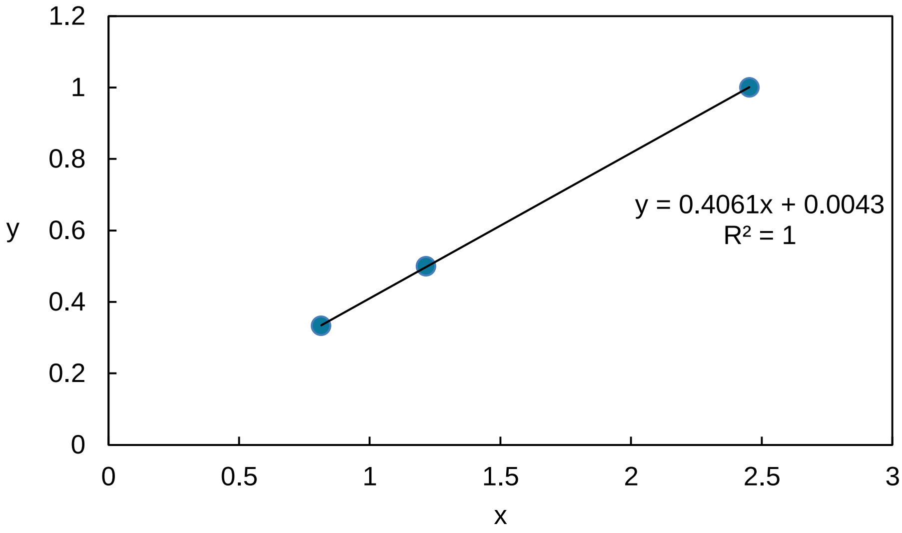
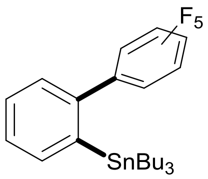


Figure S3. GC Calibration Curve for Decision of the Yield (3aa)



3aa

Table S4. Data for the GC Calibration Curve (4aaa)

Entry	GC Area		x	Amount of Substance (mmol)		y
	4aaa	**$C_{12}H_{26}O_3$**		**4aaa**	**$C_{12}H_{26}O_3$**	
1	6727060	2633692	2.5542319	0.03	0.03	1.00
2	5970068	5068912	1.1777810	0.03	0.06	0.50
3	5751109	7756233	0.7414822	0.03	0.09	0.33

x = (GC area of **4aaa**)/(GC area of $C_{12}H_{26}O_3$)

y = (amount of substance of **4aaa**)/(amount of substance of $C_{12}H_{26}O_3$)

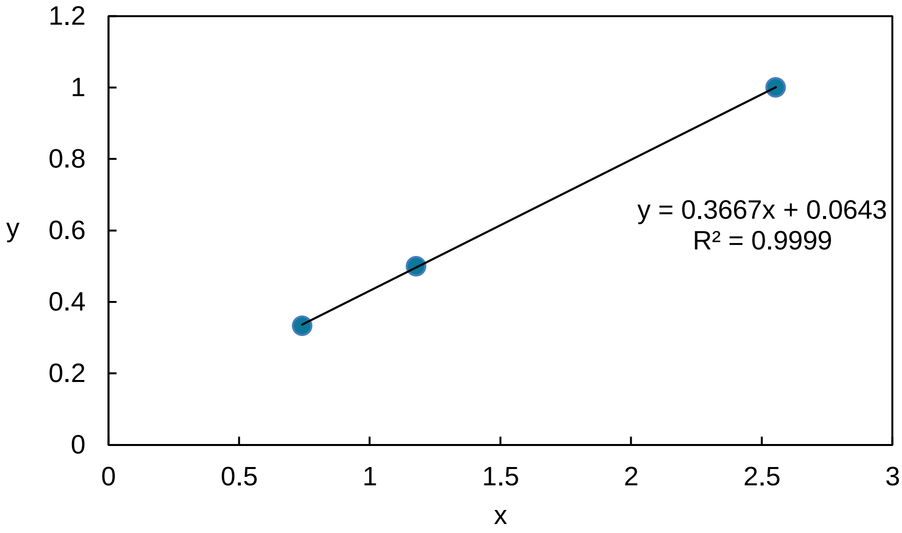
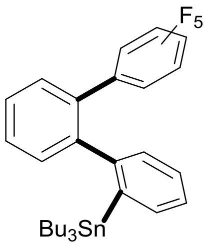


Figure S4. GC Calibration Curve for Decision of the Yield (4aaa)



4aaa

Table S5. Data for the GC Calibration Curve (1k)

Entry	GC Area		x	Amount of Substance (mmol)		y
	1k	$C_{12}H_{26}O_3$		1k	$C_{12}H_{26}O_3$	
1	12711078	6883316	1.8466504	0.05	0.05	1.00
2	11186708	11198873	0.9989137	0.05	0.10	0.50
3	12533437	18743307	0.6686887	0.05	0.15	0.33

x = (GC area of **1k**)/(GC area of $C_{12}H_{26}O_3$)

y = (amount of substance of **1k**)/(amount of substance of $C_{12}H_{26}O_3$)

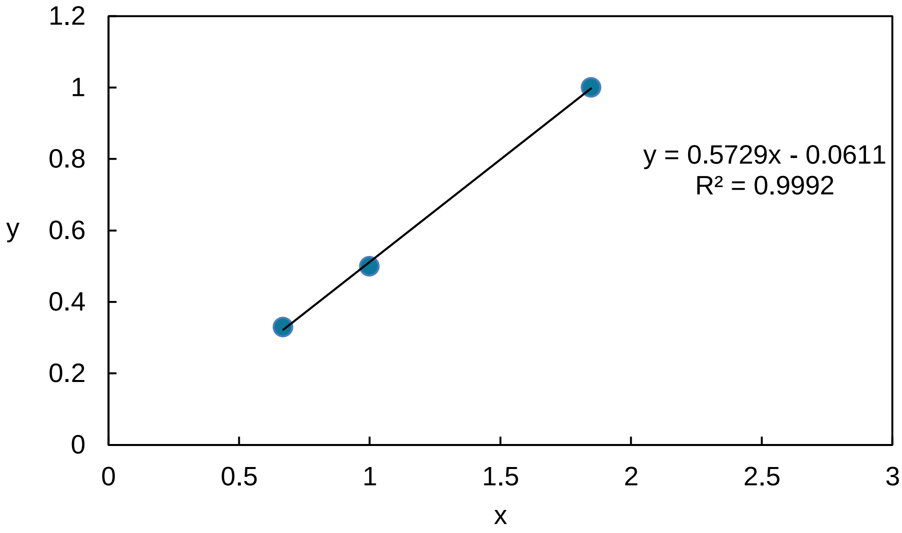
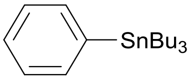


Figure S5. GC Calibration Curve for Decision of the Yield (1k)

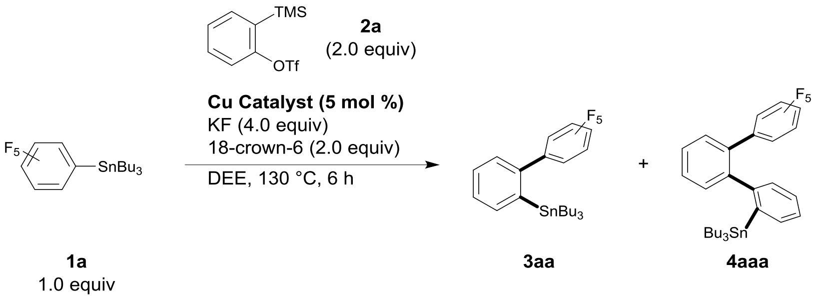


1k

3. Optimization of reaction conditions

General procedure: A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (4.0 equiv, 0.40 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (2.0 equiv, 0.20 mmol), Cu catalyst (5 mol %, 5.0 µmol), DEE (0.67 mL), **1a** (1.0 equiv, 0.10 mmol) and **2a** (2.0 equiv, 0.20 mmol) under an argon atmosphere. The resulting mixture was stirred at 130 °C for 6 h. $C_{12}H_{26}O_3$ as an internal standard (0.50 equiv, 0.050 mmol) was added to the mixture. The yields of products were determined by GC analysis based on calibration curves obtained using an authentic samples.

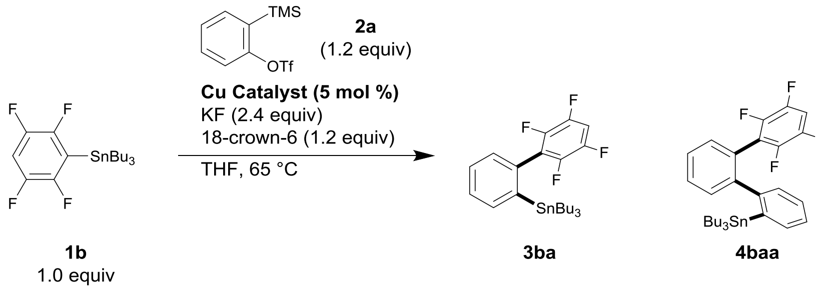
Table S6. Optimization of Copper Catalyst



Entry	Cu catalyst		$C_{12}H_{26}O_3$	3aa	4aaa
1	*CuTC*	*GC area*	*123491*	*85769*	*462338*
		Yield (%)	*–*	*14*	*72*
2	CuCl	GC area	67744	33830	236467
		Yield (%)	–	10	67
3	CuI	GC area	94550	66144	317056
		Yield (%)	–	14	65
4	*CuMS*	*GC area*	*67102*	*132560*	*65964*
		Yield (%)	*–*	*40*	*21*

The dual insertion of benzyne into the C(aryl)–Sn bond of **1a** was found to occur smoothly with copper(I) 2-thiophenecarboxylate (CuTC, 5 mol %) to provide a 72% yield of a stannylteraryl (**4aaa**) as the major product (Table S6, entry 1). Although the yields of **4aaa** observed with CuCl or CuI became slightly lower (Table S6, entries 2 and 3), the product distribution was similar on the whole, indicating that the counteranion of the copper catalysts scarcely affects a catalytic cycle of the arylstannylation. In marked contrast, the use of copper(I) 3-methylsalicylate (CuMS) resulted in the preferential formation of a *ortho*-stannylbiaryl (**3aa**) (Table S6, entry 4).

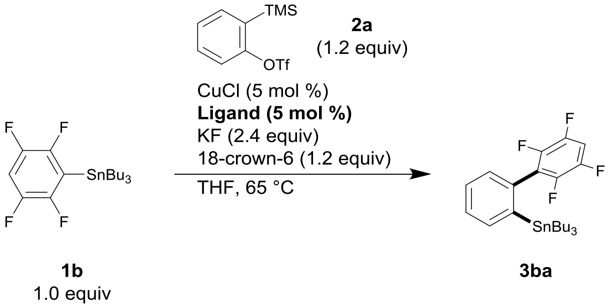
Table S7. Synthesis of *ortho*-Stannylbiaryl: Effect of Copper Catalyst[a]



Entry	Cu Catalyst	Time (h)	Yield (%)[b]	
			3ba	4baa
1[c]	CuCN	66	22	10
2	CuI	69	32	15
3	CuCl	71	35	13
4	***CuMS***	***68***	***41***	***10***
5	***CuTC***	***68***	***24***	***19***
6	Cu(II) acetylacetonate	72	6	14
7	SIMesCuCl	25	18	3
8	IMesCuCl	45	22	8
9	***$CuCl(PPh_3)_3$***	***24***	***47***	***7***

[a] **1b** (0.30 mmol), **2a** (0.36 mmol), Cu catalyst (15.0 μmol), KF (0.72 mmol), 18-crown-6 (0.36 mmol), THF (3 mL), 65 °C. [b] Isolated yields are shown (The products were isolated by preparative recycling gel permeation chromatography). [c] The conditions in Entry 1 are identical to those of our previous work.[3]

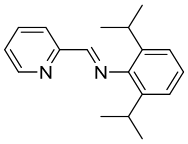
Table S8. Synthesis of *ortho*-Stannylbiaryl: Effect of Ligand[a]



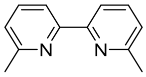
Entry	Ligand	Time (h)	NMR Yield (%)[b]
1[c]	*PPh_3*	*45*	*63*
2	PPh_3 (10 mol %)	26	63
3	PBu_3	39	0
4	di(1-adamantyl)-*n*-butylphosphine	22	0
5	dppe	43	6
6	dppp	43	40
7	dppb	20	0
8	dppo	42	0
9	dppf	28	0
10	XantPhos	28	0
11	rac-BINAP	26	0
12	$P[2,4,6\text{-}(CH_3)_3\text{-}C_6H_2]_3$	39	0
13	$P(4\text{-}Me\text{-}C_6H_4)_3$	22	16
14	$P(4\text{-}MeO\text{-}C_6H_4)_3$	22	8
15	$P(C_6F_5)_3$	21	14
16	$P[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_3$	25	0
17	$P(4\text{-}CF_3\text{-}C_6H_4)_3$	23	11
18	tri(2-furyl)phosphine	29	0
19	$AsPh_3$	24	0
20	Ligand A	24	0
21	Ligand B	42	16

[a] **1b** (0.30 mmol), **2a** (0.36 mmol), CuCl (15.0 μmol), Ligand (15.0 μmol), KF (0.72 mmol), 18-crown-6 (0.36 mmol), THF (3 mL), 65 °C. [b] Yield was determined by ^1H NMR analysis of the crude reaction mixture. [c] Transmetalation between an

arylstannane and a Cu catalyst was reported to be suppressed by adding 1 molar equiv of strong donors like PPh_3.[4] Thus, the teraryl was not formed in Entry 1 in spite of the use of 1.2 molar equiv of the benzyne precursors.

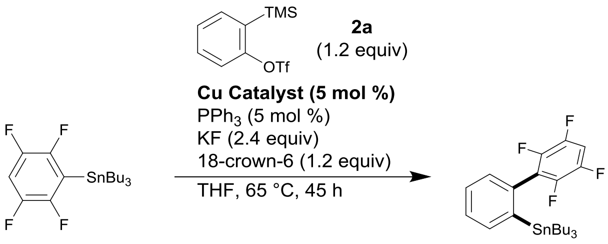


Ligand A



Ligand B

Table S9. Synthesis of *ortho*-Stannylbiaryl: Effect of Copper Catalyst in the Presence of PPh_3[a]



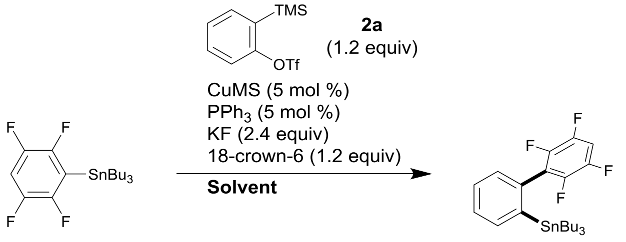
1b
1.0 equiv

3ba

Entry	Cu Catalyst	NMR Yield (%)[b]
1	CuCl	63
2	*CuMS*	*68*

[a] **1b** (0.30 mmol), **2a** (0.36 mmol), Cu catalyst (15.0 µmol), PPh_3 (15.0 µmol), KF (0.72 mmol), 18-crown-6 (0.36 mmol), THF (3 mL), 65 °C, 45 h. [b] Yield was determined by ^1H NMR analysis of the crude reaction mixture.

Table S10. Synthesis of *ortho*-Stannylbiaryl: Effect of Solvent and Temperature[a]



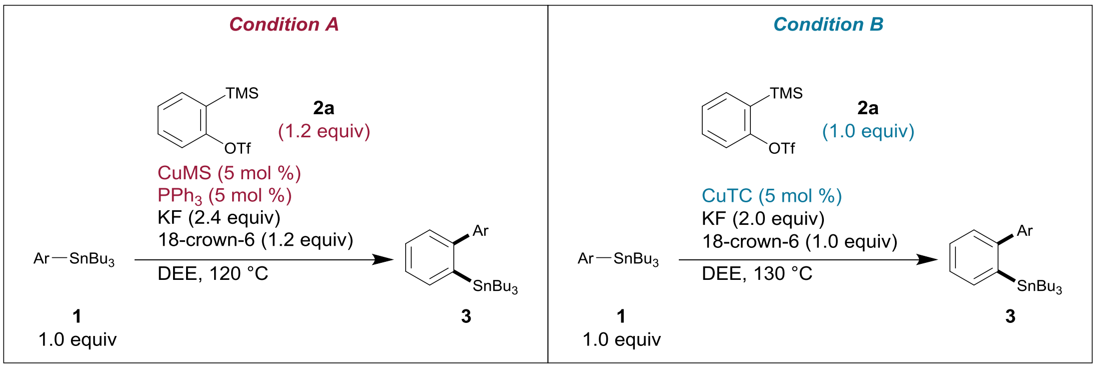
1b
1.0 equiv

3ba

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	THF	65	43	50
2	DME	80	19	0
3	***DEE***	***120***	***27***	***65***
4	diglyme	160	5	0

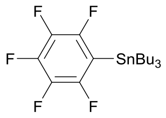
[a] **1b** (0.30 mmol), **2a** (0.36 mmol), CuMS (15.0 µmol), PPh_3 (15.0 µmol), KF (0.72 mmol), 18-crown-6 (0.36 mmol), solvent (3 mL). [b] Isolated yields are shown (The products were isolated by preparative recycling gel permeation chromatography).

Table S11. Synthesis of *ortho*-Stannylbiaryl: Comparison between *Condition A* and *B*



Entry	Ar–SnBu$_3$	*Condition A*[a]		*Condition B*[b]	
		Time (h)	Yield (%)[c]	Time (h)	Yield (%)[d]
1	**1a**	20	56	4	73
2	**1b**	27	65	4	66
3	**1c**	27	47	5	74
4	**1d**	26	36	5	60
5	**1e**	72	12	7	44
6	**1f**	24	40	6	40
7	**1g**	67	39	4	79
8	**1h**	49	39	5	69
9	**1i**	75	15	6	62
10	**1j**	69	0	6	49
11	**1k**	43	0	4	0[e]

[a] **1** (0.30 mmol), **2a** (0.36 mmol), CuMS (15.0 µmol), PPh$_3$ (15.0 µmol), KF (0.72 mmol), 18-crown-6 (0.36 mmol), DEE (3 mL), 120 °C. [b] **1** (0.10 mmol), **2a** (0.10 mmol), CuTC (5.0 µmol), KF (0.20 mmol), 18-crown-6 (0.10 mmol), DEE (0.67 mL), 130 °C. [c] Isolated yields are shown (The products were isolated by preparative recycling gel permeation chromatography). [d] Isolated yields are shown (The products were isolated by silica gel-column chromatography). [e] Yield was determined by ^{119}Sn NMR analysis of the crude reaction mixture.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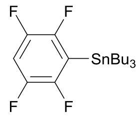
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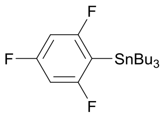
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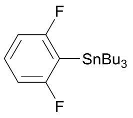
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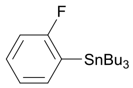
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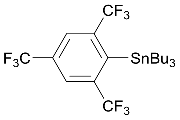
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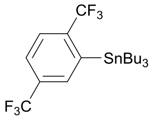
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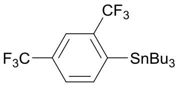
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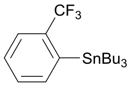
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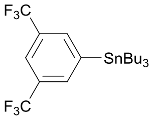
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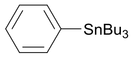
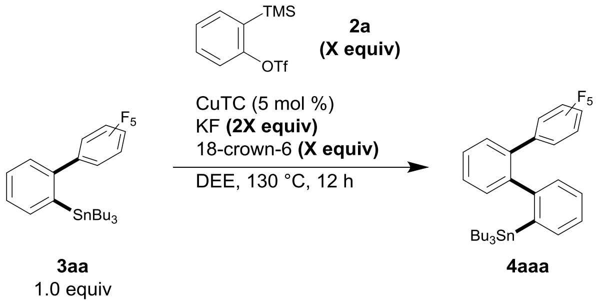

1k

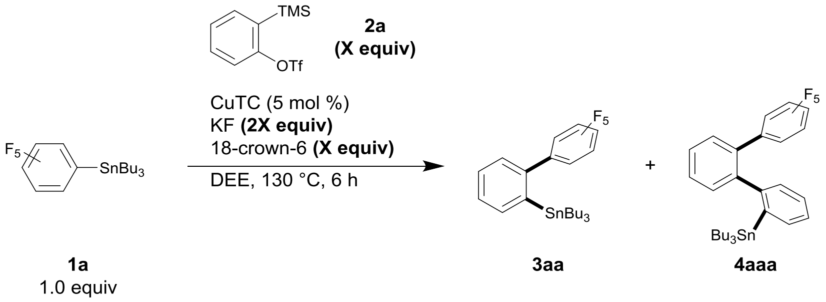
Table S12. Synthesis of Stannylteraryl: Optimization of Equivalence[a]



Entry	X	Yield (%)[b]
1	***1.5***	***55***
2	2.0	46

[a] **3aa** (0.10 mmol), **2a** (0.1 × X mmol), CuTC (5.0 µmol), KF (0.1 × 2X mmol), 18-crown-6 (0.1 × X mmol), DEE (0.67 mL), 130 °C, 12 h. [b] Isolated yields are shown (The products were isolated by silica gel-column chromatography).

Table S13. One-Pot Synthesis of Stannylteraryl: Optimization of Equivalence[a]



Entry	X		$C_{12}H_{26}O_3$	3aa	4aaa
1[b]	***2.0***	***GC area***	***123491***	***85769***	***462338***
		Yield (%)	***–***	***14***	***72***
2[c]	2.2	GC area	171135	129263	173346
		Yield (%)	–	31	44
3[d]	3.0	GC area	62675	82100	26830
		Yield (%)	–	27	11

[a] **1a** (0.10 mmol), **2a** (0.1 × X mmol), CuTC (5.0 μmol), KF (0.1 × 2X mmol), 18-crown-6 (0.1 × X mmol), DEE (0.67 mL), 130 °C, 6 h. Yield was determined by GC analysis of the crude reaction mixture. [b] $C_{12}H_{26}O_3$ (0.050 mmol) was added to the resulting mixture. [c] $C_{12}H_{26}O_3$ (0.10 mmol) was added to the resulting mixture. [d] The resulting mixture was stirred at 200 °C for 6 h under microwave irradiation. $C_{12}H_{26}O_3$ (0.050 mmol) was added to the resulting mixture. A stannyltetraaryl wasn't observed under forcing conditions with excess amount of a suitable aryne precursor.

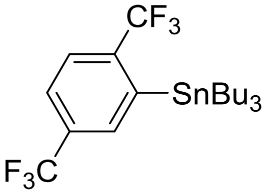
4. Synthesis of aryne precursors

2-(Trimethylsilyl)phenyl triflate (**2a**),[5] 3,6-dimethyl-2-(trimethylsilyl)phenyl triflate (**2b**),[6] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**2c**),[7] 4,5-difluoro-2-(trimethylsilyl)phenyl triflate (**2d**),[8] 3-(trimethylsilyl)-2-naphthyl triflate (**2e**),[6] 3-methoxy-2-(trimethylsilyl)phenyl triflate (**2f**),[8] 6-methoxy-2-(trimethylsilyl)phenyl triflate (**2'f**),[9] 6-chloro-2-(trimethylsilyl)phenyl triflate (**2g**),[9] 5-chloro-3-methoxy-2-(trimethylsilyl)phenyl triflate (**2h**),[10] 1-(trimethylsilyl)-2-naphthyl triflate (**2i**)[11] and 4-chloro-3-methoxy-2-(trimethylsilyl)phenyl triflate (**1j**)[3] were prepared according to literature procedures.

5. Synthesis of arylstannanes

All arylstannanes were prepared according to literature procedures.[3,12–17]

(2,5-bis(trifluoromethyl)phenyl)tributylstannane (1g)



^{1}H NMR: δ 0.89 (t, J = 7.3 Hz, 9H), 1.07 – 1.22 (m, 6H), 1.33 (sext, J = 7.3 Hz, 6H), 1.42 – 1.58 (m, 6H), 7.66 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.1 Hz, $J_{\text{Sn-H}meta}$ = 10.4 Hz, 1H), 7.84 (s, $J_{\text{Sn-H}ortho}$ = 37.0 Hz, 1H)

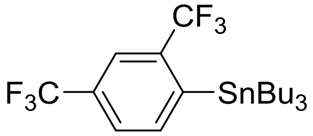
^{13}C NMR: δ 11.03 (d, J = 2.1 Hz, $J_{\text{Sn–C}}$ = 353.3, 337.6 Hz), 13.72, 27.37, 28.94, 123.97 (q, $J_{\text{C–F}}$ = 273.1 Hz), 124.57 (q, $J_{\text{C–F}}$ = 273.8 Hz), 125.28 (q, J = 3.7 Hz), 126.23 (q, J = 4.6 Hz), 132.40 (q, $J_{\text{C–CF3}}$ = 31.9 Hz), 134.02 (q, J = 3.7 Hz), 139.88 (q, $J_{\text{C–CF3}}$ = 30.3 Hz), 142.73 (q, J = 4.2 Hz)

^{19}F NMR: δ -64.76, -62.63

^{119}Sn NMR: δ -19.24

HRMS (APCI) Calcd for $C_{16}H_{21}F_6Sn$: $[M-Bu]^+$, 447.05639. Found: *m/z* 447.05652.

(2,4-bis(trifluoromethyl)phenyl)tributylstannane (1h)



^{1}H NMR: δ 0.88 (t, J = 7.3 Hz, 9H), 1.05 – 1.22 (m, 6H), 1.33 (sext, J = 7.3 Hz, 6H), 1.42 – 1.54 (m, 6H), 7.69 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.7 Hz, $J_{\text{Sn-H}ortho}$ = 35.6 Hz, 1H), 7.90 (s, 1H)

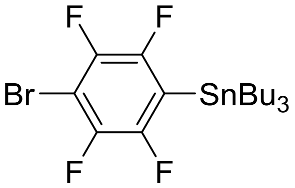
^{13}C NMR: δ 11.05 (d, J = 2.1 Hz, $J_{\text{Sn–C}}$ = 352.7, 337.1 Hz), 13.75, 27.41, 28.96, 122.53 (dt, J = 8.4, 4.1 Hz), 123.81 (q, $J_{\text{C–F}}$ = 272.2 Hz), 124.53 (q, $J_{\text{C–F}}$ = 273.6 Hz), 126.92, 130.75 (q, $J_{\text{C–CF3}}$ = 33.1 Hz), 137.38 (q, $J_{\text{C–CF3}}$ = 30.8 Hz), 138.25, 146.70 (d, J = 3.6 Hz)

^{19}F NMR: δ -64.76, -62.47

^{119}Sn NMR: δ -21.06

HRMS (APCI) Calcd for $C_{16}H_{21}F_{6}Sn$: $[M{-}Bu]^{+}$, 447.05639. Found: *m/z* 447.05640.

(4-bromo-2,3,5,6-tetrafluorophenyl)tributylstannane (1n)



^{1}H NMR: δ 0.90 (t, J = 7.3 Hz, 9H), 1.21 – 1.26 (m, 6H), 1.33 (sext, J = 7.3 Hz, 6H), 1.51 – 1.57 (m, 6H)

^{13}C NMR: δ 11.64, 13.74, 27.27, 28.94, 100.02 (tt, $J_{\text{C–CF}}$ = 22.7, $J_{\text{C–CCF}}$ = 2.8 Hz), 117.58 (tt, $J_{\text{C–CF}}$ = 50.0, $J_{\text{C–CCF}}$ = 4.1 Hz), 144.26 (dm, $J_{\text{C–F}}$ = 252.9 Hz), 148.96 (dddd, $J_{\text{C–F}}$ = 236.0, $J_{\text{C–CF}}$ = 18.9, $J_{\text{C–CCF}}$ = 12.4, $J_{\text{C–CCCF}}$ = 3.9 Hz)

^{19}F NMR: δ -134.58 (dd, J = 26.3, 11.8 Hz), -121.42 (dd, J = 26.3, 11.8 Hz)

^{119}Sn NMR: δ -18.84

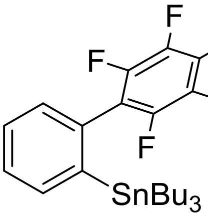
HRMS (APCI) Calcd for $C_{14}H_{18}{}^{79}BrF_{4}Sn$: $[M{-}Bu]^{+}$, 460.95445. Found: *m/z* 460.95444.

6. Synthesis of *ortho*-stannylbiaryls

NMR Yield: A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (2.0 equiv, 0.20 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (1.0 equiv, 0.10 mmol), CuTC (5 mol %, 5.0 µmol), DEE (0.67 mL), **1** (1.0 equiv, 0.10 mmol) and **2a** (1.0 equiv, 0.10 mmol) under an argon atmosphere. The resulting mixture was stirred at 130 °C for 4 h. The mixture was diluted with hexane (30 mL) before filtration. The yields of products were determined by ^{119}Sn NMR analysis of the crude reaction mixture using tributyl(vinyl)stannane as an internal standard (solvent: $CDCl_3$).

Isolated Yield: A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (2.0 equiv, 0.20 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (1.0 equiv, 0.10 mmol), CuTC (5 mol %, 5.0 µmol), DEE (0.67 mL), **1** (1.0 equiv, 0.10 mmol) and **2** (1.0 equiv, 0.10 mmol) under an argon atmosphere. The resulting mixture was stirred at 130 °C for the period as specified in Fig. 2, 3 and 9. The mixture was diluted with hexane (30 mL) before filtration. The organic solution was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography (hexane as an eluent) gave the corresponding product.

tributyl(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)stannane (3aa)



Isolated in 73% yield as a colorless oil.

^{1}H NMR: δ 0.77 – 0.83 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 9H), 1.26 (sext, *J* = 7.2 Hz, 6H), 1.32 – 1.42 (m, 6H), 7.19 – 7.25 (m, 1H), 7.39 – 7.45 (m, 2H), 7.57 – 7.62 (m, 1H)

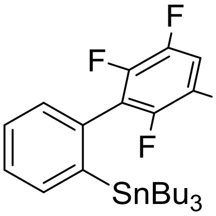
^{13}C NMR: δ 9.97 ($J_{\text{Sn–C}}$ = 342.9, 327.7 Hz), 13.68, 27.49, 29.00, 118.91 (td, *J* = 19.9, 3.3 Hz), 128.45, 128.55, 130.45, 133.81, 137.47, 137.69 (dm, $J_{\text{C–F}}$ = 253.3 Hz), 140.71 (dm, $J_{\text{C–F}}$ = 253.8 Hz), 144.52 ($J_{\text{Sn–C}}$ = 354.5, 339.3 Hz), 144.58 (dm, $J_{\text{C–F}}$ = 241.8 Hz)

^{19}F NMR: δ -163.76 (td, *J* = 22.8, 8.3 Hz), -157.12 (t, *J* = 20.8 Hz), -141.29 (dd, *J* = 23.6, 8.2 Hz)

^{119}Sn NMR: δ -39.53

HRMS (APCI) Calcd for $C_{20}H_{22}F_5Sn$: $[M-Bu]^+$, 477.06581. Found: *m/z* 477.06546.

tributyl(2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-2-yl)stannane (3ba)



Isolated in 66% yield as a colorless oil.

^{1}H NMR: δ 0.77 – 0.83 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 9H), 1.26 (sext, *J* = 7.3 Hz, 6H), 1.32 – 1.42 (m, 6H), 7.10 (tt, *J* = 9.7, 7.2 Hz, 1H), 7.22 – 7.28 (m, 1H), 7.38 – 7.45 (m, 2H), 7.60 (dd, *J* = 5.9, 2.9 Hz, 1H)

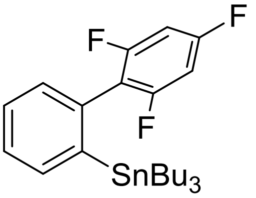
^{13}C NMR: δ 9.92 ($J_{\text{Sn–C}}$ = 342.8, 327.5 Hz), 13.70, 27.48, 28.99, 105.08 (t, $J_{\text{C–CF}}$ = 22.5 Hz), 124.66 (t, $J_{\text{C–CF}}$ = 19.3 Hz), 128.33, 128.36, 130.15, 134.95 (t, *J* = 2.2 Hz), 137.37, 144.20 (dm, $J_{\text{C–F}}$ = 236.3 Hz), 144.20 ($J_{\text{Sn–C}}$ = 358.3, 342.4 Hz), 146.09 (dm, $J_{\text{C–F}}$ = 248.8 Hz)

^{19}F NMR: δ -141.93 (ddd, *J* = 21.3, 12.7, 7.3 Hz), -140.64 (dt, *J* = 22.8, 11.5 Hz)

^{119}Sn NMR: δ -39.64

HRMS (APCI) Calcd for $C_{20}H_{23}F_4Sn$: $[M{-}Bu]^+$, 459.07524. Found: *m/z* 459.07504.

tributyl(2',4',6'-trifluoro-[1,1'-biphenyl]-2-yl)stannane (3ca)



Isolated in 74% yield as a colorless oil.

^{1}H NMR: δ 0.76 – 0.82 (m, 6H), 0.85 (t, *J* = 7.3 Hz, 9H), 1.25 (sext, *J* = 7.3 Hz, 6H), 1.36 (tt, *J* = 8.2, 5.9 Hz, 6H), 6.75 (dd, *J* = 8.8, 6.7 Hz, 2H), 7.20 – 7.25 (m, 1H), 7.38 (dt, *J* = 5.5, 2.2 Hz, 2H), 7.55 – 7.60 (m, 1H)

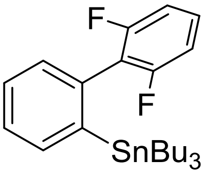
^{13}C NMR: δ 9.87 ($J_{Sn–C}$ = 341.8, 326.6 Hz), 13.74, 27.52, 29.02, 99.89 – 100.59 (m), 118.09 (td, $J_{C–CF}$ = 21.9, $J_{C–CCCF}$ = 4.7 Hz), 127.81, 128.20, 130.53, 136.02, 137.15, 144.49 ($J_{Sn–C}$ = 371.0, 354.4 Hz), 160.80 (ddd, $J_{C–F}$ = 248.0, $J_{C–CCF}$ = 14.8, 9.9 Hz), 162.16 (dt, $J_{C–F}$ = 249.1, $J_{C–CCF}$ = 15.2 Hz)

^{19}F NMR: δ -110.51, -109.64

^{119}Sn NMR: δ -39.97

HRMS (APCI) Calcd for $C_{20}H_{24}F_3Sn$: $[M{-}Bu]^+$, 441.08466. Found: *m/z* 441.08444.

tributyl(2',6'-difluoro-[1,1'-biphenyl]-2-yl)stannane (3da)



Isolated in 60% yield as a colorless oil.

^{1}H NMR: δ 0.73 – 0.78 (m, 6H), 0.84 (t, *J* = 7.2 Hz, 9H), 1.23 (sext, *J* = 7.2 Hz, 6H), 1.34 (tdd, *J* = 8.7, 7.1, 3.5 Hz, 6H), 6.96 (ddd, *J* = 8.4, 6.0, 1.1 Hz, 2H), 7.26 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.31 (tt, *J* = 8.4, 6.4 Hz, 1H), 7.35 – 7.42 (m, 2H), 7.55 – 7.60 (m, 1H)

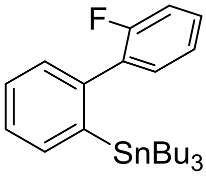
^{13}C NMR: δ 9.83 ($J_{Sn–C}$ = 341.5, 326.3 Hz), 13.75, 27.51, 29.01, 111.27 – 111.65 (m), 121.63 (t, $J_{C–CF}$ = 21.3 Hz), 127.60, 128.09, 129.18 (t, *J* = 10.0 Hz), 130.32, 136.94, 137.05, 144.25 ($J_{\text{Sn–C}}$ = 375.0, 357.9 Hz), 160.70 (dd, $J_{\text{C–F}}$ = 247.1, $J_{\text{C–CCF}}$ = 7.2 Hz)

^{19}F NMR: δ -113.05

^{119}Sn NMR: δ -40.21

HRMS (APCI) Calcd for $C_{20}H_{25}F_2Sn$: [M−Bu]$^+$, 423.09408. Found: *m/z* 423.09424.

tributyl(2'-fluoro-[1,1'-biphenyl]-2-yl)stannane (3ea)



Isolated in 44% yield as a colorless oil.

^{1}H NMR: δ 0.70 – 0.76 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 9H), 1.23 (sext, *J* = 7.2 Hz, 6H), 1.34 (tdd, *J* = 8.5, 7.1, 3.4 Hz, 6H), 7.12 (ddd, *J* = 9.5, 8.2, 1.2 Hz, 1H), 7.17 (td, *J* = 7.4, 1.2 Hz, 1H), 7.22 (td, *J* = 7.5, 2.0 Hz, 1H), 7.30 – 7.38 (m, 4H), 7.54 – 7.58 (m, 1H)

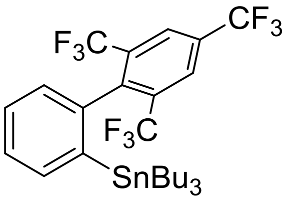
^{13}C NMR: δ 10.45 ($J_{\text{Sn–C}}$ = 341.9, 326.7 Hz), 13.77, 27.50, 29.08, 115.80 (d, *J* = 22.4 Hz), 123.91 (d, *J* = 3.7 Hz), 127.01, 127.83, 129.21 (d, *J* = 7.8 Hz), 129.83, 131.88 (d, *J* = 3.2 Hz), 132.76 (d, *J* = 16.3 Hz), 137.13, 143.14 ($J_{\text{Sn–C}}$ = 381.4, 364.9 Hz), 143.77, 159.96 (d, $J_{\text{C–F}}$ = 245.5 Hz)

^{19}F NMR: δ -116.99

^{119}Sn NMR: δ -39.77

HRMS (APCI) Calcd for $C_{20}H_{26}FSn$: [M−Bu]$^+$, 405.10350. Found: *m/z* 405.10349.

tributyl(2',4',6'-tris(trifluoromethyl)-[1,1'-biphenyl]-2-yl)stannane (3fa)



Isolated in 40% yield as a colorless oil.

^{1}H NMR: δ 0.51 – 0.57 (m, 6H), 0.82 (t, *J* = 7.3 Hz, 9H), 1.19 (sext, *J* = 7.2 Hz, 6H), 1.30 (ddt, *J* = 11.8, 8.2, 6.0 Hz, 6H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 (td, *J* = 7.4, 1.3 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 8.20 (s, 2H)

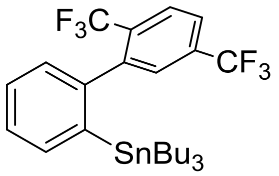
^{13}C NMR: δ 10.07 ($J_{Sn–C}$ = 342.3, 327.1 Hz), 13.59, 27.43, 28.84, 122.65 (q, $J_{C–F}$ = 275.5 Hz), 122.85 (q, $J_{C–F}$ = 272.8 Hz), 126.36, 126.56, 127.95, 130.10, 130.87 (q, $J_{C–CF3}$ = 34.5 Hz), 132.90 (q, $J_{C–CF3}$ = 30.3 Hz), 136.08, 139.42, 144.56 ($J_{Sn–C}$ = 369.9, 348.7 Hz), 146.93

^{19}F NMR: δ -64.54, -59.01

^{119}Sn NMR: δ -42.40

HRMS (APCI) Calcd for $C_{23}H_{24}F_9Sn$: $[M-Bu]^+$, 591.07508. Found: *m/z* 591.07501.

(2',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)tributylstannane (3ga)



Isolated in 79% yield as a colorless oil.

^{1}H NMR: δ 0.64 (dddd, *J* = 38.2, 13.0, 9.9, 6.5 Hz, 6H), 0.82 (t, *J* = 7.2 Hz, 9H), 1.21 (sext, *J* = 7.2 Hz, 6H), 1.26 – 1.36 (m, 6H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.35 (dtd, *J* = 20.9, 7.4, 1.5 Hz, 2H), 7.52 – 7.56 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H)

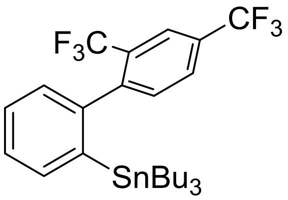
^{13}C NMR: δ 10.03 ($J_{Sn–C}$ = 342.4, 327.3 Hz), 13.64, 27.39, 28.95, 123.43 (q, $J_{C–F}$ = 273.1 Hz), 123.49 (q, $J_{C–F}$ = 274.9 Hz), 124.45 (q, *J* = 3.6 Hz), 126.98 (q, *J* = 5.2 Hz), 127.24, 127.45, 129.15, 129.31 (q, *J* = 3.4 Hz), 132.30 (q, $J_{C–CF3}$ = 30.2 Hz), 133.46 (q, $J_{C–CF3}$ = 32.9 Hz), 136.80, 142.40 ($J_{Sn–C}$ = 369.2, 352.7 Hz), 145.11, 145.43

^{19}F NMR: δ -64.78, -59.23

^{119}Sn NMR: δ -40.21

HRMS (APCI) Calcd for $C_{22}H_{25}F_6Sn$: $[M-Bu]^+$, 523.08769. Found: *m/z* 523.08771.

(2',4'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)tributylstannane (3ha)



Isolated in 69% yield as a colorless oil.

^{1}H NMR: δ 0.64 (dddd, *J* = 48.6, 13.0, 10.0, 6.5 Hz, 6H), 0.83 (t, *J* = 7.2 Hz, 9H), 1.21 (sext, *J* = 7.1 Hz, 6H), 1.26 – 1.36 (m, 6H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.43 (m, 3H), 7.54 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 8.01 (s, 1H)

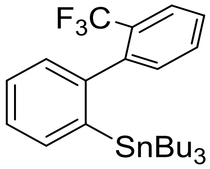
^{13}C NMR: δ 10.21 ($J_{\mathrm{Sn–C}}$ = 342.3, 327.1 Hz), 13.63, 27.41, 28.96, 123.25 – 123.51 (m), 123.43 (q, $J_{\mathrm{C–F}}$ = 274.6 Hz), 123.59 (q, $J_{\mathrm{C–F}}$ = 272.4 Hz), 127.22, 127.44, 128.01 (d, *J* = 3.3 Hz), 128.90, 129.97(q, $J_{\mathrm{C–CF3}}$ = 30.6 Hz), 130.26 (q, $J_{\mathrm{C–CF3}}$ = 33.5 Hz), 133.15, 136.73, 142.28 ($J_{\mathrm{Sn–C}}$ = 369.5, 353.2 Hz), 145.48, 147.82

^{19}F NMR: δ -64.21, -58.95

^{119}Sn NMR: δ -40.40

HRMS (APCI) Calcd for $C_{22}H_{25}F_6Sn$: $[M-Bu]^+$, 523.08769. Found: *m*/*z* 523.08734.

tributyl(2'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)stannane (3ia)



Isolated in 62% yield as a colorless oil.

^{1}H NMR: δ 0.56 – 0.72 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 9H), 1.21 (sext, *J* = 7.2 Hz, 6H), 1.26 – 1.40 (m, 6H), 7.25 (d, *J* = 10.9 Hz, 2H), 7.32 (quin d, *J* = 7.3, 1.6 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.58 (m, 2H), 7.73 (d, *J* = 7.8 Hz, 1H)

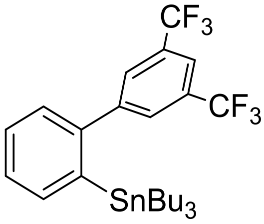
^{13}C NMR: δ 10.13 ($J_{\mathrm{Sn–C}}$ = 341.4, 326.3 Hz), 13.72, 27.45, 29.00, 124.25 (q, $J_{\mathrm{C–F}}$ = 274.3 Hz), 126.12 (q, *J* = 5.2 Hz), 126.84, 127.02, 127.51, 129.00 (q, $J_{\mathrm{C–CF3}}$ = 29.4 Hz), 129.18 (d, *J* = 1.8 Hz), 131.27, 132.30, 136.49, 142.54 ($J_{\mathrm{Sn–C}}$ = 385.8, 368.6 Hz), 144.01 (d, *J* = 1.7 Hz), 147.00

^{19}F NMR: δ -58.41

^{119}Sn NMR: δ -41.38

HRMS (APCI) Calcd for $C_{21}H_{26}F_3Sn$: $[M-Bu]^+$, 455.10031. Found: *m*/*z* 455.10010.

(3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)tributylstannane (3ja)



Isolated in 49% yield as a colorless oil.

^{1}H NMR: δ 0.70 – 0.76 (m, 6H), 0.82 (t, J = 7.2 Hz, 9H), 1.21 (sext, J = 7.2 Hz, 6H), 1.26 – 1.40 (m, 6H), 7.32 (dd, J = 6.9, 2.1 Hz, 1H), 7.40 (ddd, J = 5.9, 3.2, 1.9 Hz, 2H), 7.56 – 7.60 (m, 1H), 7.79 (s, 2H), 7.89 (s, 1H)

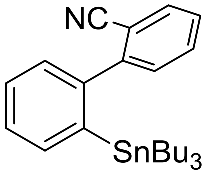
^{13}C NMR: δ 10.74 ($J_{\text{Sn–C}}$ = 343.4, 328.1 Hz), 13.63, 27.39, 29.07, 120.99 (quin, J = 3.8 Hz), 123.48 (q, $J_{\text{C–F}}$ = 272.9 Hz), 127.68, 128.50, 129.04, 131.70 (q, $J_{\text{C–CF3}}$ = 33.2 Hz), 137.66, 141.96 ($J_{\text{Sn–C}}$ = 358.4, 342.3 Hz), 147.36, 147.74

^{19}F NMR: δ -64.40

^{119}Sn NMR: δ -37.20

HRMS (APCI) Calcd for $C_{22}H_{25}F_6Sn$: [M−Bu]$^{+}$, 523.08769. Found: *m*/*z* 523.08795.

2'-(tributylstannyl)-[1,1'-biphenyl]-2-carbonitrile (3la)



Isolated in 24% yield as a colorless oil.

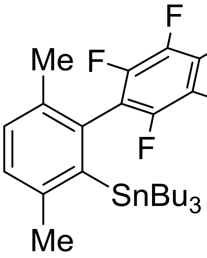
^{1}H NMR: δ 0.63 – 0.78 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H), 1.22 (sext, J = 7.2 Hz, 6H), 1.29 – 1.41 (m, 6H), 7.34 – 7.41 (m, 4H), 7.46 (td, J = 7.7, 1.0 Hz, 1H), 7.55 – 7.58 (m, 1H), 7.61 (td, J = 7.6, 1.2 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H)

^{13}C NMR: δ 10.66 ($J_{\text{Sn–C}}$ = 342.4, 327.3 Hz), 13.75, 27.49, 29.07, 112.98, 118.26, 127.75, 127.80, 128.14, 129.27, 130.71, 132.33, 133.08, 137.36, 142.30, 146.22, 149.05

^{119}Sn NMR: δ -39.23

HRMS (ESI) Calcd for $C_{25}H_{36}NSn$: [M+H]$^{+}$, 470.18642. Found: *m*/*z* 470.18655.

tributyl(2',3',4',5',6'-pentafluoro-3,6-dimethyl-[1,1'-biphenyl]-2-yl)stannane (3ab)



Isolated in 78% yield as a colorless oil.

^{1}H NMR: δ 0.66 – 0.72 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 9H), 1.24 (sext, *J* = 7.1 Hz, 6H), 1.29 – 1.42 (m, 6H), 1.96 (s, 3H), 2.46 (s, 3H), 7.18 (d, *J* = 5.2 Hz, $J_{\text{Sn-H}meta}$ = 15.3 Hz, 2H)

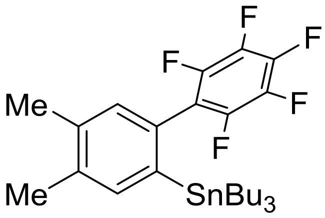
^{13}C NMR: δ 11.20 ($J_{\text{Sn–C}}$ = 338.5, 323.6 Hz), 13.62, 20.41, 25.02, 27.41, 28.90, 118.03 (td, *J* = 21.2, 3.6 Hz), 130.49, 130.71, 133.57, 134.10, 137.98 (dm, $J_{\text{C–F}}$ = 251.9 Hz), 140.79 (dm, $J_{\text{C–F}}$ = 253.8 Hz), 143.05, 144.21 ($J_{\text{Sn–C}}$ = 382.4, 364.3 Hz), 144.44 (dm, $J_{\text{C–F}}$ = 241.3 Hz)

^{19}F NMR: δ -163.63 (td, *J* = 23.3, 8.4 Hz), -157.35 (t, *J* = 20.7 Hz), -141.04 (dd, *J* = 23.8, 8.3 Hz)

^{119}Sn NMR: δ -48.89

HRMS (APCI) Calcd for $C_{22}H_{26}F_5Sn$: [M−Bu]$^+$, 505.09711. Found: *m/z* 505.09677.

tributyl(2',3',4',5',6'-pentafluoro-4,5-dimethyl-[1,1'-biphenyl]-2-yl)stannane (3ac)



Isolated in 66% yield as a colorless oil.

^{1}H NMR: δ 0.76 – 0.81 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 9H), 1.26 (sext, *J* = 7.1 Hz, 6H), 1.37 (tt, *J* = 8.0, 5.8 Hz, 6H), 2.29 (s, 3H), 2.33 (s, 3H), 7.01 (s, $J_{\text{Sn-H}meta}$ = 13.8 Hz, 1H), 7.32 (s, $J_{\text{Sn-H}ortho}$ = 40.0 Hz, 1H)

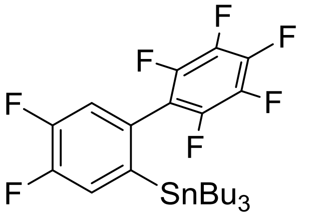
^{13}C NMR: δ 9.89 ($J_{\text{Sn–C}}$ = 342.2, 326.9 Hz), 13.69, 19.77, 19.78, 27.51, 29.02, 118.95 (td, *J* = 20.0, 3.5 Hz), 131.20, 131.57, 137.09, 137.16, 137.64 (dm, $J_{\text{C–F}}$ = 251.6 Hz), 138.82, 140.54 (dm, $J_{C–F}$ = 253.3 Hz), 140.75 ($J_{Sn–C}$ = 367.2, 350.8 Hz), 144.64 (dm, $J_{C–F}$ = 241.3 Hz)

^{19}F NMR: δ -163.99 (td, J = 23.3, 8.3 Hz), -157.56 (t, J = 20.8 Hz), -141.31 (dd, J = 23.9, 8.3 Hz)

^{119}Sn NMR: δ -40.91

HRMS (APCI) Calcd for $C_{22}H_{26}F_5Sn$: [M−Bu]$^+$, 505.09711. Found: *m/z* 505.09653.

tributyl(2',3',4,4',5,5',6'-heptafluoro-[1,1'-biphenyl]-2-yl)stannane (3ad)



Isolated in 40% yield as a colorless oil.

^{1}H NMR: δ 0.77 – 0.83 (m, 6H), 0.86 (t, J = 7.2 Hz, 9H), 1.25 (sext, J = 7.1 Hz, 6H), 1.35 (tt, J = 7.9, 5.7 Hz, 6H), 7.07 (dd, J = 10.9, 6.9 Hz, $J_{\text{Sn-H}meta}$ = 10.5 Hz, 1H), 7.34 (t, J = 9.3 Hz, $J_{\text{Sn-H}ortho}$ = 37.3 Hz, 1H)

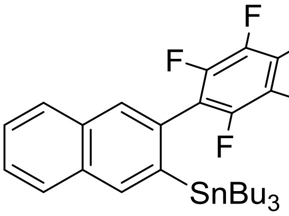
^{13}C NMR: δ 10.17 ($J_{Sn–C}$ = 347.4, 331.9 Hz), 13.64, 27.41, 28.88, 117.12 (td, J = 18.9, 3.2 Hz), 119.92 (d, J = 16.8 Hz), 125.59 (d, J = 14.1 Hz), 129.90, 137.74 (dm, $J_{C–F}$ = 254.4 Hz), 141.13 (dm, $J_{C–F}$ = 255.1 Hz), 141.91 (d, J = 4.9 Hz), 144.59 (dm, $J_{C–F}$ = 242.5 Hz), 150.20 (dd, J = 250.2, 12.4 Hz), 150.58 (dd, J = 255.0, 11.1 Hz)

^{19}F NMR: δ -163.21 (td, J = 22.6, 8.3 Hz), -155.84 (t, J = 20.8 Hz), -141.19 (dd, J = 23.4, 8.3 Hz), -139.95 – -139.77 (m), -139.30 (dt, J = 19.9, 9.7 Hz)

^{119}Sn NMR: δ -33.37 (d, J = 7.1 Hz)

HRMS (APCI) Calcd for $C_{20}H_{20}F_7Sn$: [M−Bu]$^+$, 513.04697. Found: *m/z* 513.04645.

tributyl(3-(perfluorophenyl)naphthalen-2-yl)stannane (3ae)



Isolated in 66% yield as a colorless oil.

^{1}H NMR: δ 0.84 – 0.91 (m, 15H), 1.29 (sext, J = 7.3 Hz, 6H), 1.36 – 1.49 (m, 6H), 7.55 (dt, J = 20.7, 6.9 Hz, 2H), 7.74 (s, $J_{\text{Sn-H}meta}$ = 12.4 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.06 (s, $J_{\text{Sn-H}ortho}$ = 44.3 Hz, 1H)

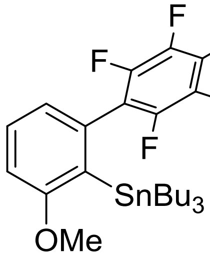
^{13}C NMR: δ 10.10 ($J_{\text{Sn–C}}$ = 342.9, 327.7 Hz), 13.70, 27.51, 29.03, 118.89 (td, J = 19.8, 3.4 Hz), 126.81, 127.11, 127.75, 128.00, 129.65, 130.46, 132.94, 137.74 (dm, $J_{\text{C–F}}$ = 251.5 Hz), 137.93, 140.80 (dm, $J_{\text{C–F}}$ = 254.0 Hz), 141.03 ($J_{\text{Sn–C}}$ = 353.8, 338.0 Hz), 144.76 (dm, $J_{\text{C–F}}$ = 242.1 Hz)

^{19}F NMR: δ -163.65 (td, J = 23.3, 8.3 Hz), -156.89 (t, J = 20.8 Hz), -140.94 (dd, J = 23.7, 8.2 Hz)

^{119}Sn NMR: δ -36.89

HRMS (APCI) Calcd for $C_{24}H_{24}F_5Sn$: $[M{-}Bu]^+$, 527.08146. Found: *m*/*z* 527.08105.

tributyl(2',3',4',5',6'-pentafluoro-3-methoxy-[1,1'-biphenyl]-2-yl)stannane (3af)



Isolated in 79% yield as a colorless oil.

^{1}H NMR: δ 0.69 – 0.74 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H), 1.22 (sext, J = 7.2 Hz, 6H), 1.31 – 1.40 (m, 6H), 3.83 (s, 3H), 6.82 (d, J = 7.4 Hz, $J_{\text{Sn-H}meta}$ = 10.2 Hz, 1H), 6.91 (d, J = 8.1 Hz, $J_{\text{Sn-H}meta}$ = 13.0 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H)

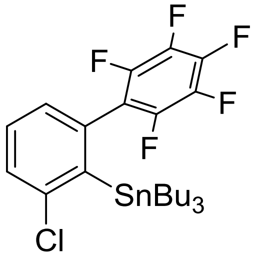
^{13}C NMR: δ 10.84 ($J_{\text{Sn–C}}$ = 355.0, 339.1 Hz), 13.70, 27.43, 29.02, 55.44, 109.57, 118.48 (td, J = 19.5, 3.4 Hz), 123.74, 129.99, 133.25 ($J_{\text{Sn–C}}$ = 346.4, 331.0 Hz), 134.73, 137.68 (dm, $J_{\text{C–F}}$ = 249.9 Hz), 140.61 (dm, $J_{\text{C–F}}$ = 253.4 Hz), 144.58 (dm, $J_{\text{C–F}}$ = 241.7 Hz), 163.96

^{19}F NMR: δ -164.16 (td, *J* = 22.8, 8.1 Hz), -157.88 (t, *J* = 20.8 Hz), -142.44 (dd, *J* = 23.6, 8.0 Hz)

^{119}Sn NMR: δ -46.49

HRMS (APCI) Calcd for $C_{21}H_{24}F_5OSn$: $[M-Bu]^+$, 507.07638. Found: *m/z* 507.07593.

tributyl(3-chloro-2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)stannane (3ag)



Isolated in 55% yield as a colorless oil.

^{1}H NMR: δ 0.78 – 0.83 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 9H), 1.23 (sext, *J* = 7.3 Hz, 6H), 1.30 – 1.47 (m, 6H), 7.06 (d, *J* = 7.4 Hz, $J_{\text{Sn-H}meta}$ = 7.6 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, $J_{\text{Sn-H}meta}$ = 8.4 Hz, 1H)

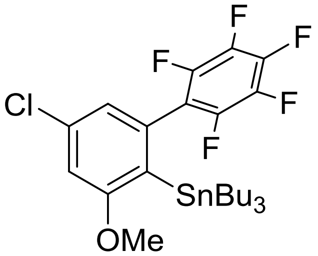
^{13}C NMR: δ 11.99 ($J_{\text{Sn–C}}$ = 352.9, 337.4 Hz), 13.64, 27.35, 28.81, 118.07 (td, *J* = 19.6, 3.7 Hz), 129.13, 129.53, 129.84, 135.55, 137.77 (dm, $J_{\text{C–F}}$ = 253.6 Hz), 140.94 (dm, $J_{\text{C–F}}$ = 254.4 Hz), 143.57, 144.57 (dm, $J_{\text{C–F}}$ = 242.7 Hz), 145.14 ($J_{\text{Sn–C}}$ = 319.9, 305.2 Hz)

^{19}F NMR: δ -163.54 (td, *J* = 23.0, 8.4 Hz), -156.77 (t, *J* = 20.8 Hz), -142.09 (dd, *J* = 23.5, 8.3 Hz)

^{119}Sn NMR: δ -33.39

HRMS (APCI) Calcd for $C_{20}H_{21}{}^{35}ClF_5Sn$: $[M-Bu]^+$, 511.02684. Found: *m/z* 511.02655.

tributyl(5-chloro-2',3',4',5',6'-pentafluoro-3-methoxy-[1,1'-biphenyl]-2-yl)stannane (3ah)



Isolated in 68% yield as a colorless oil.

^{1}H NMR: δ 0.67 – 0.73 (m, 6H), 0.83 (t, *J* = 7.3 Hz, 9H), 1.21 (sext, *J* = 7.2 Hz, 6H), 1.33 (tt, *J* = 8.1, 6.1 Hz, 6H), 3.83 (s, 3H), 6.84 (s, $J_{\text{Sn-H}meta}$ = 10.2 Hz, 1H), 6.87 (s, $J_{\text{Sn-H}meta}$ = 12.0 Hz, 1H)

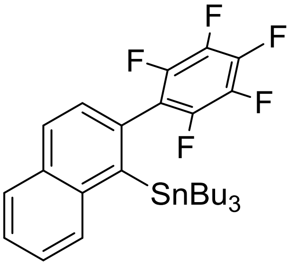
^{13}C NMR: δ 10.85 ($J_{\text{Sn–C}}$ = 356.6, 340.8 Hz), 13.68, 27.38, 28.95, 55.73, 110.41, 117.44 (td, *J* = 19.3, 3.7 Hz), 123.53, 131.91 ($J_{\text{Sn–C}}$ = 330.2, 315.7 Hz), 135.60, 135.63, 137.71 (dm, $J_{\text{C–F}}$ = 253.0 Hz), 140.89 (dm, $J_{\text{C–F}}$ = 254.3 Hz), 144.49 (dm, $J_{\text{C–F}}$ = 242.7 Hz), 164.65

^{19}F NMR: δ -163.87 (td, *J* = 22.7, 8.2 Hz), -157.09 (t, *J* = 20.8 Hz), -142.40 (dd, *J* = 23.4, 8.2 Hz)

^{119}Sn NMR: δ -43.70

HRMS (APCI) Calcd for $C_{21}H_{23}{}^{35}ClF_5OSn$: [M−Bu]$^+$, 541.03741. Found: *m*/*z* 541.03711.

tributyl(2-(perfluorophenyl)naphthalen-1-yl)stannane (3ai)



Isolated in 68% yield as a colorless oil.

^{1}H NMR: δ 0.82 (t, *J* = 7.3 Hz, 9H), 0.84 – 0.89 (m, 6H), 1.23 (sext, *J* = 7.3 Hz, 6H), 1.31 – 1.47 (m, 6H), 7.22 (d, *J* = 8.2 Hz, $J_{\text{Sn-H}meta}$ = 9.6 Hz, 1H), 7.53 – 7.60 (m, $J_{\text{Sn-H}peri}$ = 12.0 Hz, 2H), 7.89 (t, *J* = 7.7 Hz, 2H), 7.95 – 8.01 (m, 1H)

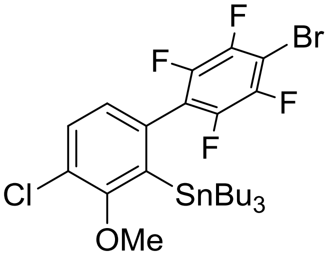
^{13}C NMR: δ 11.75 ($J_{\text{Sn–C}}$ = 341.4, 326.3 Hz), 13.61, 27.36, 28.94, 119.36 (td, *J* = 20.0, 3.5 Hz), 126.36, 126.53, 127.87, 129.15, 129.23, 130.38, 132.63, 133.26, 137.83 (dm, $J_{\text{C–F}}$ = 252.6 Hz), 139.14, 140.84 (dm, $J_{\text{C–F}}$ = 254.1 Hz), 144.83 (dm, $J_{\text{C–F}}$ = 242.2 Hz), 146.04 ($J_{\text{Sn–C}}$ = 353.7, 337.4 Hz)

^{19}F NMR: δ -163.68 (td, *J* = 23.1, 22.6, 7.8 Hz), -157.13 (t, *J* = 20.7 Hz), -141.82 – -141.61 (m)

^{119}Sn NMR: δ -46.37

HRMS (APCI) Calcd for $C_{24}H_{24}F_5Sn$: [M−Bu]$^+$, 527.08146. Found: *m*/*z* 527.08118.

(4'-bromo-4-chloro-2',3',5',6'-tetrafluoro-3-methoxy-[1,1'-biphenyl]-2-yl)tributylstannane (3nj)



Isolated in 59% yield as a colorless oil.

^{1}H NMR: δ 0.72 – 0.80 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H), 1.22 (sext, J = 7.3 Hz, 6H), 1.29 – 1.44 (m, 6H), 3.95 (s, 3H), 6.91 (d, J = 8.0 Hz, $J_{\text{Sn-H}meta}$ = 11.5 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H)

^{13}C NMR: δ 11.22 ($J_{\text{Sn–C}}$ = 353.0, 337.4 Hz), 13.67, 27.46, 28.97, 61.51 (d, J = 2.1 Hz), 99.32 (t, $J_{\text{C–CF}}$ = 22.5 Hz), 121.96 (t, $J_{\text{C–CF}}$ = 19.3 Hz), 127.40, 127.43, 131.60, 133.76, 140.16 ($J_{\text{Sn–C}}$ = 316.3, 302.0 Hz), 144.48 (ddt, $J_{\text{C–F}}$ = 247.9, $J_{\text{C–CF}}$ = 14.2, $J_{\text{C–CCF}}$ = $J_{\text{C–CCCF}}$ = 4.6 Hz), 145.10 (ddt, $J_{\text{C–F}}$ = 248.9, $J_{\text{C–CF}}$ = 16.2, $J_{\text{C–CCF}}$ = $J_{\text{C–CCCF}}$ = 4.1 Hz), 160.69

^{19}F NMR: δ -140.89 (dd, J = 22.7, 9.4 Hz), -135.06 (dd, J = 22.4, 9.1 Hz)

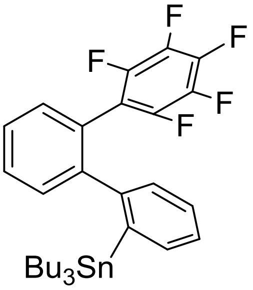
^{119}Sn NMR: δ -44.54

HRMS (APCI) Calcd for $C_{21}H_{23}{}^{79}Br^{35}ClF_4OSn$: [M−Bu]$^+$, 600.95734. Found: m/z 600.95624.

7. Synthesis of stannylteraryls via sequential insertion of different arynes to tributyl(pentafluorophenyl)stannanes

General procedure: A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (3.0 equiv, 0.30 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (1.5 equiv, 0.15 mmol), CuTC (5 mol %, 5.0 µmol), DEE (0.67 mL), **3** (1.0 equiv, 0.10 mmol) and **2** (1.5 equiv, 0.15 mmol) under an argon atmosphere. The resulting mixture was stirred at 130 °C for 12 h. The mixture was diluted with hexane (30 mL) before filtration. The organic solution was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography (hexane as an eluent) gave the corresponding product.

tributyl(2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-2-yl)stannane (4aaa)



Isolated in 55% yield as a colorless oil.

^{1}H NMR: δ 0.58 – 0.81 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H), 1.24 (sext, J = 7.3 Hz, 6H), 1.30 – 1.48 (m, 6H), 6.86 (d, J = 7.6 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.49 (dq, J = 21.2, 7.4 Hz, 3H)

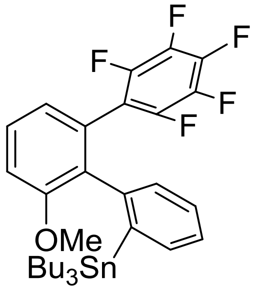
^{13}C NMR: δ 10.58 (J_{Sn-C} = 341.8, 327.1 Hz), 13.75, 27.47, 29.13, 115.94 (td, J = 19.4, 3.4 Hz), 125.75, 126.67, 127.10, 127.49, 128.48, 129.71, 130.74, 131.20, 137.33, 137.39 (dm, J_{C-F} = 252.5 Hz), 140.56 (dm, J_{C-F} = 253.2 Hz), 143.42 (J_{Sn-C} = 384.9, 366.6 Hz), 143.44 (J_{Sn-C} = 384.1, 367.8 Hz), 143.65 (dm, J_{C-F} = 248.3 Hz), 144.67 (dm, J_{C-F} = 249.4 Hz), 146.07, 147.42

^{19}F NMR: δ -164.39 – -163.79 (m), -156.88 (t, J = 20.6 Hz), -142.35 (d, J = 16.7 Hz), -138.25 (d, J = 17.7 Hz)

^{119}Sn NMR: δ -41.34, -41.30

HRMS (APCI) Calcd for $C_{26}H_{26}F_5Sn$: $[M-Bu]^+$, 553.09711. Found: *m/z* 553.09705.

tributyl(2'',3'',4'',5'',6''-pentafluoro-6'-methoxy-[1,1':2',1''-terphenyl]-2-yl)stannane (4afa)



Isolated in 87% yield as a colorless oil.

^{1}H NMR: δ 0.70 (qt, *J* = 17.8, 8.7 Hz, 6H), 0.85 (t, *J* = 7.2 Hz, 9H), 1.25 (sext, *J* = 7.1 Hz, 6H), 1.31 – 1.45 (m, 6H), 3.75 (s, 3H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.46 (m, 2H)

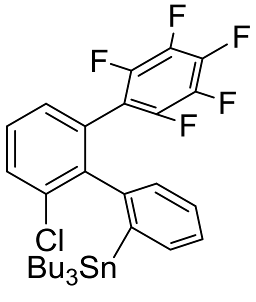
^{13}C NMR: δ 10.22 ($J_{\text{Sn–C}}$ = 340.8, 325.7 Hz), 13.76, 27.58, 29.13, 55.74, 111.82, 115.96 (td, *J* = 19.9, 3.6 Hz), 122.83, 126.52, 127.35, 127.91, 128.64, 129.06, 134.34, 136.53, 137.20 (dm, $J_{\text{C–F}}$ = 251.1 Hz), 140.42 (dm, $J_{\text{C–F}}$ = 253.0 Hz), 143.15, 143.43 (dm, $J_{\text{C–F}}$ = 247.0 Hz), 144.36 (dm, $J_{\text{C–F}}$ = 247.9 Hz), 144.89 ($J_{\text{Sn–C}}$ = 405.0, 387.4 Hz), 144.92 ($J_{\text{Sn–C}}$ = 405.2, 386.8 Hz), 157.38

^{19}F NMR: δ -164.89 – -164.55 (m), -157.28 (t, *J* = 20.8 Hz), -141.76 (d, *J* = 23.2 Hz), -138.25 (d, *J* = 22.8 Hz)

^{119}Sn NMR: δ -45.16, -45.09

HRMS (APCI) Calcd for $C_{27}H_{28}F_5OSn$: $[M-Bu]^+$, 583.10768. Found: *m/z* 583.10809.

tributyl(6'-chloro-2'',3'',4'',5'',6''-pentafluoro-[1,1':2',1''-terphenyl]-2-yl)stannane (4aga)



Isolated in 63% yield as a colorless oil.

^{1}H NMR: δ 0.62 – 0.79 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 9H), 1.24 (sext, *J* = 7.2 Hz, 6H), 1.30 – 1.46 (m, 6H), 6.93 (d, J = 7.4 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.37 – 7.44 (m, 2H), 7.59 (d, J = 8.1 Hz, 1H)

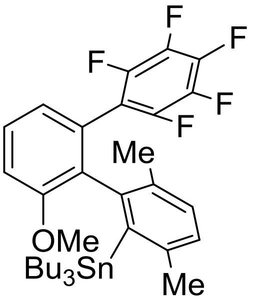
^{13}C NMR: δ 10.50 ($J_{\text{Sn–C}}$ = 341.8, 326.6 Hz), 10.52 ($J_{\text{Sn–C}}$ = 341.8, 326.7 Hz), 13.71, 27.54, 29.11, 115.31 (td, J = 19.8, 3.8 Hz), 127.14, 127.46, 128.49, 128.65, 128.67, 129.23, 130.98, 135.14, 137.01, 137.25 (dm, $J_{\text{C–F}}$ = 247.6 Hz), 140.72 (dm, $J_{\text{C–F}}$ = 254.1 Hz), 143.46 (dm, $J_{\text{C–F}}$ = 239.7 Hz), 143.99, 144.15 (dm, $J_{\text{C–F}}$ = 249.7 Hz), 144.19 ($J_{\text{Sn–C}}$ = 377.6, 360.4 Hz), 144.21 ($J_{\text{Sn–C}}$ = 378.0, 363.2 Hz), 144.36

^{19}F NMR: δ -164.12 (dtd, J = 67.2, 22.7, 7.1 Hz), -156.17 (t, J = 20.8 Hz), -140.49 (d, J = 23.2 Hz), -138.18 (d, J = 23.1 Hz)

^{119}Sn NMR: δ -45.92, -45.84

HRMS (APCI) Calcd for $C_{26}H_{25}{}^{35}ClF_5Sn$: $[M-Bu]^+$, 587.05814. Found: *m/z* 587.05792.

tributyl(2'',3'',4'',5'',6''-pentafluoro-6'-methoxy-3,6-dimethyl-[1,1':2',1''-terphenyl]-2-yl)stannane (4afb)



Isolated in 54% yield as a colorless oil.

^{1}H NMR: δ 0.51 – 0.68 (m, 6H), 0.84 (t, J = 7.2 Hz, 9H), 1.22 (sext, J = 7.2 Hz, 6H), 1.27 – 1.40 (m, 6H), 1.77 (s, 3H), 2.36 (s, 3H), 3.75 (s, 3H), 6.92 (q, J = 7.6 Hz, 3H), 7.05 (d, J = 8.2 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H)

^{13}C NMR: δ 11.39 ($J_{\text{Sn–C}}$ = 337.2, 322.2 Hz), 11.42 ($J_{\text{Sn–C}}$ = 337.4, 322.5 Hz), 13.76, 19.84 (d, J = 5.6 Hz), 24.78, 27.57, 29.15, 55.65, 111.86, 115.58 (td, J = 19.0, 3.3 Hz), 123.41, 128.37, 128.57, 128.80, 129.60, 133.30, 133.79, 137.21 (dm, $J_{\text{C–F}}$ = 250.8 Hz), 140.25 (dm, $J_{\text{C–F}}$ = 253.3 Hz), 141.30, 142.52, 143.85 (dm, $J_{\text{C–F}}$ = 247.2 Hz), 144.22 (dm, $J_{\text{C–F}}$ = 242.9 Hz), 144.51, 144.55, 157.85

^{19}F NMR: δ -164.60 (dtd, J = 92.4, 23.6, 23.0, 7.3 Hz), -157.30 (t, J = 21.1 Hz), -141.31 (dd, J = 23.3, 6.6 Hz), -135.91 (d, J = 23.9 Hz)

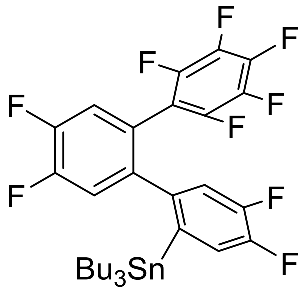
^{119}Sn NMR: δ -52.96, -52.77

HRMS (APCI) Calcd for $C_{29}H_{32}F_5OSn$: $[M-Bu]^+$, 611.13898. Found: *m/z* 611.13959.

8. A one-pot sequential insertion of the same arynes

General procedure: A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (4.0 equiv, 0.40 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (2.0 equiv, 0.20 mmol), CuTC (5 mol %, 5.0 µmol), DEE (0.67 mL), **1a** (1.0 equiv, 0.10 mmol) and **2** (2.0 equiv, 0.20 mmol) under an argon atmosphere. The resulting mixture was stirred at 130 °C for the period as specified in Fig. 5. The mixture was diluted with hexane (30 mL) before filtration. The organic solution was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography (hexane as an eluent) gave the corresponding product.

tributyl(2'',3'',4,4',4'',5,5',5'',6''-nonafluoro-[1,1':2',1''-terphenyl]-2-yl)stannane (4add)



Isolated in 16% yield as a colorless oil.

^{1}H NMR (400 MHz): δ 0.68 – 0.83 (m, 6H), 0.86 (t, *J* = 7.2 Hz, 9H), 1.26 (sext, *J* = 7.2 Hz, 6H), 1.33 – 1.47 (m, 6H), 6.67 (dd, *J* = 11.2, 7.0 Hz, 1H), 7.13 (dd, *J* = 10.4, 7.9 Hz, 1H), 7.17 – 7.26 (m, 2H)

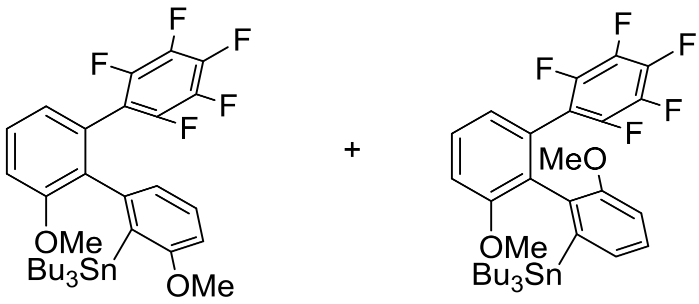
^{13}C NMR (100 MHz): δ 10.77 ($J_{Sn–C}$ = 347.6, 332.1 Hz), 13.66, 27.39, 28.98, 113.32 (td, *J* = 19.0, 3.5 Hz), 117.62 (d, *J* = 16.4 Hz), 119.87 (d, *J* = 17.5 Hz), 120.52 (d, *J* = 18.0 Hz), 122.22, 125.42 (d, *J* = 13.7 Hz), 136.05 – 136.67 (m), 138.41 – 139.25 (m), 139.76 – 140.20 (m), 140.63, 141.42, 141.96, 142.16 – 142.66 (m), 143.02 – 143.43 (m), 144.64 – 145.03 (m), 145.51 – 145.90 (m), 149.16 (dd, *J* = 250.0, 13.0 Hz), 149.70 (dd, *J* = 251.9, 13.0 Hz), 149.72 (dd, *J* = 254.4, 11.2 Hz), 150.73 (dd, *J* = 254.1, 12.5 Hz)

^{19}F NMR: δ -162.42 (dtd, *J* = 152.6, 22.4, 7.5 Hz), -154.04 (t, *J* = 21.0 Hz), -141.88 (d, *J* = 23.1 Hz), -141.25 (dt, *J* = 17.1, 7.8 Hz), -139.82 (dt, *J* = 20.1, 9.9 Hz), -138.97 (dt, *J* = 18.6, 8.7 Hz), -138.55 (d, *J* = 23.1 Hz), -136.16 (dt, *J* = 18.7, 8.7 Hz)

^{119}Sn NMR: δ -34.33

HRMS (APCI) Calcd for $C_{26}H_{22}F_9Sn$: $[M{-}Bu]^+$, 625.05943. Found: *m*/*z* 625.05927.

mixture of tributyl(2",3",4",5",6"-pentafluoro-3,6'-dimethoxy-[1,1':2',1"-terphenyl]-2-yl)stannane and tributyl(2",3",4",5",6"-pentafluoro-6,6'-dimethoxy-[1,1':2',1"-terphenyl]-2-yl)stannane (4aff)



75 : 25

Isolated in 87% yield as a colorless oil.

^{1}H NMR: δ 0.54 – 0.76 (m, 8H), 0.81 – 0.89 (m, 12H), 1.23 (dq, *J* = 14.3, 7.2 Hz, 8H), 1.29 – 1.45 (m, 8H), 3.45 (s, 1H), 3.74 (s, 3H), 3.74 (s, 1H), 3.76 (s, 3H), 6.51 (dm, *J* = 6.5 Hz, $J_{\text{Sn-H}meta}$ = 11.8 Hz, 1H), 6.59 (d, *J* = 7.3 Hz, 0.3H), 6.67 (d, *J* = 7.5 Hz, $J_{\text{Sn-H}meta}$ = 14.8 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 0.3H), 7.02 (ddd, *J* = 8.4, 3.7, 0.9 Hz, 1.3H), 7.06 – 7.12 (m, 1.3H), 7.16 (dd, *J* = 8.1, 7.3 Hz, 0.3H), 7.38 – 7.46 (m, 1.3H)

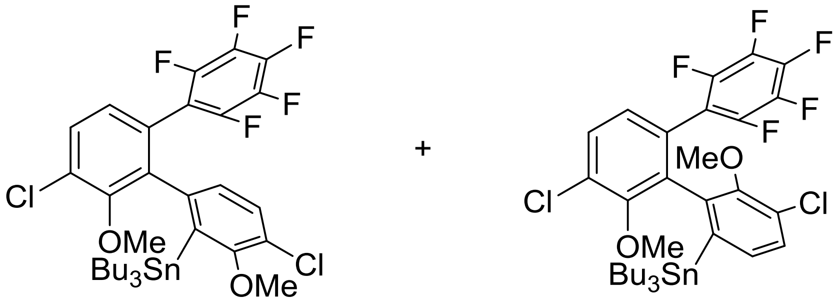
^{13}C NMR: δ 10.29 ($J_{\text{Sn–C}}$ = 341.2, 325.0 Hz), 10.31 ($J_{\text{Sn–C}}$ = 340.6, 325.5 Hz), 10.87 ($J_{\text{Sn–C}}$ = 354.8, 339.0 Hz), 10.89 ($J_{\text{Sn–C}}$ = 354.9, 339.1 Hz), 13.78, 13.81, 27.61, 29.16, 29.21, 54.48, 55.12, 55.66, 55.74, 107.82, 109.56, 111.69, 112.18, 116.05 (td, *J* = 19.7, 3.6 Hz), 122.53, 122.62, 127.64, 128.19, 128.53, 128.58, 128.66, 128.93, 129.39, 129.95, 130.49, 133.18, 133.21, 133.89, 137.27 (dm, $J_{\text{C–F}}$ = 250.7 Hz), 140.39 (dm, $J_{\text{C–F}}$ = 252.7 Hz), 143.63 (dm, $J_{\text{C–F}}$ = 243.3 Hz), 144.35 (dm, $J_{\text{C–F}}$ = 242.3 Hz), 144.39, 147.79, 147.84, 155.79, 157.46, 157.54, 163.00

^{19}F NMR: δ -165.65 (dtd, *J* = 206.0, 23.3, 22.4, 7.0 Hz), -164.72 (dtd, *J* = 99.2, 23.0, 22.5, 7.5 Hz), -157.95 (t, *J* = 20.9 Hz), -157.45 (t, *J* = 20.9 Hz), -143.28 (dd, *J* = 23.1, 7.1 Hz), -141.37 (dd, *J* = 23.7, 7.2 Hz), -138.17 (dd, *J* = 23.9, 6.2 Hz), -137.66 (dd, *J* = 23.8, 6.6 Hz)

^{119}Sn NMR: δ -49.90, -49.83, -43.69, -43.57

HRMS (APCI) Calcd for $C_{28}H_{30}F_5O_2Sn$: [M−Bu]$^+$, 613.11824. Found: *m*/*z* 613.11877.

mixture of tributyl(4,5'-dichloro-2'',3'',4'',5'',6''-pentafluoro-3,6'-dimethoxy-[1,1':2',1''-terphenyl]-2-yl)stannane and tributyl(5,5'-dichloro-2'',3'',4'',5'',6''-pentafluoro-6,6'-dimethoxy-[1,1':2',1''-terphenyl]-2-yl)stannane (4ajj)



94 : 6

Isolated in 45% yield as a colorless oil.

^{1}H NMR: δ 0.61 – 0.80 (m, 6.4H), 0.85 (t, *J* = 7.3 Hz, 9.6H), 1.24 (sext, *J* = 7.2 Hz, 6.4H), 1.28 – 1.47 (m, 6.4H), 3.35 (s, 3H), 3.40 (s, 0.2H), 3.78 (s, 0.2H), 3.92 (s, 3H), 6.54 (d, *J* = 8.0 Hz, $J_{\text{Sn-H}meta}$ = 11.6 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, $J_{\text{Sn-H}meta}$ = 15.1 Hz, 0.07H), 7.02 (d, *J* = 8.3 Hz, 1H), 7.05 (s, 0.07H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 0.07H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 0.2H)

^{13}C NMR: δ 11.37, 11.39, 11.48 ($J_{\text{Sn–C}}$ = 356.8, 340.9 Hz), 11.49 ($J_{\text{Sn–C}}$ = 356.4, 340.9 Hz), 13.77, 13.82, 27.54, 27.59, 29.04, 29.07, 55.59, 59.76, 59.94, 61.34, 114.73 (td, *J* = 19.5, 3.8 Hz), 125.36, 126.09, 126.40, 127.17, 129.76, 130.39, 130.51, 137.40 (dm, $J_{\text{C–F}}$ = 251.8 Hz), 139.54, 140.83 (dm, $J_{\text{C–F}}$ = 254.3 Hz), 141.21, 141.23, 142.11, 143.54 (dm, $J_{\text{C–F}}$ = 243.2 Hz), 144.31 (dm, $J_{\text{C–F}}$ = 241.6 Hz), 154.39, 159.96

^{19}F NMR: δ -164.72 (td, *J* = 23.3, 7.4 Hz), -163.76 (dtd, *J* = 67.7, 22.6, 7.6 Hz), -156.49 (t, *J* = 21.0 Hz), -155.84 (t, *J* = 20.9 Hz), -142.30 (dd, *J* = 23.4, 7.0 Hz), -141.36 (d, *J* = 23.5 Hz), -138.15 (d, *J* = 23.5 Hz), -136.27 (d, *J* = 22.8 Hz)

^{119}Sn NMR: δ -48.07, -48.01, -43.71, -43.56

HRMS (APCI) Calcd for $C_{28}H_{28}{}^{35}Cl_2F_5O_2Sn$: [M−Bu]$^+$, 681.04030. Found: *m*/*z* 681.04004.

9. GC trace of a one-pot sequential insertion of benzynes

A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (4.0 equiv, 0.40 mmol, 0.0231 g) under an argon atmosphere. The tube was charged with 18-crown-6 (2.0 equiv, 0.20 mmol, 0.0534 g), CuTC (5 mol %, 5.2 µmol, 0.0010 g), DEE (0.67 mL), **1a** (1.0 equiv, 0.10 mmol, 0.0456 g), **2a** (2.0 equiv, 0.20 mmol, 0.0599 g) and $C_{12}H_{26}O_3$ as an internal standard (0.50 equiv, 0.050 mmol, 0.0111 g) under an argon atmosphere. The resulting mixture was stirred at 130 °C and monitored by GC analysis based on calibration curves obtained using an authentic samples.

Table S14. GC Trace of a One-Pot Sequential Insertion of Benzynes

Entry	Time (h)		$C_{12}H_{26}O_3$	1a	2a	3aa	4aaa
1	0.5	GC area	33156	74486	–	35977	0
		Yield (%)	–	60	83[a]	22	0
2	1	GC area	53325	12292	90548	169755	7133
		Yield (%)	–	6	55	65	6
3	1.5	GC area	47569	0	53693	123622	98058
		Yield (%)	–	0	36	53	41
4	2	GC area	82256	0	56593	136548	242807
		Yield (%)	–	0	22	34	57
5	2.5	GC area	52332	0	26056	71136	168400
		Yield (%)	–	0	15	28	62
6	3	GC area	80711	0	27155	90843	274952
		Yield (%)	–	0	10	23	66
7	4.5	GC area	58436	0	8920	51600	220553
		Yield (%)	–	0	4	18	72
8	6	GC area	123491	0	10175	85769	462338
		Yield (%)	–	0	2	14	72

[a] The GC yield of **2a** was determined by using 0.2 mmol of $\mathbf{C_{12}H_{26}O_3}$ instead of 0.05 mmol.

Entry	Time (h)		$C_{12}H_{26}O_3$	2a
1’	0.5	GC area	188959	125307
		Yield (%)	–	83

10. Mechanistic studies on the proposed catalytic cycle

Fig. 7A

A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (3.0 equiv, 0.30 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (1.5 equiv, 0.15 mmol), CuTC (1.0 equiv, 0.10 mmol), DEE (0.67 mL) and **1** (1.0 equiv, 0.10 mmol) under an argon atmosphere. The resulting mixture was stirred at 30 °C for 1 h. The mixture was diluted with hexane (30 mL) before filtration. The conversions and yields were determined by ^{119}Sn NMR analysis of the crude reaction mixture using tributyl(vinyl)stannane as an internal standard (solvent: $CDCl_3$).

Fig. 7B

A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (3.0 equiv, 0.30 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (1.5 equiv, 0.15 mmol), **5** (1.0 equiv, 0.10 mmol) and DEE (0.67 mL) under an argon atmosphere. The resulting mixture was stirred at 30 °C for 5 min. The mixture was diluted with hexane (30 mL) before filtration. The conversion of **5** was determined by ^{119}Sn NMR analysis of the crude reaction mixture using tributyl(vinyl)stannane as an internal standard (solvent: $CDCl_3$).

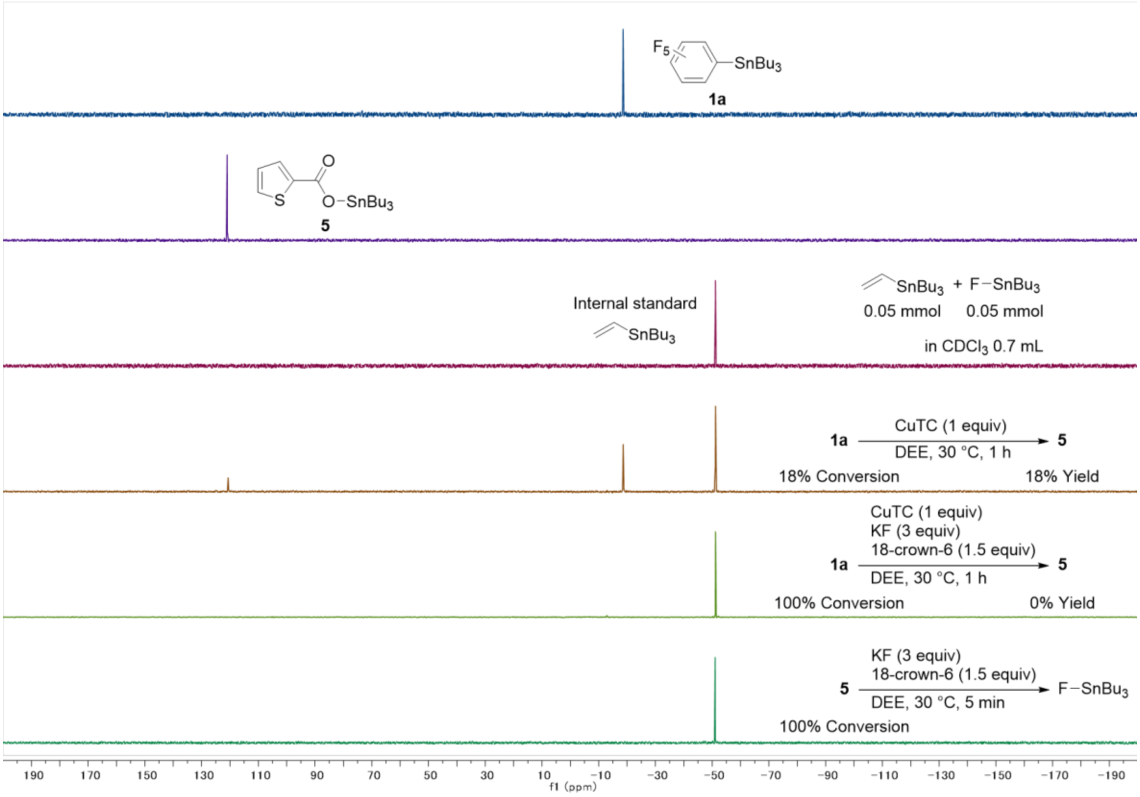


Figure S6. ^{119}**Sn NMR Spectra of the Experiments Described in Fig. 7**

Fig. 7C

Phenylcopper was prepared according to a literature procedure.[18]

A round-bottom flask equipped with a magnetic stirring bar was flame-dried under an argon atmosphere. The flask was charged with phenyl bromide (1.0 equiv, 1.0 mmol, 0.1569 g) and THF (2.0 mL) and cooled to -78 °C under an argon atmosphere. To this solution, *n*-butyllithium (1.55 M in *n*-hexane, 1.0 equiv, 1.0 mmol, 0.65 mL) was added dropwise via syringe. The resulting mixture was stirred at -78 °C for 1 h. To this mixture, cuprous bromide (1.05 equiv, 1.05 mmol, 0.1506 g) in THF (6.2 mL) was added dropwise via syringe over a period of 15 min before the resulting mixture was stirred at -10 °C for 3 h (mixture X). A mixture Y of KF (3.0 equiv, 3.0 mmol, 0.1747 g), 18-crown-6 (0.116 M in THF, 1.5 equiv, 1.5 mmol, 13.0 mL) and Bu_3SnF (1.0 equiv, 1.0 mmol, 0.3086 g) were added to the mixture X (mixture Z). The resulting mixture Z was stirred at -10 °C for 10 min. $C_{12}H_{26}O_3$ as an internal standard (0.50 equiv, 0.50 mmol, 0.1093 g) was added to the mixture. The yields of products were determined by GC analysis based on calibration curves obtained using an authentic samples.

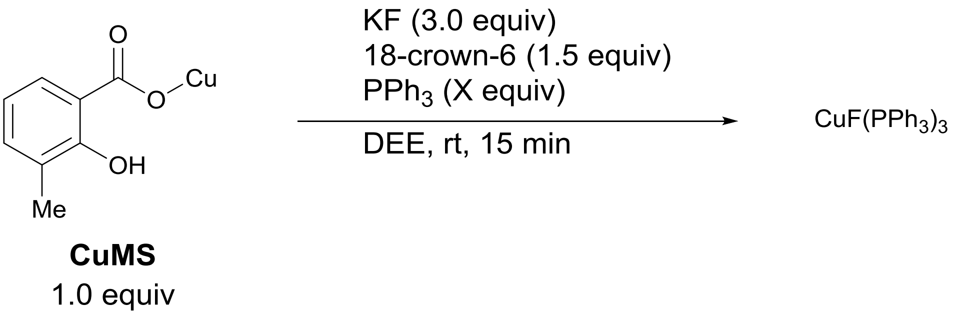
GC area: 1605631 (**1k**), 803189 ($C_{12}H_{26}O_3$).

Yield of **1k**: 54%

Formation of CuF as an actual catalytic intermediate

General procedure: A Schlenk tube equipped with a magnetic stirring bar was flame-dried after addition of KF (3.0 equiv, 0.30 mmol) under an argon atmosphere. The tube was charged with 18-crown-6 (1.5 equiv, 0.15 mmol), CuMS (1.0 equiv, 0.10 mmol), PPh_3 (X equiv, 0.1 × X mmol), DEE (0.20 mL), under an argon atmosphere. The resulting mixture was stirred at room temperature for 15 min. The formation of $CuF(PPh_3)_3$ was determined by ^{19}F, ^{31}P NMR analysis of the crude reaction mixture (solvent: $CDCl_3$).

Table S15. Formation of CuF as an Actual Catalytic Intermediate



Entry	X	^{19}F NMR Chemical Shift (ppm)	^{31}P NMR Chemical Shift (ppm)
1	0	–	–
2	*3.0*	***-210.5***	***-3.51***

$CuF(PPh_3)_3 \cdot 2MeOH$ is known.[19]

^{19}F NMR (282 MHz, CD_3CN) δ -204.8

^{31}P NMR (202 MHz, $CDCl_3$) δ **-3.55**

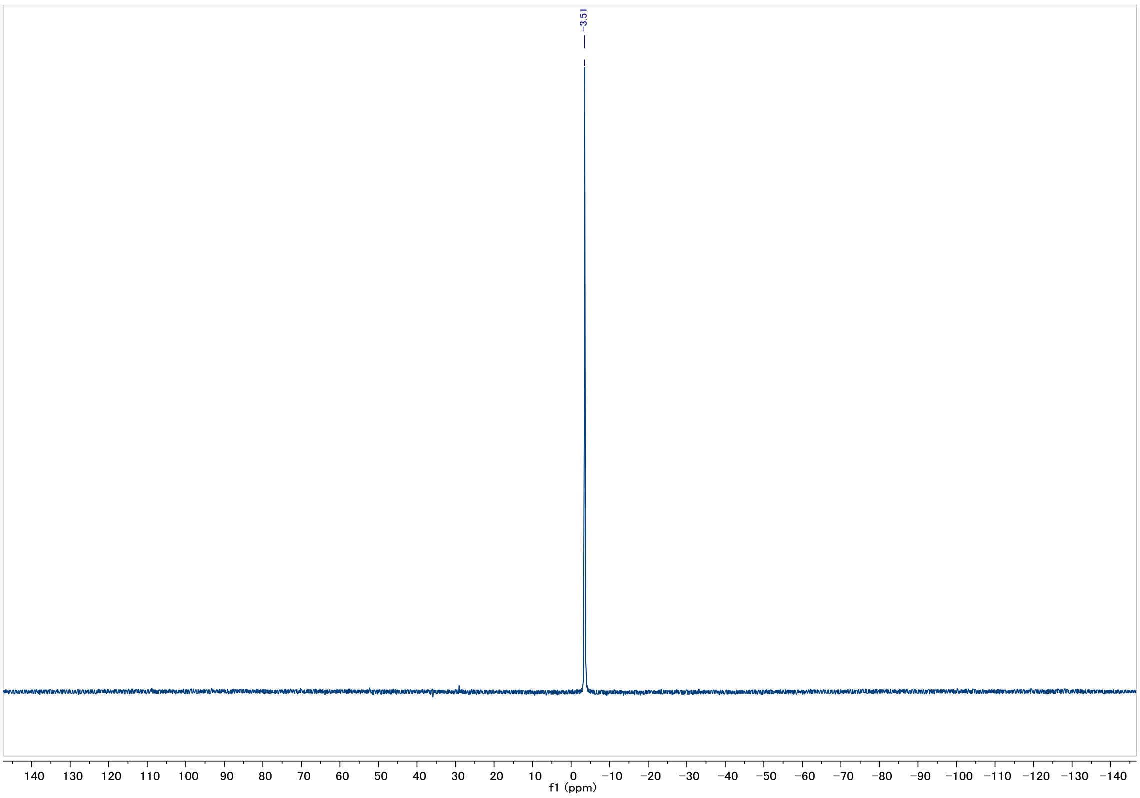
Commercially available $CuF(PPh_3)_3 \cdot 2MeOH$ (actual chemical shift)

^{19}F NMR (470 MHz, $CDCl_3$) δ **-203.3**

In addition, the counteranion-independent catalytic activity observed with CuTC, CuCl or CuI (Table S6, entries 1–3) indicates that these Cu(I) salts are swiftly converted into CuF, which serves as the actual catalytic intermediate.

^{19}F NMR (Table S15, Entry 2, $CDCl_3$)

^{31}P NMR (Table S15, Entry 2, $CDCl_3$)



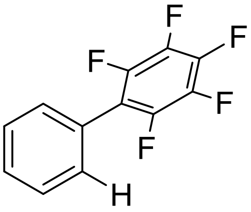
11. Gram-scale arylstannylation and transformations of the resulting *ortho*-stannylbiaryl

Gram-scale arylstannylation

A round-bottom flask equipped with a magnetic stirring bar was flame-dried after addition of KF (2.0 equiv, 8.0 mmol, 0.4650 g) under an argon atmosphere. The tube was charged with 18-crown-6 (1.0 equiv, 4.0 mmol, 1.0577 g), CuTC (5 mol %, 0.2 mmol, 0.0380 g), DEE (26.7 mL), **1a** (1.0 equiv, 4.0 mmol, 1.8288 g) and **2a** (1.0 equiv, 4.0 mmol, 1.1934 g) under an argon atmosphere. The resulting mixture was stirred at 130 °C for 6 h. The mixture was diluted with hexane before filtration. The organic solution was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography (hexane as an eluent) gave **3aa** (74%, 1.5702 g) as a colorless oil.

Fig. 8A

2,3,4,5,6-pentafluoro-1,1'-biphenyl (6)



6 was prepared according to a literature procedure.[20]

A Schlenk tube equipped with a magnetic stirring bar was charged with **3aa** (1.0 equiv, 0.10 mmol, 0.0534 g), THF (1.0 mL) and aq. HCl (12 M, 10 equiv, 1.0 mmol, 0.08 mL) under an argon atmosphere. The resulting mixture was stirred at 25 °C for 3 h. After the mixture was quenched with saturated $NaHCO_3$ aqueous solution and diluted with hexane, the organic layer was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography using 10% w/w anhydrous potassium carbonate-silica as a stationary phase (ethyl acetate as an eluent) gave **6** (97%) as a white solid.

This compound is known.[21]

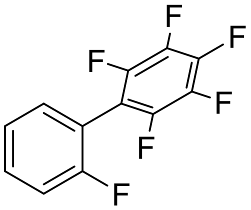
Nuclear magnetic resonance spectrum of **6** were taken on a Varian 400-MR (^1H, 400 MHz; ^{13}C, 100 MHz; ^{19}F, 376 MHz).

^{1}H NMR (400 MHz): δ 7.40 – 7.54 (m, 5H)

^{13}C NMR (100 MHz): δ 116.06 (td, $J_{\text{C–CF}}$ = 17.4, $J_{\text{C–CCF}}$ = 4.2 Hz), 126.53, 128.86, 129.44, 130.28, 137.95 (dm, $J_{\text{C–F}}$ = 249.9 Hz), 140.50 (dm, $J_{\text{C–F}}$ = 253.6 Hz), 144.26 (dm, $J_{\text{C–F}}$ = 247.5 Hz)

^{19}F NMR (376 MHz): δ -163.98 (td, *J* = 22.2, 7.7 Hz), -157.35 (t, *J* = 20.9 Hz), -144.99 (dd, *J* = 22.6, 7.6 Hz).

2,2',3,4,5,6-hexafluoro-1,1'-biphenyl (7)



7 was prepared according to a literature procedure.[22]

A Schlenk tube equipped with a magnetic stirring bar was charged with AgOTf (2.0 equiv, 0.20 mmol, 0.0514 g), 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA, 1.2 equiv, 0.12 mmol, 0.0425 g), acetone (1 mL) and **3aa** (1.0 equiv, 0.10 mmol, 0.0537 g) under an argon atmosphere. The resulting mixture was stirred at 25 °C for 30 min. After the mixture was diluted with hexane, the organic solution was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography using 10% w/w anhydrous potassium carbonate-silica as a stationary phase (hexane as an eluent) gave a mixture of **7** (61%) and **6** (19%) as a white solid.

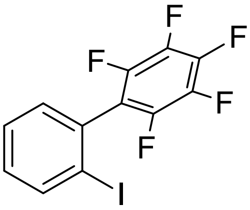
This compound is known.[23]

^{1}H NMR: δ 7.20 – 7.32 (m, 2H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.45 – 7.54 (m, 1H)

^{13}C NMR: δ 110.29 (td, $J_{\text{C–CF}}$ = 18.5, $J_{\text{C–CCF}}$ = 3.9 Hz), 114.32 (d, $J_{\text{C–CF}}$ = 17.0 Hz), 116.32 (d, $J_{\text{C–CF}}$ = 21.6 Hz), 124.49 (d, $J_{\text{C–CCF}}$ = 3.6 Hz), 131.85 (d, $J_{\text{C–CCF}}$ = 8.3 Hz), 132.12, 137.87 (dm, $J_{\text{C–F}}$ = 252.8 Hz), 141.24 (dm, $J_{\text{C–F}}$ = 254.7 Hz), 144.47 (dm, $J_{\text{C–F}}$ = 249.2 Hz), 160.03 (d, $J_{\text{C–F}}$ = 250.7 Hz)

^{19}F NMR: δ -163.81 (td, *J* = 21.8, 7.5 Hz), -155.84 (t, *J* = 20.8 Hz), -142.04 (dd, *J* = 20.7, 10.1 Hz), -114.53

2,3,4,5,6-pentafluoro-2'-iodo-1,1'-biphenyl (8)



8 was prepared according to a literature procedure.[20]

A Schlenk tube equipped with a magnetic stirring bar was charged with **3aa** (1.0 equiv, 0.10 mmol, 0.0537 g), DCM (1.0 mL) and I_2 (1.5 equiv, 0.15 mmol, 0.0380 mL) under an argon atmosphere. The resulting mixture was stirred at 25 °C for 30 min. After the mixture was quenched with saturated $Na_2S_2O_3$ aqueous solution and saturated $NaHCO_3$ aqueous solution and diluted with DCM, the organic layer was washed twice with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography using 10% w/w anhydrous potassium carbonate-silica as a stationary phase (ethyl acetate as an eluent) gave **8** (95%) as a white solid.

This compound is known.[24]

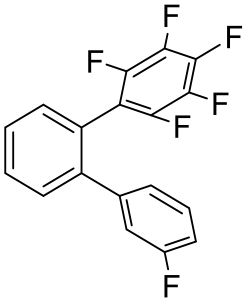
^{1}H NMR: δ 7.19 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H)

^{13}C NMR: δ 99.73, 118.47 (td, $J_{C\text{–}CF}$ = 19.3, $J_{C\text{–}CCF}$ = 4.0 Hz), 128.53, 131.16, 131.32, 132.63, 137.83 (dm, $J_{C\text{–}F}$ = 253.0 Hz), 139.68, 141.41 (dm, $J_{C\text{–}F}$ = 254.5 Hz), 144.08 (dm, $J_{C\text{–}F}$ = 248.0 Hz)

^{19}F NMR: δ -163.58 (dt, J = 22.0, 11.3 Hz), -155.71 (t, J = 20.8 Hz), -141.39 (dd, J = 22.6, 7.3 Hz)

Fig. 8B

2,3,3'',4,5,6-hexafluoro-1,1':2',1''-terphenyl (9)



9 was prepared according to a literature procedure.[25]

A reaction tube equipped with a magnetic stirring bar was flame-dried after addition of LiBr (6.0 equiv, 0.60 mmol, 0.0525 g) under an argon atmosphere. The tube was charged with CuCl (5.0 equiv, 0.50 mmol, 0.0500 g), $Pd(PPh_3)_4$ (10 mol %, 10.0 µmol, 0.0116 g), DMF (1.0 mL), 1-fluoro-3-iodobenzene (1.8 equiv, 0.18 mmol, 0.0402 g) and **3aa** (1.0 equiv, 0.10 mmol, 0.0542 g) under an argon atmosphere. The resulting mixture was stirred at 160 °C for 30 min under microwave irradiation. After the mixture was diluted with diethyl ether (30 mL), the organic solution was washed four times with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography using 10% w/w anhydrous potassium carbonate-silica as a stationary phase (hexane as an eluent) gave **9** (53%) as a white solid.

Mp: 66–68 °C

^{1}H NMR: δ 6.89 (d, J = 7.3 Hz, 2H), 6.93 – 7.01 (m, 1H), 7.18 – 7.27 (m, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.44 – 7.52 (m, 2H), 7.56 (td, J = 7.5, 1.3 Hz, 1H)

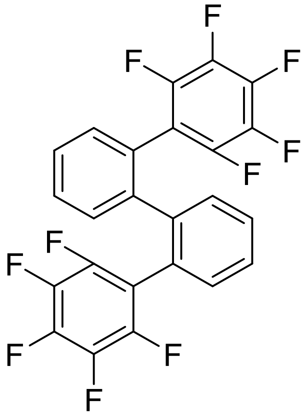
^{13}C NMR: δ 114.57 (d, $J_{C–CF}$ = 21.0 Hz), 115.60 (t, $J_{C–CF}$ = 19.1 Hz), 115.73 (d, $J_{C–CF}$ = 21.9 Hz), 124.41 (d, $J_{C–CCCF}$ = 2.8 Hz), 124.97, 128.11, 129.81 (d, $J_{C–CCF}$ = 8.4 Hz), 130.02, 130.39, 131.41, 137.56 (dm, $J_{C–F}$ = 251.5 Hz), 140.77 (dm, $J_{C–F}$ = 248.8 Hz), 141.81, 142.63 (d, $J_{C–CCF}$ = 7.7 Hz), 144.12 (dm, $J_{C–F}$ = 242.8 Hz), 162.53 (d, $J_{C–F}$ = 246.5 Hz)

^{19}F NMR: δ -163.86 (td, J = 22.5, 7.8 Hz), -156.54 (t, J = 20.9 Hz), -141.95 (dd, J = 23.0, 7.8 Hz), -114.73 (q, J = 8.8 Hz)

HRMS (EI) Calcd for $C_{18}H_8F_6$: M^+, 338.05302. Found: m/z 338.05385.

Fig. 8C

2,2''',3,3''',4,4''',5,5''',6,6'''-decafluoro-1,1':2',1'':2'',1'''-tetraphenyl (10)



10 was prepared according to a literature procedure.[26]

A Schlenk tube equipped with a magnetic stirring bar was charged with CuCl (2.6 equiv, 0.129 mmol, 0.0128 g), DMF (0.5 mL) and **3aa** (1.0 equiv, 0.05 mmol, 0.0272 g) under an argon atmosphere. The resulting mixture was stirred at 25 °C for 6 h. After the mixture was diluted with diethyl ether (30 mL), the organic solution was washed three times with brine and dried over $MgSO_4$. Evaporation of the solvent followed by silica gel-column chromatography using 10% w/w anhydrous potassium carbonate-silica as a stationary phase (hexane as an eluent) gave **10** (41%) as a white solid.

Mp: 120–122 °C

^{1}H NMR: δ 7.11 (d, J = 7.7 Hz, 2H), 7.39 – 7.45 (m, 2H), 7.53 (d, J = 4.6 Hz, 4H)

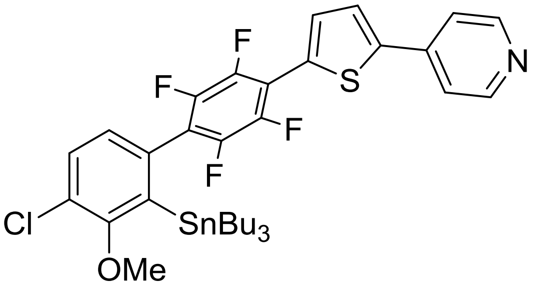
^{13}C NMR: δ 114.78 (td, J = 18.7, 3.3 Hz), 125.04, 128.23, 129.67, 130.90, 131.96, 137.56 (dm, $J_{C–F}$ = 249.2 Hz), 140.82 (dm, $J_{C–F}$ = 254.5 Hz), 141.11, 143.54 (dm, $J_{C–F}$ = 252.8 Hz), 144.09 (dm, $J_{C–F}$ = 243.7 Hz)

^{19}F NMR: δ -164.06 (dt, J = 105.6, 18.2 Hz), -156.49 (t, J = 20.7 Hz), -145.90 (d, J = 21.3 Hz), -138.71 (d, J = 22.8 Hz)

HRMS (EI) Calcd for $C_{24}H_8F_{10}$: M^+, 486.04663. Found: m/z 486.04662.

12. Synthesis of π-extended arylstannane by chemoselective MKS reaction of an *ortho*-stannylbiaryl generated from 11

4-(5-(4'-chloro-2,3,5,6-tetrafluoro-3'-methoxy-2'-(tributylstannyl)-[1,1'-biphenyl]-4-yl)thiophen-2-yl)pyridine (11)



A reaction tube equipped with a magnetic stirring bar was charged with Pd(PPh$_3$)$_4$ (9.7 mol %, 12.5 μmol, 0.0145 g), 4-(5-(trimethylstannyl)thiophen-2-yl)pyridine (1.2 equiv, 0.16 mmol, 0.0506 g), **3lj** (1.0 equiv, 0.13 mmol, 0.0849 g) and DMF (1.3 mL) under an argon atmosphere. The resulting mixture was stirred at 160 °C for 1 h under microwave irradiation. After the mixture was diluted with diethyl ether (30 mL), the organic solution was washed four times with brine and dried over MgSO$_4$. Evaporation of the solvent followed by preparative recycling gel permeation chromatography gave **11** (76%) as a yellow oil.

^{1}H NMR: δ 0.73 – 0.90 (m, 15H), 1.22 (sext, J = 7.3 Hz, 6H), 1.29 – 1.45 (m, 6H), 3.96 (s, 3H), 6.97 (d, J = 8.0 Hz, $J_{\text{Sn-H}meta}$ = 11.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 6.1 Hz, 2H), 7.59 (d, J = 3.9 Hz, 1H), 7.67 (d, J = 3.9 Hz, 1H), 8.65 (d, J = 6.0 Hz, 2H)

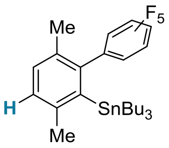
^{13}C NMR: δ 11.27 ($J_{\text{Sn–C}}$ = 352.8, 337.2 Hz), 13.68, 27.47, 28.98, 61.51, 113.30 (t, $J_{\text{C–CF}}$ = 14.6 Hz), 120.03, 121.11 (t, $J_{\text{C–CF}}$ = 19.2 Hz), 125.61, 127.31, 127.58, 129.36, 131.55, 131.61, 133.97, 140.25 ($J_{\text{Sn–C}}$ = 318.9, 304.1 Hz), 140.67, 143.74, 143.74 (dm, $J_{\text{C–F}}$ = 245.0 Hz), 144.75 (dm, $J_{\text{C–F}}$ = 236.5 Hz), 150.71, 160.67

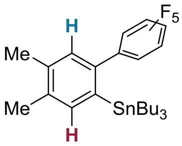
^{19}F NMR: δ -142.29 (dd, J = 22.6, 11.6 Hz), -141.49 (dd, J = 22.5, 11.5 Hz)

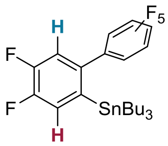
^{119}Sn NMR: δ -44.53

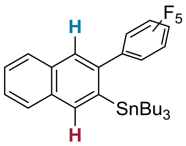
HRMS (ESI) Calcd for $C_{34}H_{39}{}^{35}ClF_4NOSSn$: $[M+H]^+$, 740.13935. Found: *m/z* 740.13977.

13. Tin-proton coupling constants in products (^{1}H NMR)

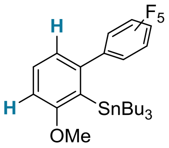


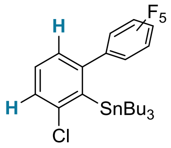


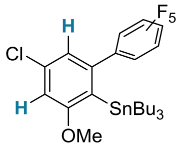


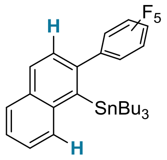


	3ab	**3ac**	**3ad**	**3ae**
$J_{\text{Sn-H}ortho}$ (Hz)	–	40.0	37.3	44.3
$J_{\text{Sn-H}meta}$ (Hz)	15.3	13.8	10.5	12.4

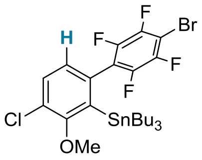


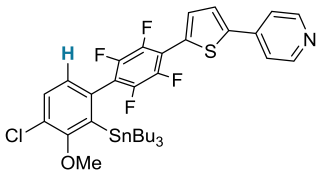




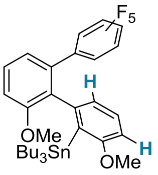


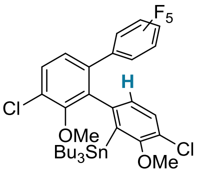
	3af	**3ag**	**3ah**	**3ai**
$J_{\text{Sn-H}ortho}$ (Hz)	–	–	–	–
$J_{\text{Sn-H}meta}$ (Hz)	10.2 13.0	7.6 8.4	10.2 12.0	9.6 (*meta*) 12.0 (*peri*)





	3nj	**11**
$J_{\text{Sn-H}ortho}$ (Hz)	–	–
$J_{\text{Sn-H}meta}$ (Hz)	11.5	11.8





	4aff	**4ajj**
$J_{\text{Sn-H}ortho}$ (Hz)	–	–
$J_{\text{Sn-H}meta}$ (Hz)	11.8 14.8	11.6

Figure S7. Tin-Proton Coupling Constants in Products (^{1}H NMR)

The structure of the arylstannylation products could be determined by tin-proton coupling constants in their ^{1}H NMR spectra.

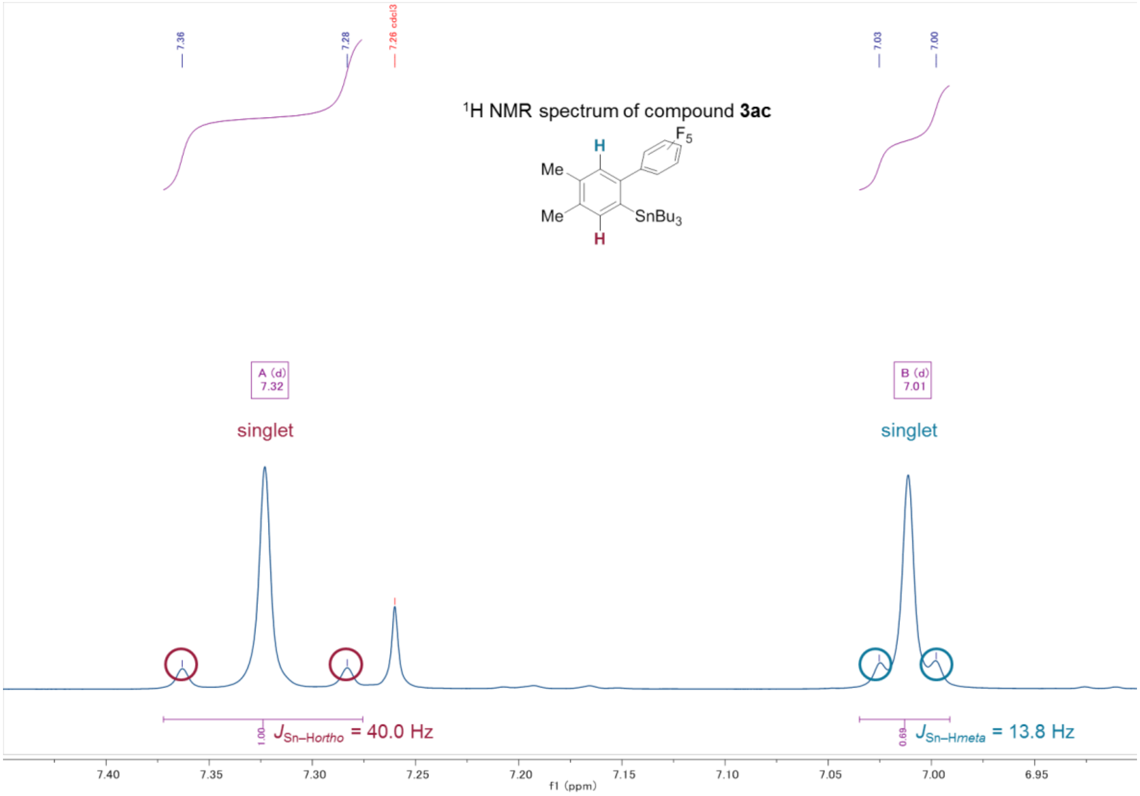


Figure S8. Evaluation of Tin-Proton Coupling Constants (singlet)

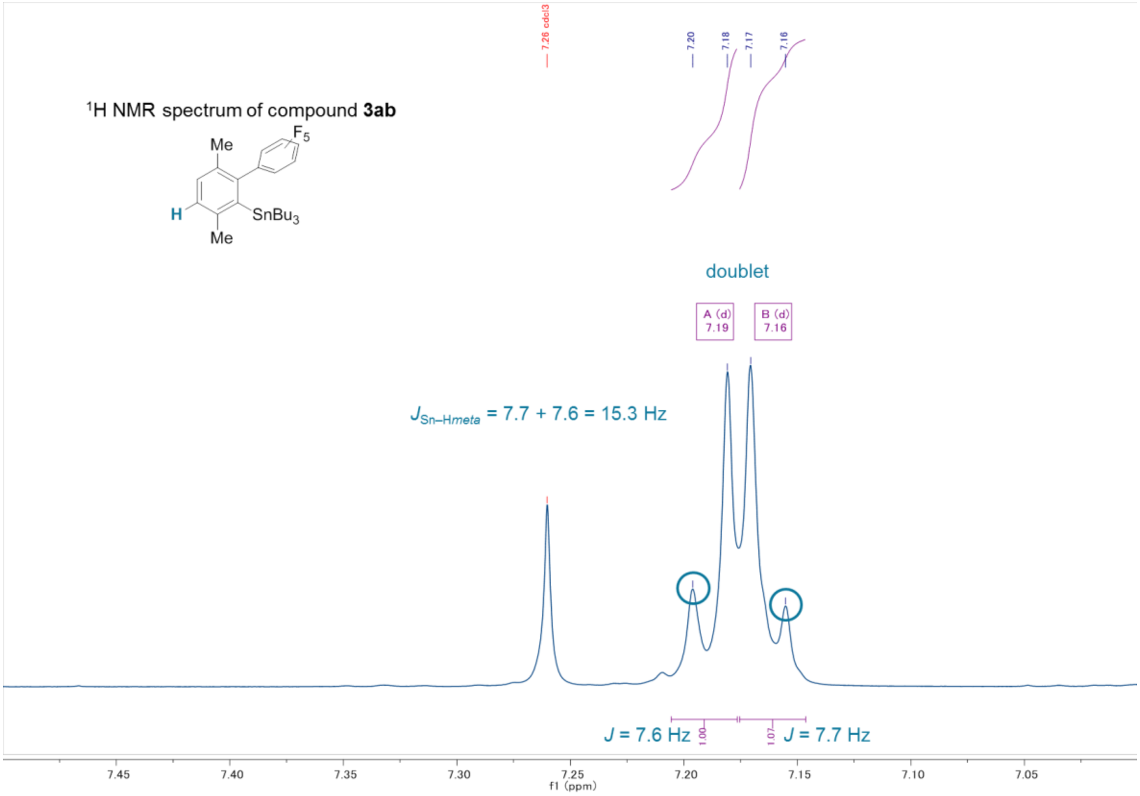


Figure S9. Evaluation of Tin-Proton Coupling Constants (doublet)

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15. Acknowledgements

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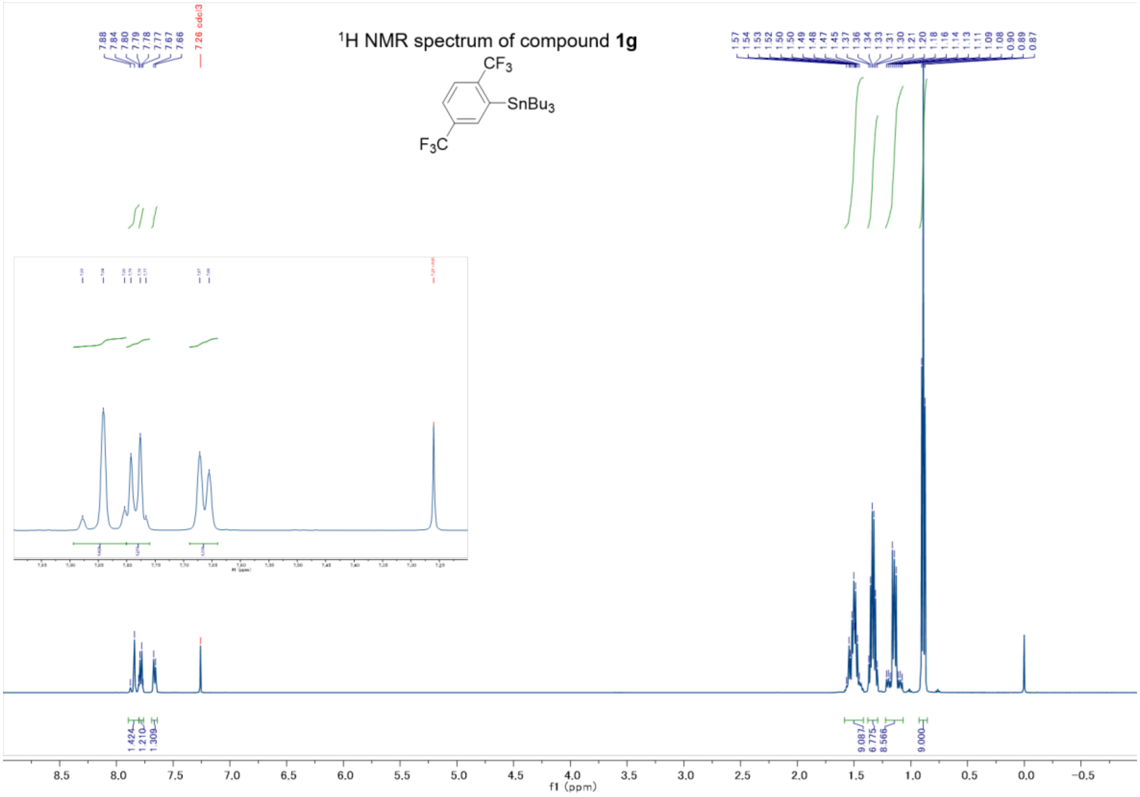
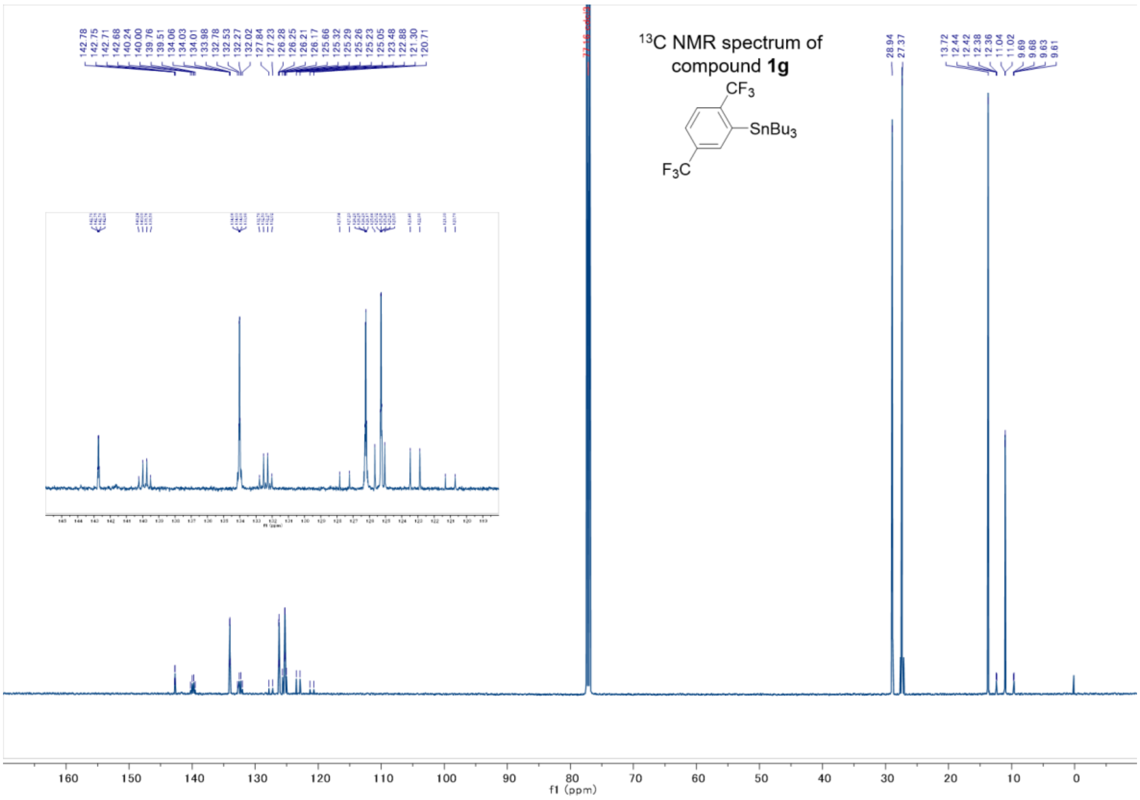
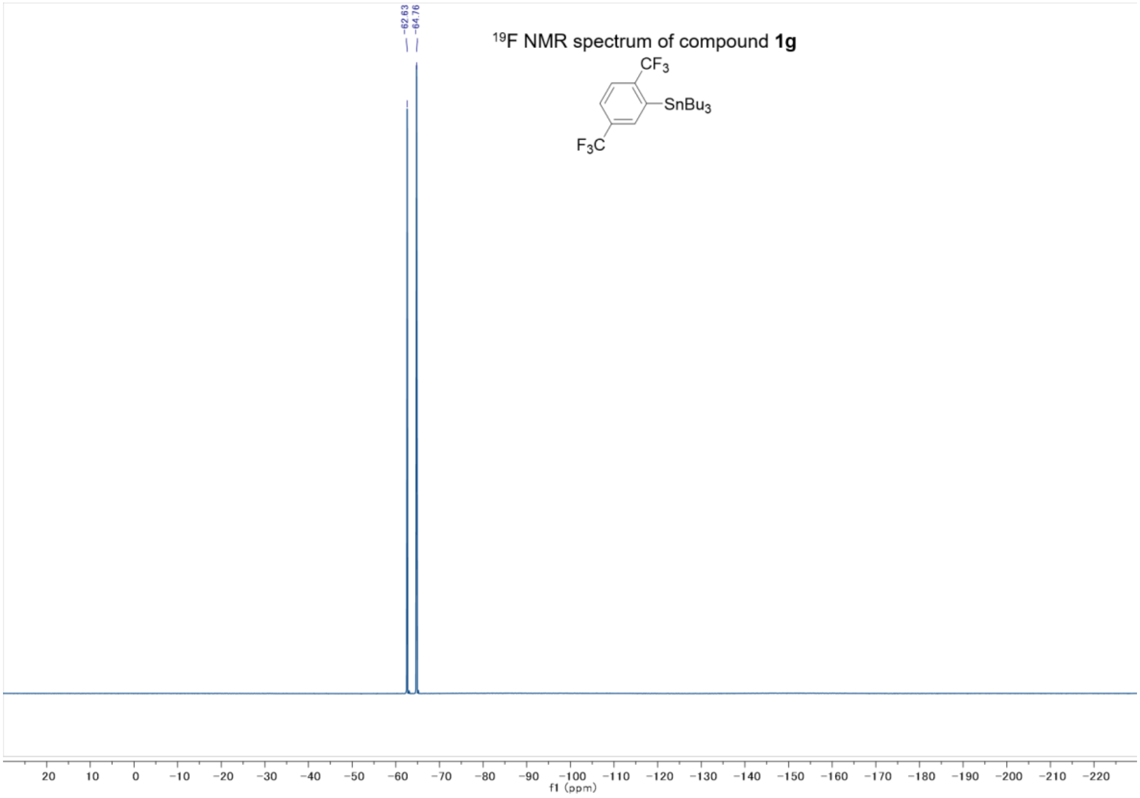
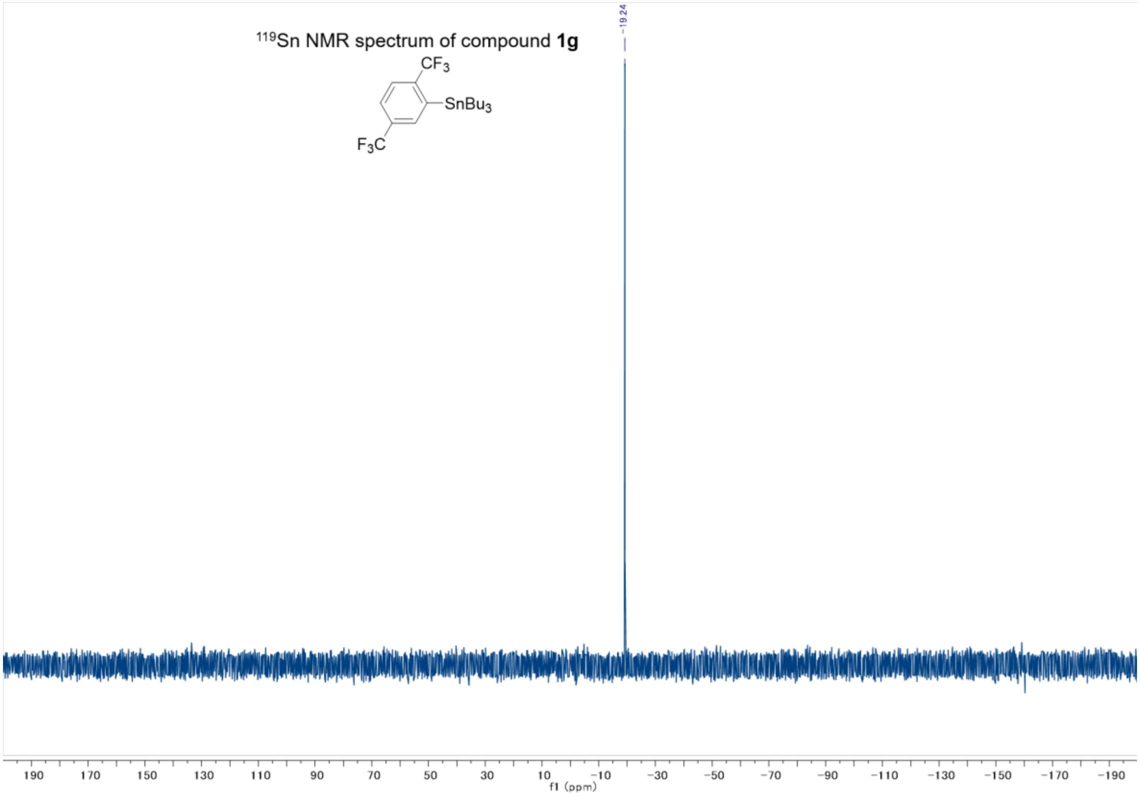
16. NMR spectra



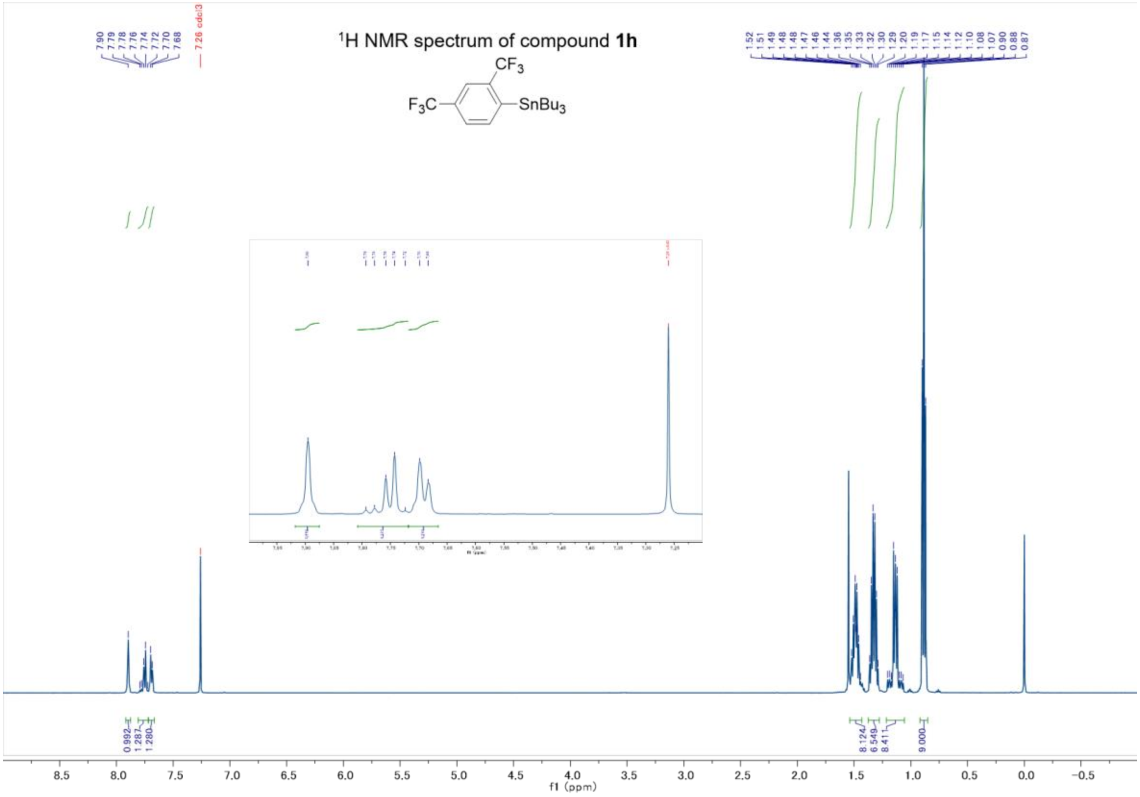




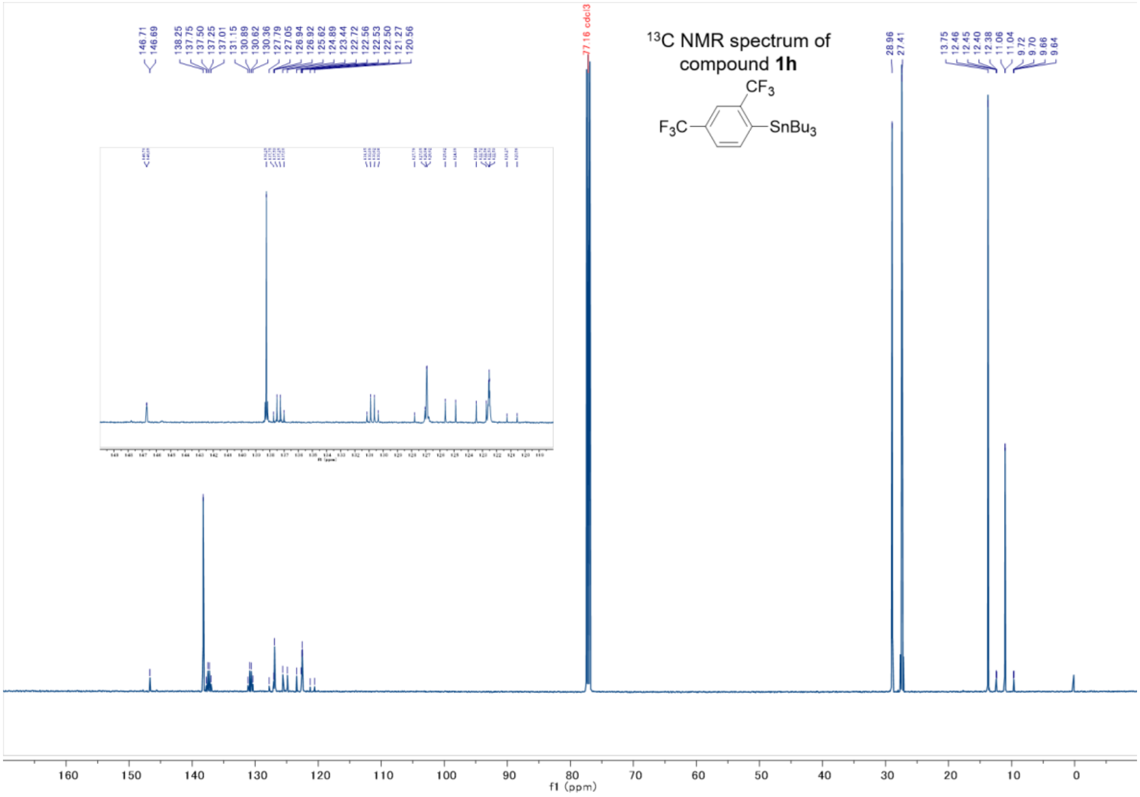
-62.63
-64.76
^{19}F NMR spectrum of compound **1g**
CF_3
$SnBu_3$
F_3C
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)



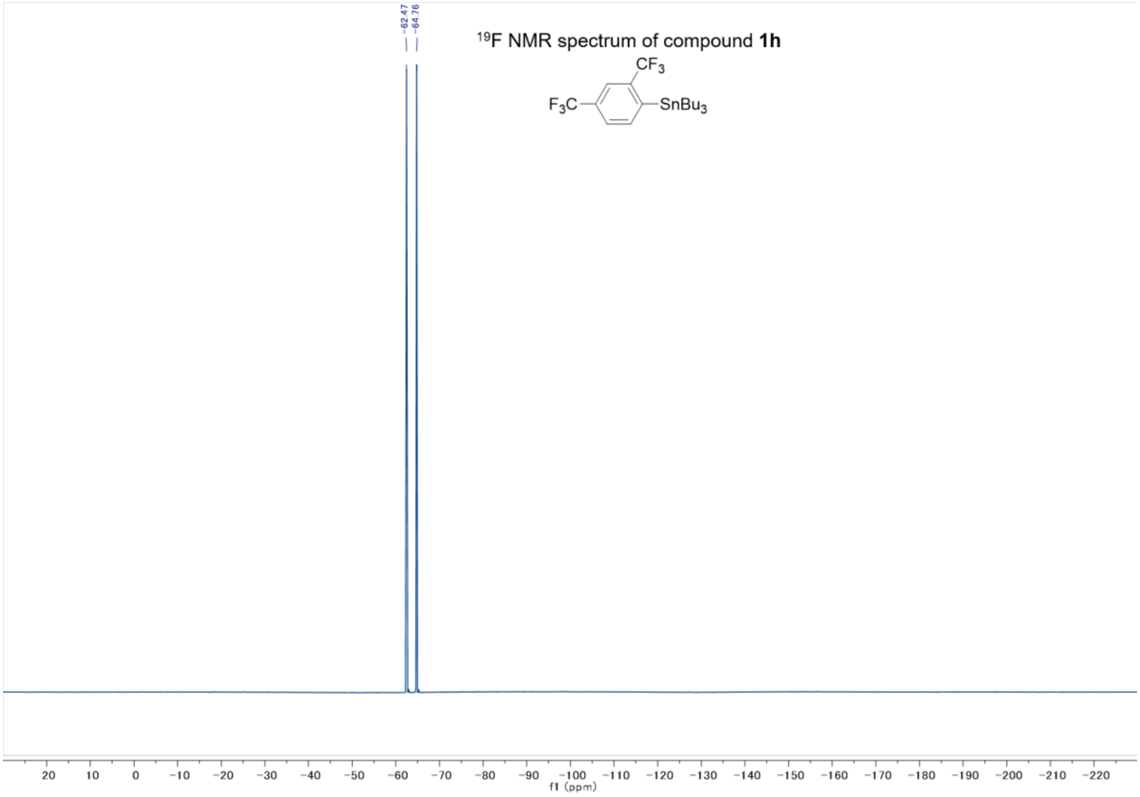
-19.24
^{119}Sn NMR spectrum of compound **1g**
CF_3
$SnBu_3$
F_3C
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)



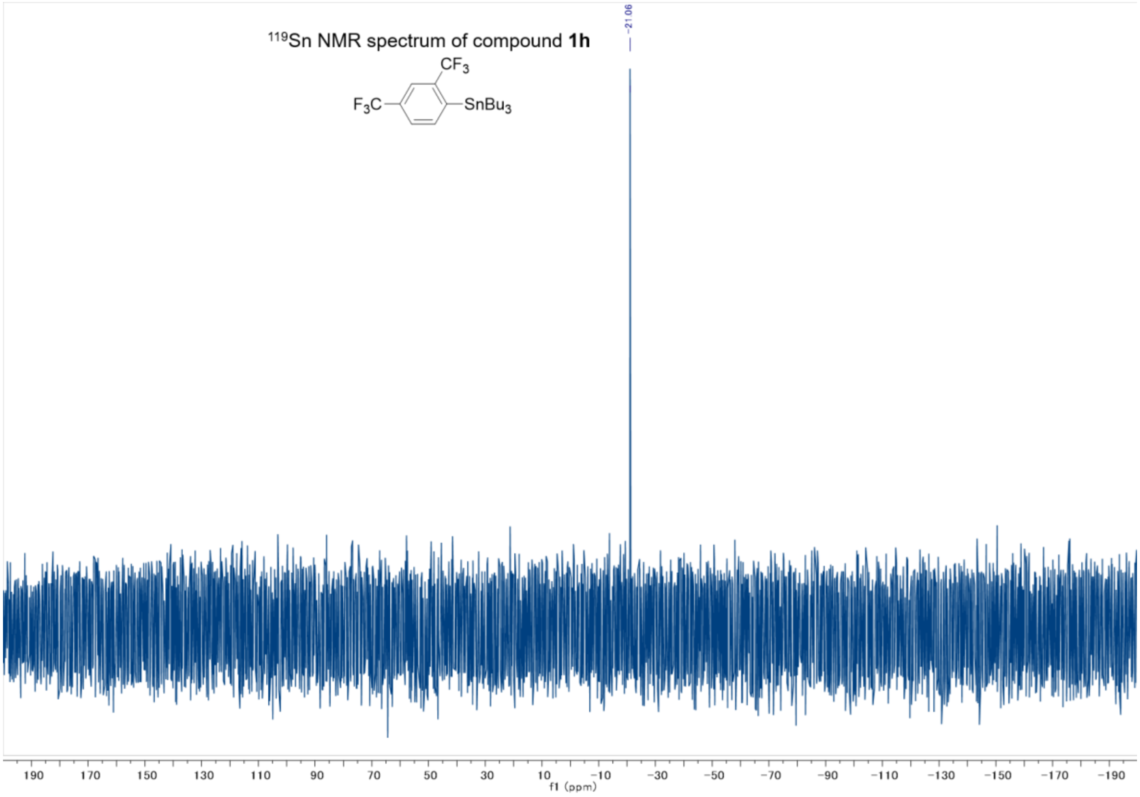
¹H NMR spectrum of compound **1h**
CF3
F3C
SnBu3
7.90
7.79
7.78
7.76
7.74
7.72
7.70
7.68
7.26 cdcl3
1.52
1.51
1.49
1.48
1.48
1.47
1.46
1.44
1.36
1.35
1.33
1.32
1.30
1.29
1.20
1.19
1.17
1.15
1.14
1.12
1.10
1.08
1.07
0.90
0.88
0.87
0.992
1.287
1.280
8.124
6.549
8.41
9.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)



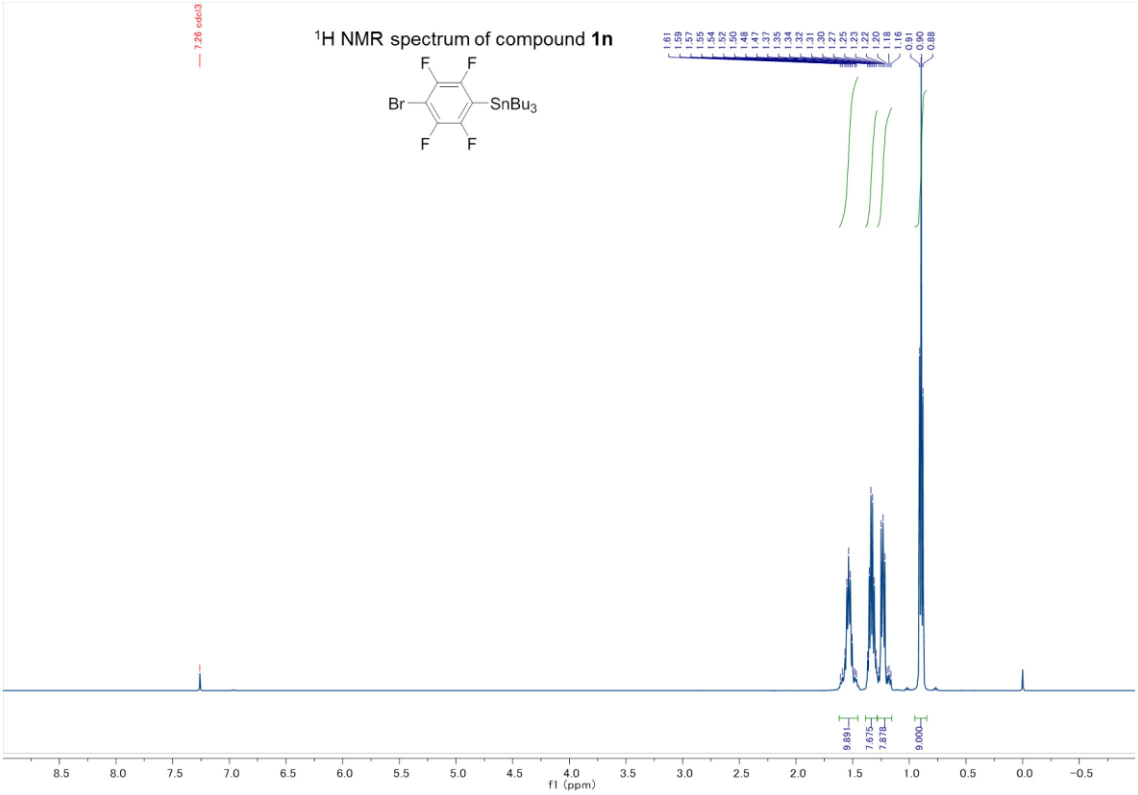
¹³C NMR spectrum of compound **1h**
CF3
F3C
SnBu3
146.71
146.69
138.25
137.75
137.50
137.25
137.01
131.15
130.89
130.62
130.36
127.79
127.05
126.94
126.92
125.62
124.89
123.44
122.72
122.56
122.53
122.50
121.27
120.56
77.16 cdcl3
28.96
27.41
13.75
12.46
12.45
12.40
12.38
11.06
11.04
9.72
9.70
9.66
9.64
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

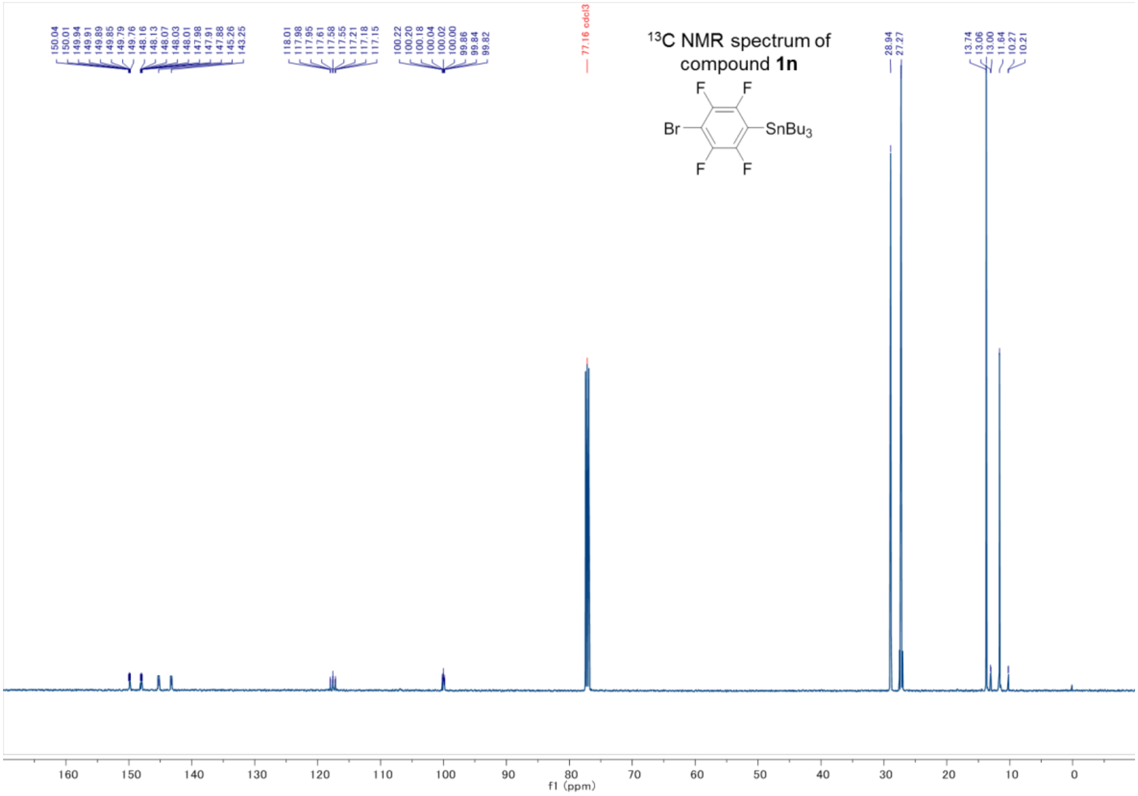


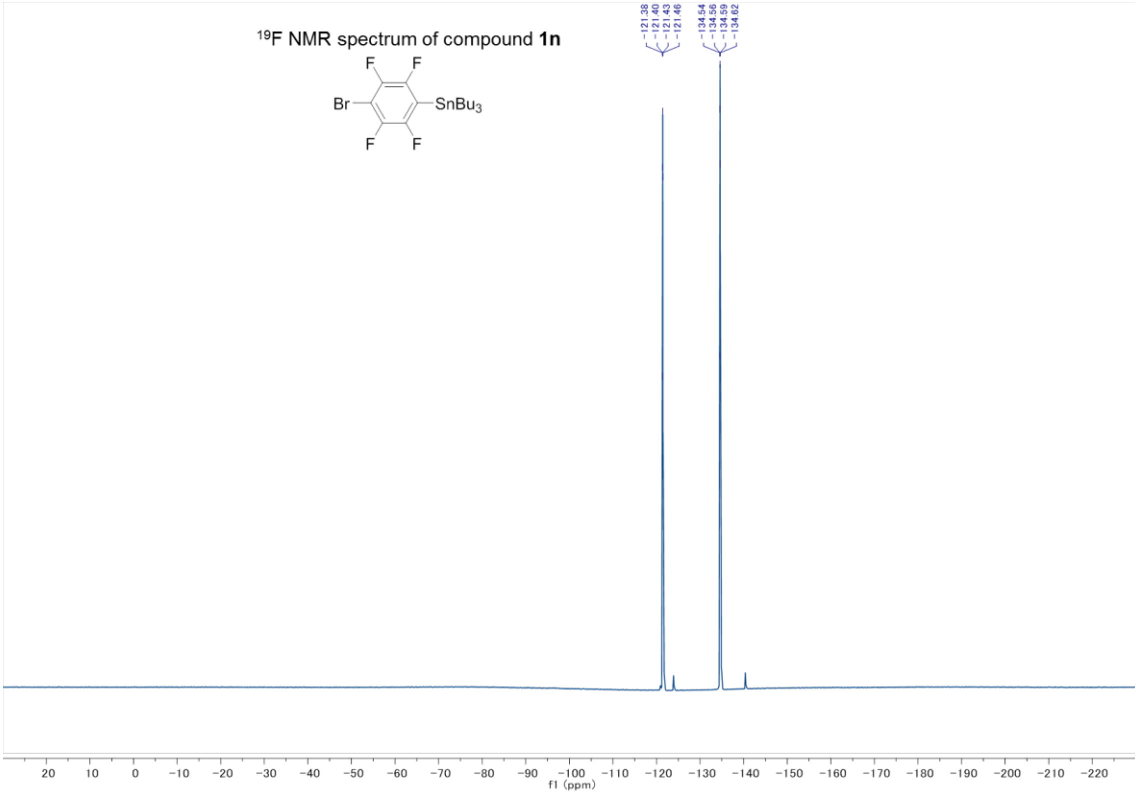
^{19}F NMR spectrum of compound **1h**

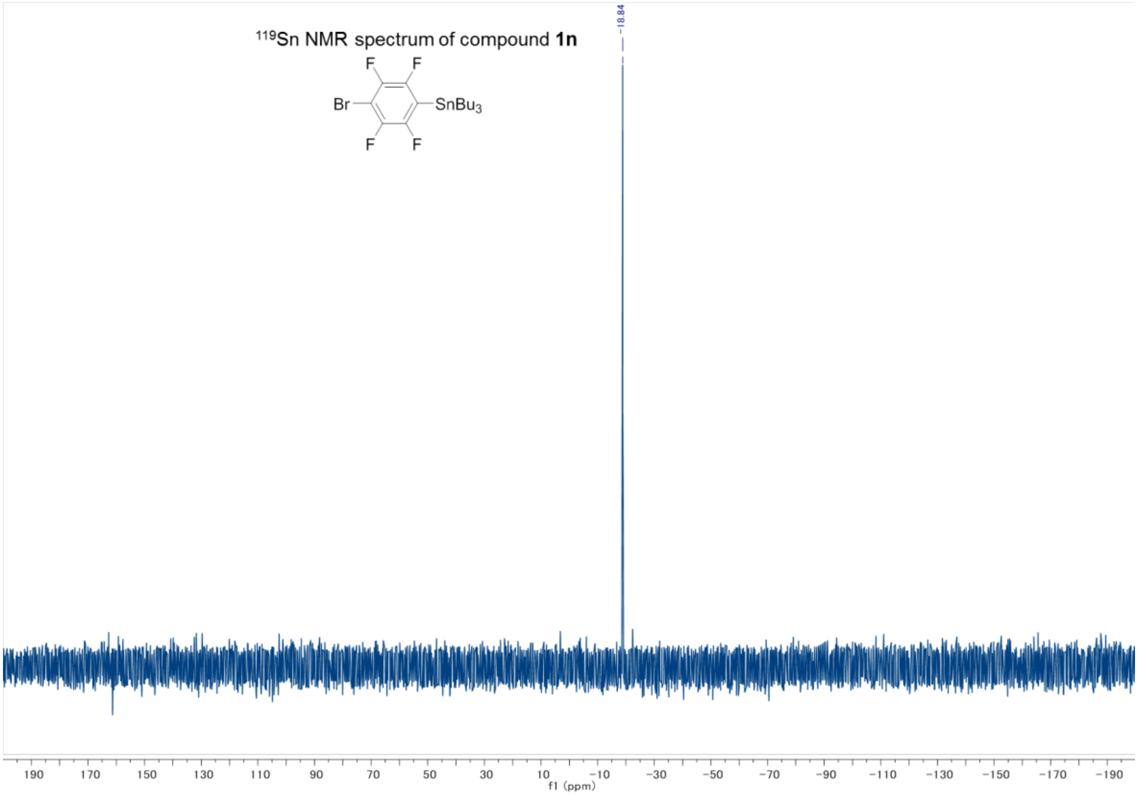


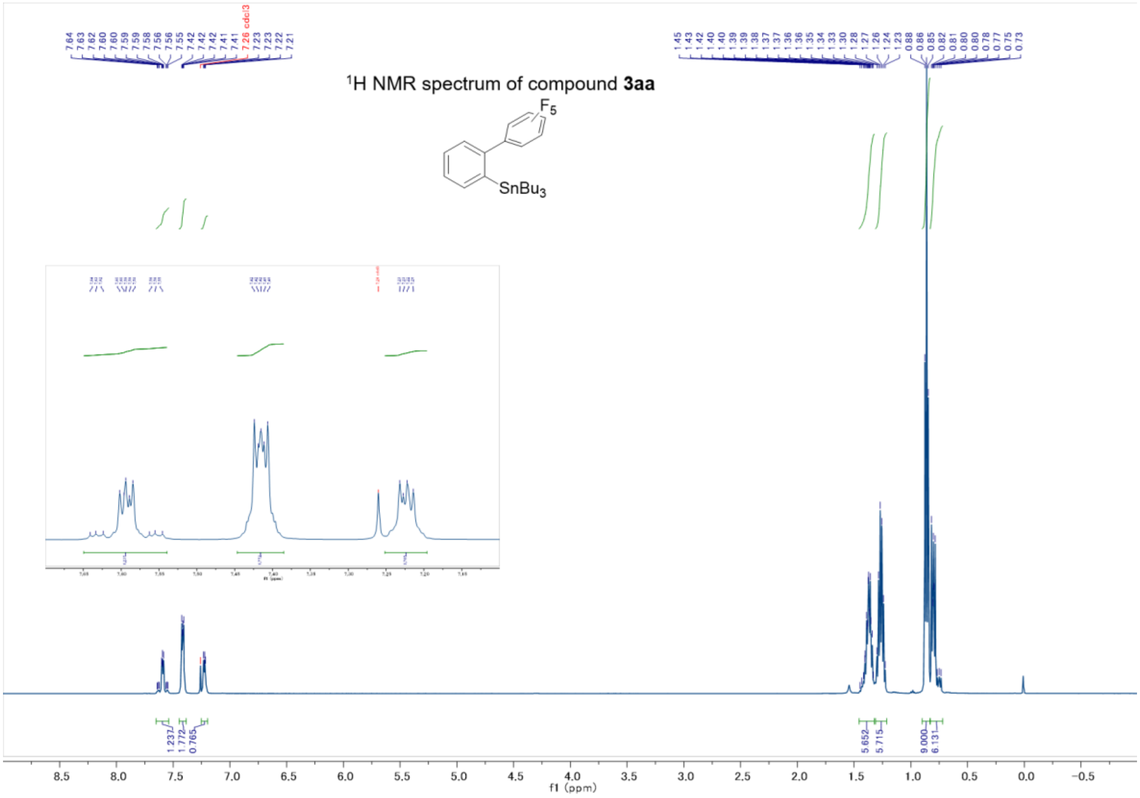
^{119}Sn NMR spectrum of compound **1h**


1H NMR spectrum of compound 1n
Br
F
F
F
F
SnBu3
7.26 cdcl3
1.61
1.59
1.57
1.55
1.54
1.52
1.50
1.48
1.47
1.37
1.35
1.34
1.32
1.31
1.30
1.27
1.25
1.23
1.22
1.20
1.18
1.16
0.91
0.90
0.88
9.891
7.675
7.878
9.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

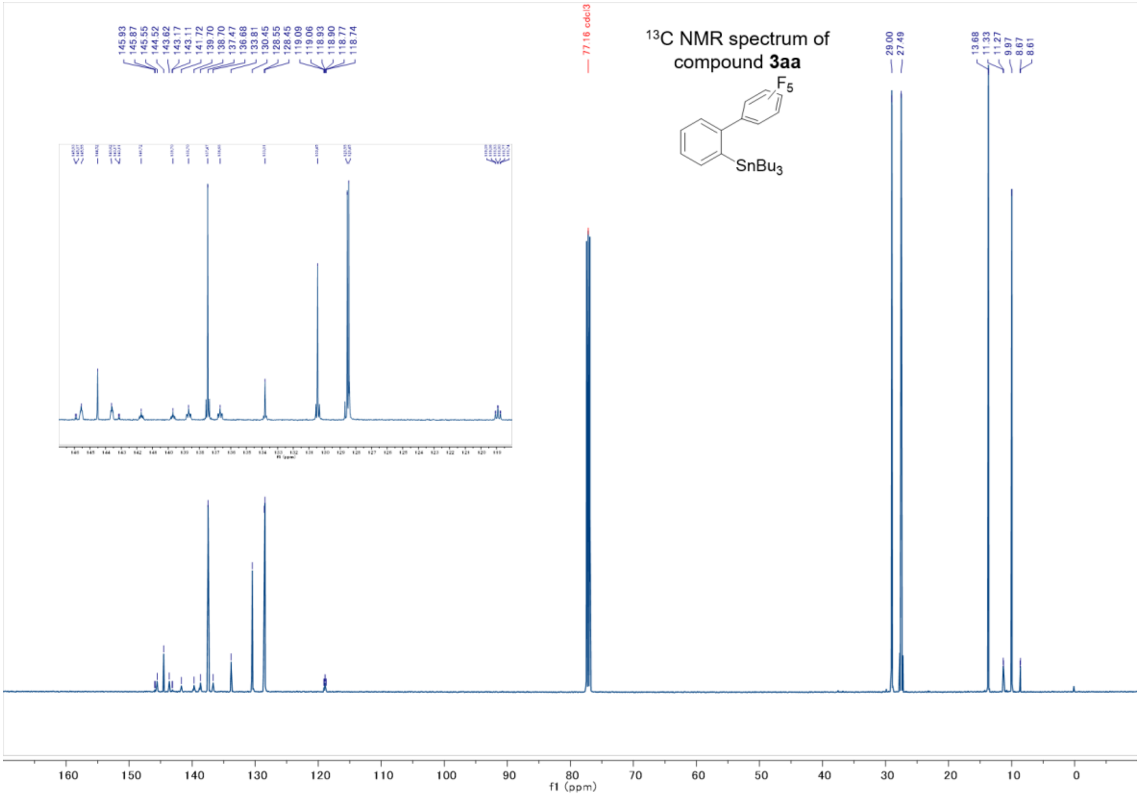

13C NMR spectrum of compound 1n
Br
F
F
F
F
SnBu3
150.04
150.01
149.94
149.91
149.89
149.85
149.79
149.76
148.16
148.13
148.07
148.03
148.01
147.98
147.91
147.88
145.26
143.25
118.01
117.98
117.95
117.61
117.58
117.55
117.21
117.18
117.15
100.22
100.20
100.18
100.04
100.02
100.00
99.86
99.84
99.82
77.16 cdcl3
28.94
27.27
13.74
13.06
13.00
11.64
10.27
10.21
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


^{19}F NMR spectrum of compound **1n**

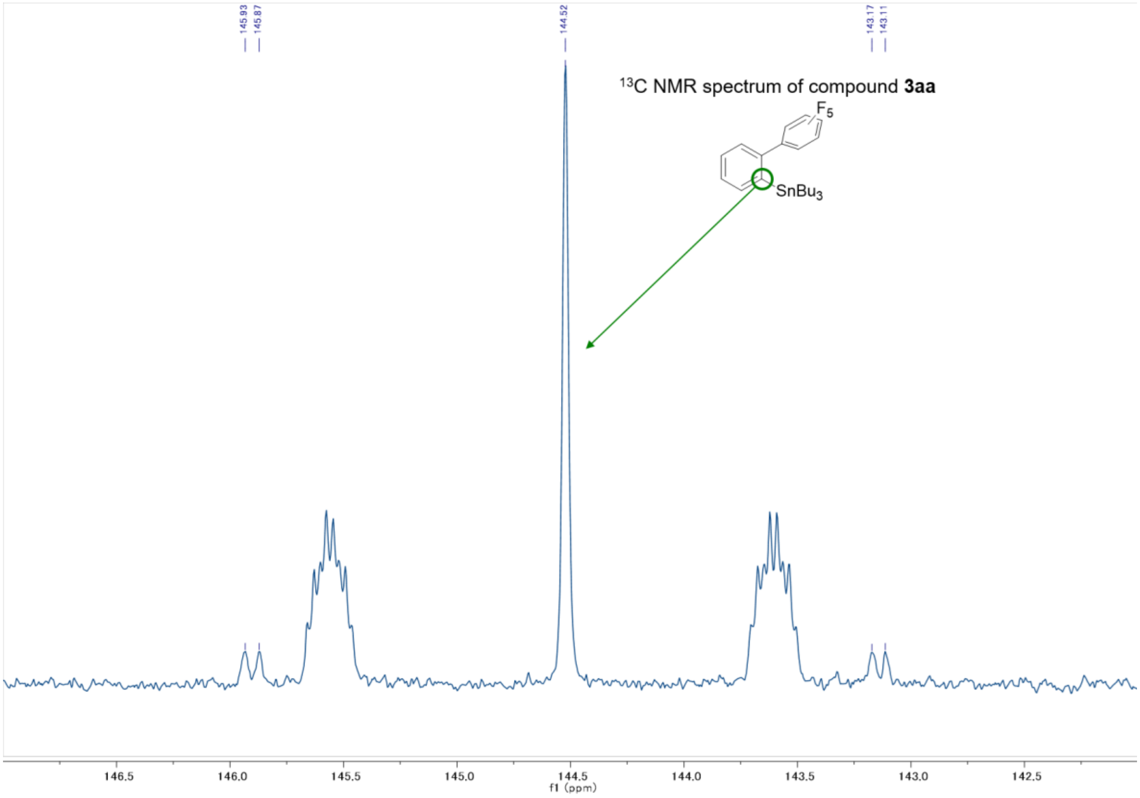

^{119}Sn NMR spectrum of compound **1n**

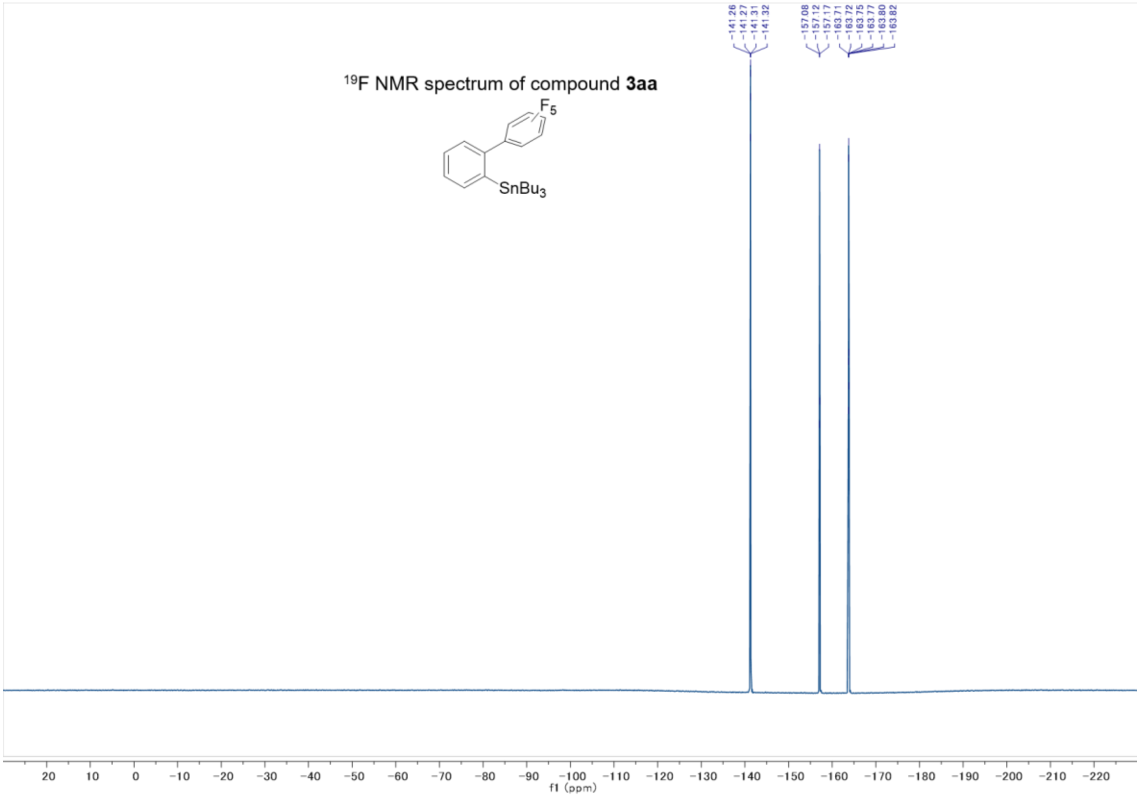


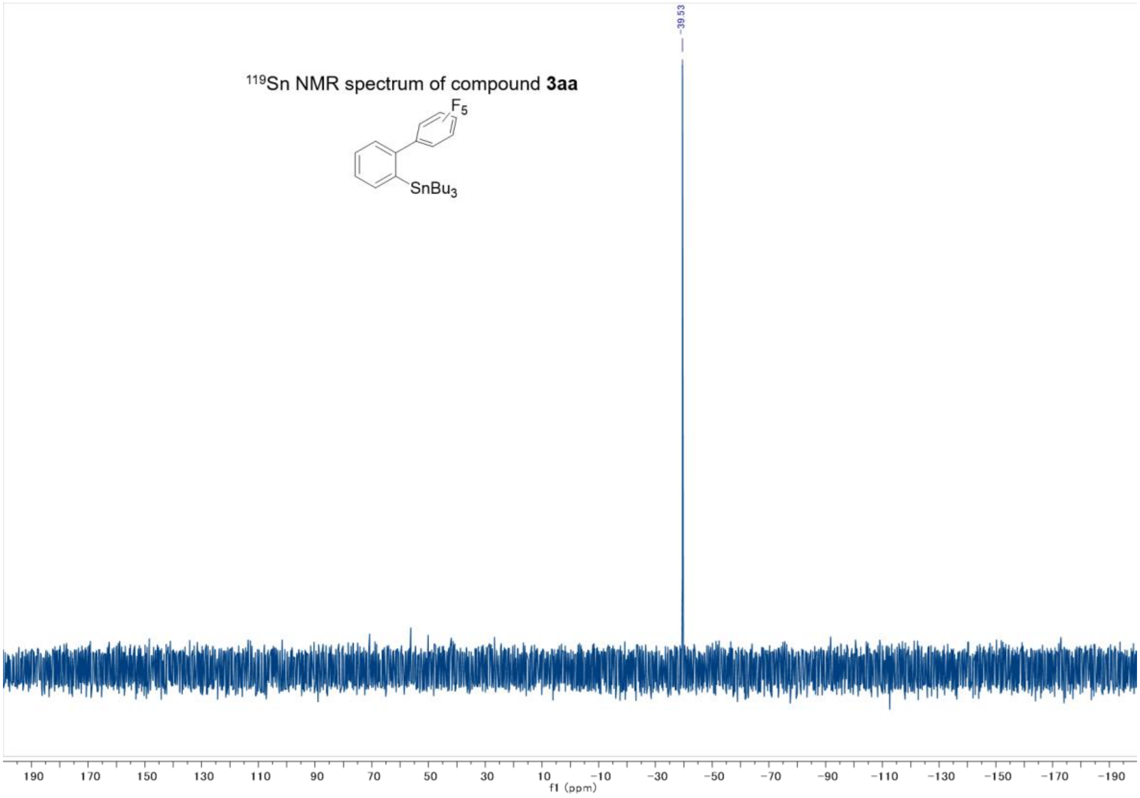
^{1}H NMR spectrum of compound **3aa**



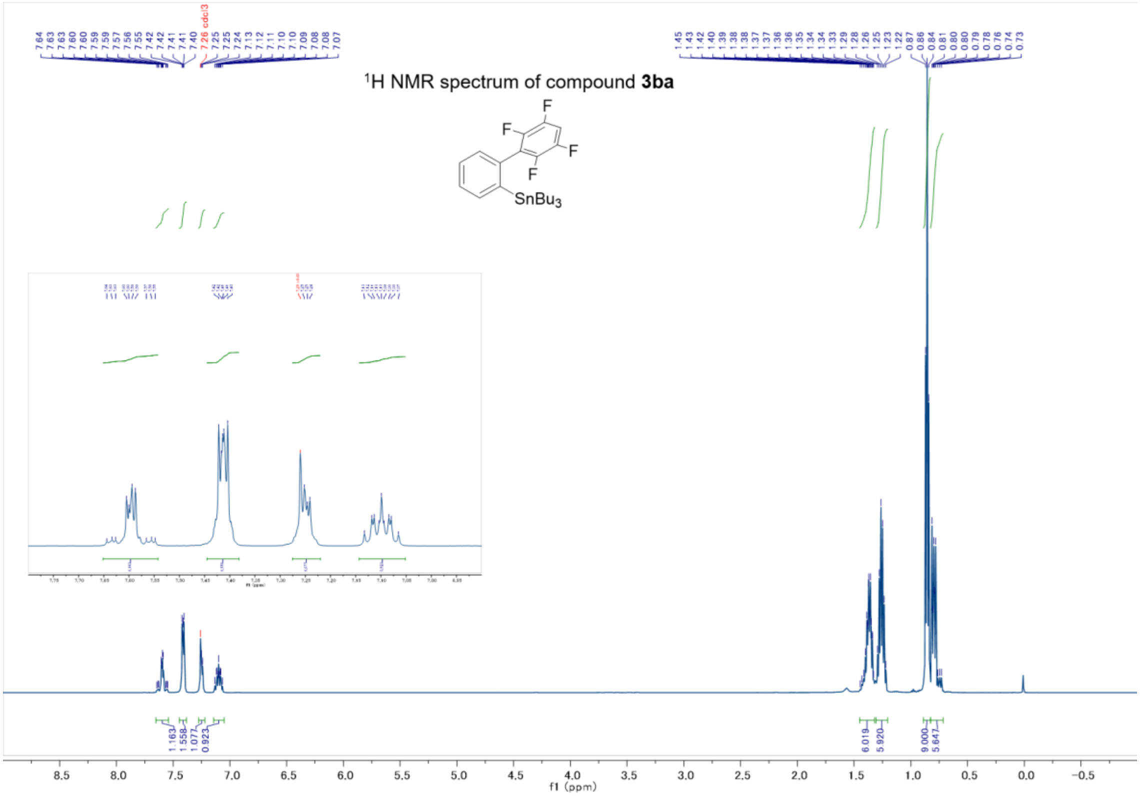
^{13}C NMR spectrum of compound **3aa**


145.93
145.87
144.52
143.17
143.11
^{13}C NMR spectrum of compound **3aa**
F5
SnBu3
146.5
146.0
145.5
145.0
144.5
144.0
143.5
143.0
142.5
f1 (ppm)

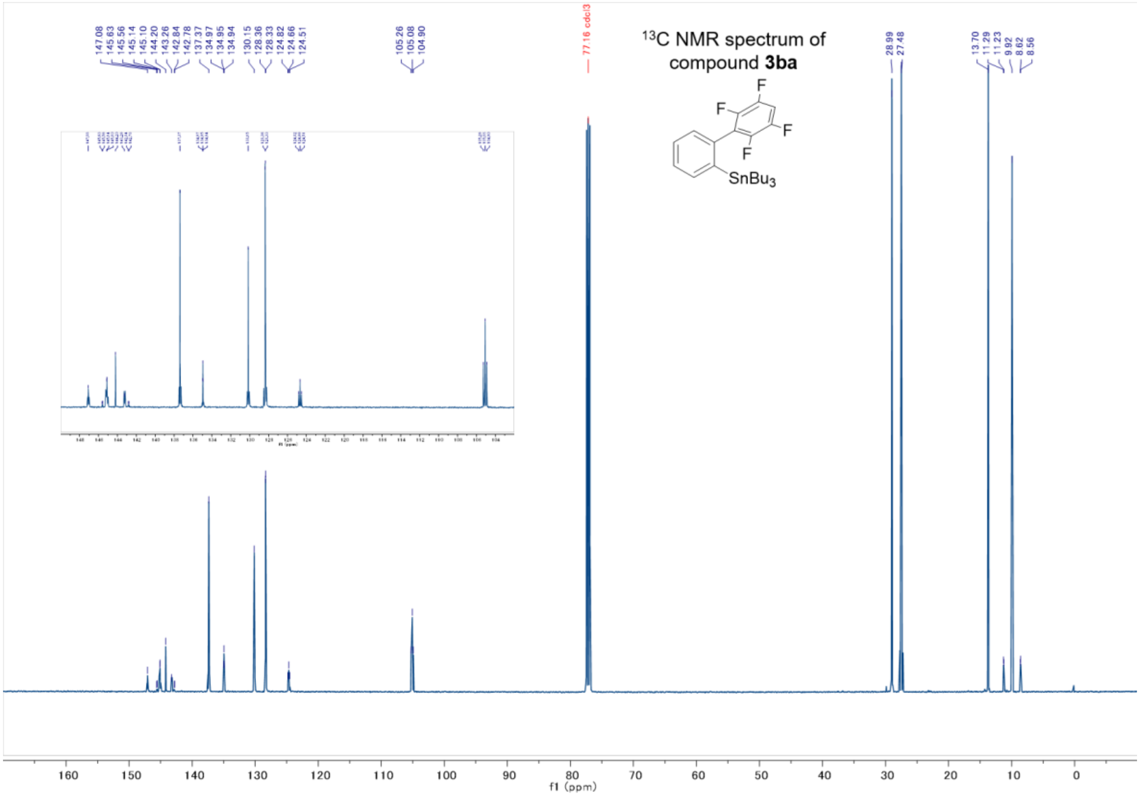

-141.26
-141.27
-141.31
-141.32
-157.08
-157.12
-157.17
-163.71
-163.72
-163.75
-163.77
-163.80
-163.82
^{19}F NMR spectrum of compound **3aa**
F5
SnBu3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)



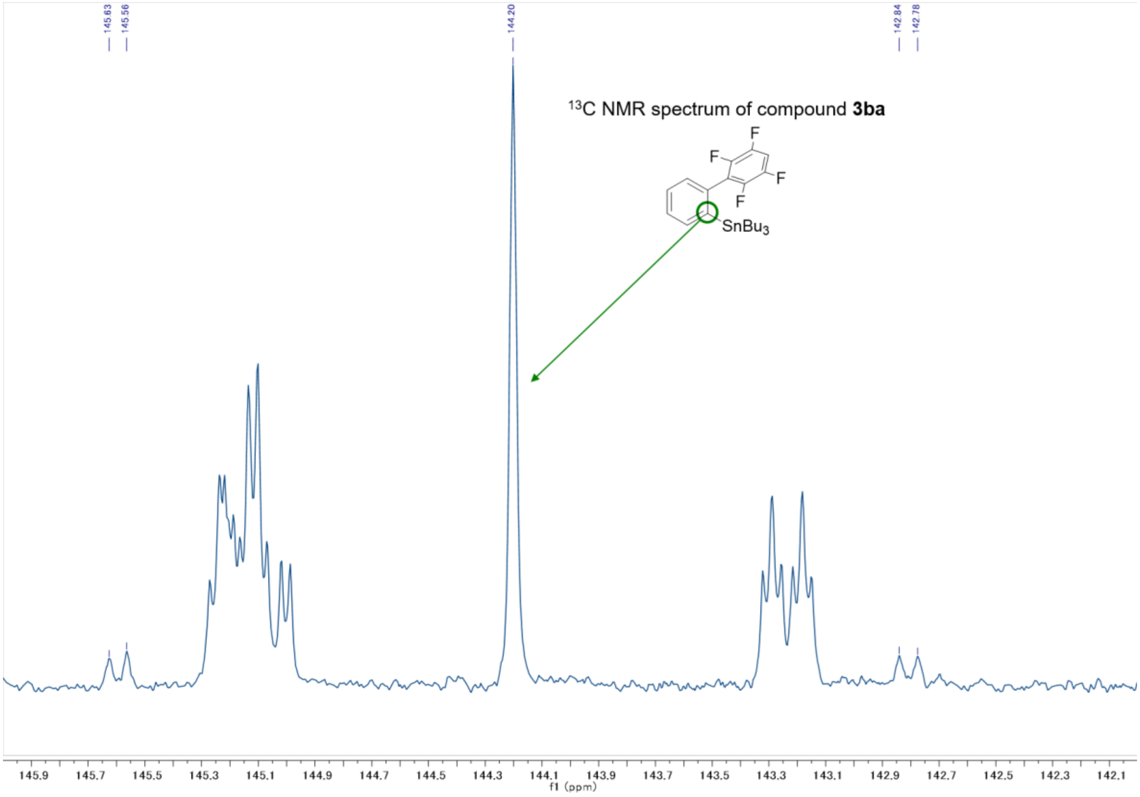
-39.53
^{119}Sn NMR spectrum of compound **3aa**
F5
SnBu3
190
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)



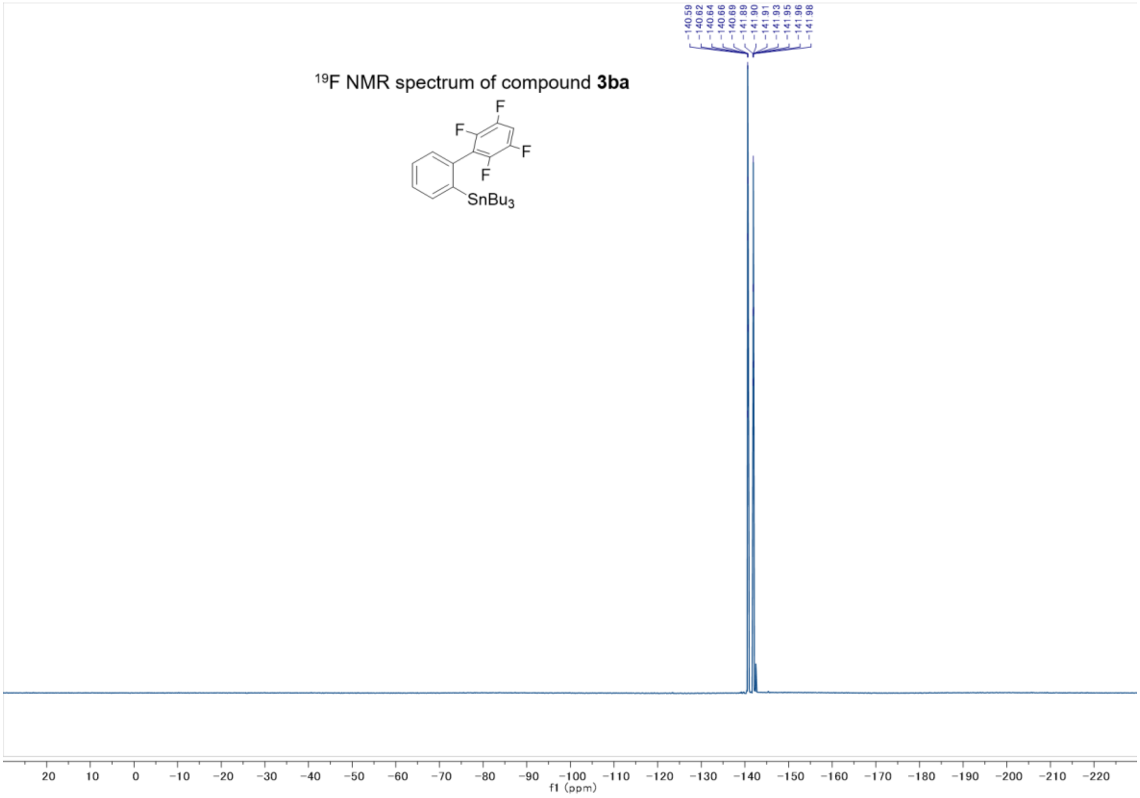
7.64
7.63
7.63
7.60
7.60
7.59
7.59
7.57
7.56
7.55
7.42
7.42
7.41
7.41
7.40
7.26 cdcl3
7.25
7.25
7.24
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.08
7.07
1.45
1.43
1.42
1.40
1.39
1.38
1.38
1.37
1.37
1.36
1.35
1.34
1.34
1.33
1.29
1.28
1.26
1.25
1.23
1.22
0.87
0.86
0.84
0.81
0.80
0.80
0.79
0.78
0.76
0.74
0.73
^{1}H NMR spectrum of compound **3ba**
F
F
F
F
SnBu3
1.163
1.558
1.077
0.923
6.019
5.920
9.000
5.647
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

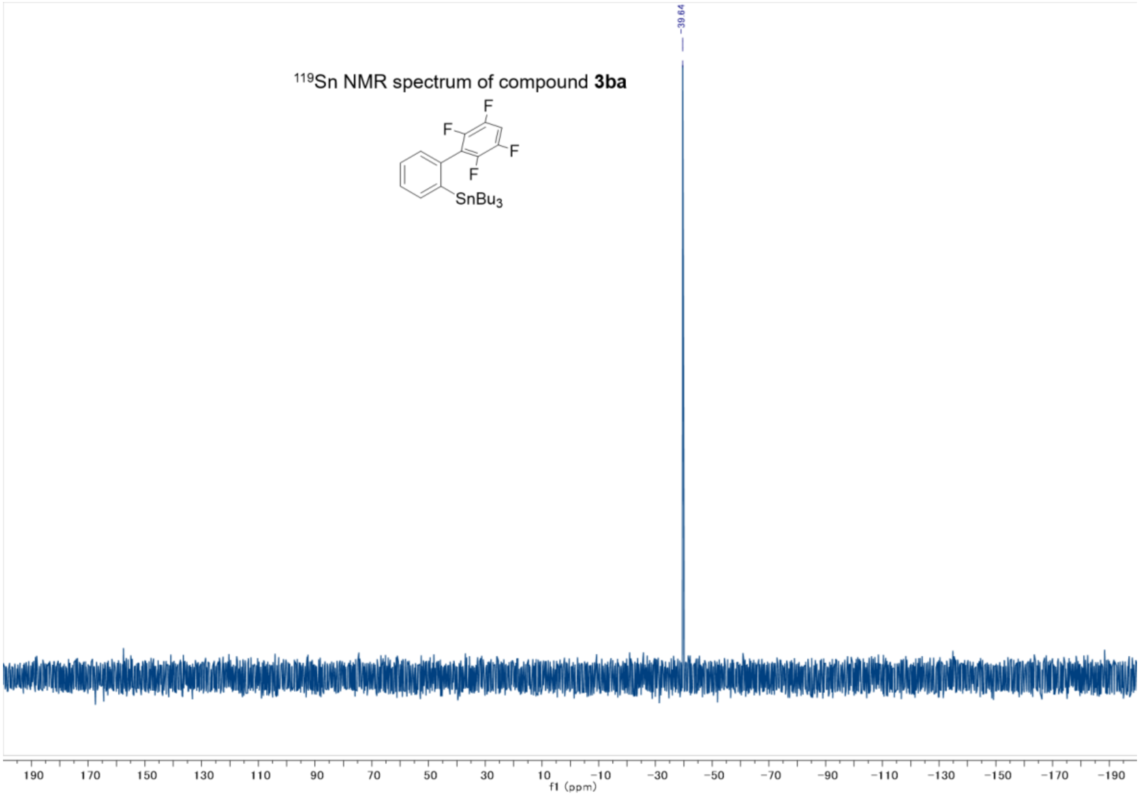


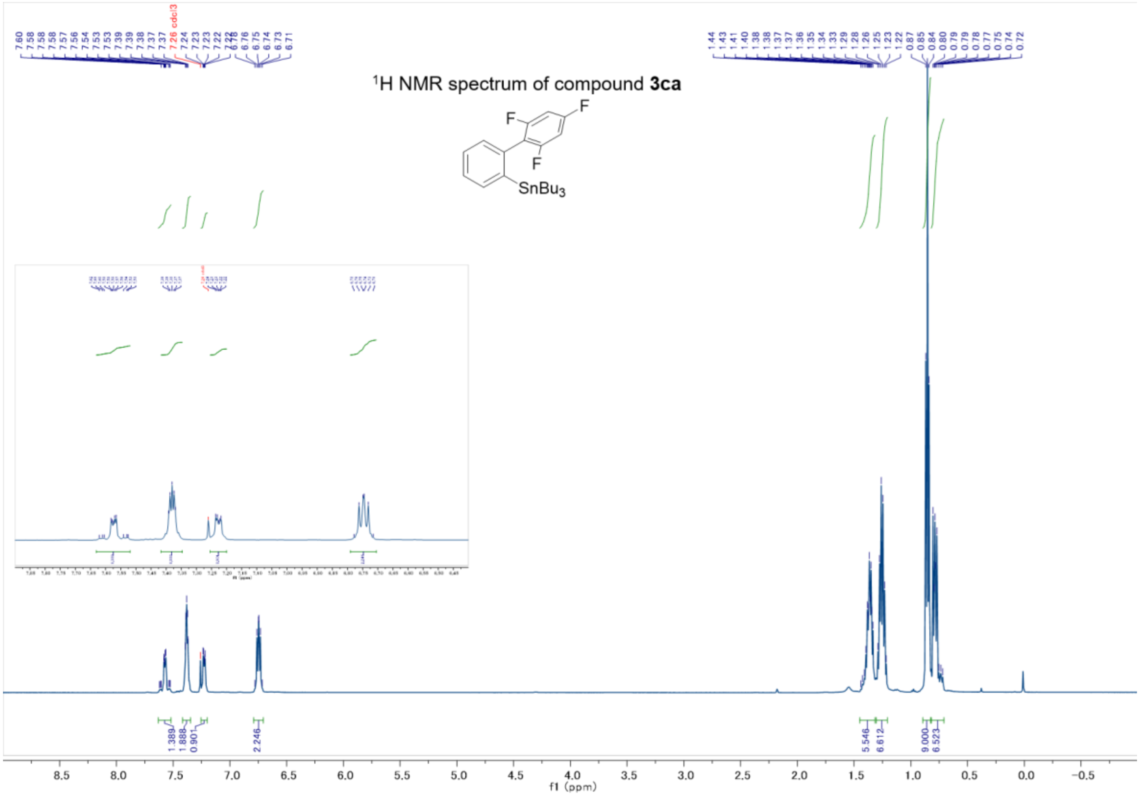
^{13}C NMR spectrum of compound **3ba**
F
F
F
F
SnBu$_3$
147.08
145.63
145.56
145.14
145.10
144.20
143.26
142.84
142.78
137.37
134.97
134.95
134.94
130.15
128.36
128.33
124.82
124.66
124.51
105.26
105.08
104.90
77.16 cdcl3
28.99
27.48
13.70
11.29
11.23
9.92
8.62
8.56
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

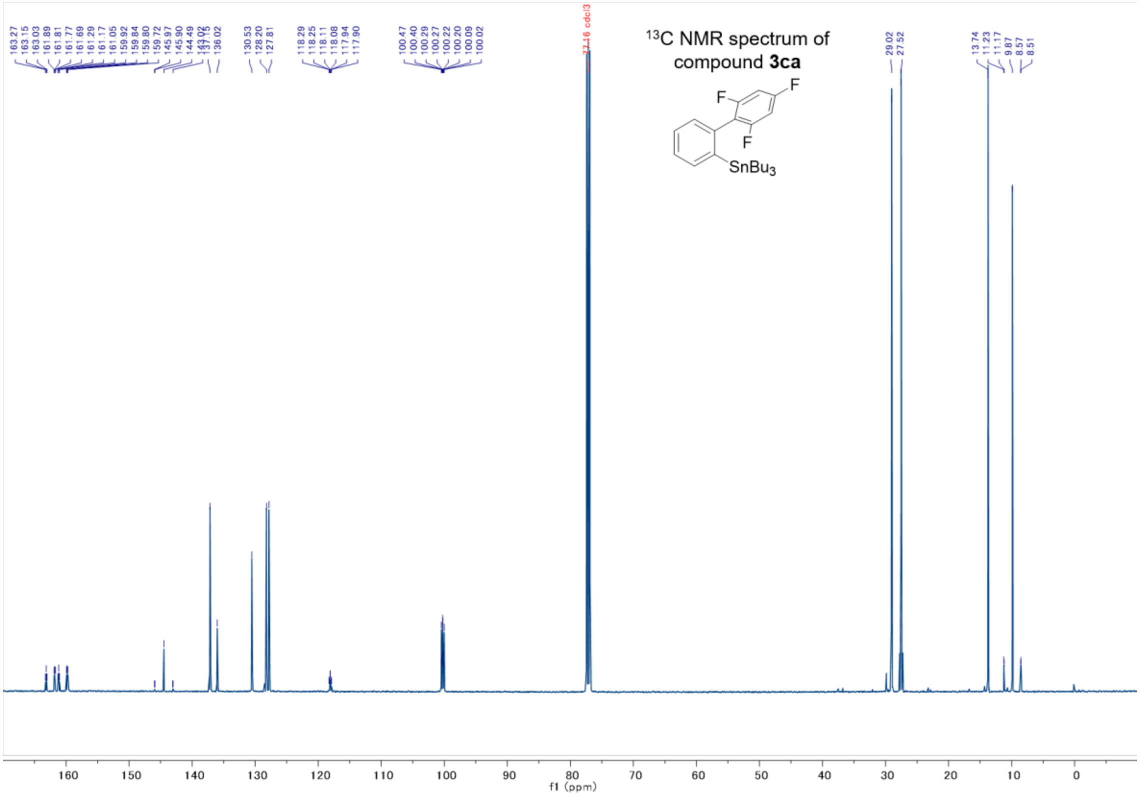


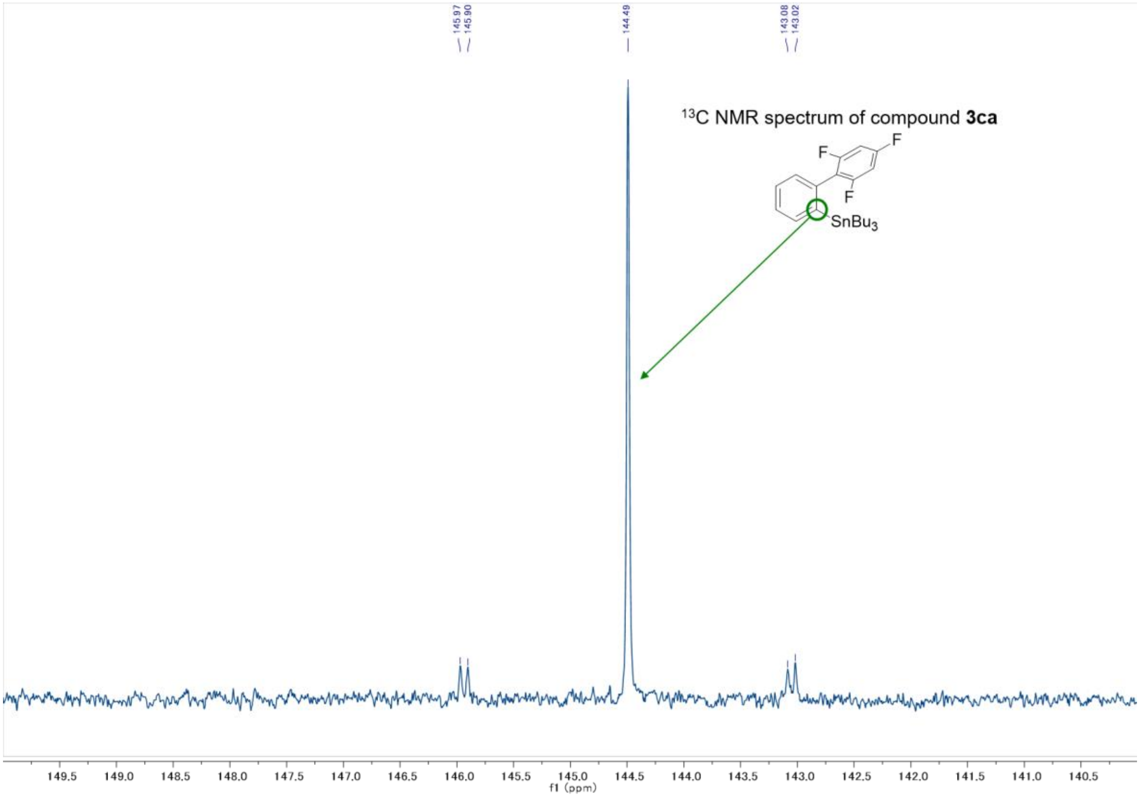
^{13}C NMR spectrum of compound **3ba**
F
F
F
F
SnBu$_3$
145.63
145.56
144.20
142.84
142.78
145.9
145.7
145.5
145.3
145.1
144.9
144.7
144.5
144.3
144.1
143.9
143.7
143.5
143.3
143.1
142.9
142.7
142.5
142.3
142.1
f1 (ppm)

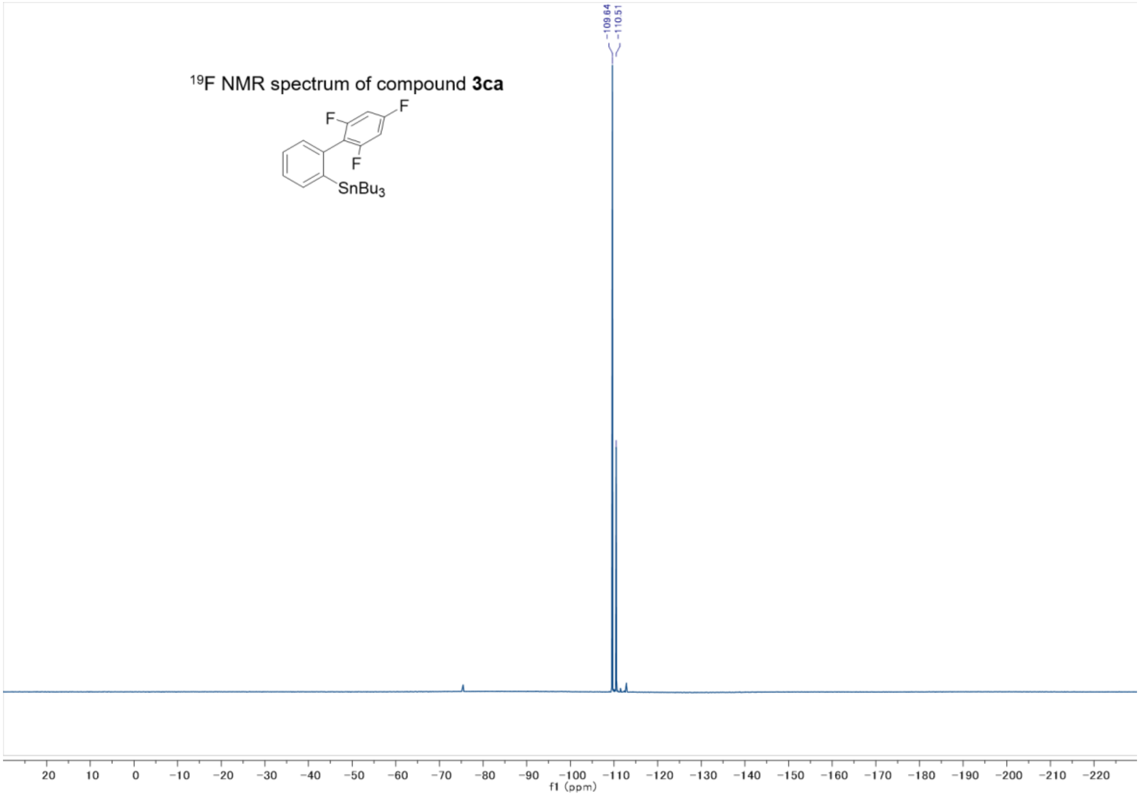

-140.59
-140.62
-140.64
-140.66
-140.69
-141.89
-141.90
-141.91
-141.93
-141.95
-141.96
-141.98
^{19}F NMR spectrum of compound **3ba**
F
F
F
F
SnBu$_3$
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

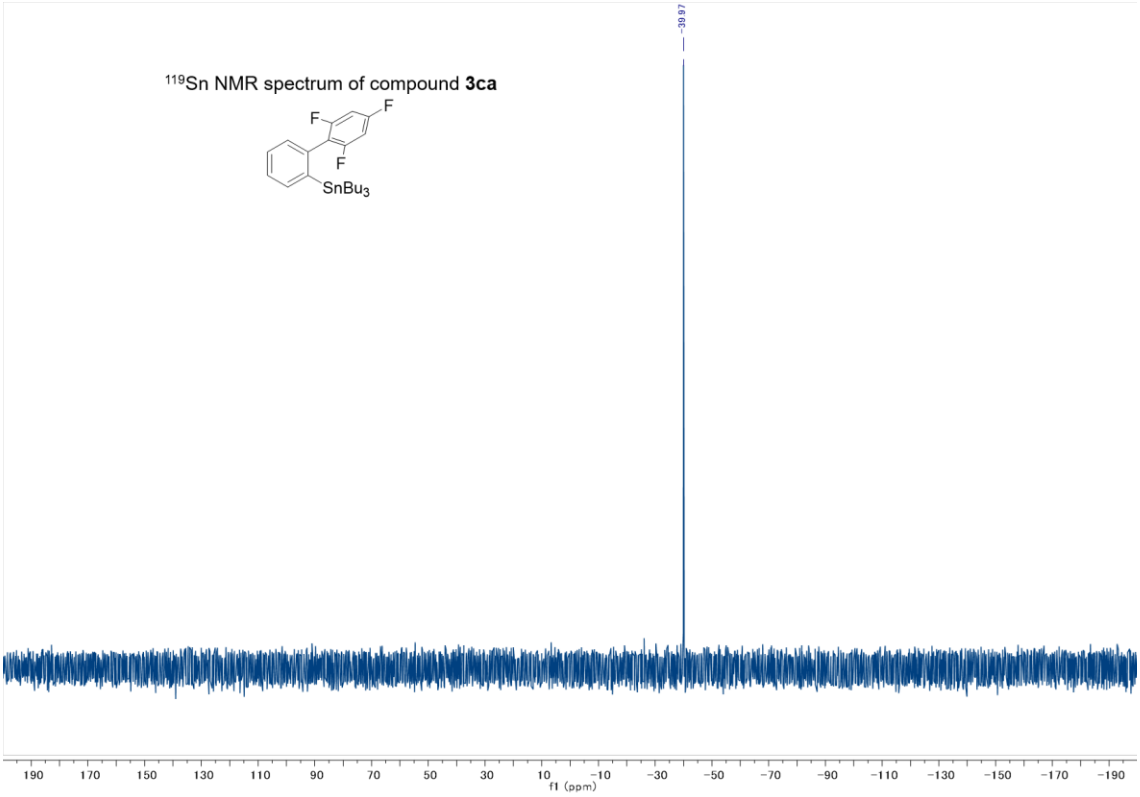

-39.64
^{119}Sn NMR spectrum of compound **3ba**
F
F
F
F
SnBu$_3$
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)


^{1}H NMR spectrum of compound **3ca**

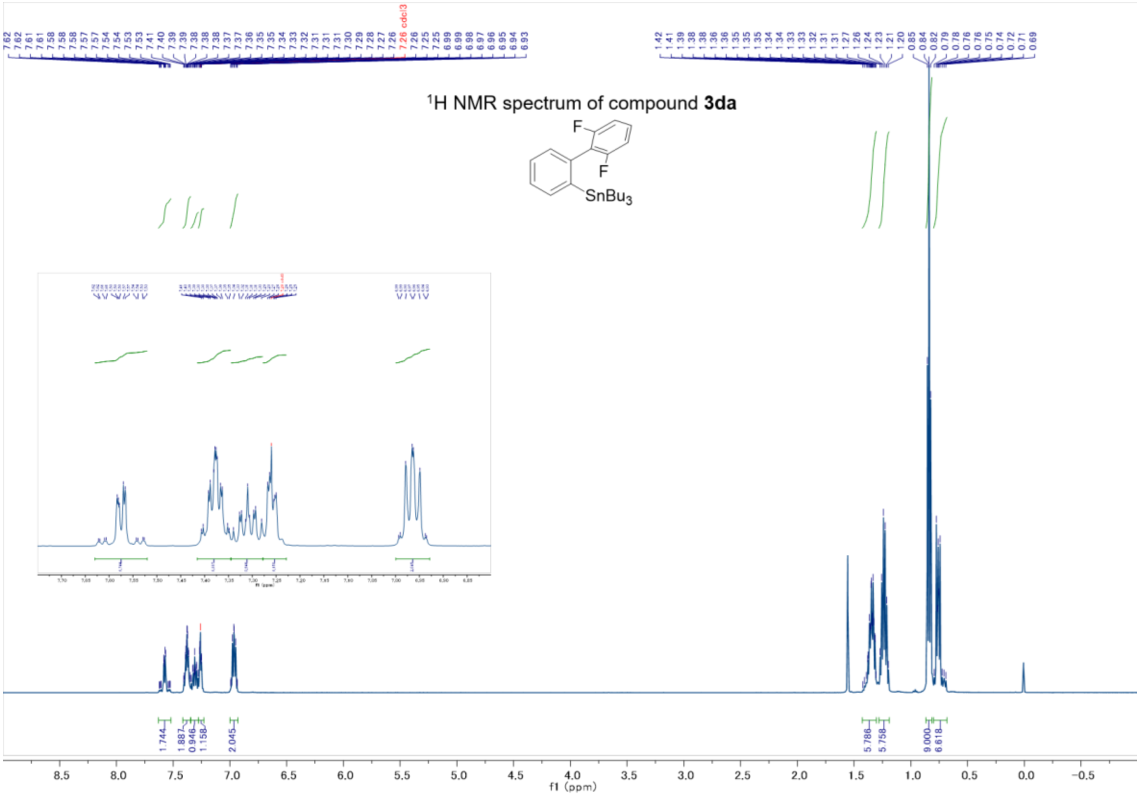

^{13}C NMR spectrum of compound **3ca**


145.97
145.90
144.49
143.08
143.02
^{13}C NMR spectrum of compound **3ca**
F
F
F
SnBu$_3$
149.5
149.0
148.5
148.0
147.5
147.0
146.5
146.0
145.5
145.0
144.5
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)

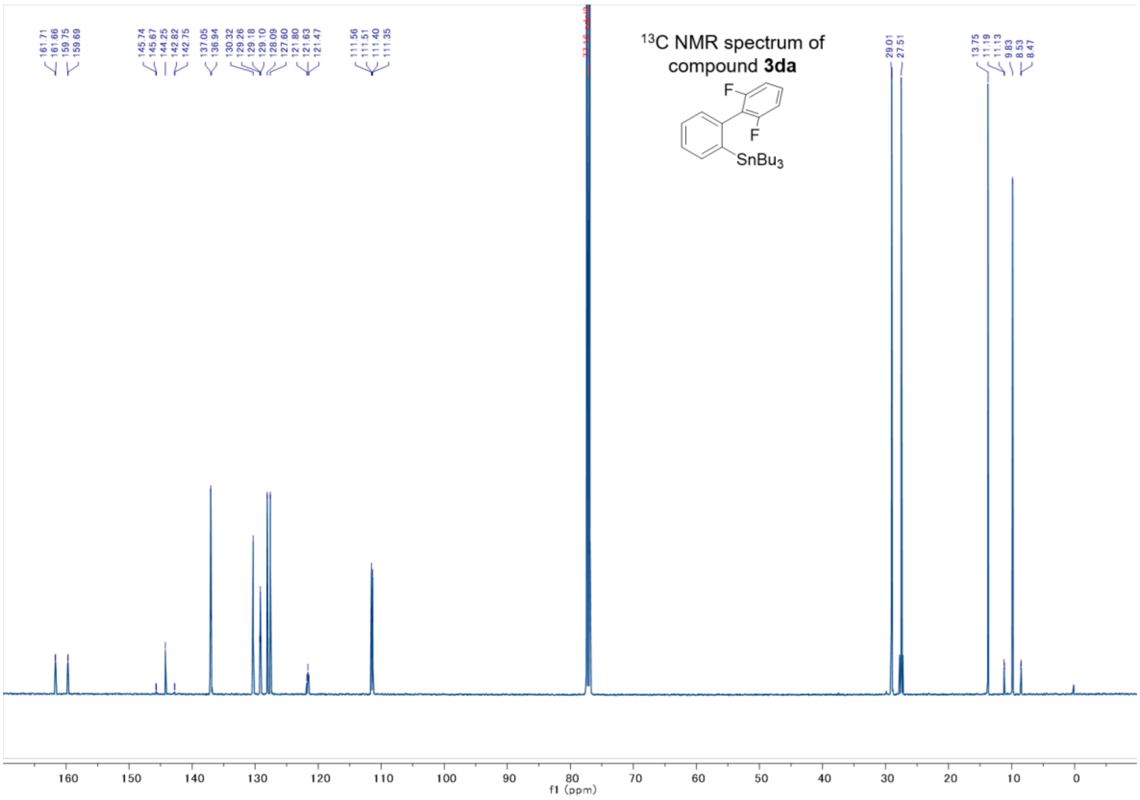

-109.64
-110.51
^{19}F NMR spectrum of compound **3ca**
F
F
F
SnBu$_3$
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

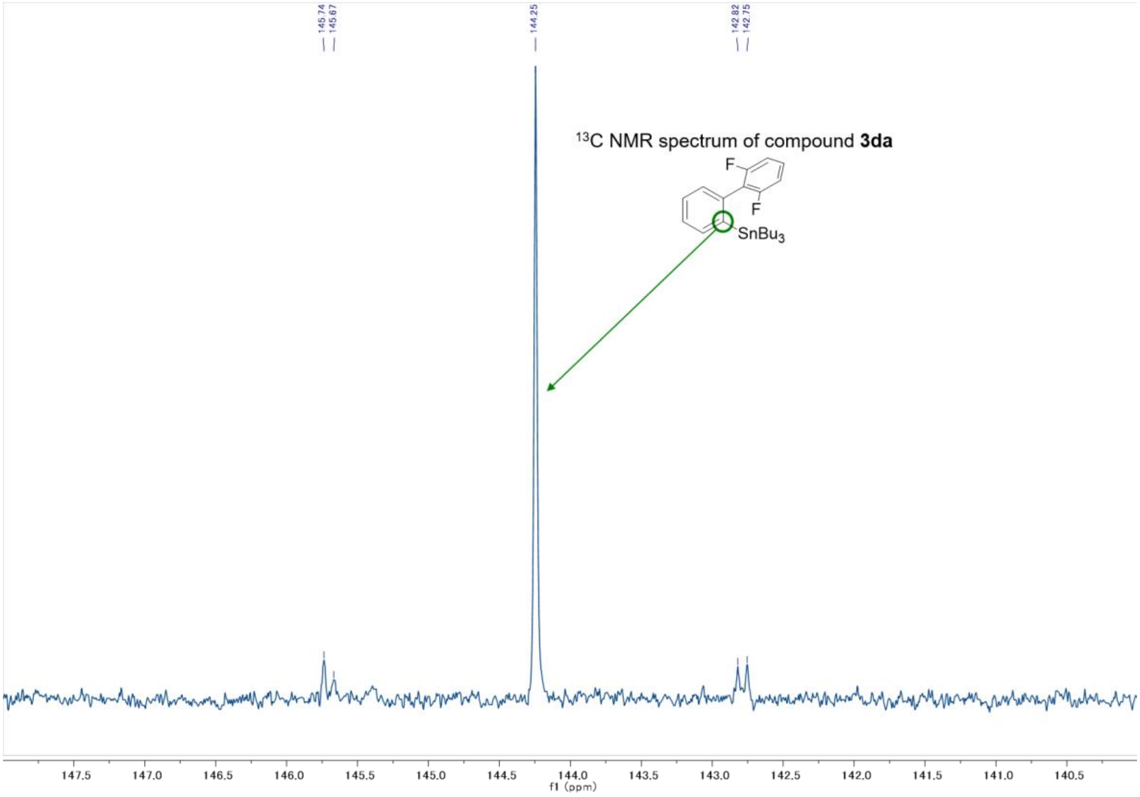


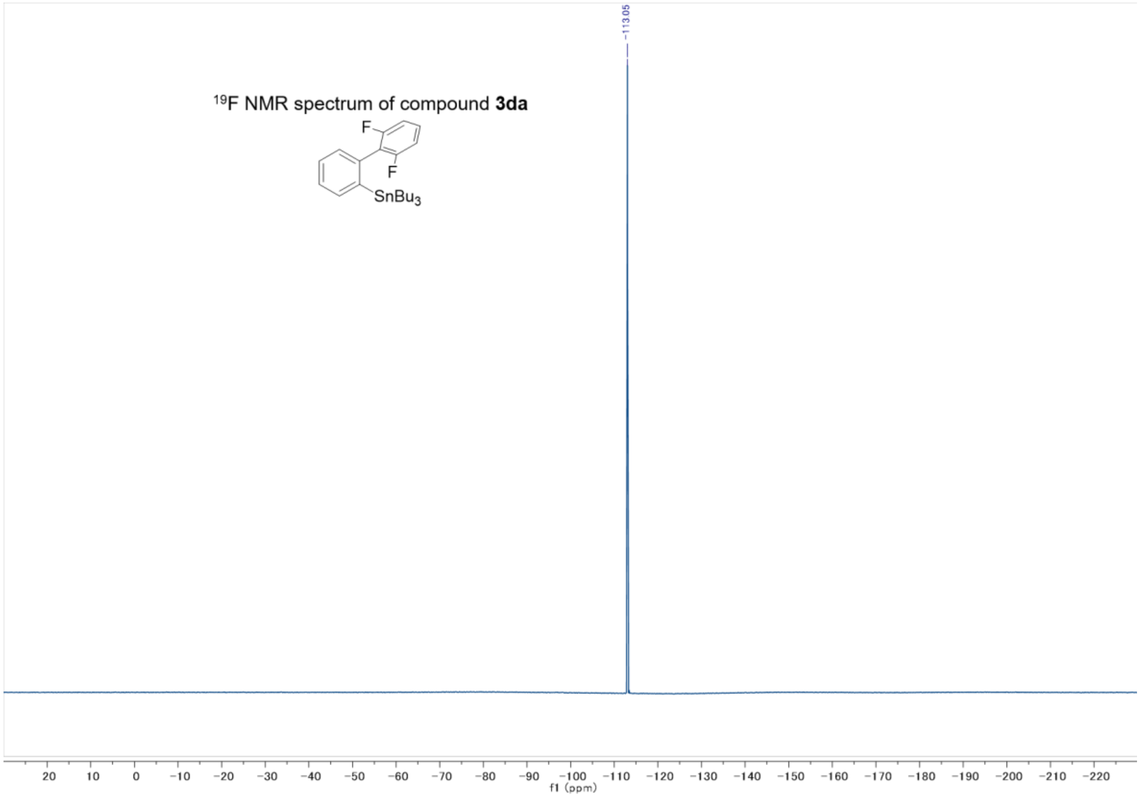
^{119}Sn NMR spectrum of compound **3ca**



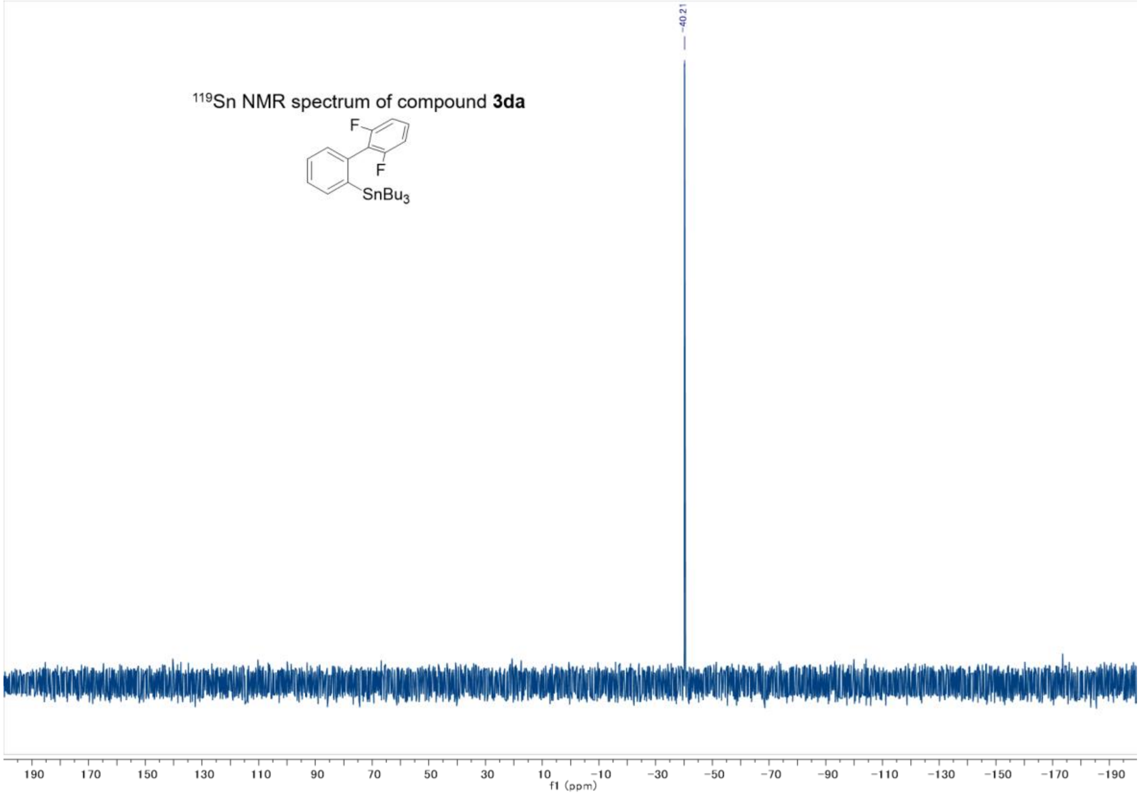
^{1}H NMR spectrum of compound **3da**


161.71
161.66
159.75
159.68
145.74
145.67
144.25
142.82
142.75
137.05
136.94
130.32
129.26
129.18
129.10
128.09
127.60
121.80
121.63
121.47
111.56
111.51
111.40
111.35
29.01
27.51
13.75
11.19
11.13
9.83
8.53
8.47
^{13}C NMR spectrum of compound **3da**
F
F
SnBu$_3$
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

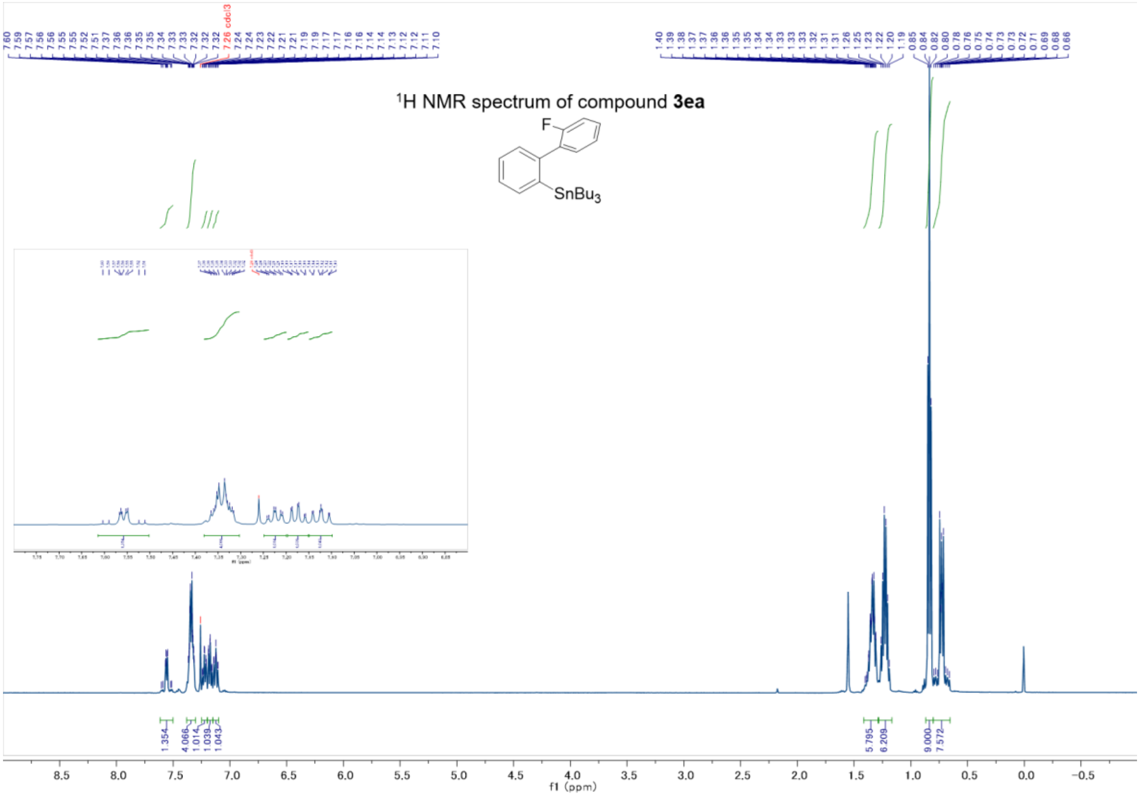

145.74
145.67
144.25
142.82
142.75
^{13}C NMR spectrum of compound **3da**
F
F
SnBu$_3$
147.5
147.0
146.5
146.0
145.5
145.0
144.5
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)



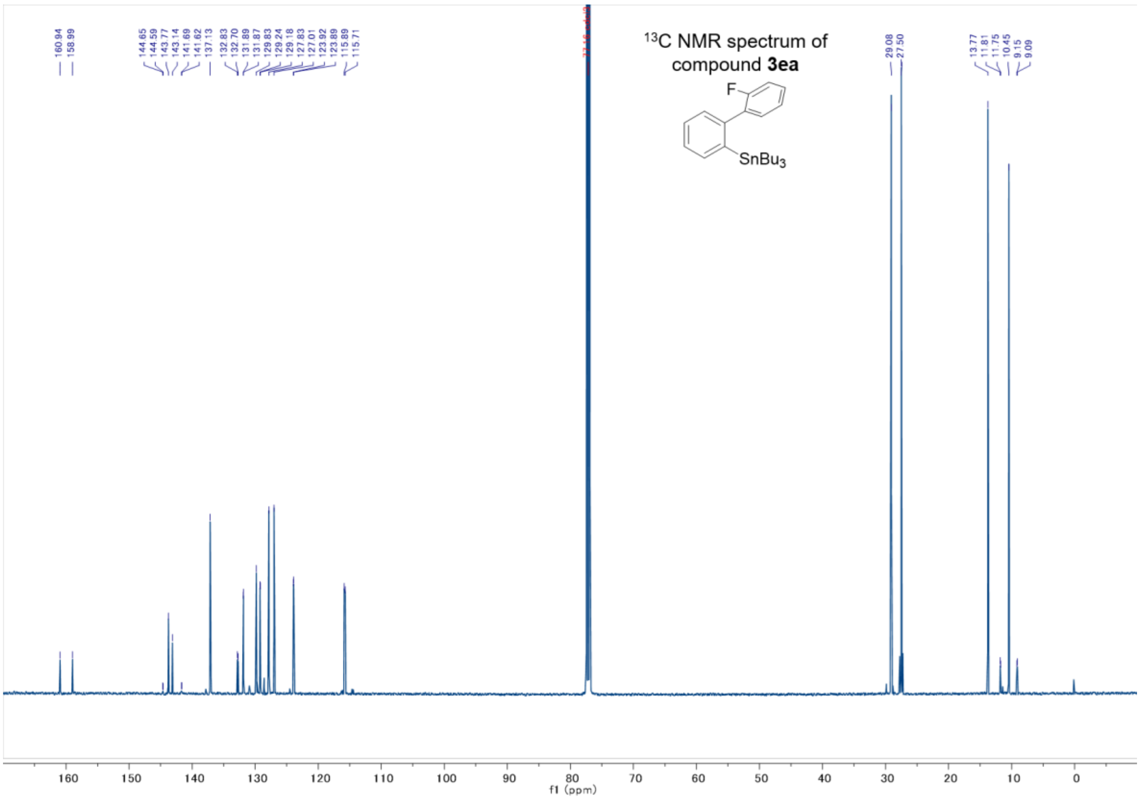
^{19}F NMR spectrum of compound **3da**



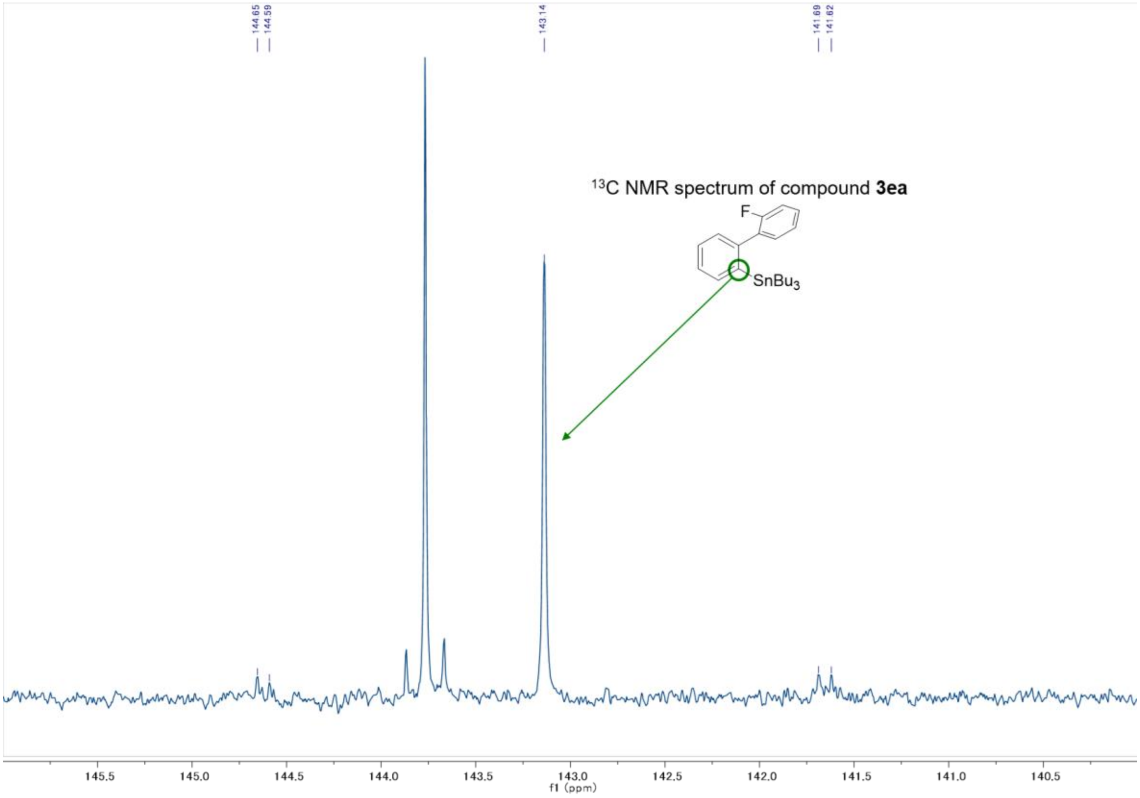
^{119}Sn NMR spectrum of compound **3da**

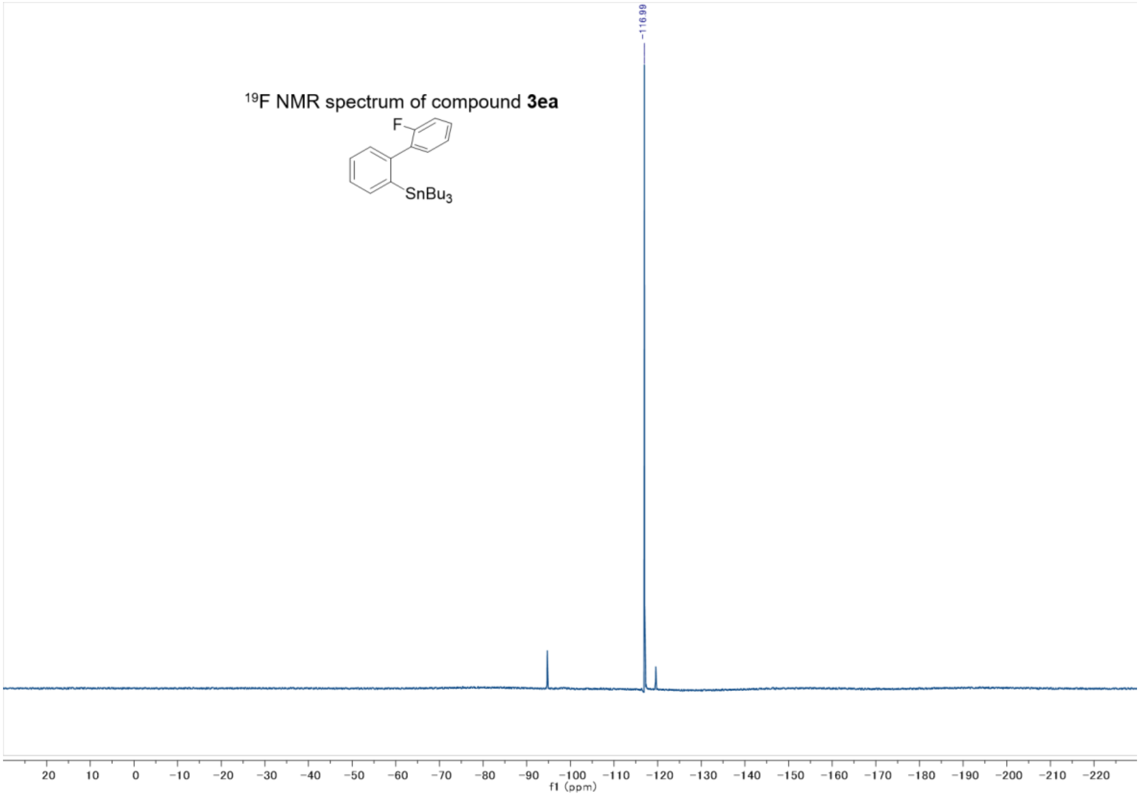


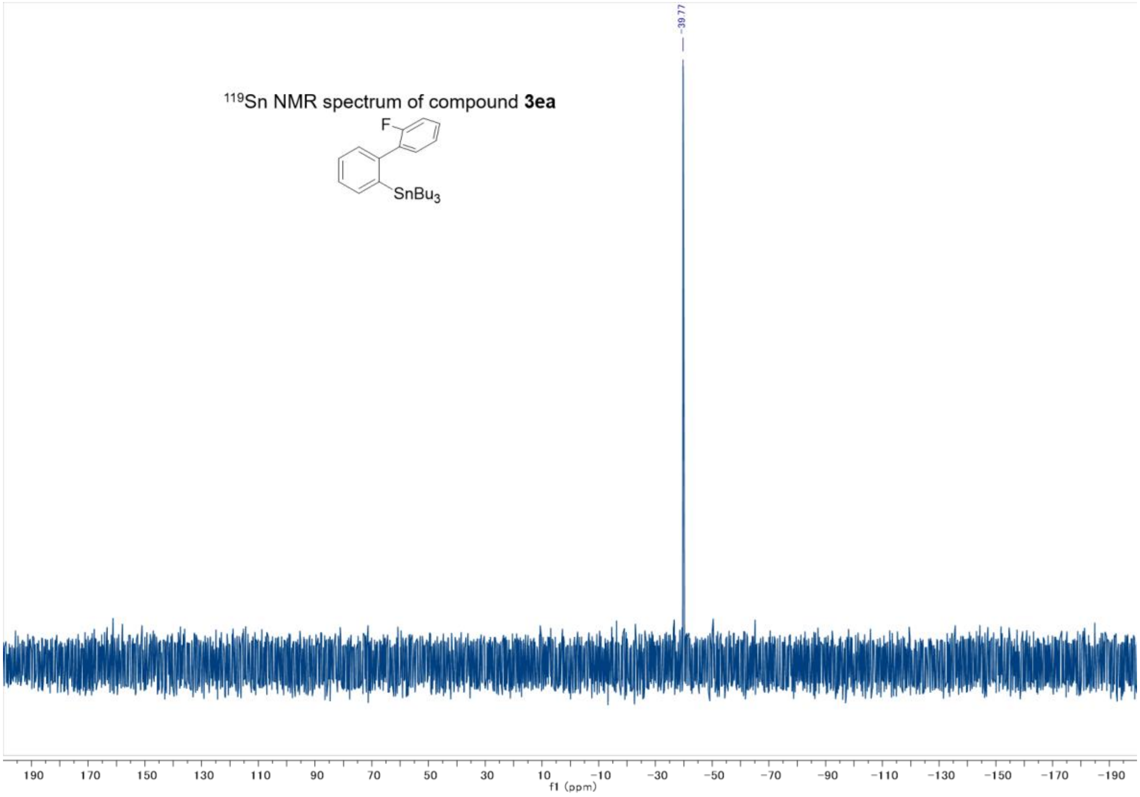
^{1}H NMR spectrum of compound **3ea**

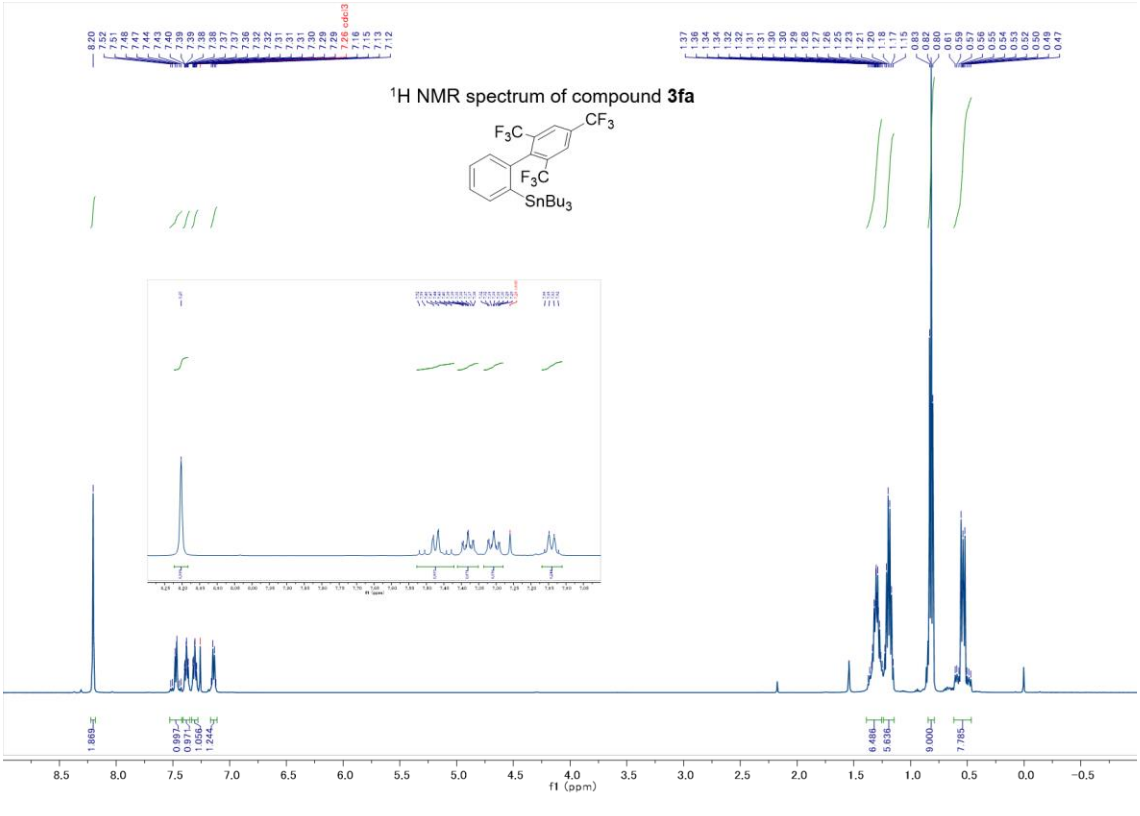


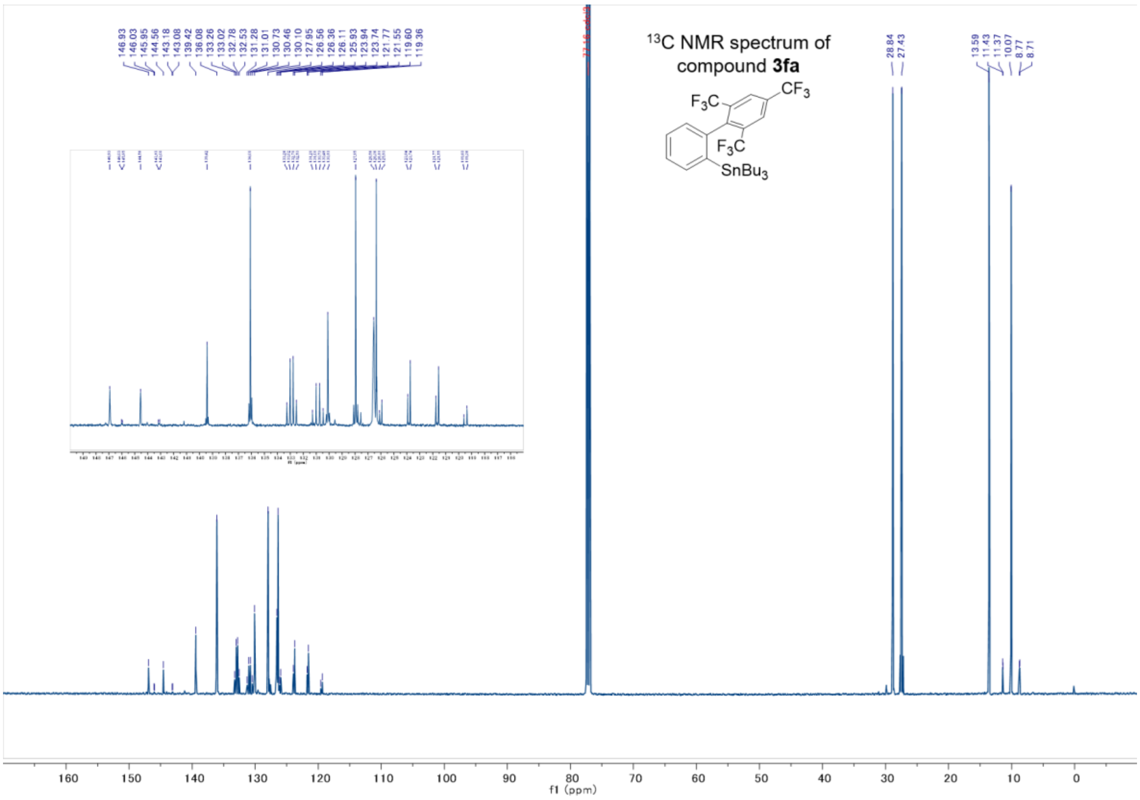
^{13}C NMR spectrum of compound **3ea**

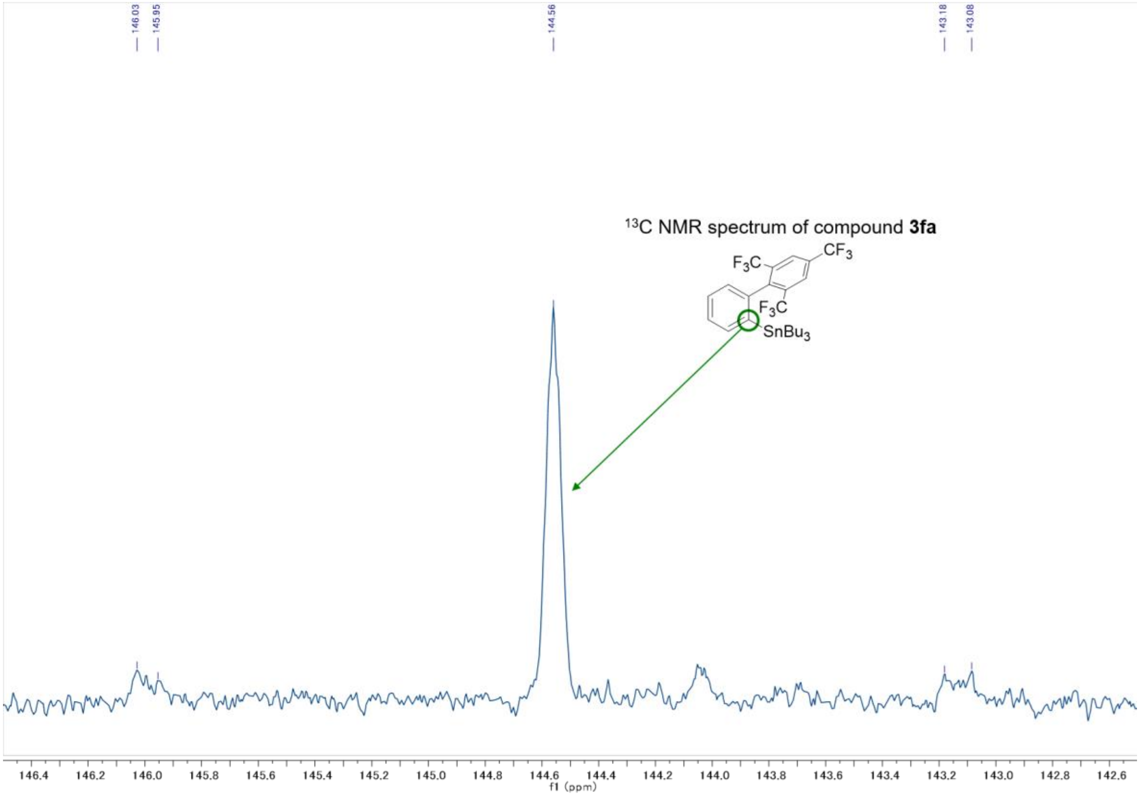

144.65
144.59
143.14
141.69
141.62
^{13}C NMR spectrum of compound **3ea**
F
SnBu$_3$
145.5
145.0
144.5
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)

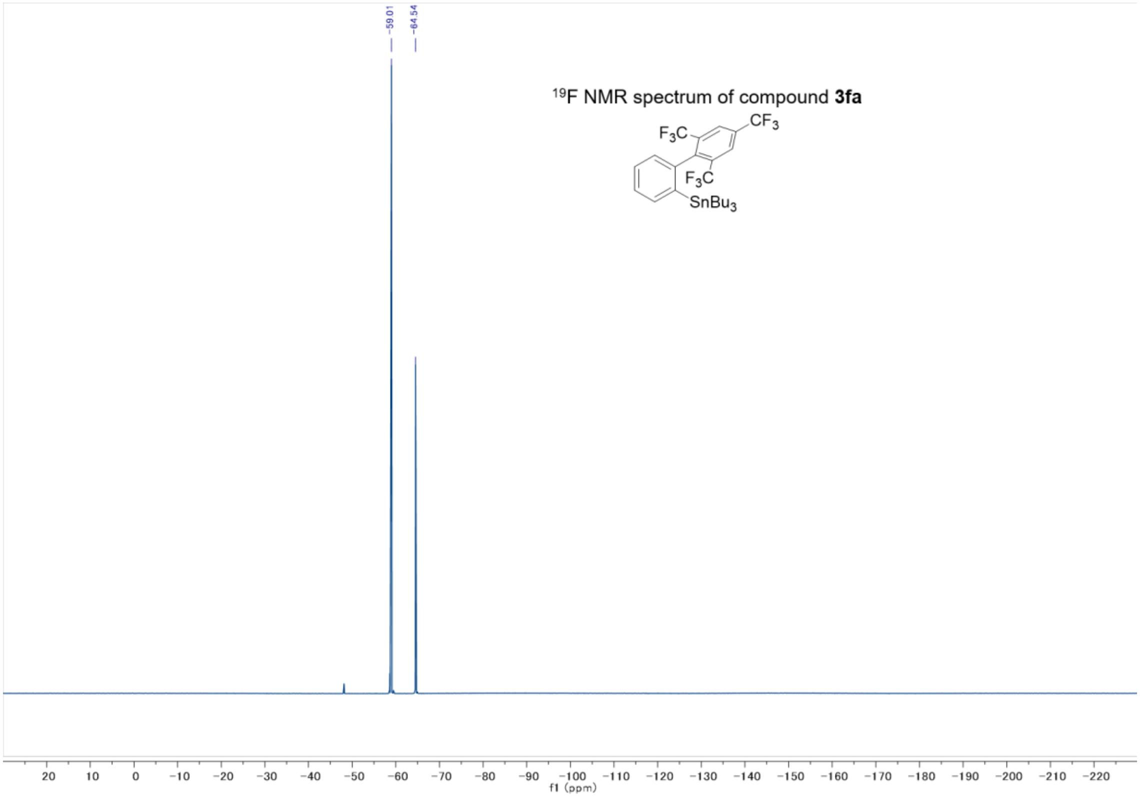

−116.99
^{19}F NMR spectrum of compound **3ea**
F
SnBu$_3$
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

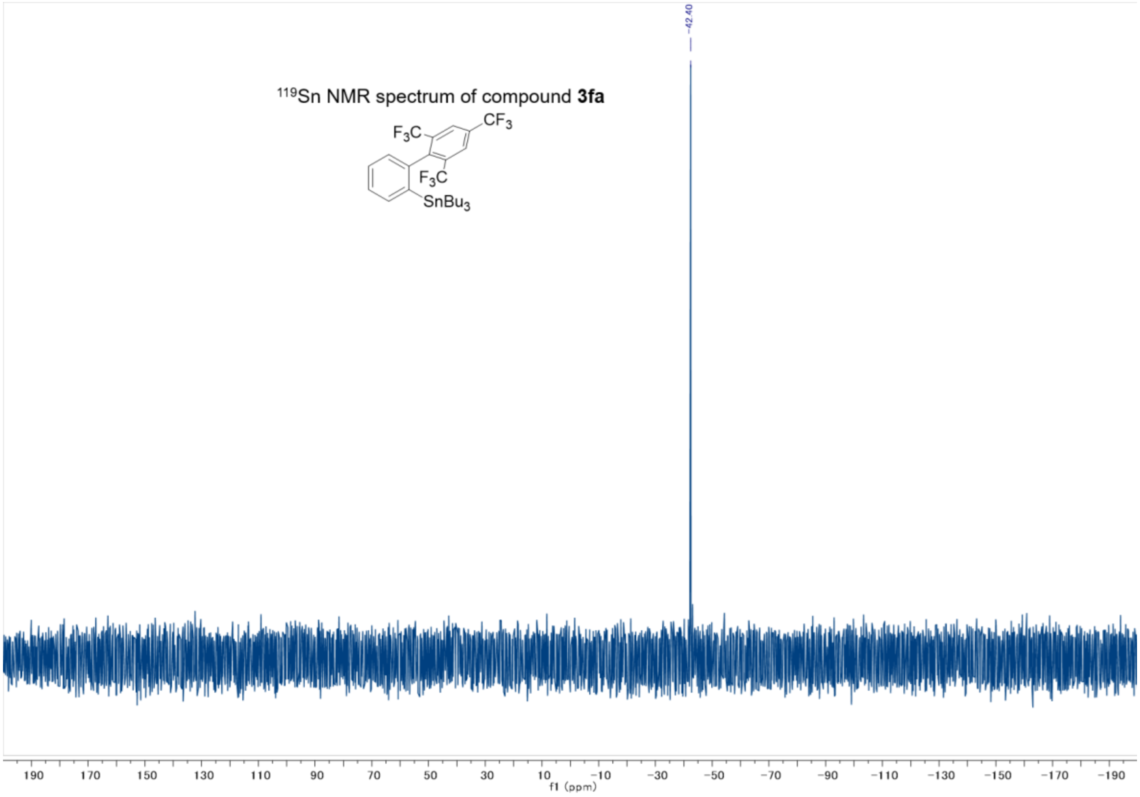

−39.77
^{119}Sn NMR spectrum of compound **3ea**
F
SnBu$_3$
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

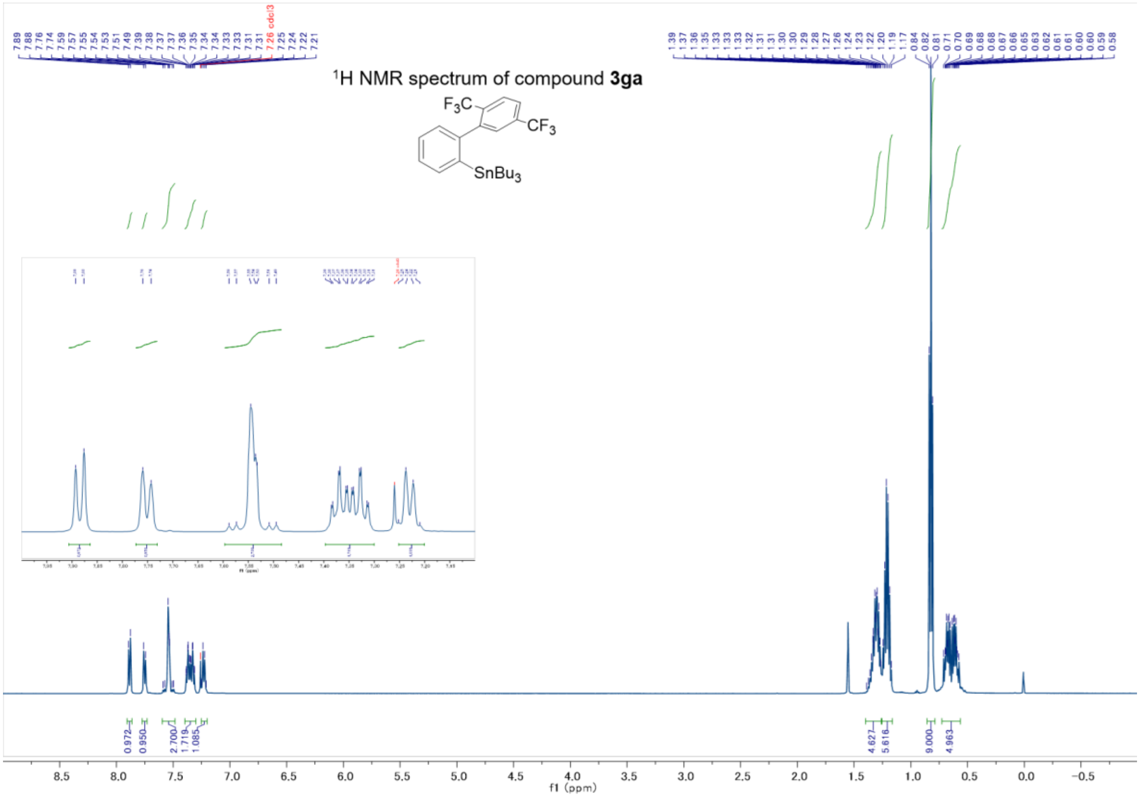

8.20 7.52 7.51 7.48 7.47 7.44 7.43 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.26 cdcl3 7.16 7.15 7.13 7.12
1.37 1.36 1.34 1.34 1.32 1.32 1.31 1.31 1.30 1.30 1.29 1.28 1.27 1.26 1.25 1.23 1.21 1.20 1.18 1.17 1.15 0.83 0.82 0.80 0.61 0.59 0.57 0.56 0.55 0.54 0.53 0.52 0.50 0.49 0.47
^{1}H NMR spectrum of compound **3fa**
F$_3$C
CF$_3$
F$_3$C
SnBu$_3$
1.869
0.997
0.971
1.056
1.244
6.486
5.636
9.000
7.785
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

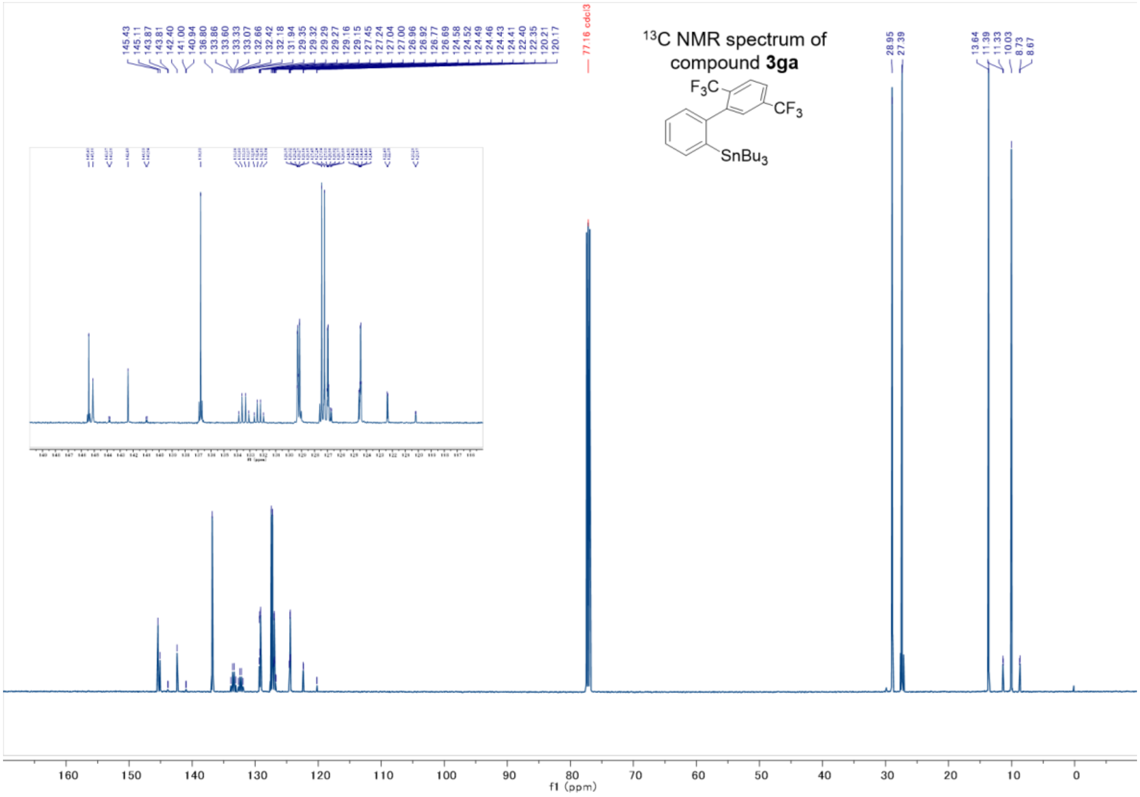

13C NMR spectrum of compound 3fa
F3C
CF3
F3C
SnBu3
146.93
146.03
145.95
144.56
143.18
143.08
139.42
136.08
133.26
133.02
132.78
132.53
131.28
131.01
130.73
130.46
130.10
127.95
126.56
126.36
126.11
125.93
123.94
123.74
121.77
121.55
119.60
119.36
28.84
27.43
13.59
11.43
11.37
10.07
8.77
8.71
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

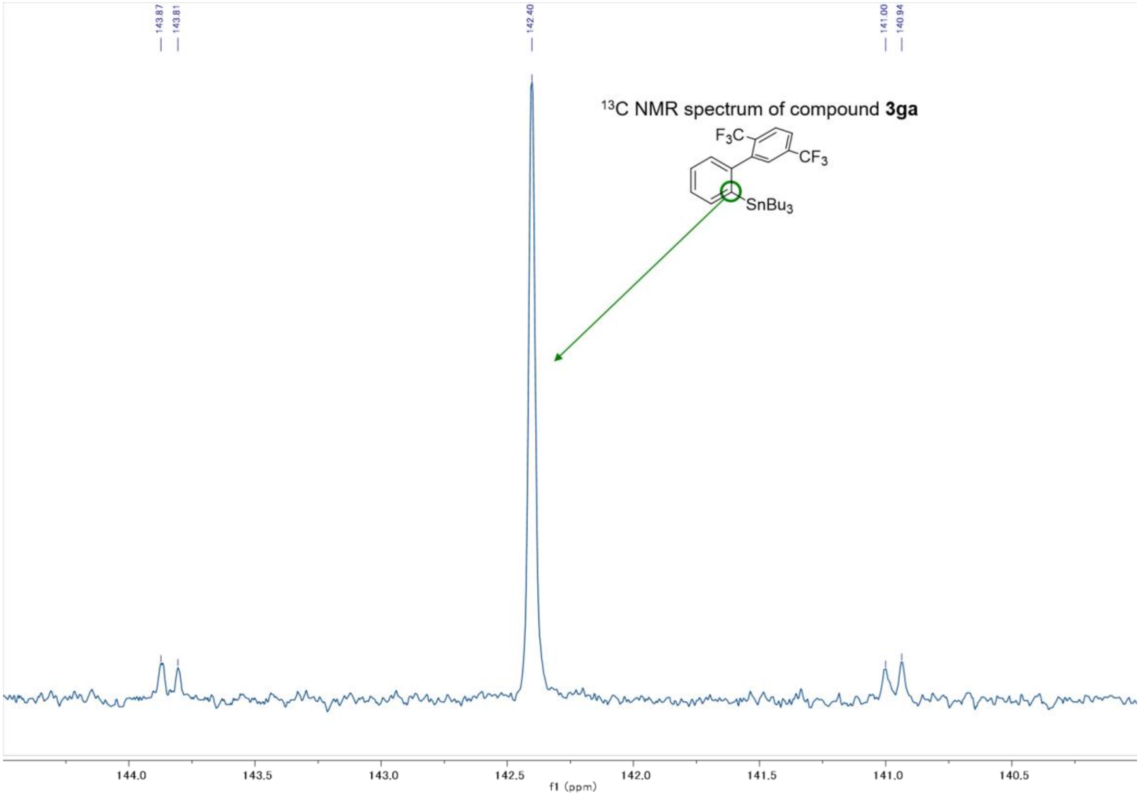

146.03
145.95
144.56
143.18
143.08
13C NMR spectrum of compound 3fa
F3C
CF3
F3C
SnBu3
146.4
146.2
146.0
145.8
145.6
145.4
145.2
145.0
144.8
144.6
144.4
144.2
144.0
143.8
143.6
143.4
143.2
143.0
142.8
142.6
f1 (ppm)

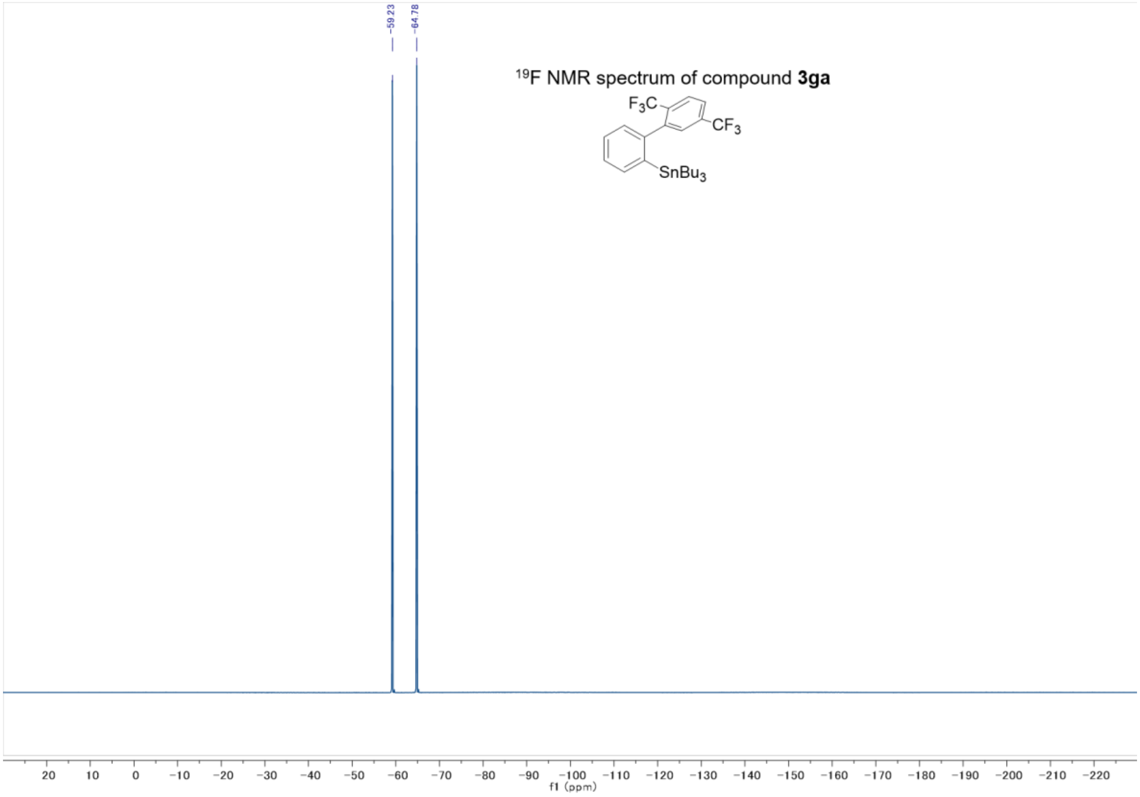

−59.01
−64.54
^{19}F NMR spectrum of compound **3fa**
F_3C
CF_3
F_3C
$SnBu_3$
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

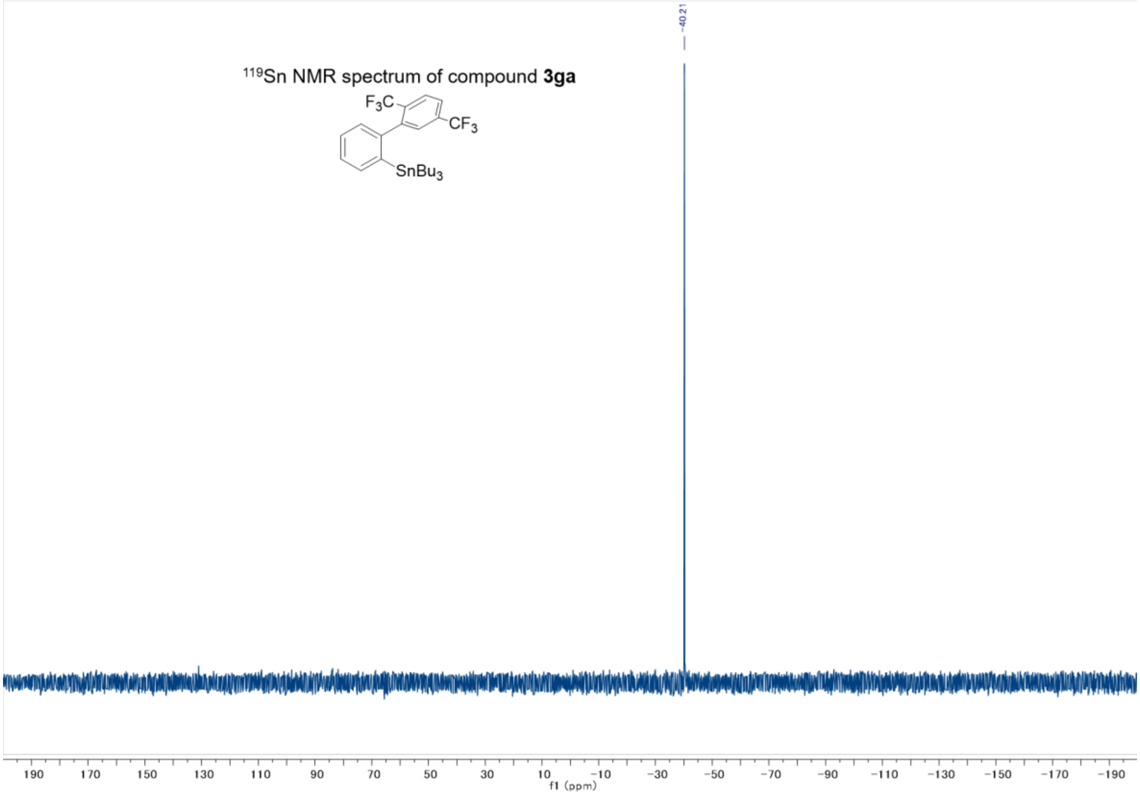

−42.40
^{119}Sn NMR spectrum of compound **3fa**
F_3C
CF_3
F_3C
$SnBu_3$
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

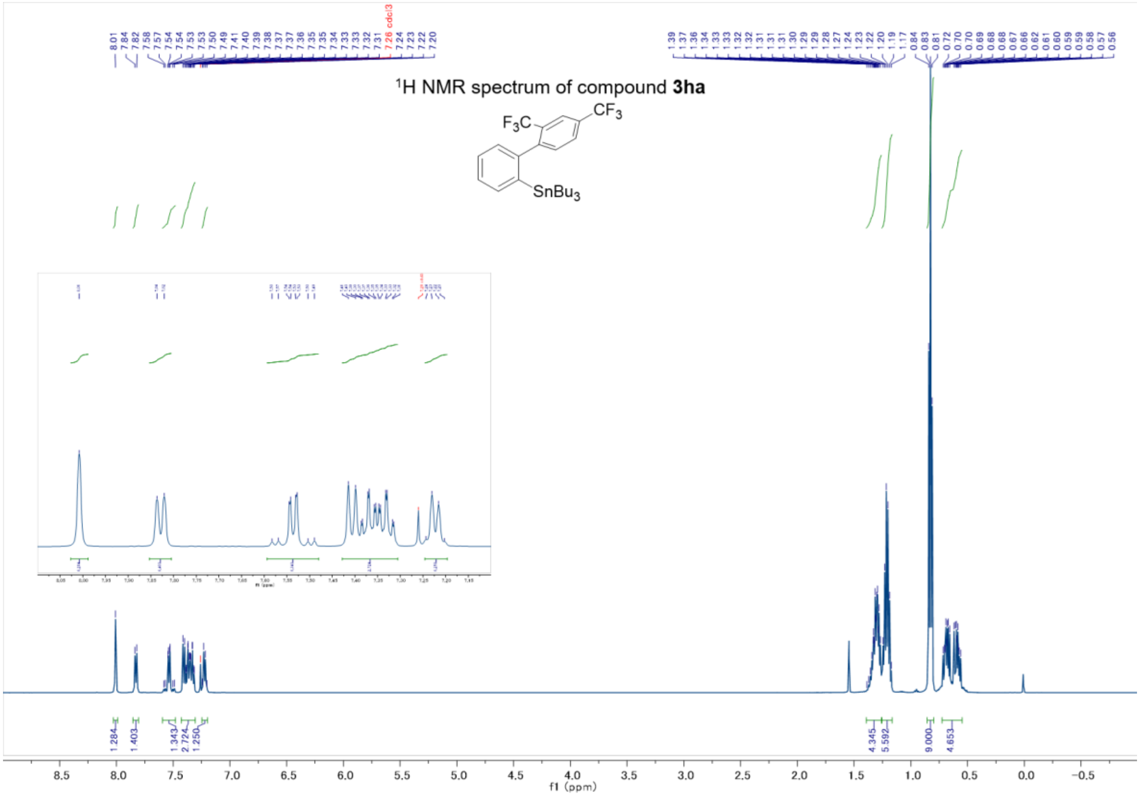

^{1}H NMR spectrum of compound **3ga**

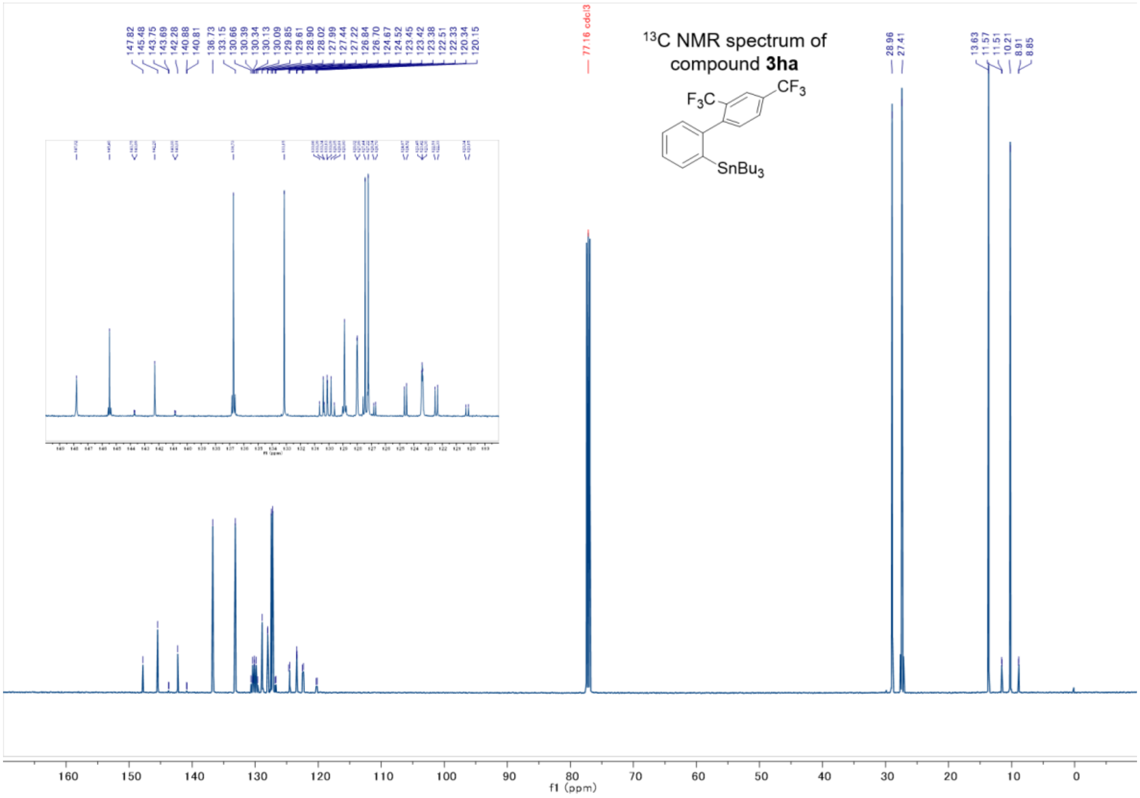

^{13}C NMR spectrum of compound **3ga**

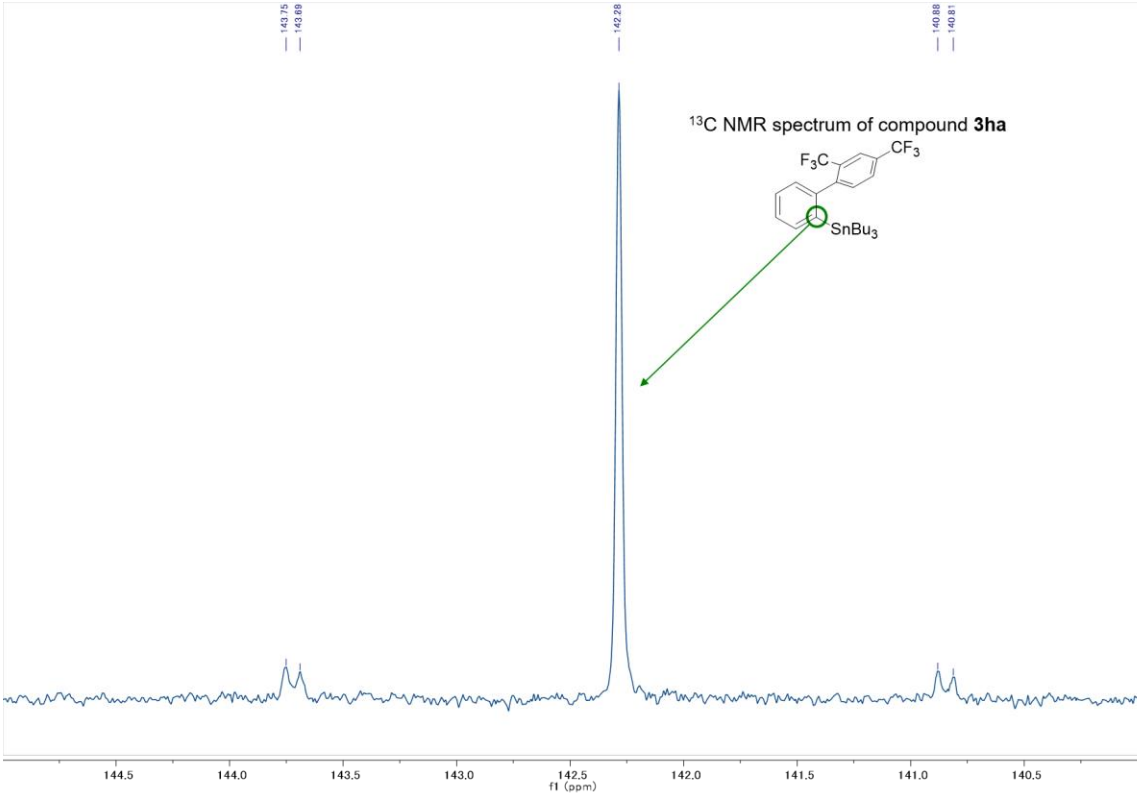

143.87
143.81
142.40
141.00
140.94
^{13}C NMR spectrum of compound **3ga**
F$_3$C
CF$_3$
SnBu$_3$
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)

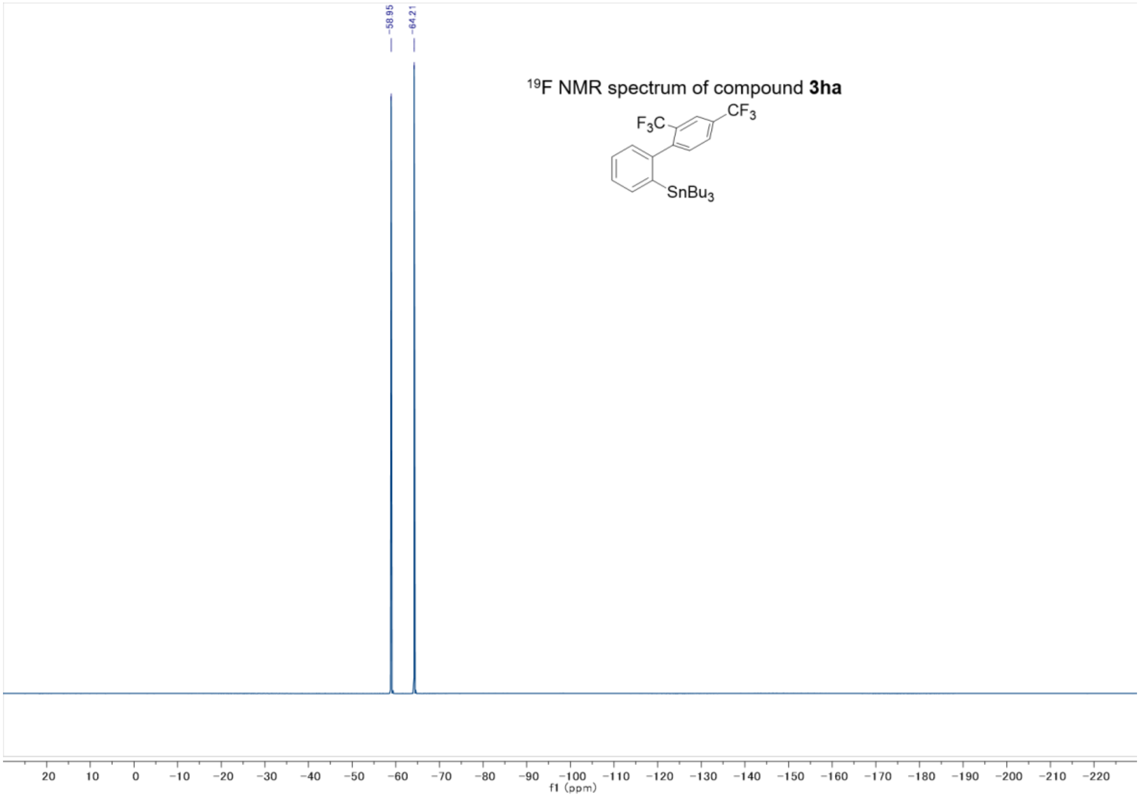

-59.23
-64.78
^{19}F NMR spectrum of compound **3ga**
F$_3$C
CF$_3$
SnBu$_3$
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

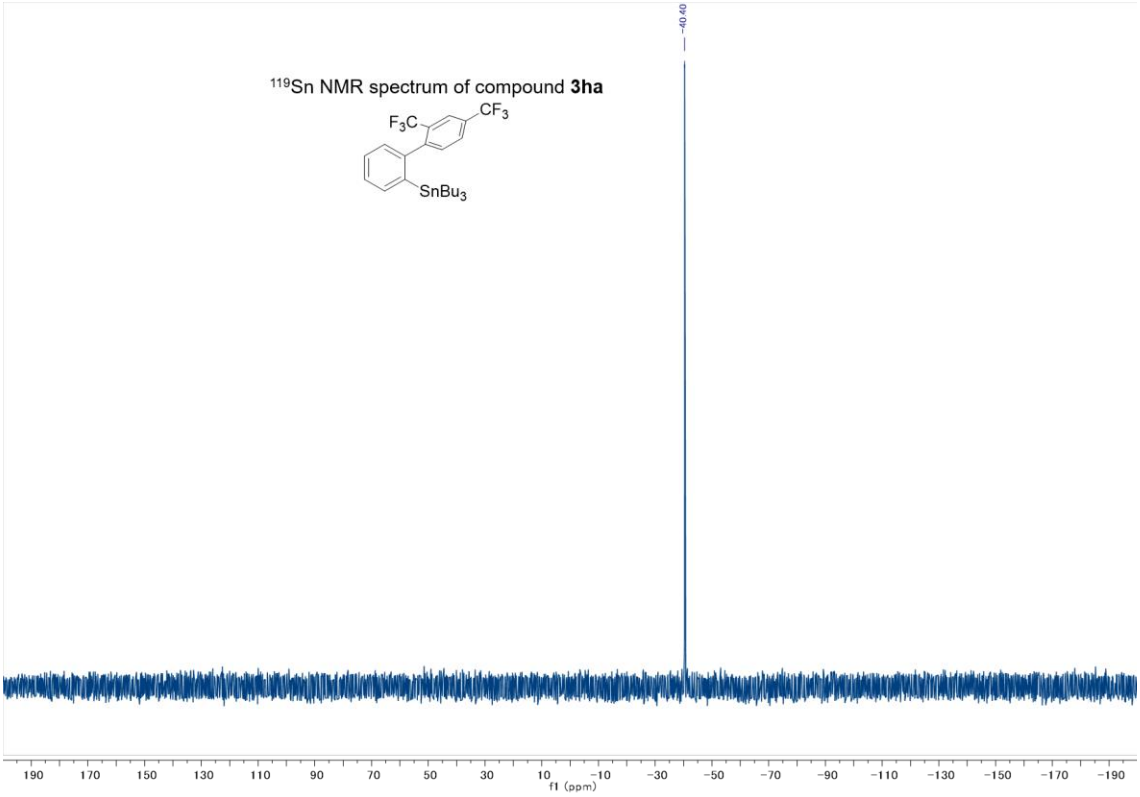

^{119}Sn NMR spectrum of compound **3ga**

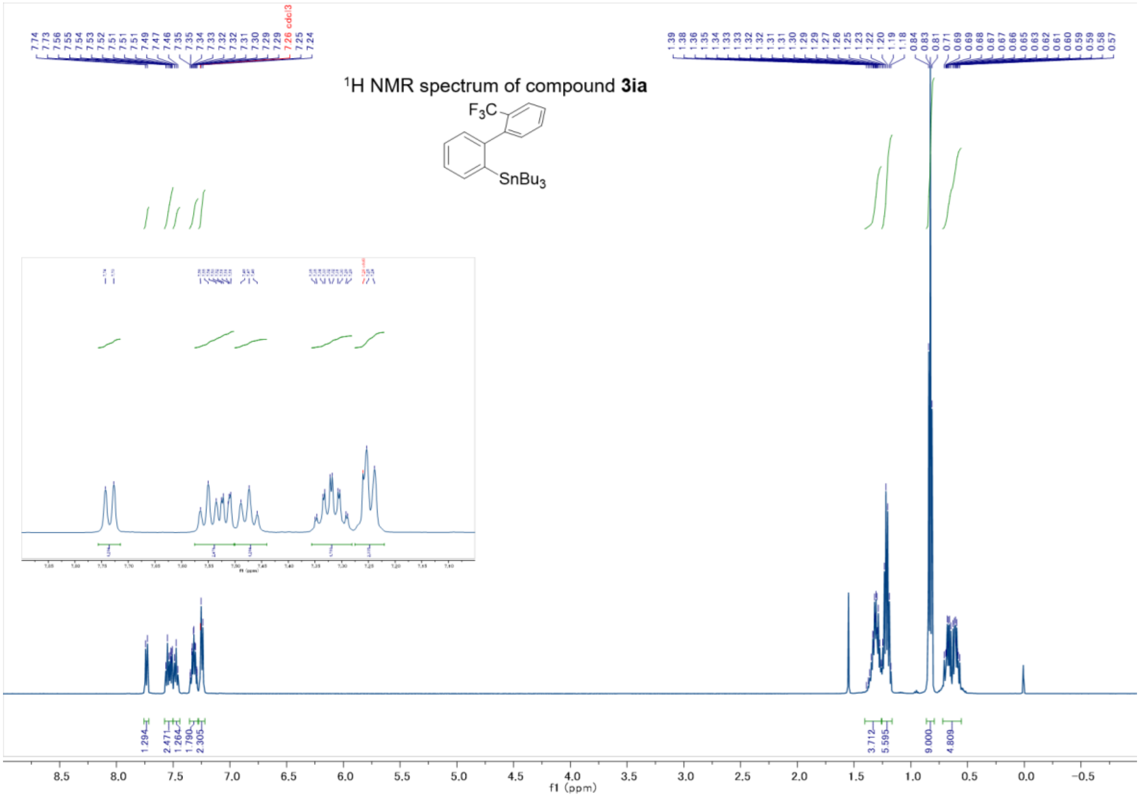

^{1}H NMR spectrum of compound **3ha**

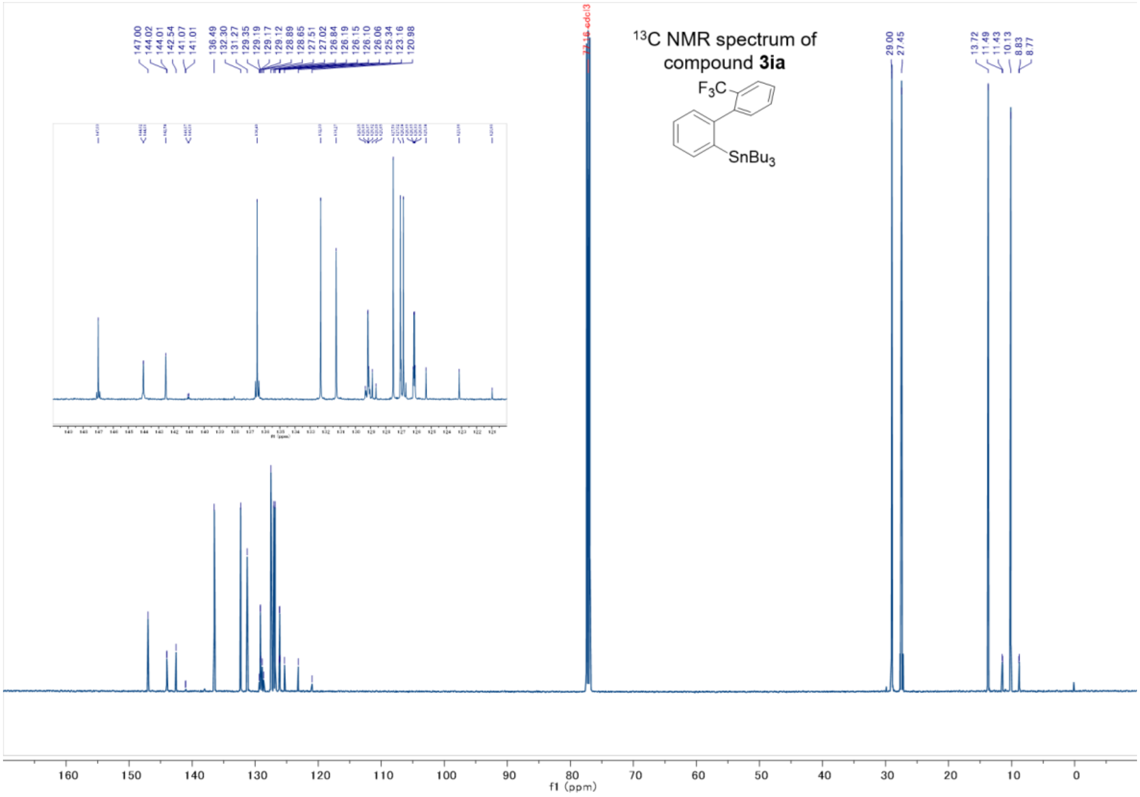

13C NMR spectrum of compound 3ha
F3C
CF3
SnBu3
147.82
145.48
143.75
143.69
142.28
140.88
140.81
136.73
133.15
130.66
130.39
130.34
130.13
130.09
129.85
129.61
128.90
128.02
127.99
127.44
127.22
126.84
126.70
124.67
124.52
123.45
123.42
123.38
122.51
122.33
120.34
120.15
77.16 cdcl3
28.96
27.41
13.63
11.57
11.51
10.21
8.91
8.85
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

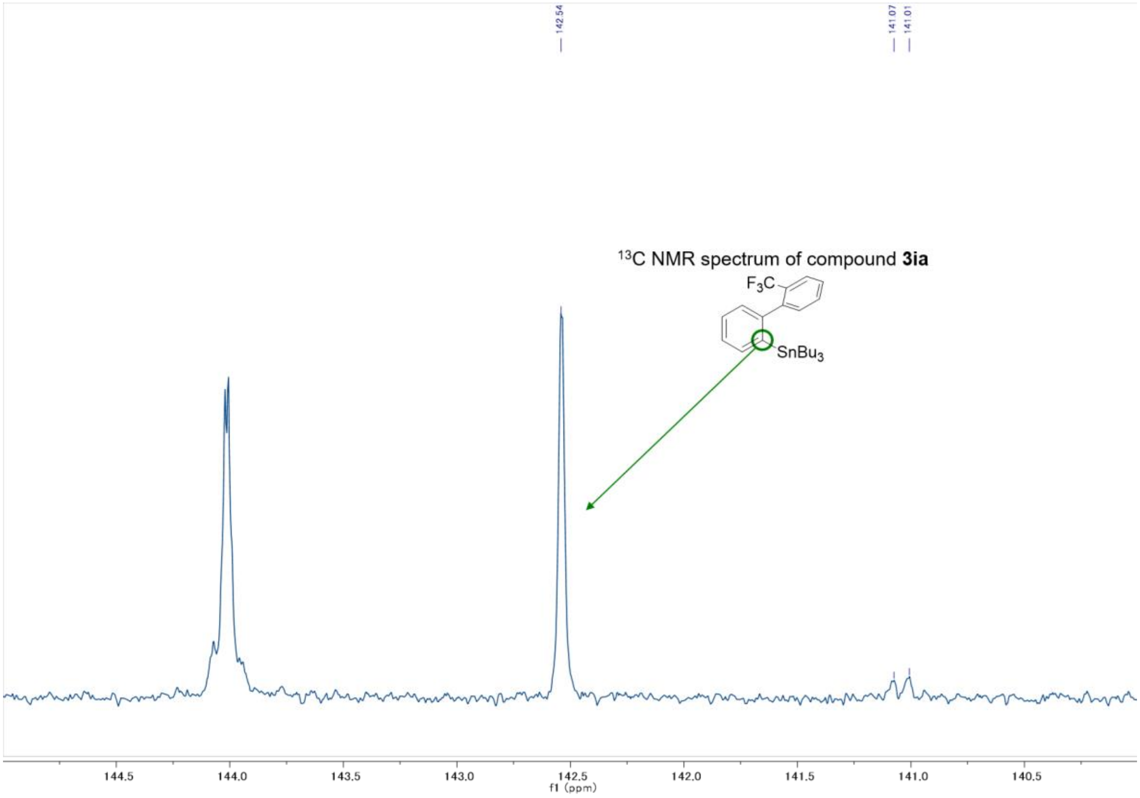

143.75
143.69
142.28
140.88
140.81
13C NMR spectrum of compound 3ha
F3C
CF3
SnBu3
144.5
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)

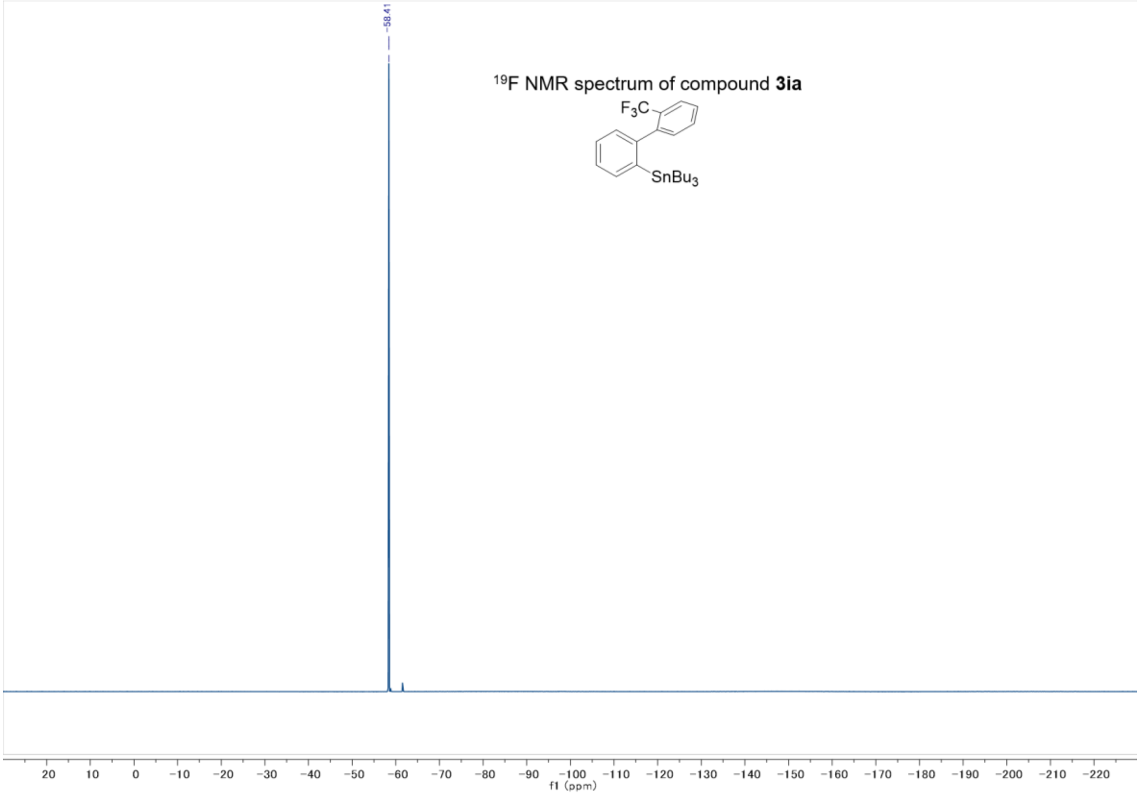

^{19}F NMR spectrum of compound **3ha**
-58.95
-64.21
F_3C
CF_3
$SnBu_3$
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

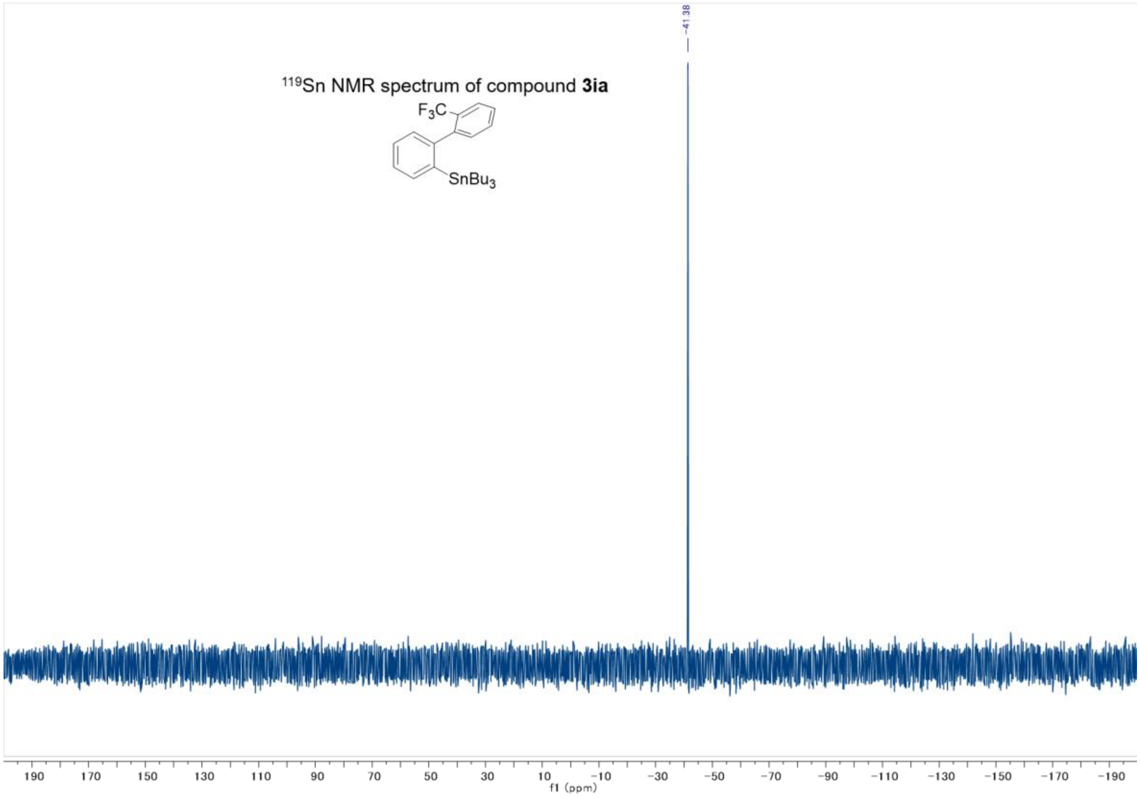

^{119}Sn NMR spectrum of compound **3ha**
-40.40
F_3C
CF_3
$SnBu_3$
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

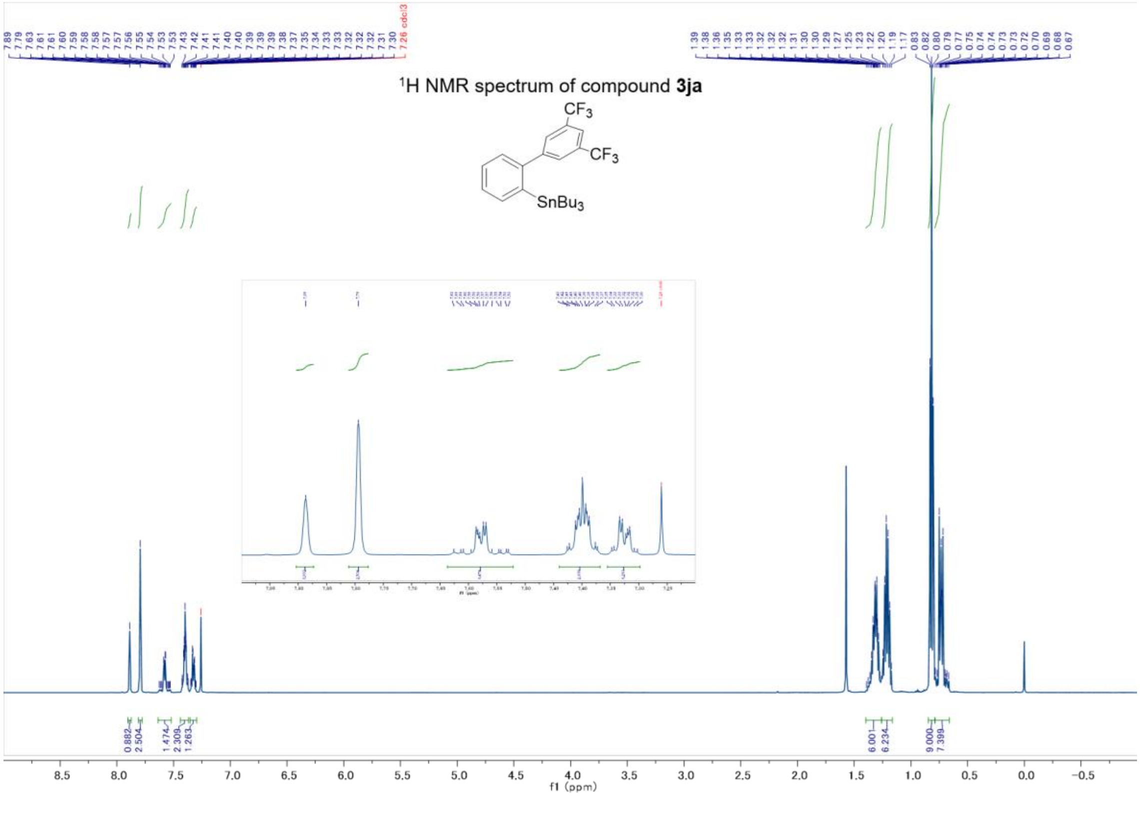

7.74
7.73
7.56
7.55
7.54
7.53
7.52
7.51
7.51
7.51
7.49
7.47
7.46
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.26 cdcl3
7.25
7.24
1.39
1.38
1.36
1.35
1.34
1.33
1.33
1.32
1.32
1.31
1.31
1.30
1.29
1.29
1.27
1.26
1.25
1.23
1.22
1.20
1.19
1.18
0.84
0.83
0.81
0.71
0.69
0.69
0.68
0.67
0.67
0.66
0.65
0.63
0.62
0.61
0.60
0.59
0.59
0.58
0.57
¹H NMR spectrum of compound **3ia**
F₃C
SnBu₃
1.294
2.471
1.264
1.790
2.305
3.712
5.595
9.000
4.809
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

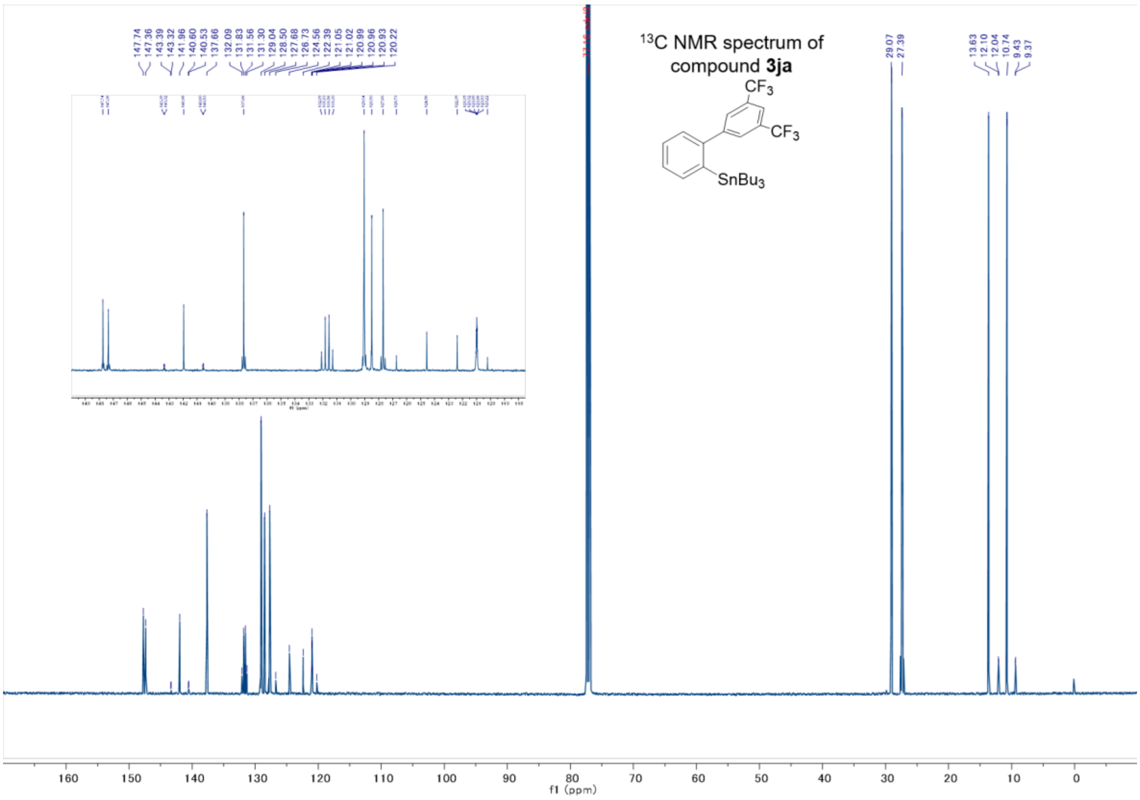

147.00
144.02
144.01
142.54
141.07
141.01
136.49
132.30
131.27
129.35
129.19
129.17
129.12
128.89
128.65
127.51
127.02
126.84
126.19
126.15
126.10
126.06
125.34
123.16
120.98
77.16 cdcl3
¹³C NMR spectrum of compound **3ia**
F₃C
SnBu₃
29.00
27.45
13.72
11.49
11.43
10.13
8.83
8.77
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

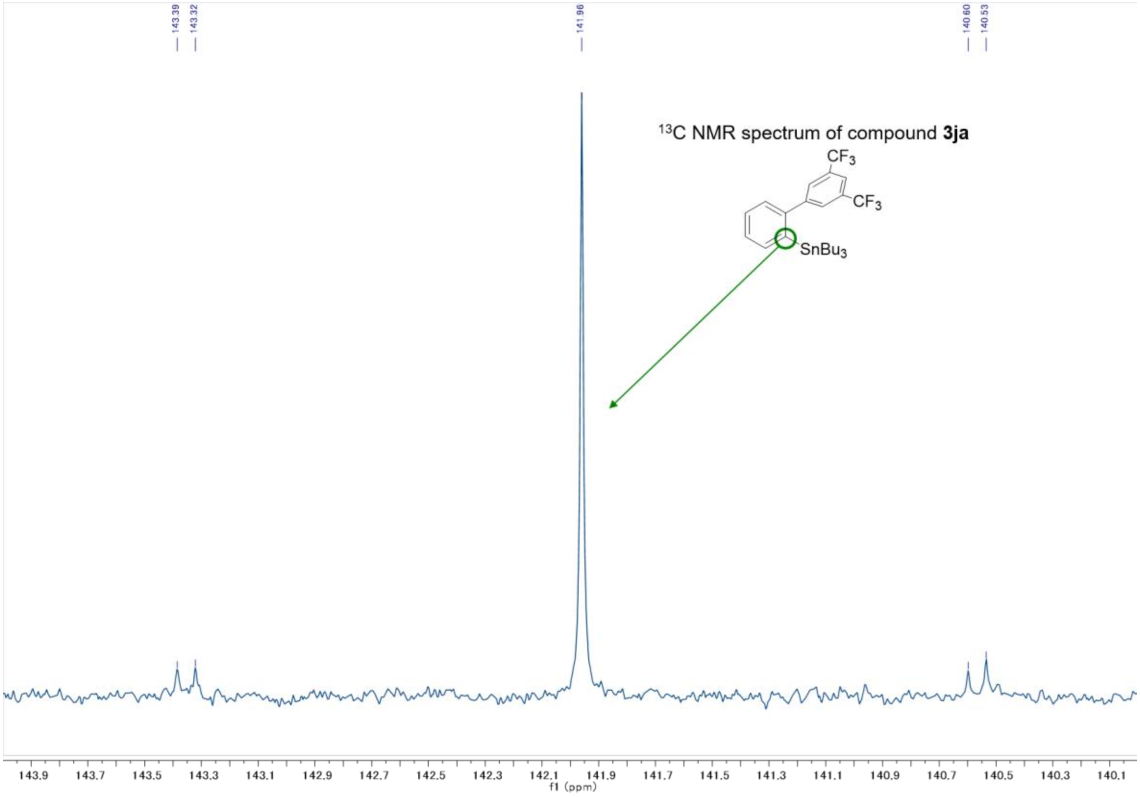

142.54
141.07
141.01
^{13}C NMR spectrum of compound **3ia**
F3C
SnBu3
144.5
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)

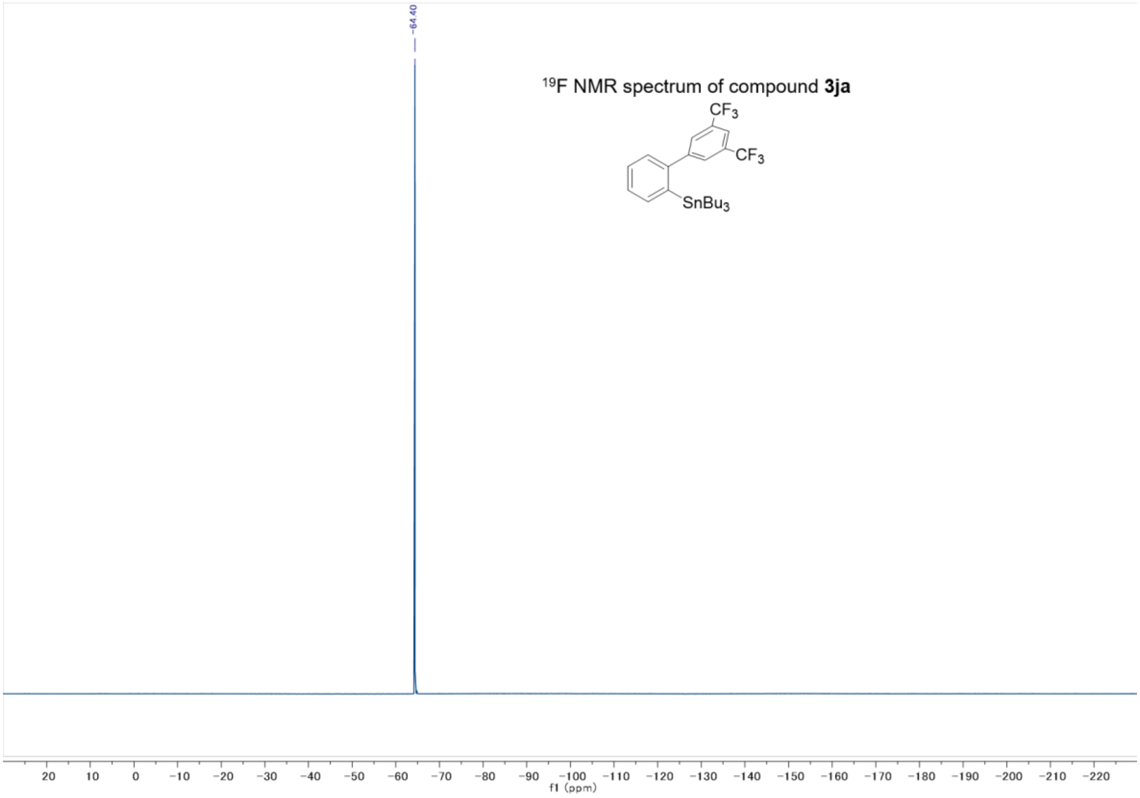

-58.41
^{19}F NMR spectrum of compound **3ia**
F3C
SnBu3
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

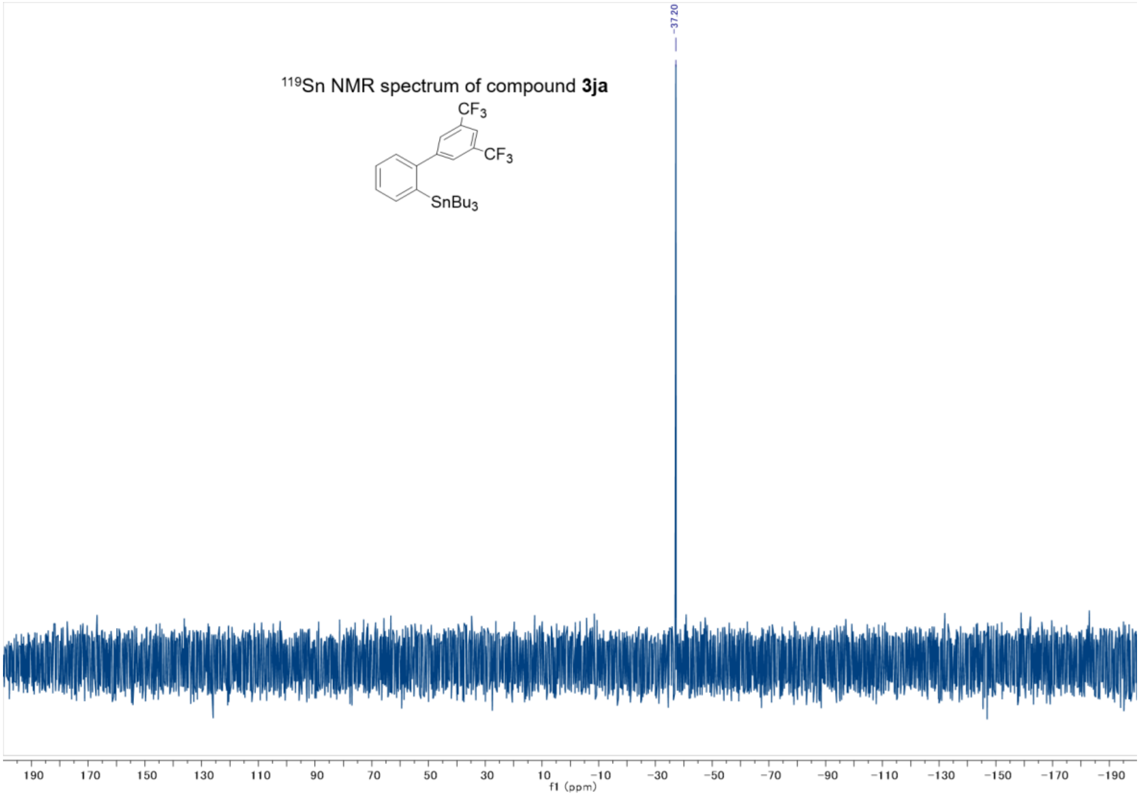

^{119}Sn NMR spectrum of compound **3ia**

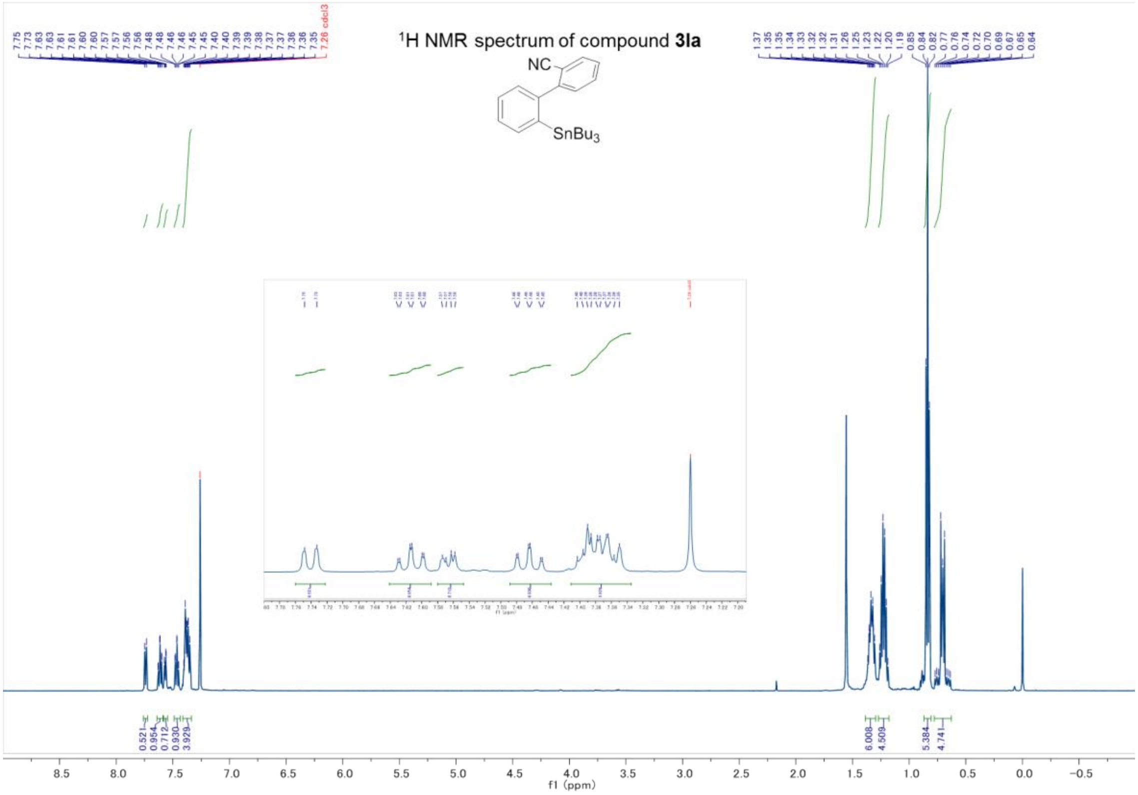

^{1}H NMR spectrum of compound **3ja**


^{13}C NMR spectrum of compound **3ja**

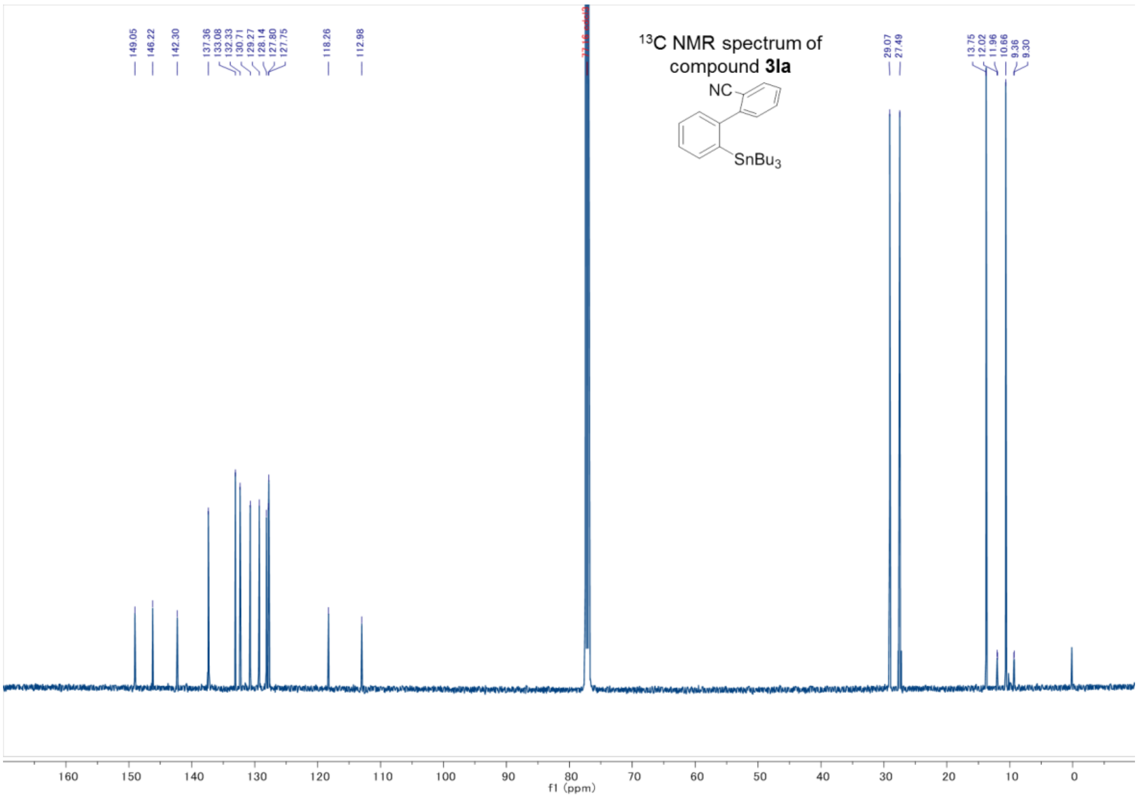

^{13}C NMR spectrum of compound **3ja**


–64.40
^{19}F NMR spectrum of compound **3ja**
CF3
CF3
SnBu3
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

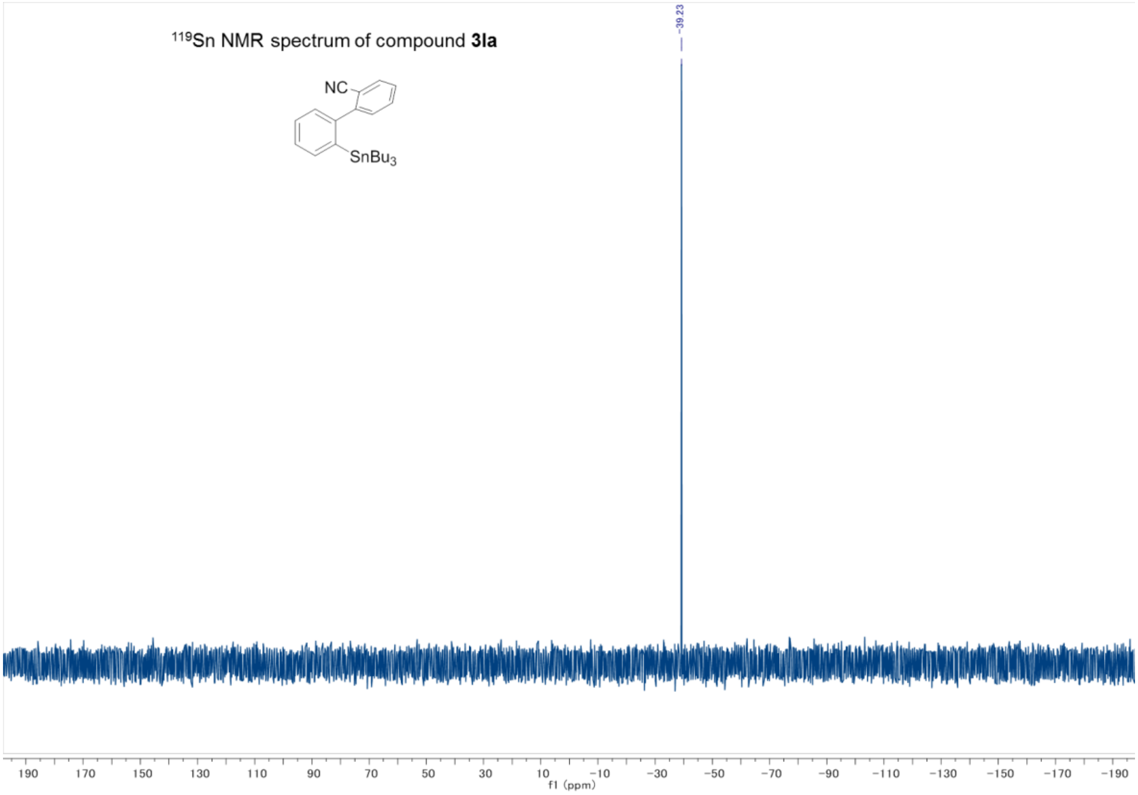

–37.20
^{119}Sn NMR spectrum of compound **3ja**
CF3
CF3
SnBu3
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)



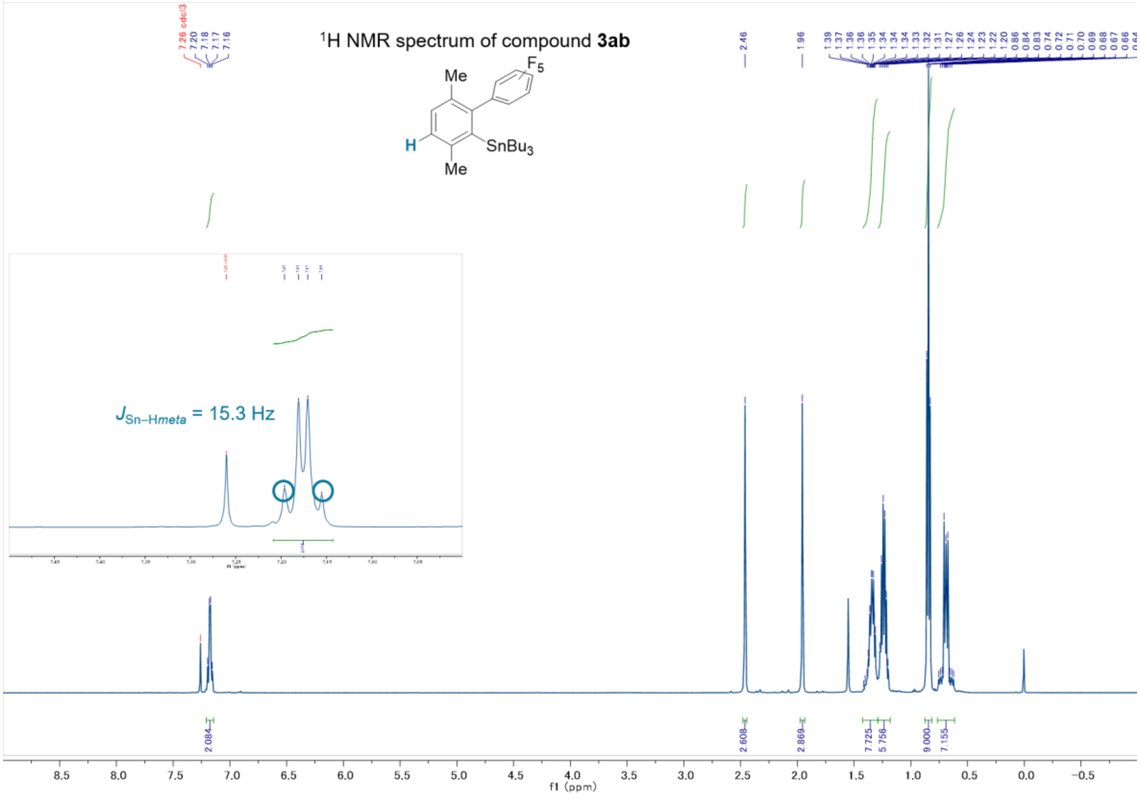
^{1}H NMR spectrum of compound **3la**



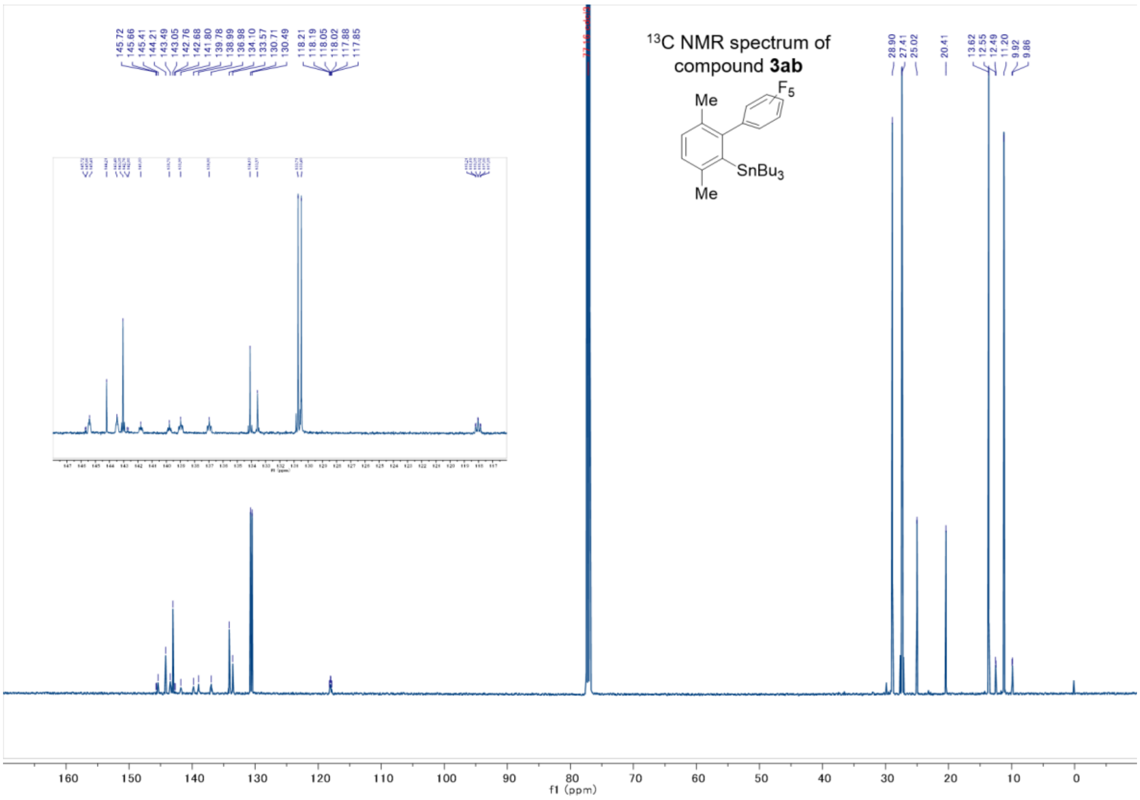
^{13}C NMR spectrum of compound **3la**

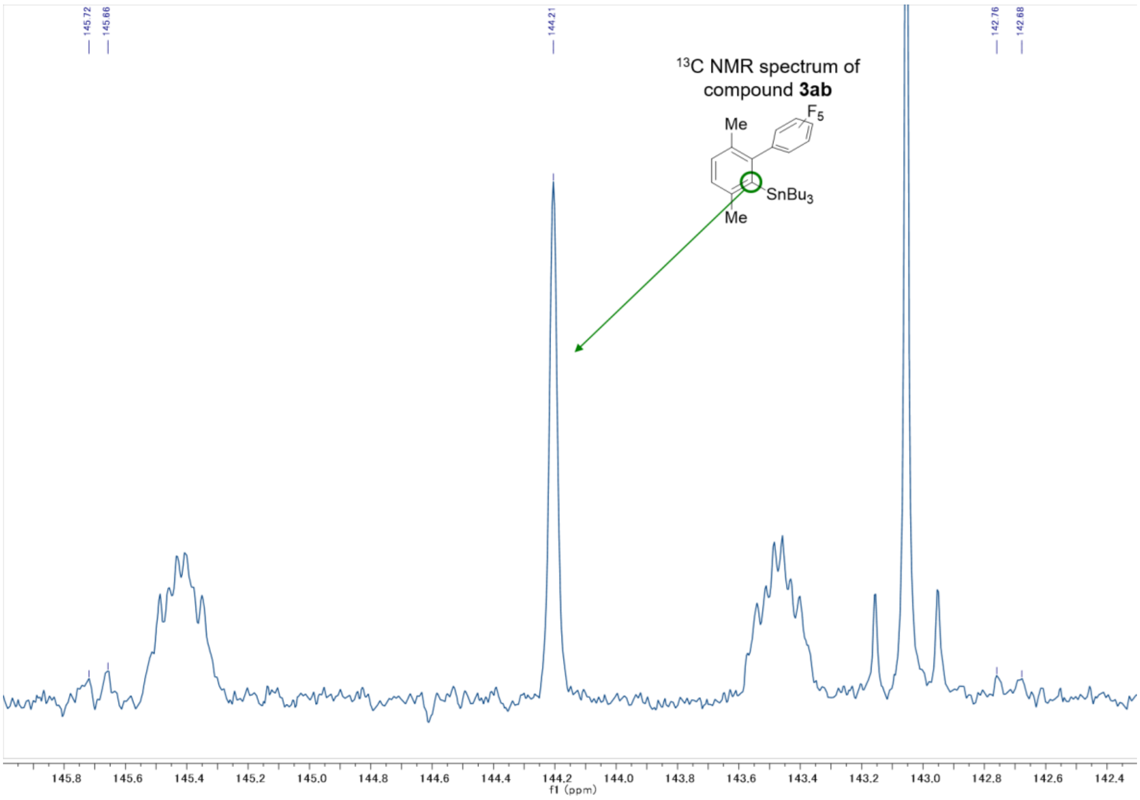


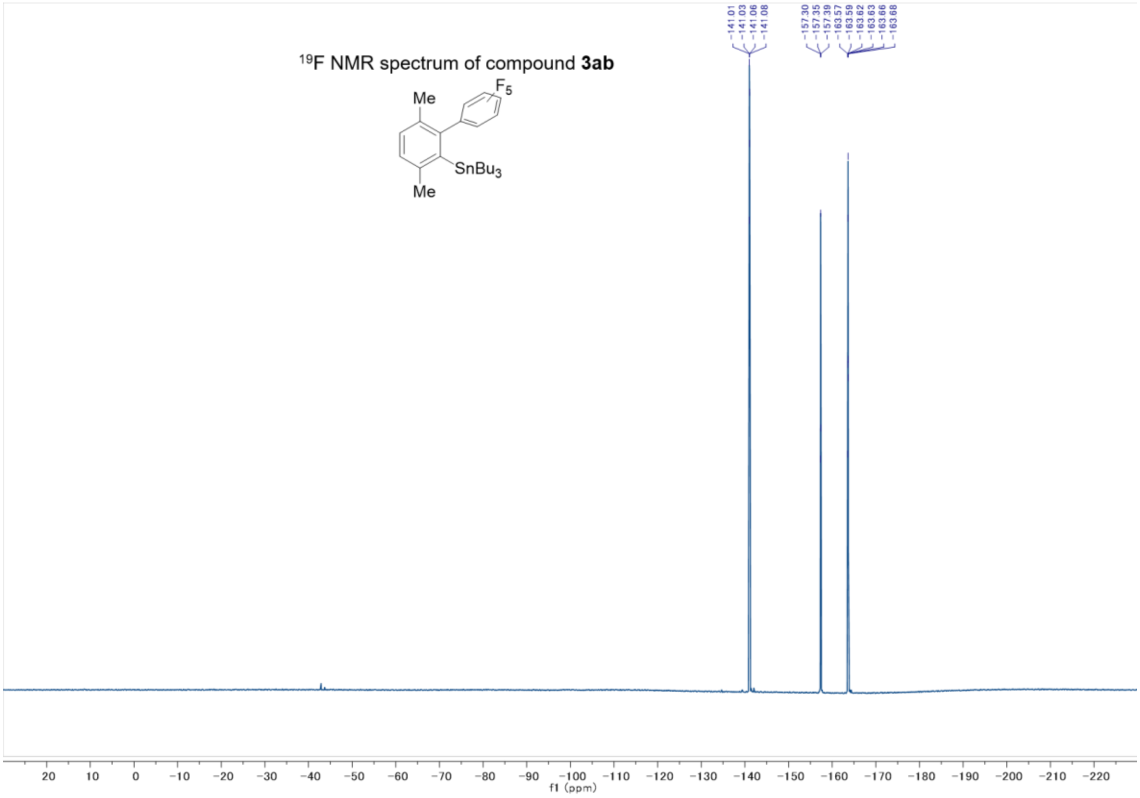
^{119}Sn NMR spectrum of compound **3la**
NC
SnBu$_3$
−39.23
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

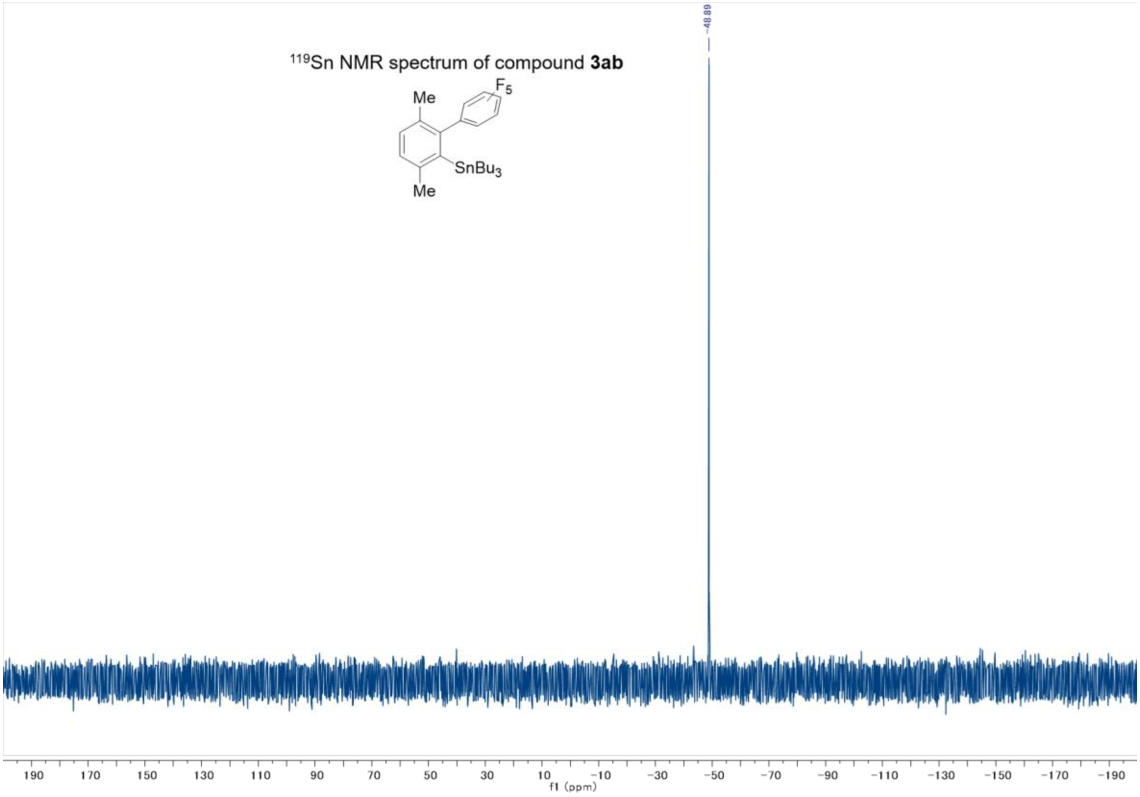


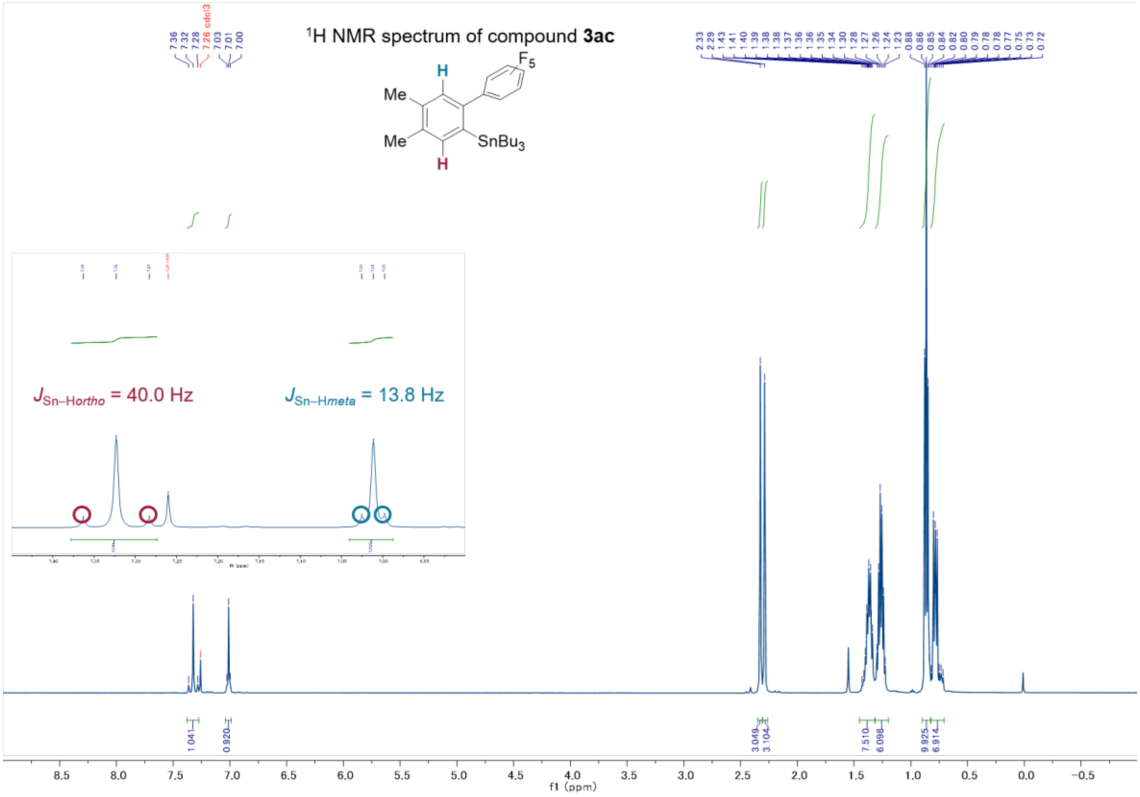
^{1}H NMR spectrum of compound **3ab**
Me
F$_5$
H
SnBu$_3$
Me
7.26 cdcl3
7.20
7.18
7.17
7.16
2.46
1.96
1.39
1.37
1.36
1.36
1.35
1.34
1.34
1.33
1.32
1.31
1.27
1.26
1.24
1.23
1.22
1.20
0.86
0.84
0.83
0.74
0.72
0.71
0.70
0.69
0.68
0.67
0.66
0.64
$J_{\text{Sn–H}meta}$ = 15.3 Hz
2.084
2.608
2.869
7.725
5.756
9.000
7.155
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

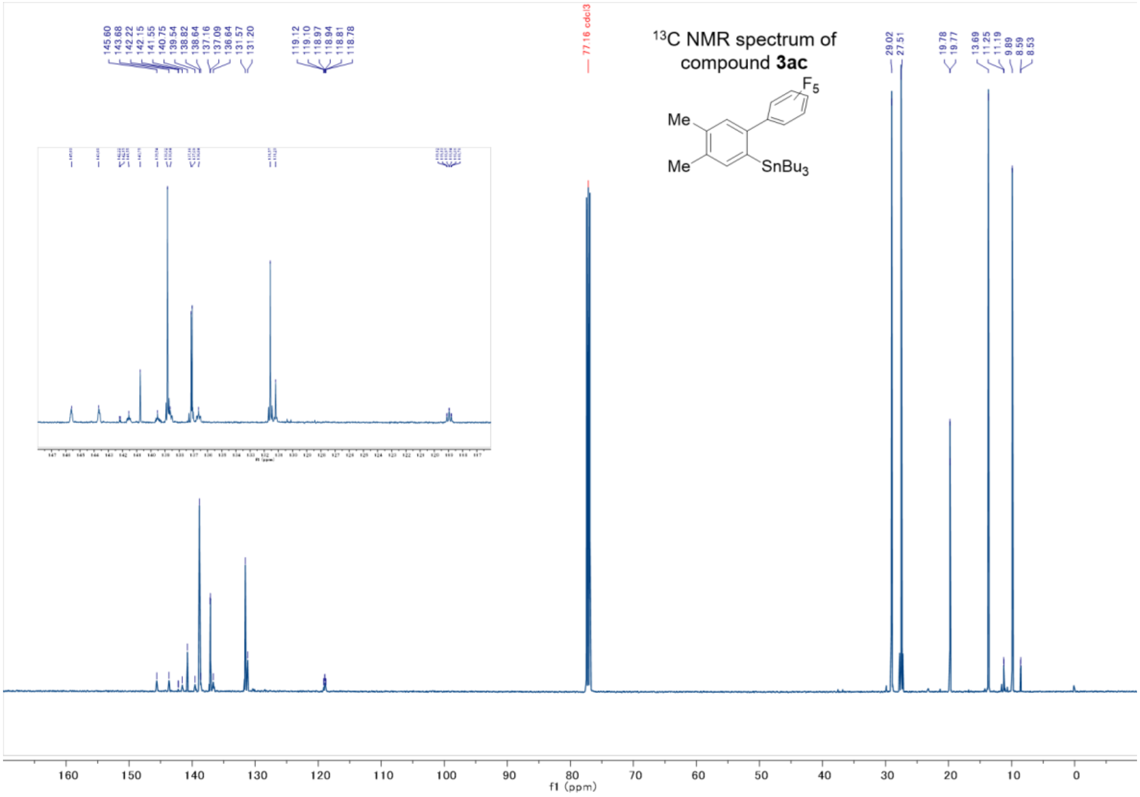

145.72
145.66
145.41
144.21
143.49
143.05
142.76
142.68
141.80
139.78
138.99
136.98
134.10
133.57
130.71
130.49
118.21
118.19
118.05
118.02
117.88
117.85
28.90
27.41
25.02
20.41
13.62
12.55
12.49
11.20
9.92
9.86
^{13}C NMR spectrum of compound **3ab**
Me
F_5
$SnBu_3$
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

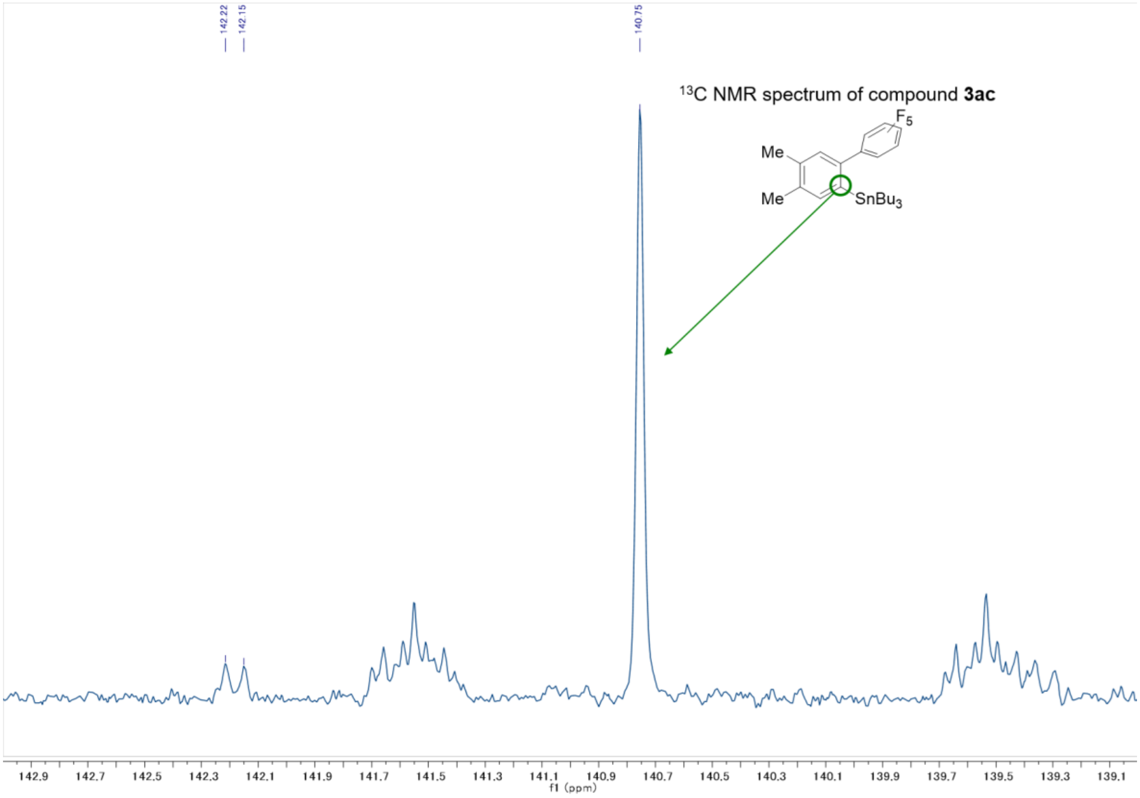

145.72
145.66
144.21
142.76
142.68
^{13}C NMR spectrum of compound **3ab**
Me
F_5
$SnBu_3$
Me
145.8
145.6
145.4
145.2
145.0
144.8
144.6
144.4
144.2
144.0
143.8
143.6
143.4
143.2
143.0
142.8
142.6
142.4
f1 (ppm)


^{19}F NMR spectrum of compound **3ab**

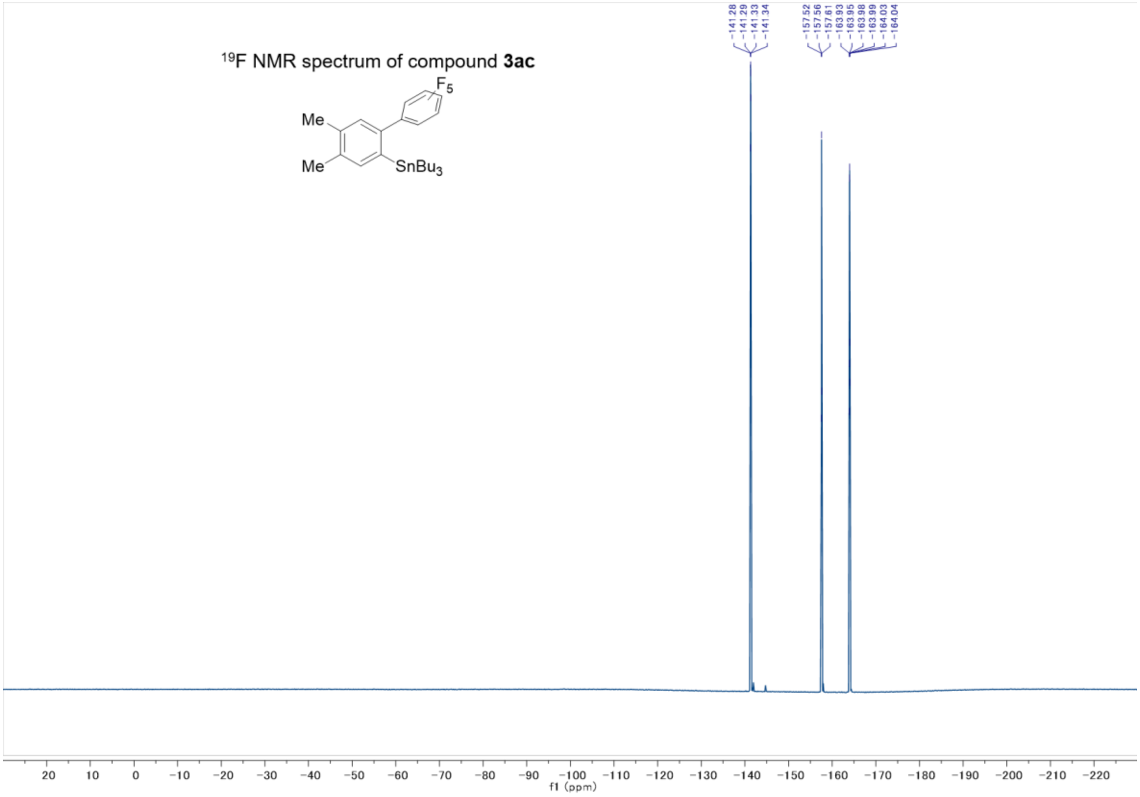

^{119}Sn NMR spectrum of compound **3ab**


1H NMR spectrum of compound 3ac
Me
Me
H
H
F5
SnBu3
7.36
7.32
7.28
7.26 cdcl3
7.03
7.01
7.00
2.33
2.29
1.43
1.41
1.40
1.39
1.38
1.38
1.37
1.36
1.36
1.35
1.34
1.30
1.28
1.27
1.26
1.24
1.23
0.88
0.86
0.85
0.84
0.82
0.80
0.79
0.78
0.78
0.77
0.75
0.73
0.72
$J_{Sn-Hortho}$ = 40.0 Hz
$J_{Sn-Hmeta}$ = 13.8 Hz
1.041
0.920
3.049
3.104
7.510
6.098
9.925
6.914
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

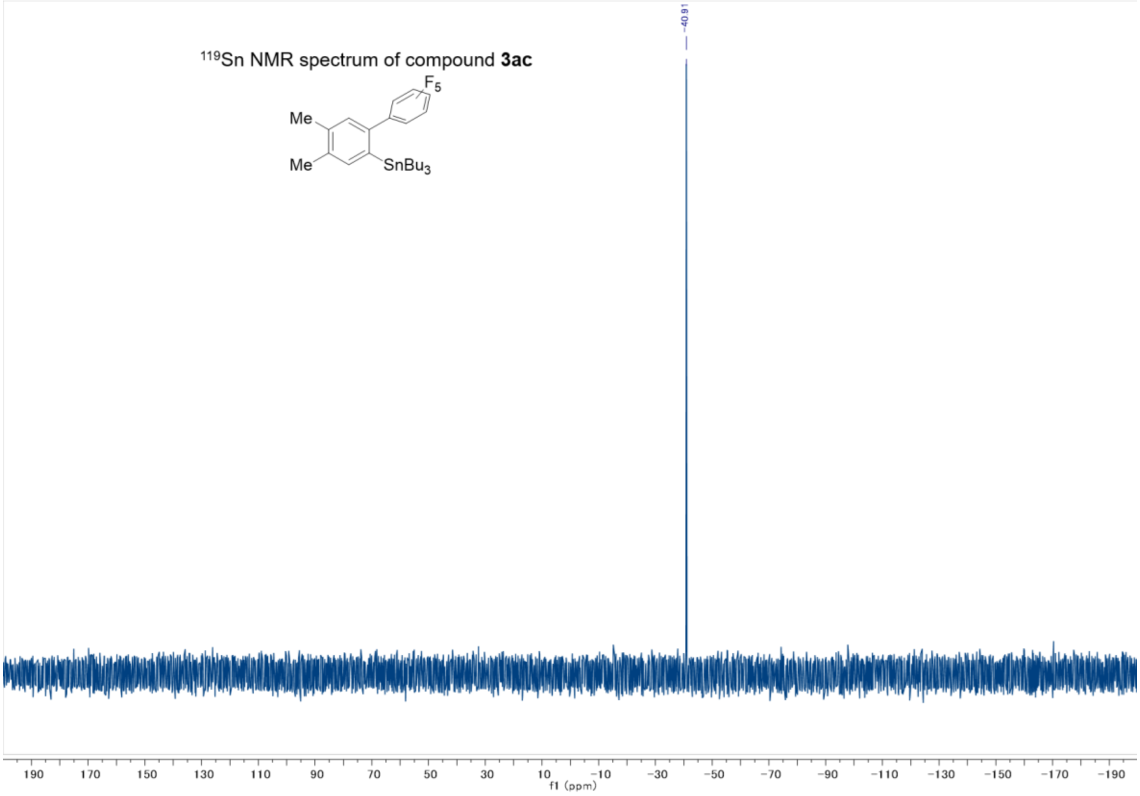

13C NMR spectrum of compound 3ac
Me
Me
F5
SnBu3
145.60
143.68
142.22
142.15
141.55
140.75
139.54
138.82
138.64
137.16
137.09
136.64
131.57
131.20
119.12
119.10
118.97
118.94
118.81
118.78
77.16 cdcl3
29.02
27.51
19.78
19.77
13.69
11.25
11.19
9.89
8.59
8.53
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

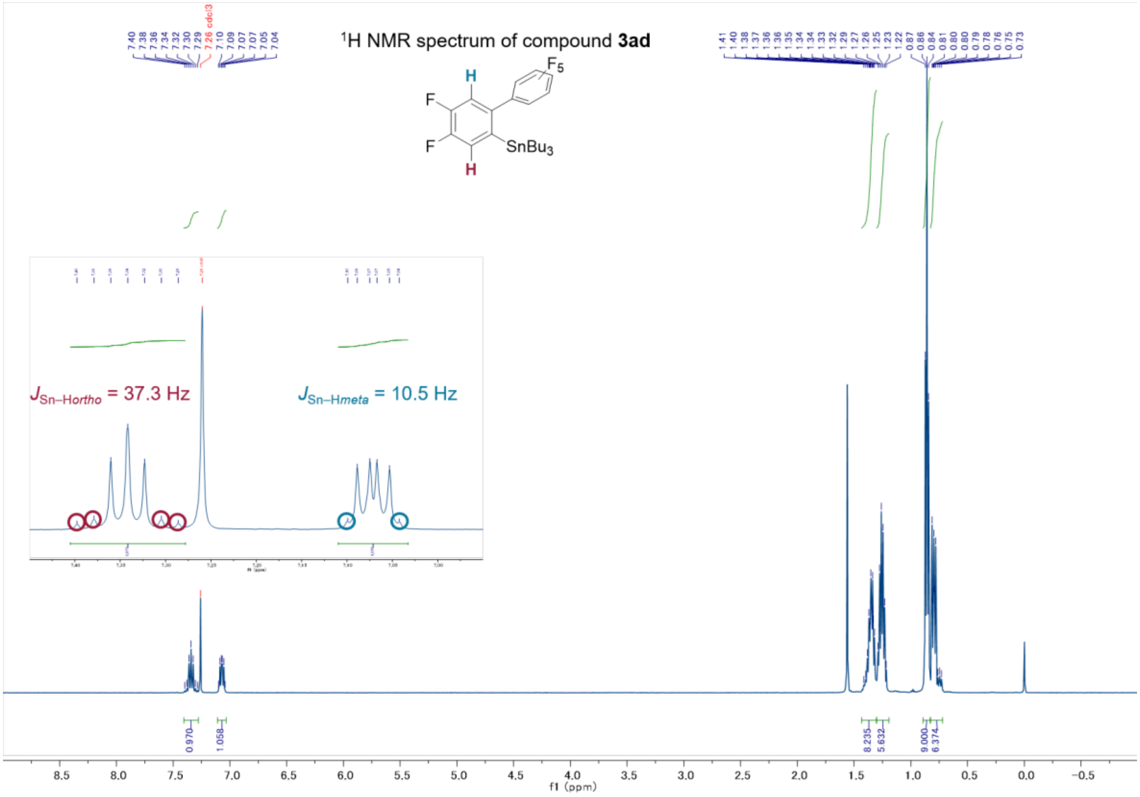


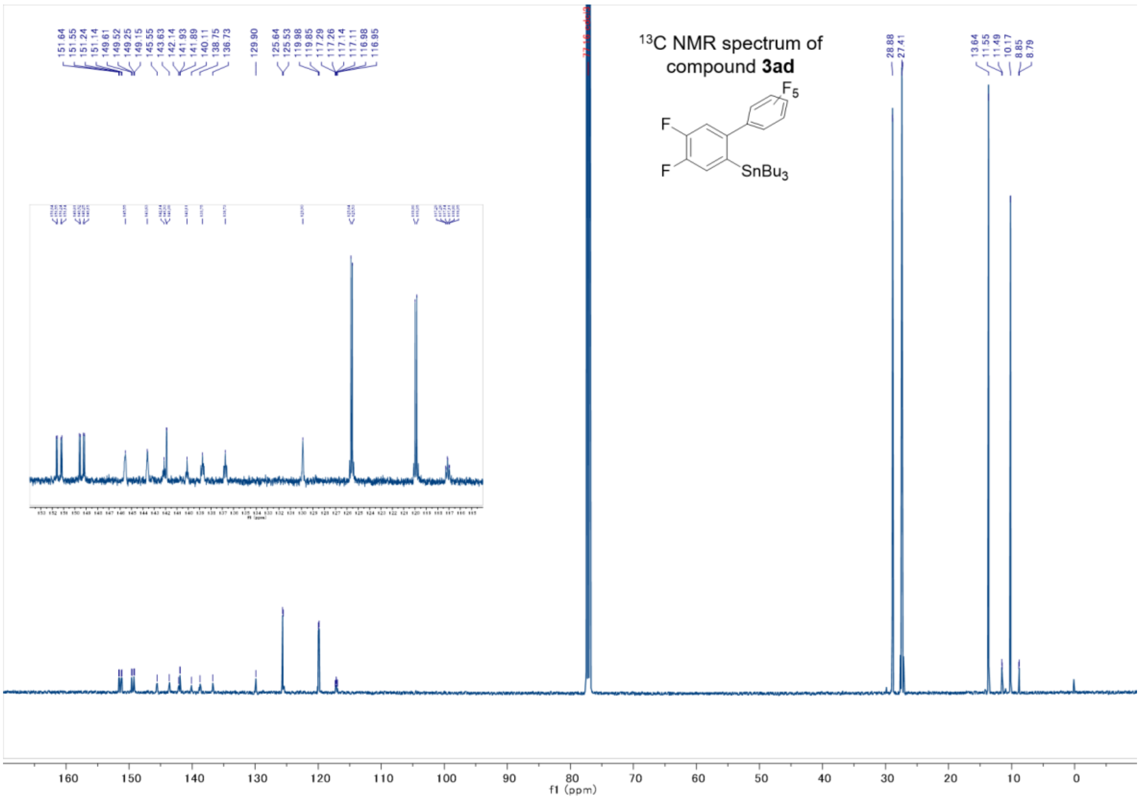
^{13}C NMR spectrum of compound **3ac**



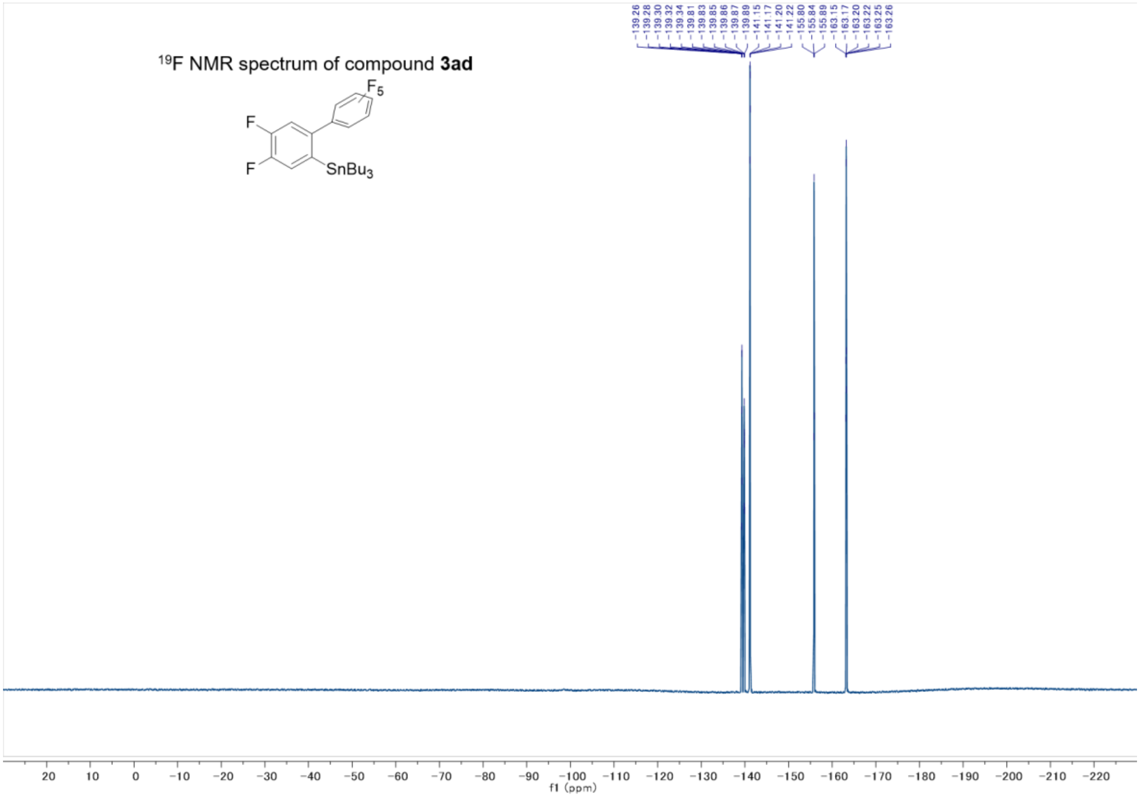
^{19}F NMR spectrum of compound **3ac**


^{119}Sn NMR spectrum of compound **3ac**

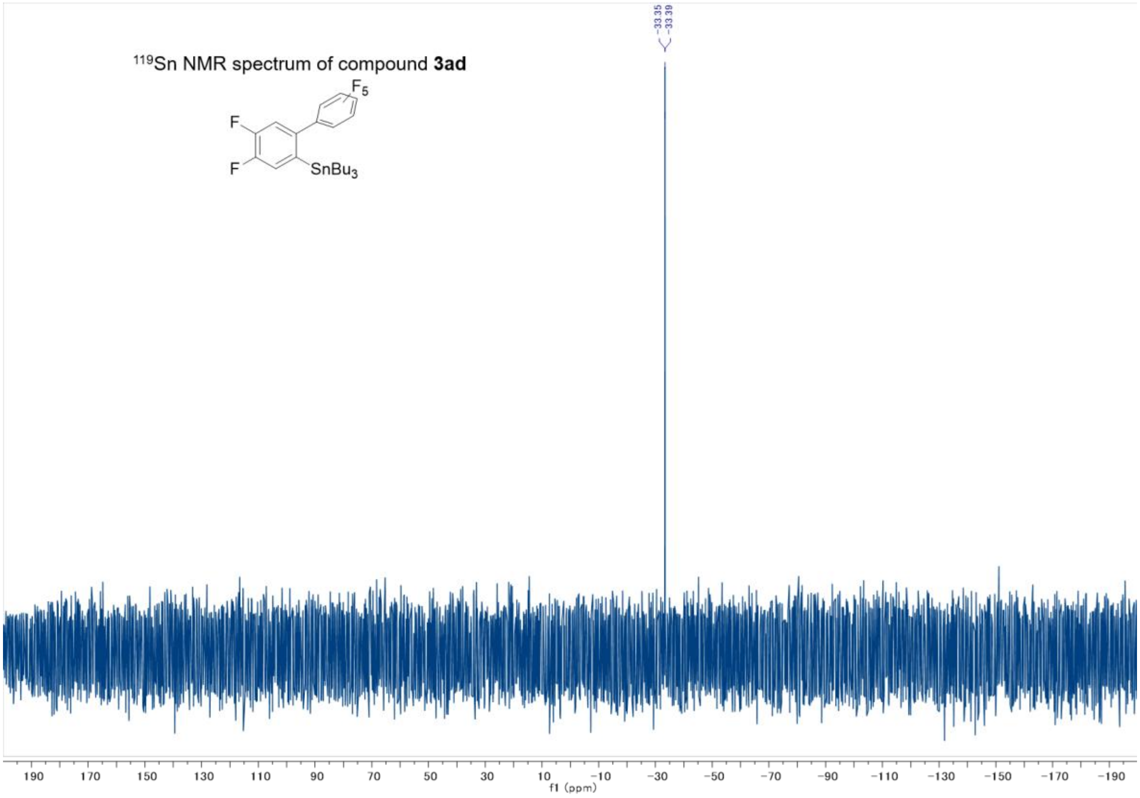

^{1}H NMR spectrum of compound **3ad**

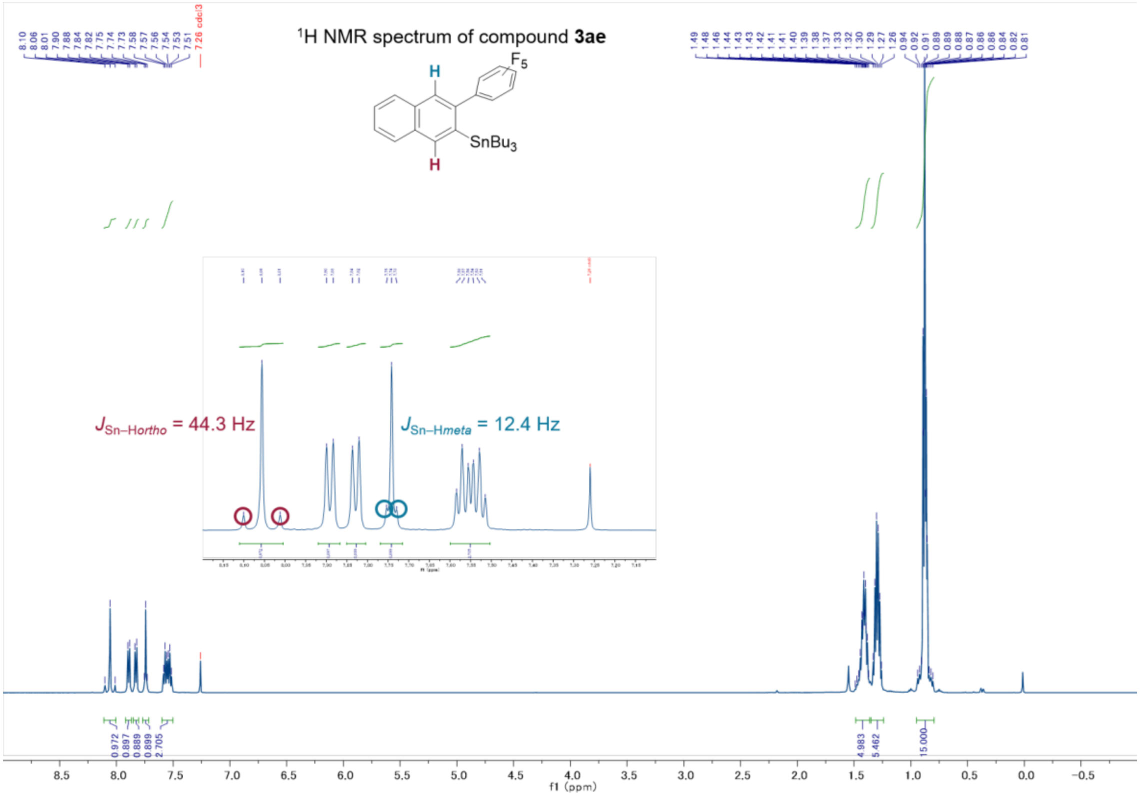


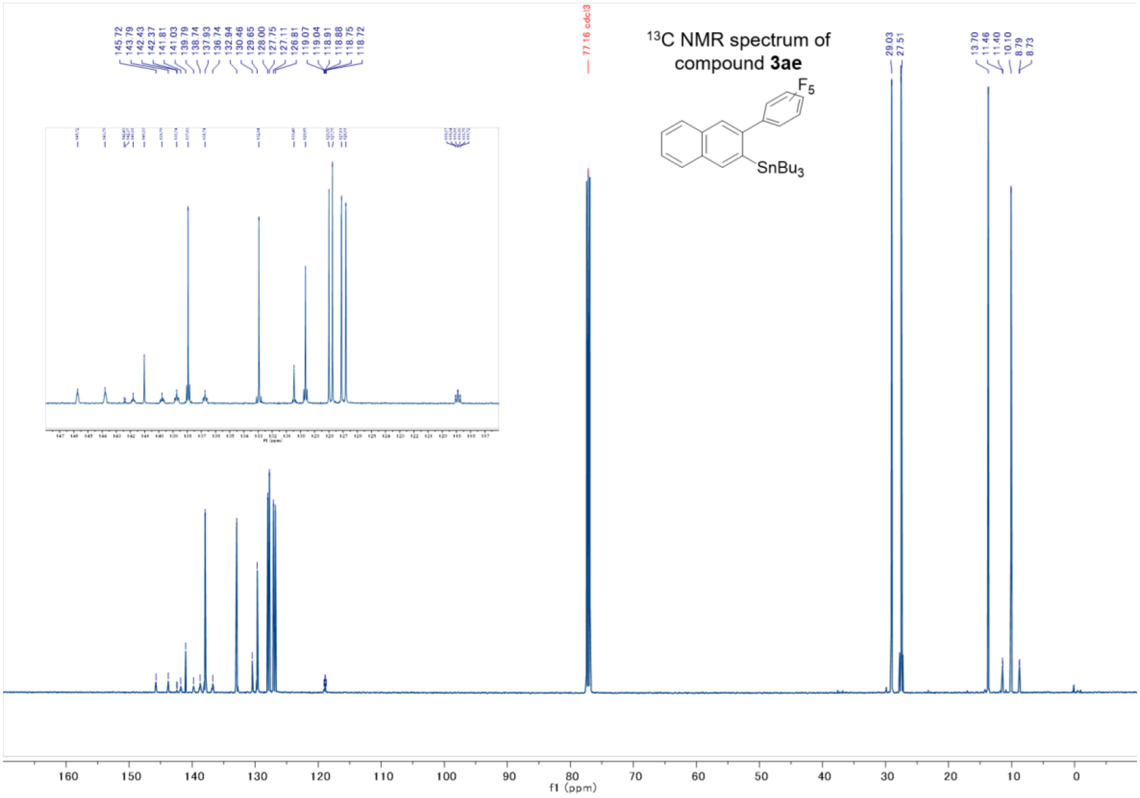
¹³C NMR spectrum of compound **3ad**
F
F
F5
SnBu3
151.64
151.55
151.24
151.14
149.61
149.52
149.25
149.15
145.55
143.63
142.14
141.93
141.89
140.11
138.75
136.73
129.90
125.64
125.53
119.98
119.85
117.29
117.26
117.14
117.11
116.98
116.95
28.88
27.41
13.64
11.55
11.49
10.17
8.85
8.79
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

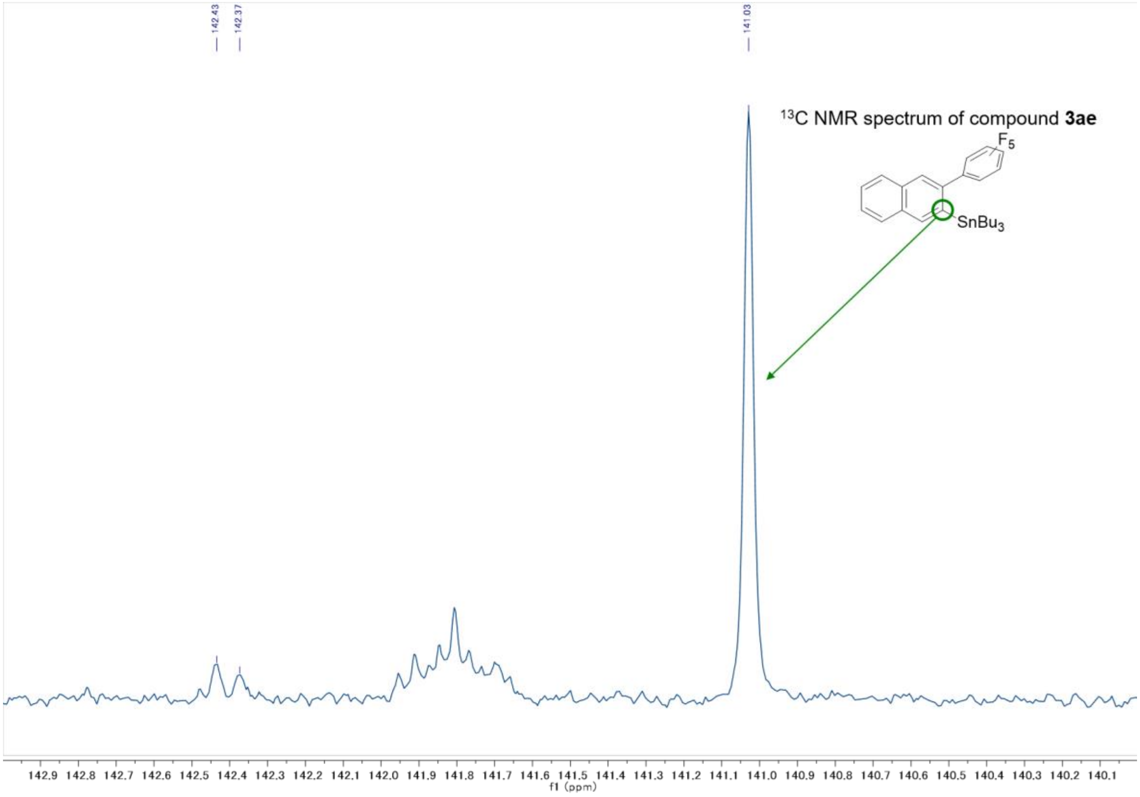


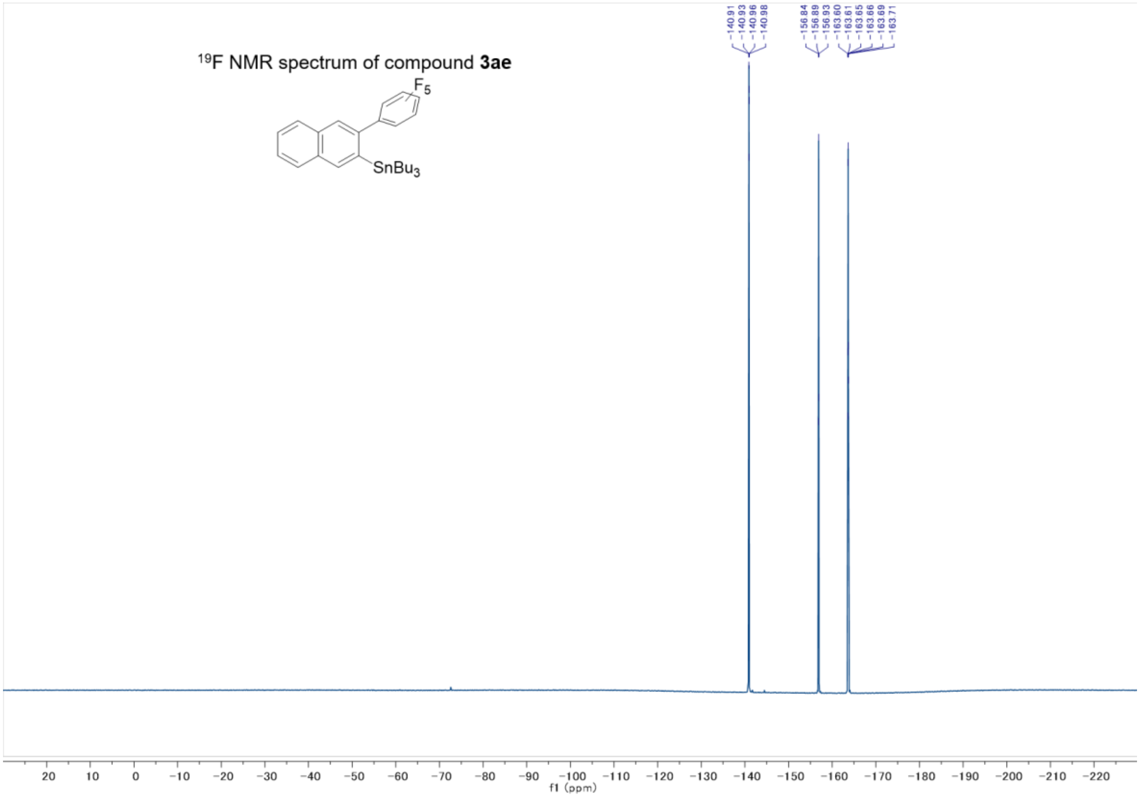
¹⁹F NMR spectrum of compound **3ad**
F
F
F5
SnBu3
-139.26
-139.28
-139.30
-139.32
-139.34
-139.81
-139.83
-139.85
-139.86
-139.87
-139.89
-141.15
-141.17
-141.20
-141.22
-155.80
-155.84
-155.89
-163.15
-163.17
-163.20
-163.22
-163.25
-163.26
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

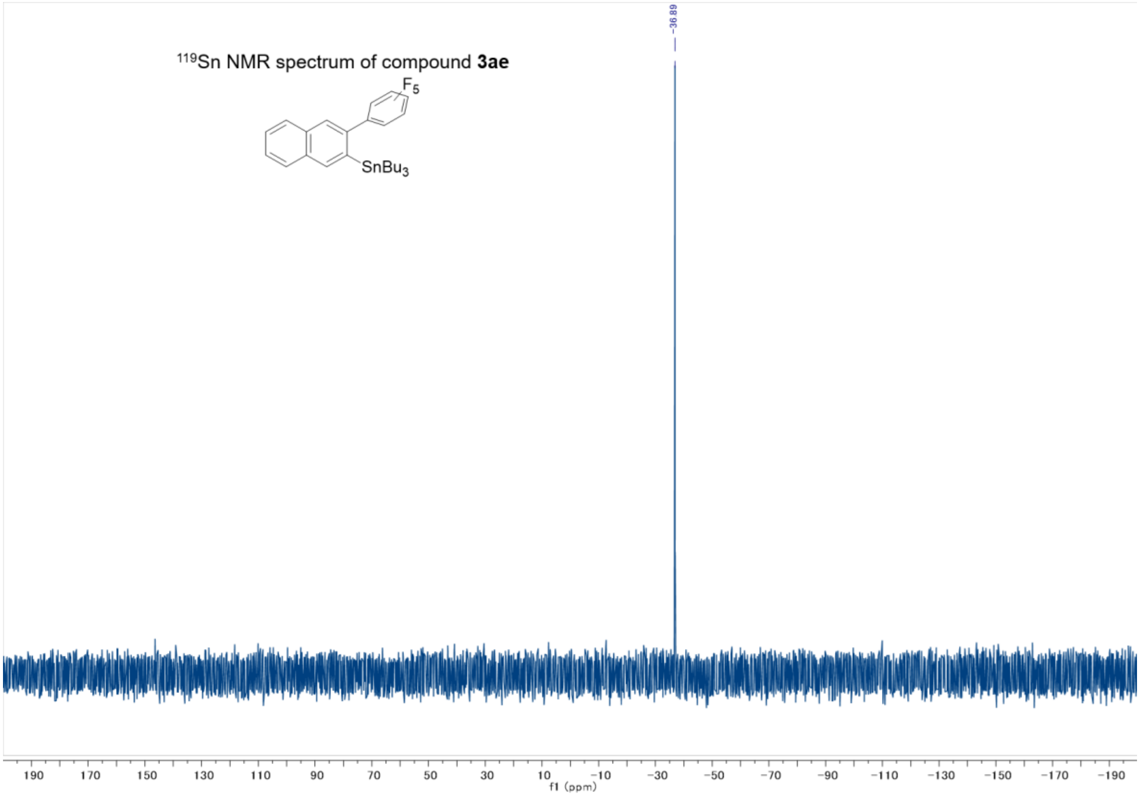

^{119}Sn NMR spectrum of compound **3ad**
F
F
F_5
$SnBu_3$
-33.35
-33.39
190
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

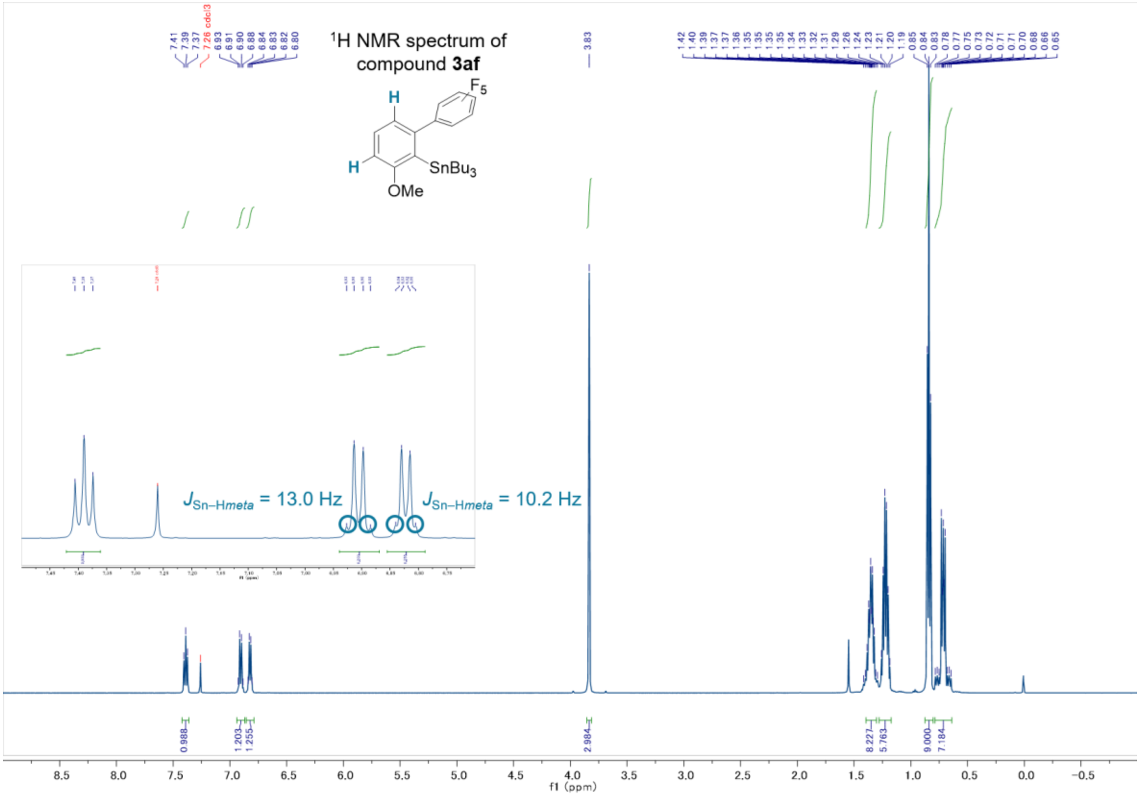

^{1}H NMR spectrum of compound **3ae**
H
H
F_5
$SnBu_3$
8.10
8.06
8.01
7.90
7.88
7.84
7.82
7.75
7.74
7.73
7.58
7.57
7.56
7.54
7.53
7.51
7.26 cdcl3
1.49
1.48
1.46
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.39
1.38
1.37
1.33
1.32
1.30
1.29
1.27
1.26
0.94
0.92
0.91
0.89
0.89
0.88
0.87
0.86
0.86
0.84
0.82
0.81
$J_{\text{Sn–H}ortho}$ = 44.3 Hz
$J_{\text{Sn–H}meta}$ = 12.4 Hz
0.972
0.897
0.889
0.899
2.705
4.983
5.462
15.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


145.72
143.79
142.43
142.37
141.81
141.03
139.79
138.74
137.93
136.74
132.94
130.46
129.65
128.00
127.75
127.11
126.81
119.07
119.04
118.91
118.88
118.75
118.72
77.16 cdcl3
^{13}C NMR spectrum of compound **3ae**
F5
SnBu3
29.03
27.51
13.70
11.46
11.40
10.10
8.79
8.73
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

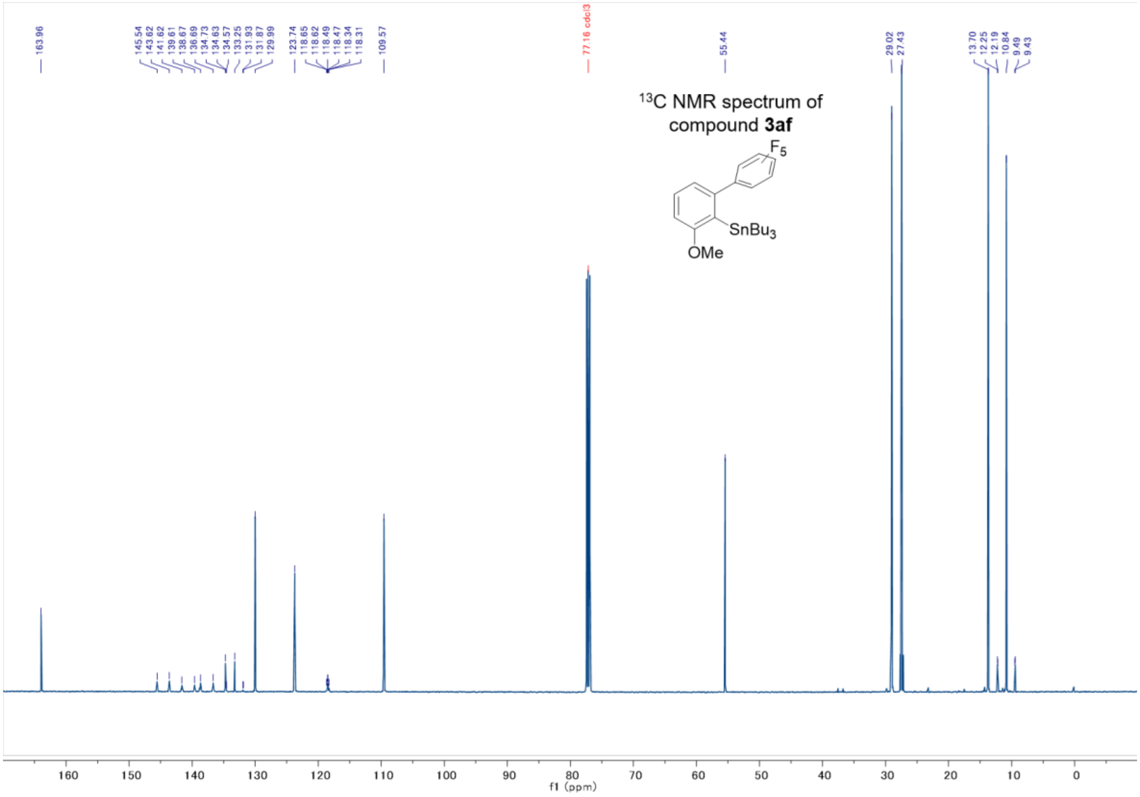

142.43
142.37
141.03
^{13}C NMR spectrum of compound **3ae**
F5
SnBu3
142.9
142.8
142.7
142.6
142.5
142.4
142.3
142.2
142.1
142.0
141.9
141.8
141.7
141.6
141.5
141.4
141.3
141.2
141.1
141.0
140.9
140.8
140.7
140.6
140.5
140.4
140.3
140.2
140.1
f1 (ppm)


^{19}F NMR spectrum of compound **3ae**

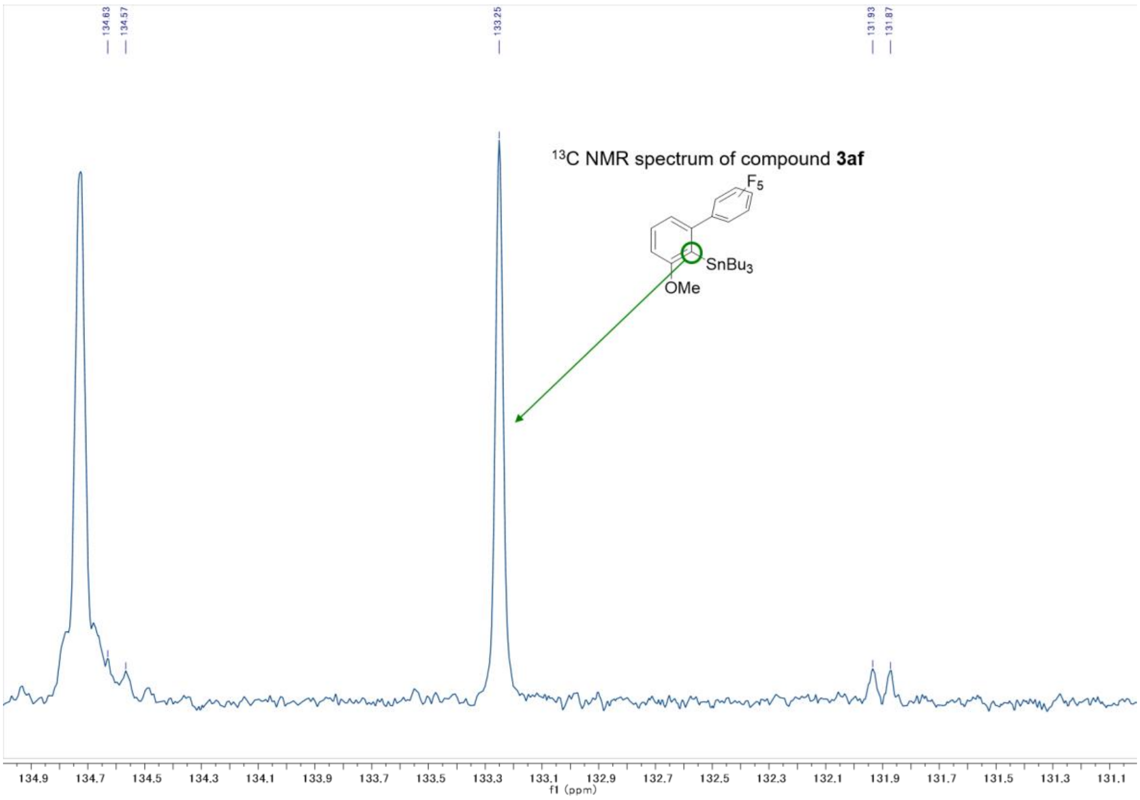

^{119}Sn NMR spectrum of compound **3ae**

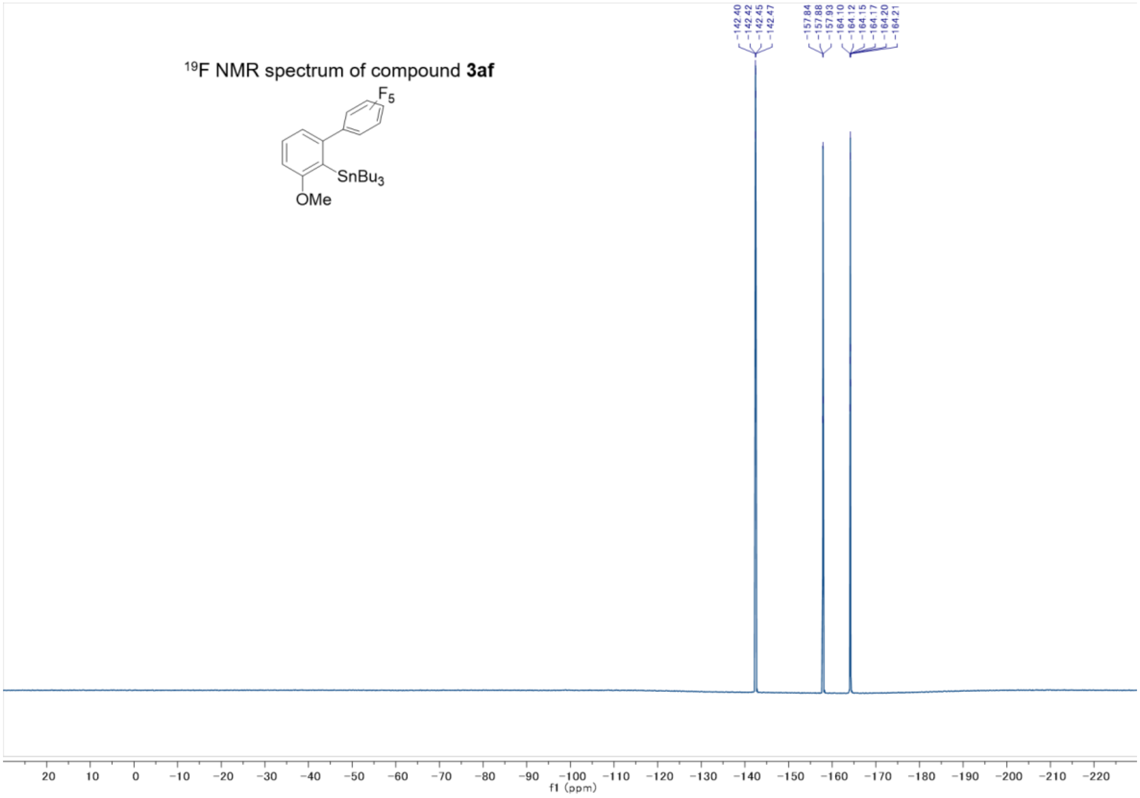


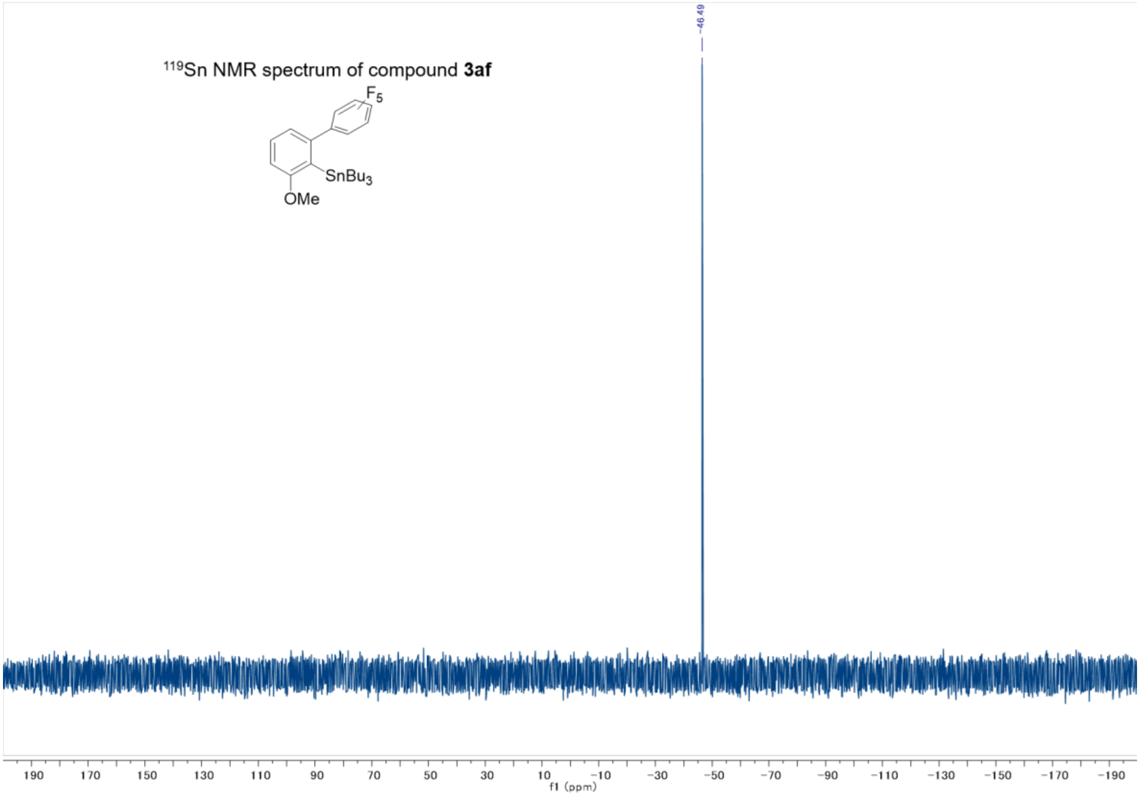
7.41
7.39
7.37
7.26 cdcl3
6.93
6.91
6.90
6.88
6.84
6.83
6.82
6.80
^{1}H NMR spectrum of compound **3af**
H
H
F$_5$
SnBu$_3$
OMe
3.83
1.42
1.40
1.39
1.37
1.37
1.36
1.35
1.35
1.35
1.35
1.34
1.33
1.32
1.31
1.29
1.26
1.24
1.23
1.21
1.20
1.19
0.85
0.84
0.83
0.78
0.77
0.75
0.73
0.72
0.71
0.71
0.70
0.68
0.66
0.65
$J_{\text{Sn–H}meta}$ = 13.0 Hz
$J_{\text{Sn–H}meta}$ = 10.2 Hz
0.988
1.203
1.255
2.984
8.227
5.763
9.000
7.184
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

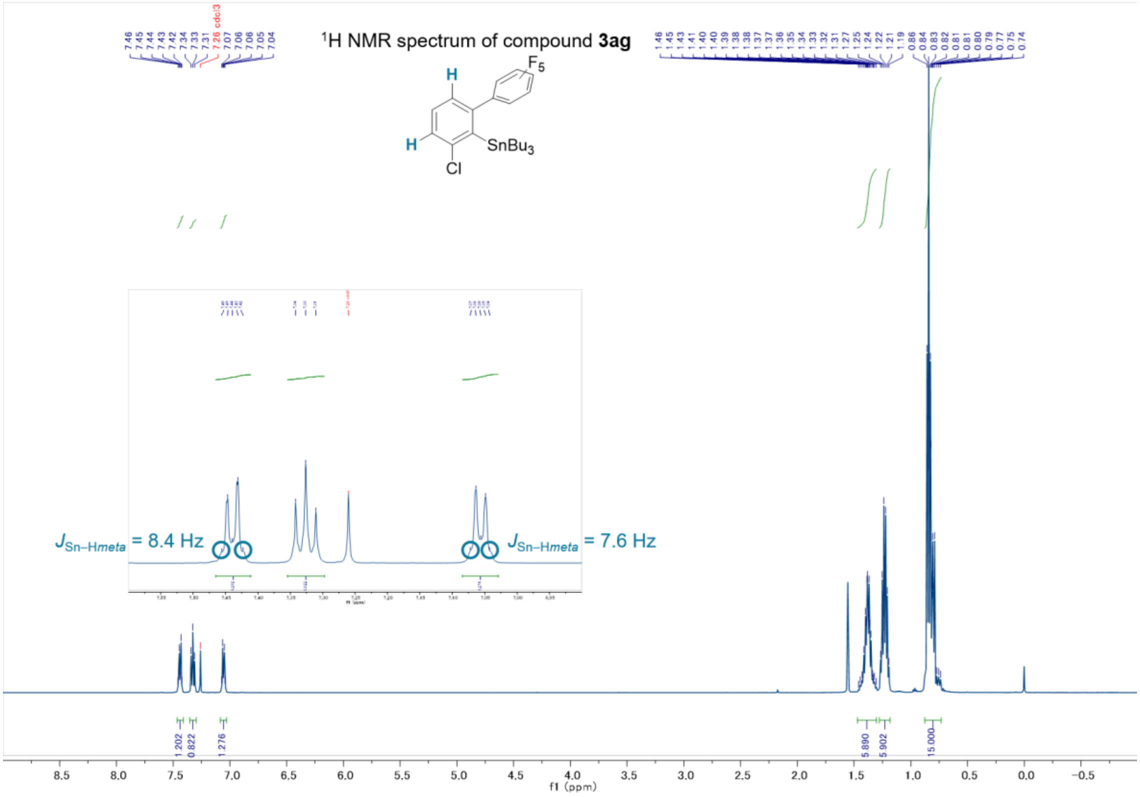


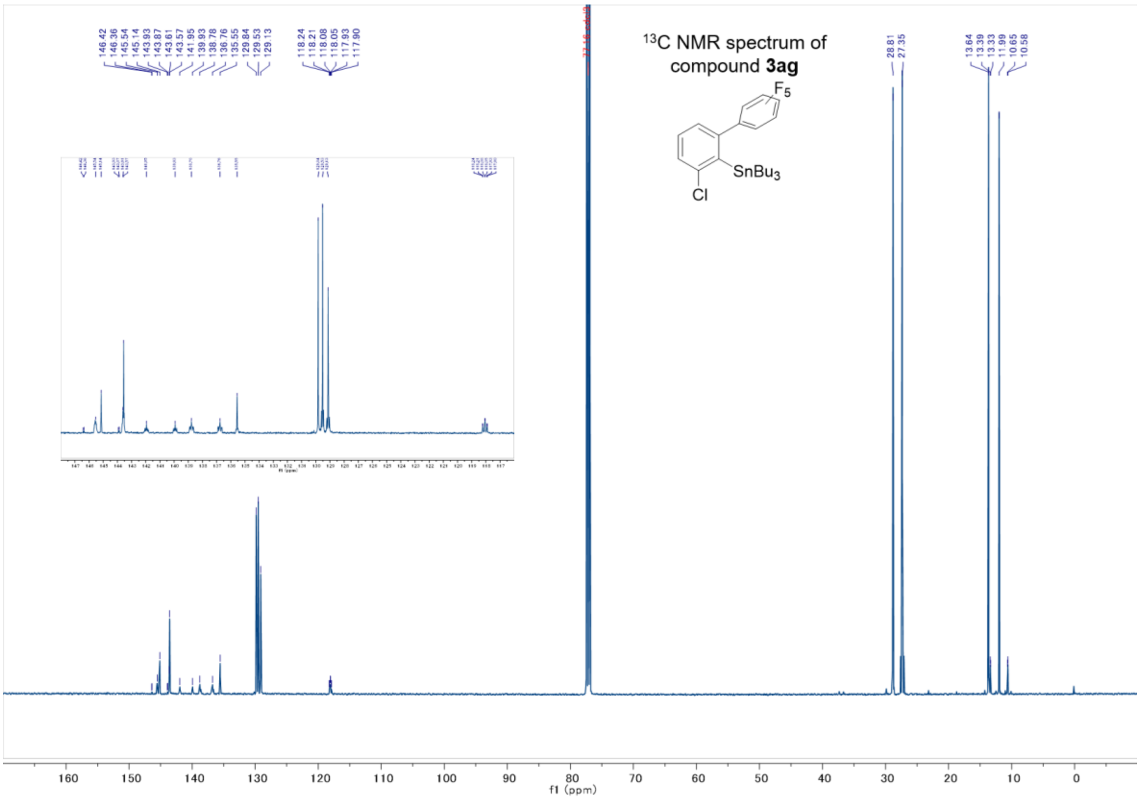
163.96
145.54
143.62
141.62
139.61
138.67
136.69
134.73
134.63
134.57
133.25
131.93
131.87
129.99
123.74
118.65
118.62
118.49
118.47
118.34
118.31
109.57
77.16 cdcl3
55.44
29.02
27.43
13.70
12.25
12.19
10.84
9.49
9.43
^{13}C NMR spectrum of compound **3af**
F$_5$
SnBu$_3$
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

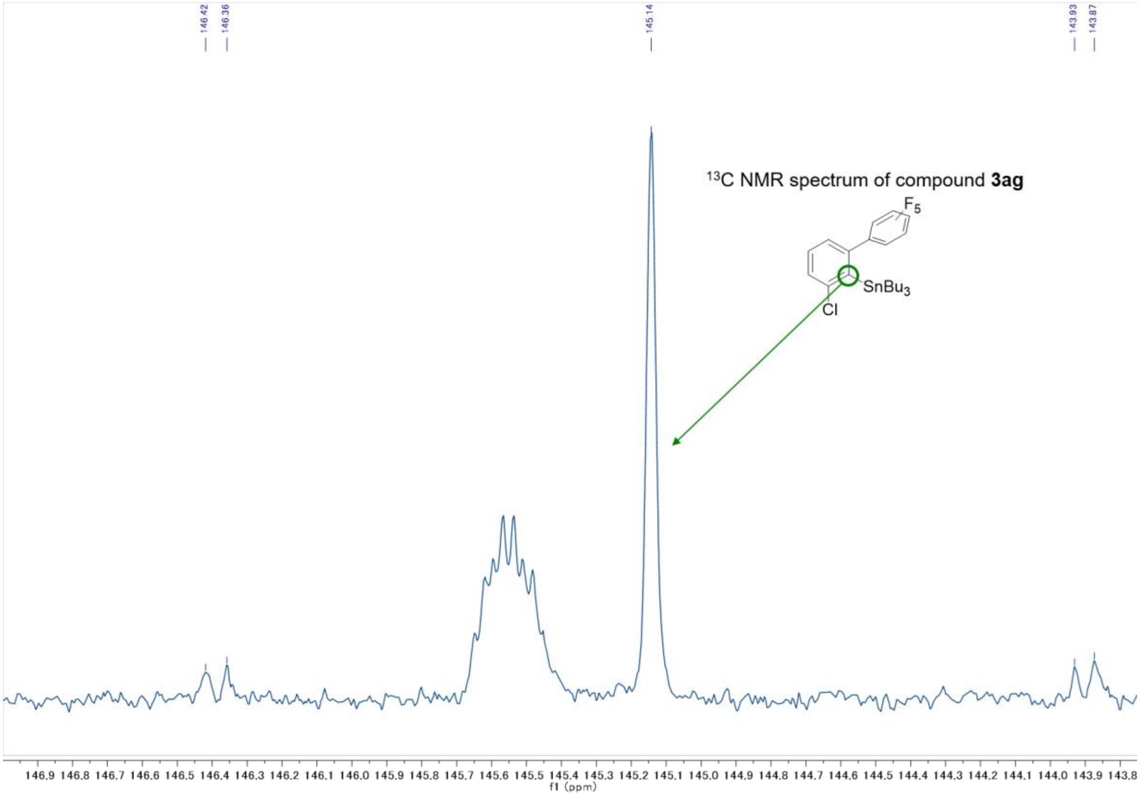

134.63
134.57
133.25
131.93
131.87
^{13}C NMR spectrum of compound **3af**
F5
SnBu3
OMe
134.9 134.7 134.5 134.3 134.1 133.9 133.7 133.5 133.3 133.1 132.9 132.7 132.5 132.3 132.1 131.9 131.7 131.5 131.3 131.1
f1 (ppm)

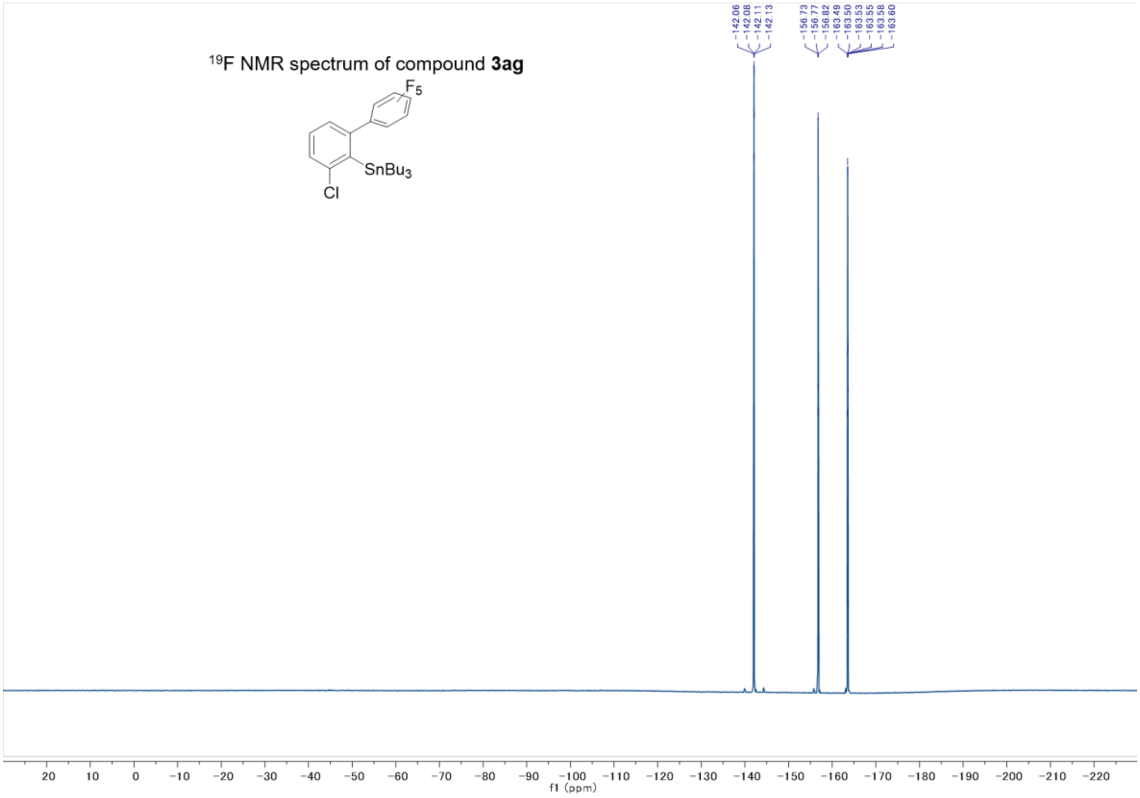

-142.40
-142.42
-142.45
-142.47
-157.84
-157.88
-157.93
-164.10
-164.12
-164.15
-164.17
-164.20
-164.21
^{19}F NMR spectrum of compound **3af**
F5
SnBu3
OMe
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


^{119}Sn NMR spectrum of compound **3af**
F5
SnBu3
OMe
-46.49
190
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

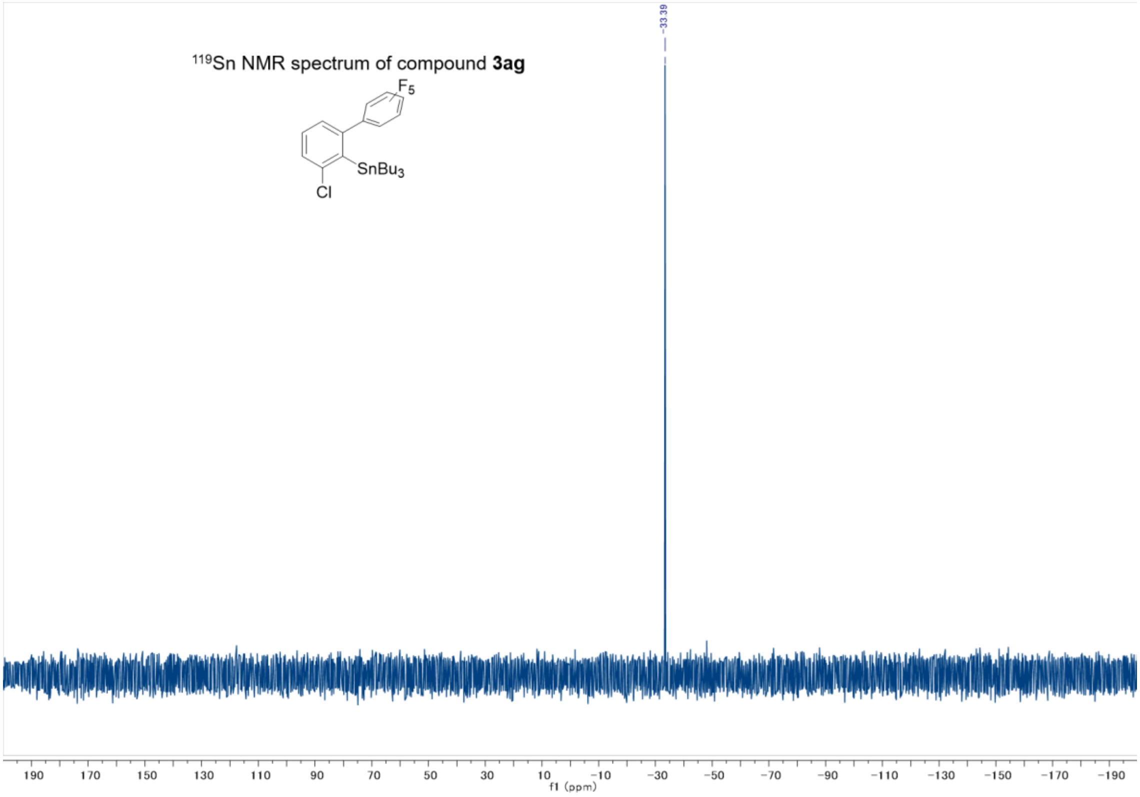

^{1}H NMR spectrum of compound **3ag**
H
F5
H
SnBu3
Cl
7.46
7.45
7.44
7.43
7.42
7.34
7.33
7.31
7.26 cdcl3
7.07
7.06
7.06
7.05
7.04
1.46
1.45
1.43
1.41
1.40
1.40
1.39
1.38
1.38
1.37
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.27
1.25
1.24
1.22
1.21
1.19
0.86
0.84
0.83
0.82
0.81
0.81
0.80
0.79
0.77
0.75
0.74
$J_{Sn-Hmeta}$ = 8.4 Hz
$J_{Sn-Hmeta}$ = 7.6 Hz
1.202
0.822
1.276
5.890
5.902
15.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


146.42
146.36
145.54
145.14
143.93
143.87
143.61
143.57
141.95
139.93
138.78
136.76
135.55
129.84
129.53
129.13
118.24
118.21
118.08
118.05
117.93
117.90
28.81
27.35
13.64
13.39
13.33
11.99
10.65
10.58
^{13}C NMR spectrum of compound **3ag**
F5
SnBu3
Cl
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

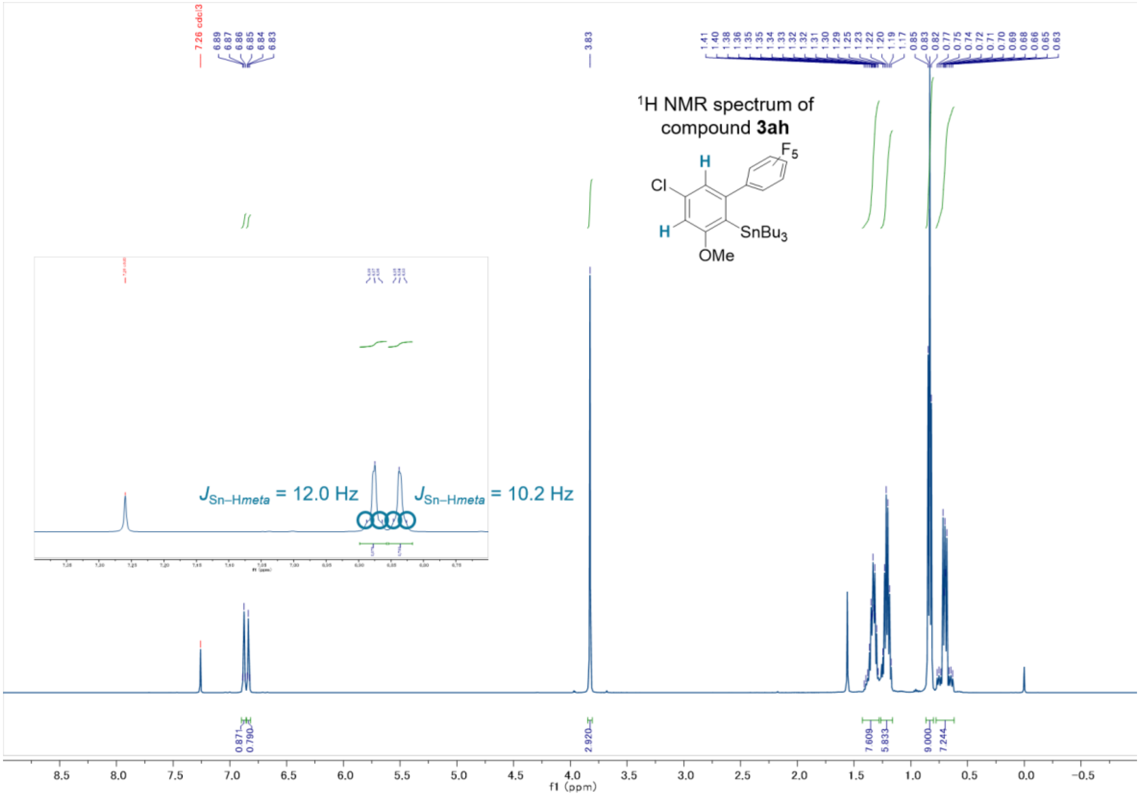

146.42
146.36
145.14
143.93
143.87
^{13}C NMR spectrum of compound **3ag**
F5
SnBu3
Cl
146.9 146.8 146.7 146.6 146.5 146.4 146.3 146.2 146.1 146.0 145.9 145.8 145.7 145.6 145.5 145.4 145.3 145.2 145.1 145.0 144.9 144.8 144.7 144.6 144.5 144.4 144.3 144.2 144.1 144.0 143.9 143.8
f1 (ppm)

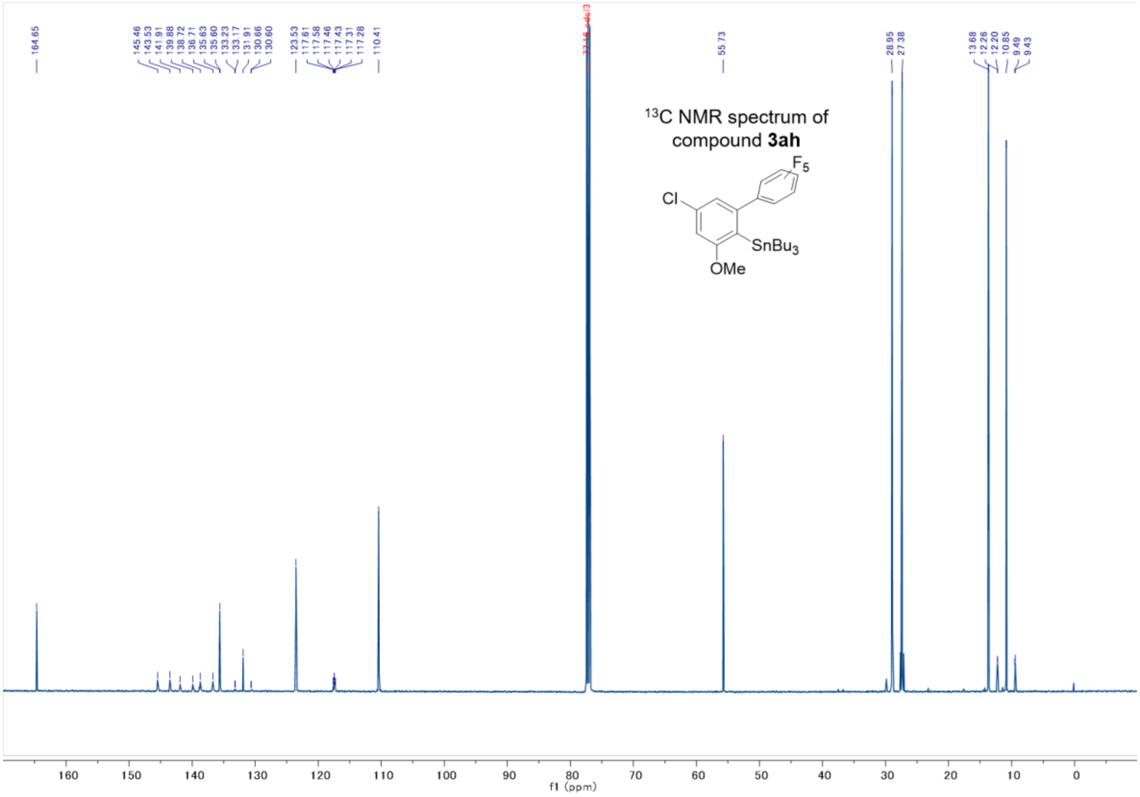


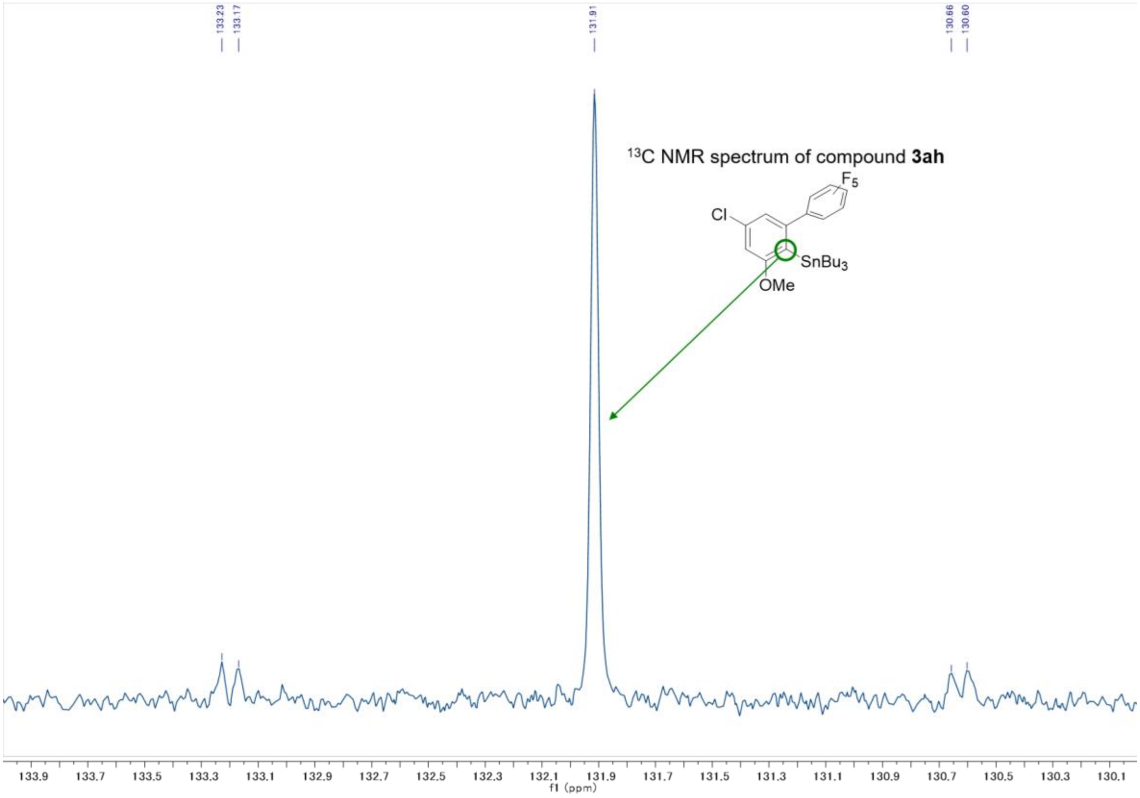
^{19}F NMR spectrum of compound **3ag**



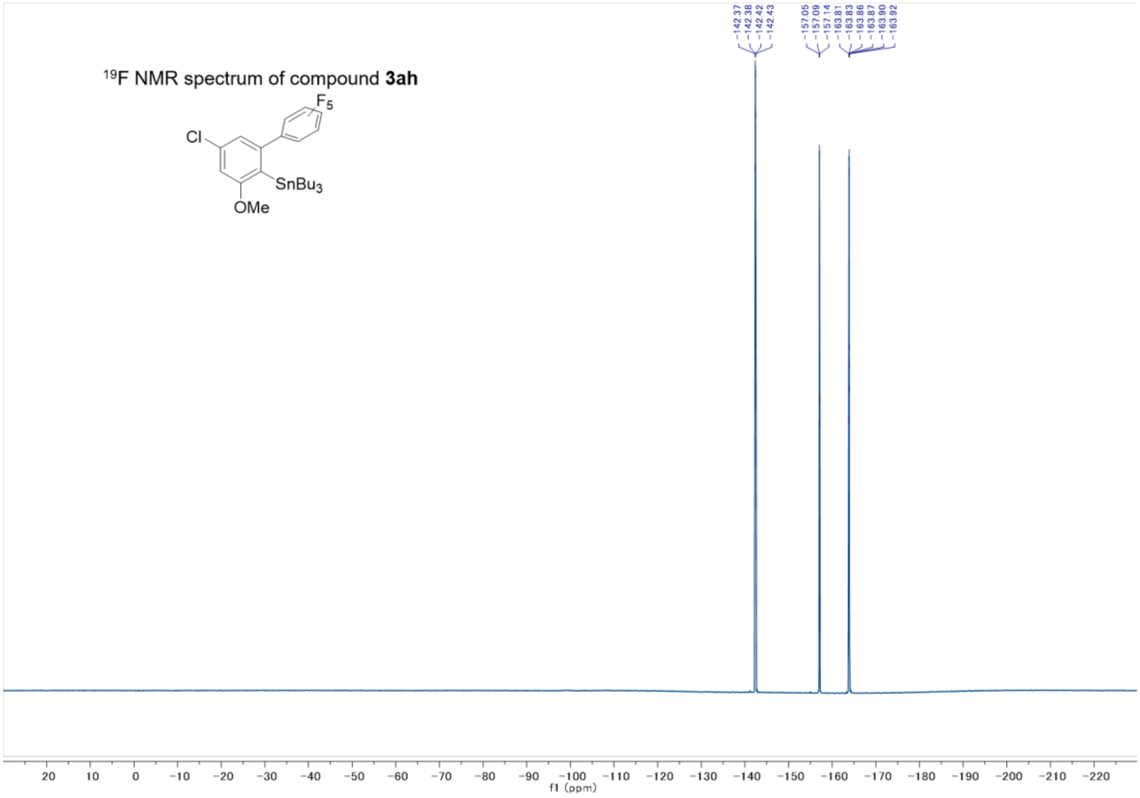
^{119}Sn NMR spectrum of compound **3ag**


7.26 cdcl3
6.89
6.87
6.86
6.85
6.84
6.83
3.83
1.41
1.40
1.38
1.36
1.35
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.29
1.25
1.23
1.22
1.20
1.19
1.17
0.85
0.83
0.82
0.77
0.75
0.74
0.72
0.71
0.70
0.69
0.68
0.66
0.65
0.63
^{1}H NMR spectrum of compound **3ah**
Cl
H
H
OMe
SnBu$_3$
F$_5$
$J_{\text{Sn–H}meta}$ = 12.0 Hz
$J_{\text{Sn–H}meta}$ = 10.2 Hz
0.871
0.790
2.920
7.609
5.833
9.000
7.244
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
f1 (ppm)

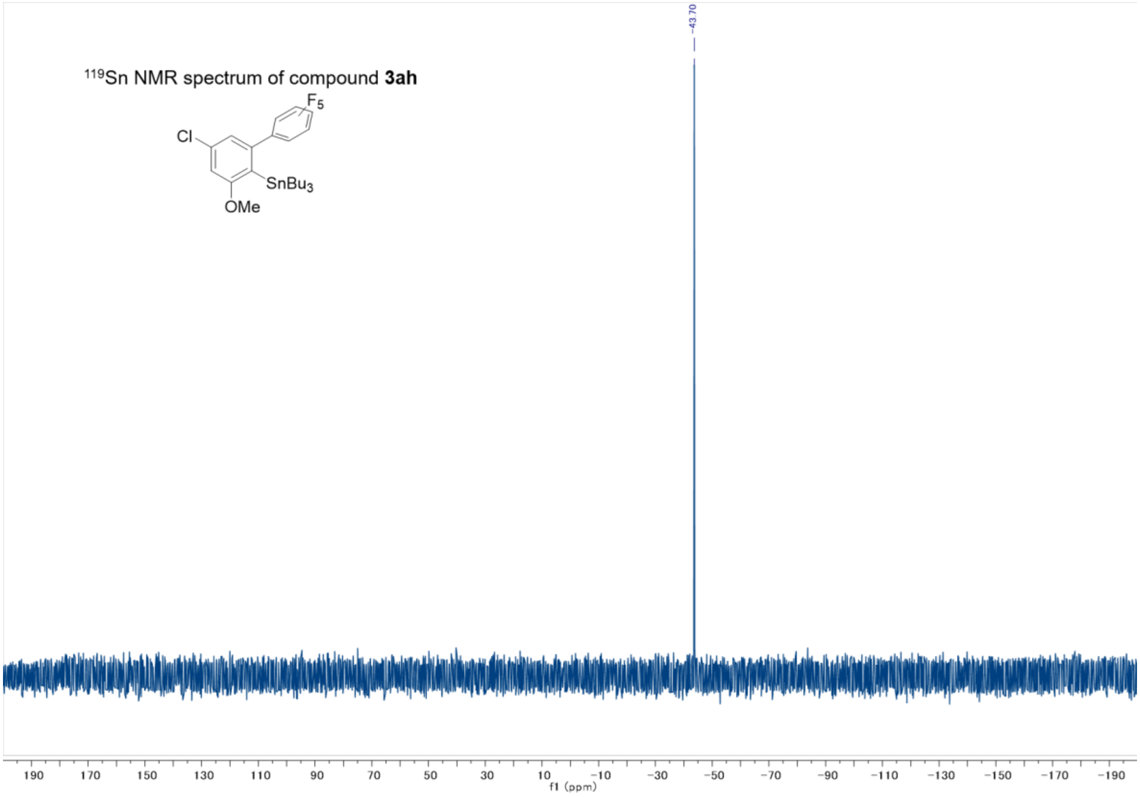

164.65
145.46
143.53
141.91
139.88
138.72
136.71
135.63
135.60
133.23
133.17
131.91
130.66
130.60
123.53
117.61
117.58
117.46
117.43
117.31
117.28
110.41
77.16 cdcl3
55.73
28.95
27.38
13.68
12.26
12.20
10.85
9.49
9.43
^{13}C NMR spectrum of compound **3ah**
Cl
OMe
SnBu$_3$
F$_5$
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



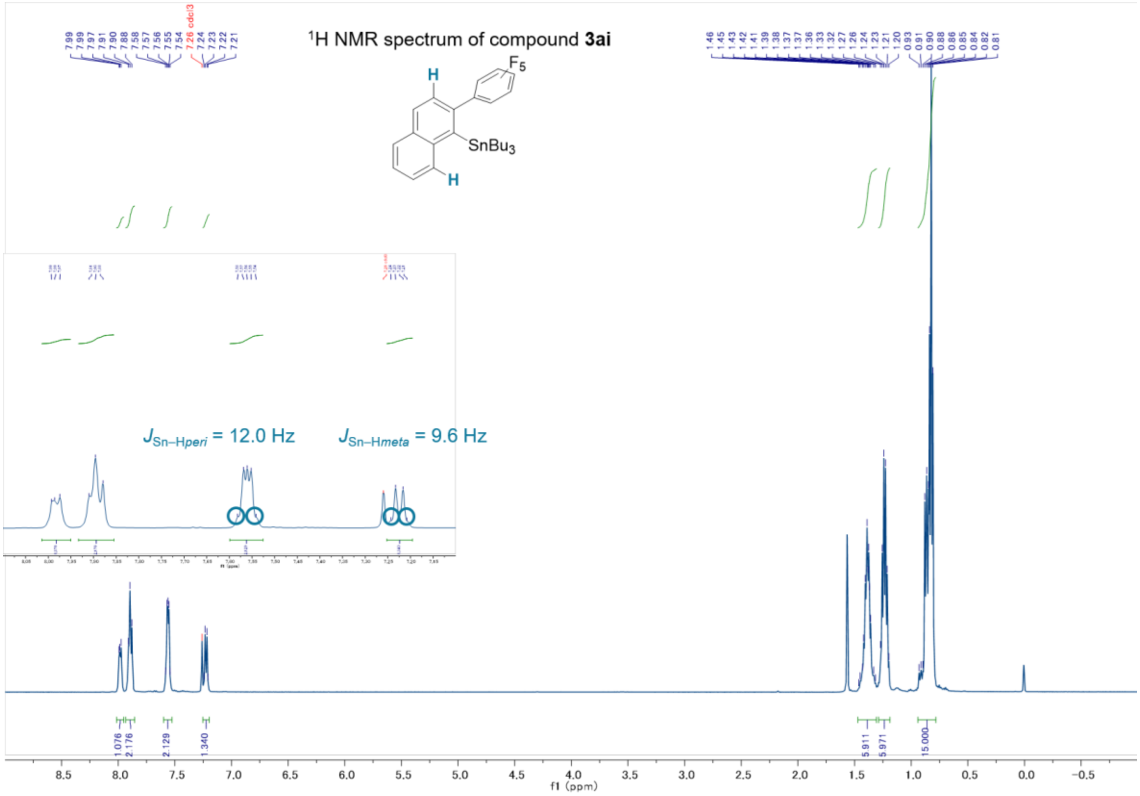
^{13}C NMR spectrum of compound **3ah**



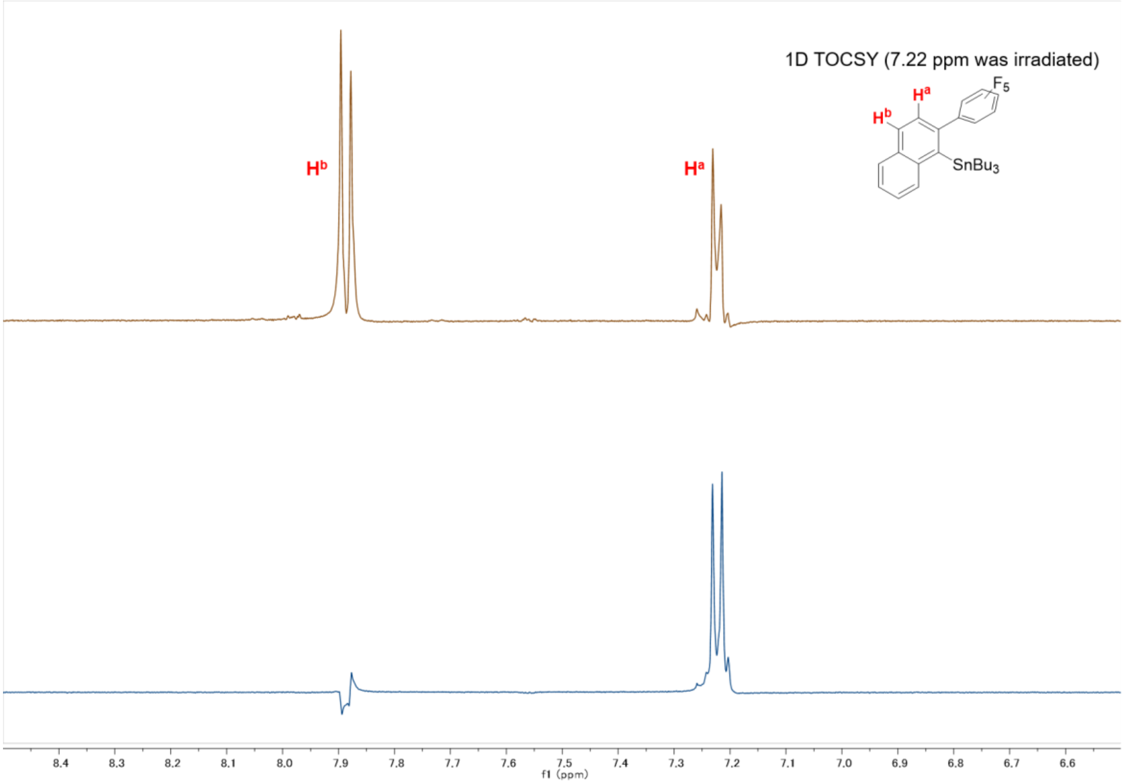
^{19}F NMR spectrum of compound **3ah**



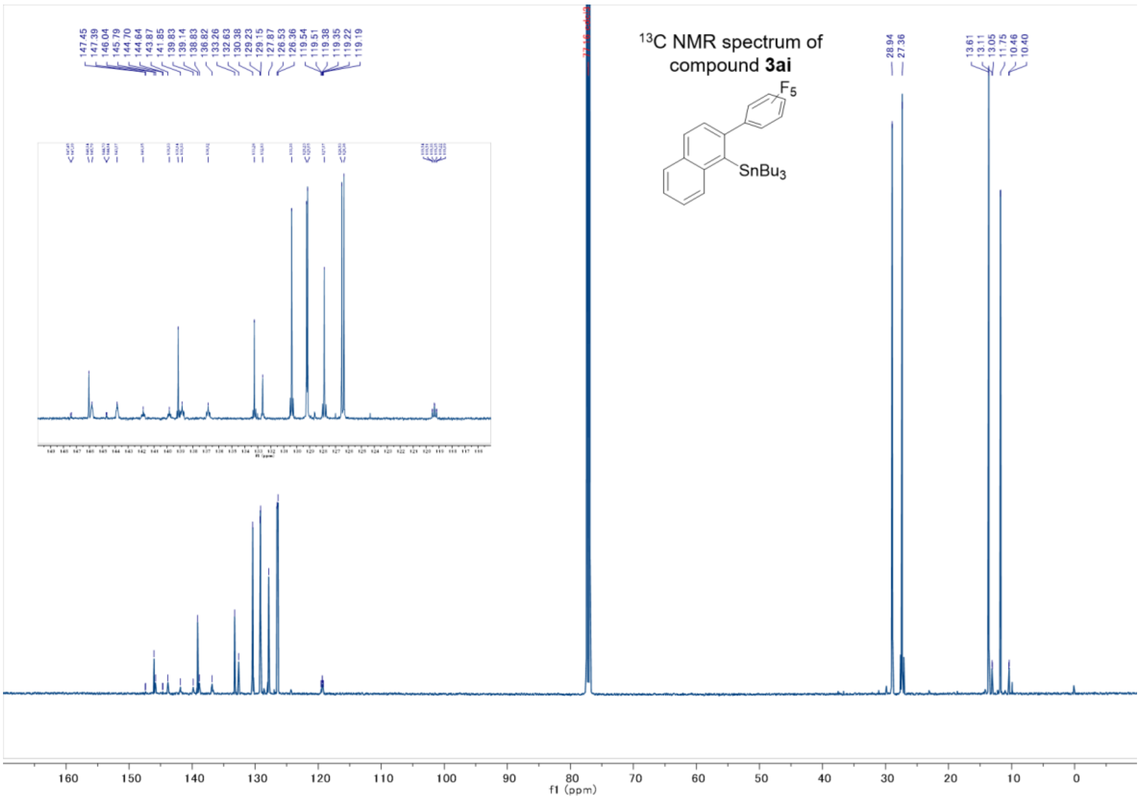
^{119}Sn NMR spectrum of compound **3ah**
F5
Cl
SnBu3
OMe
−43.70
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)



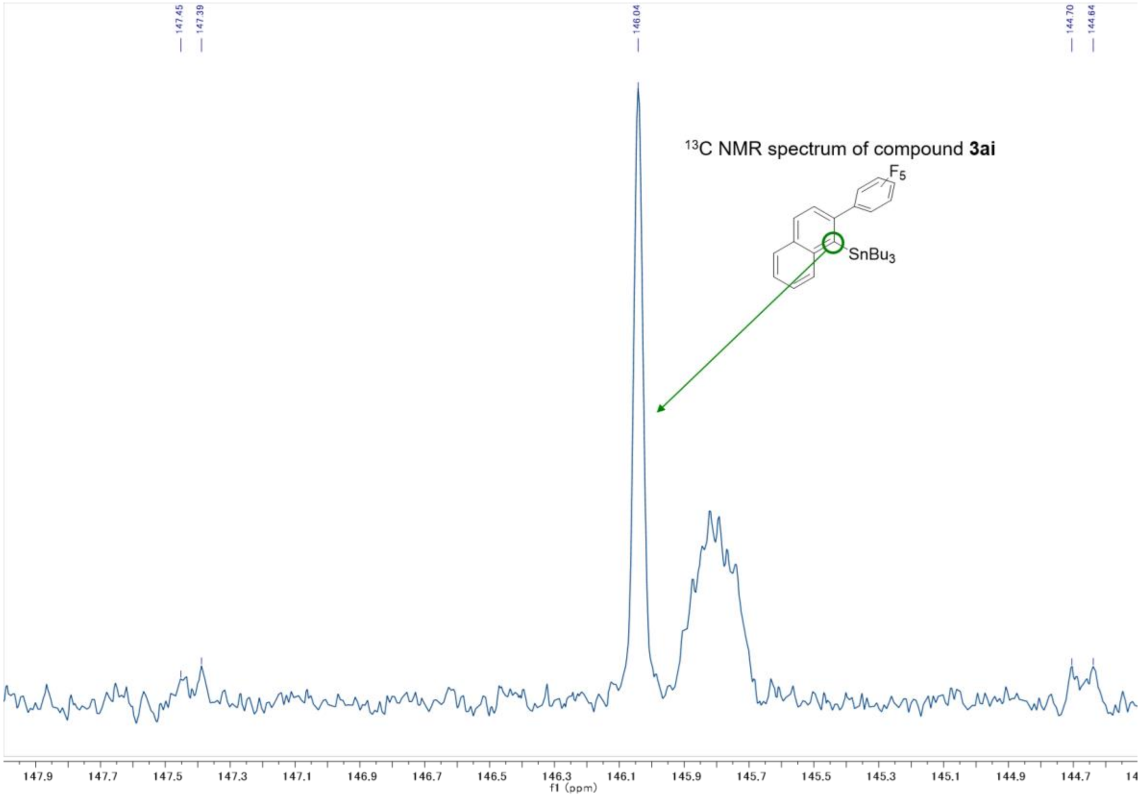
^{1}H NMR spectrum of compound **3ai**
H
F5
SnBu3
H
7.99 7.99 7.97 7.91 7.90 7.88 7.58 7.57 7.56 7.55 7.54 7.26 cdcl3 7.24 7.23 7.22 7.21
1.46 1.45 1.43 1.42 1.41 1.39 1.38 1.37 1.37 1.36 1.33 1.32 1.27 1.26 1.24 1.23 1.21 1.20 0.93 0.91 0.90 0.88 0.88 0.86 0.85 0.84 0.82 0.81
$J_{\text{Sn–H}peri}$ = 12.0 Hz
$J_{\text{Sn–H}meta}$ = 9.6 Hz
1.076 2.176 2.129 1.340 5.911 5.971 15.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

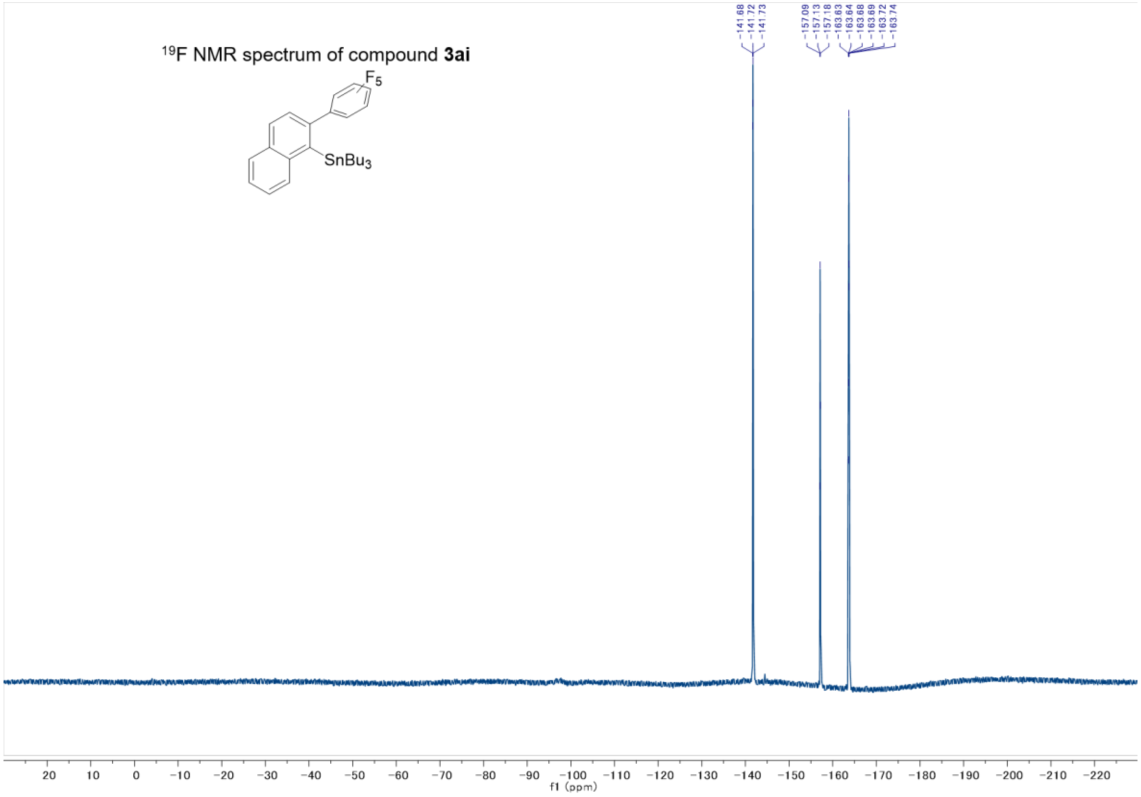


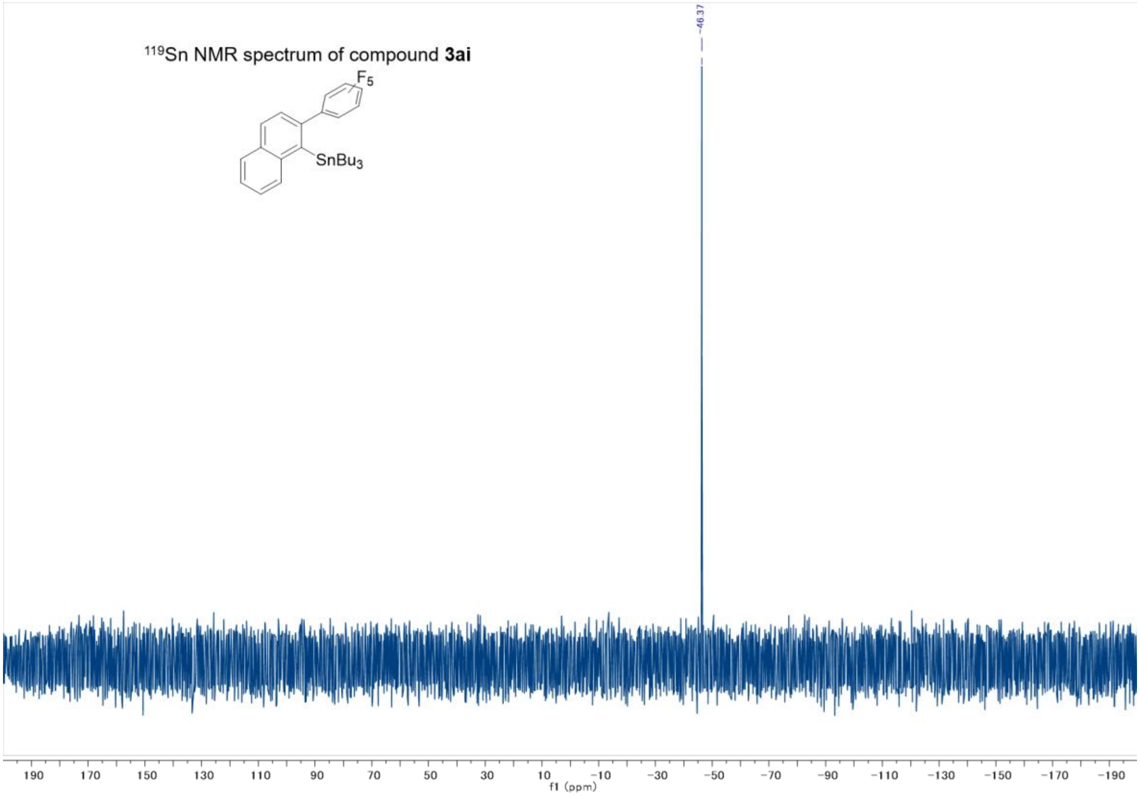
1D TOCSY (7.22 ppm was irradiated)
F5
H^a
H^b
SnBu3
H^b
H^a
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)



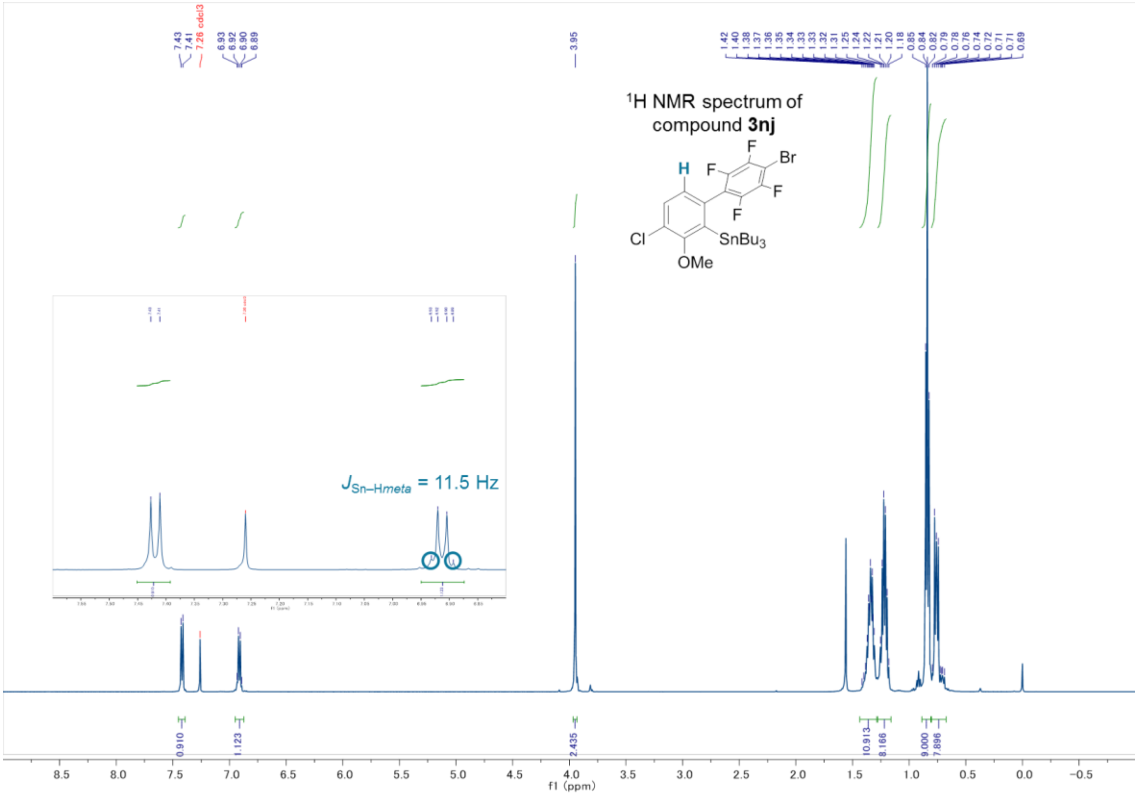
13C NMR spectrum of compound 3ai
F5
SnBu3
147.45
147.39
146.04
145.79
144.70
144.64
143.87
141.85
139.83
139.14
138.83
136.82
133.26
132.63
130.38
129.23
129.15
127.87
126.53
126.36
119.54
119.51
119.38
119.35
119.22
119.19
28.94
27.36
13.61
13.11
13.05
11.75
10.46
10.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


147.45
147.39
146.04
144.70
144.64
^{13}C NMR spectrum of compound **3ai**
F5
SnBu3
147.9
147.7
147.5
147.3
147.1
146.9
146.7
146.5
146.3
146.1
145.9
145.7
145.5
145.3
145.1
144.9
144.7
14
f1 (ppm)

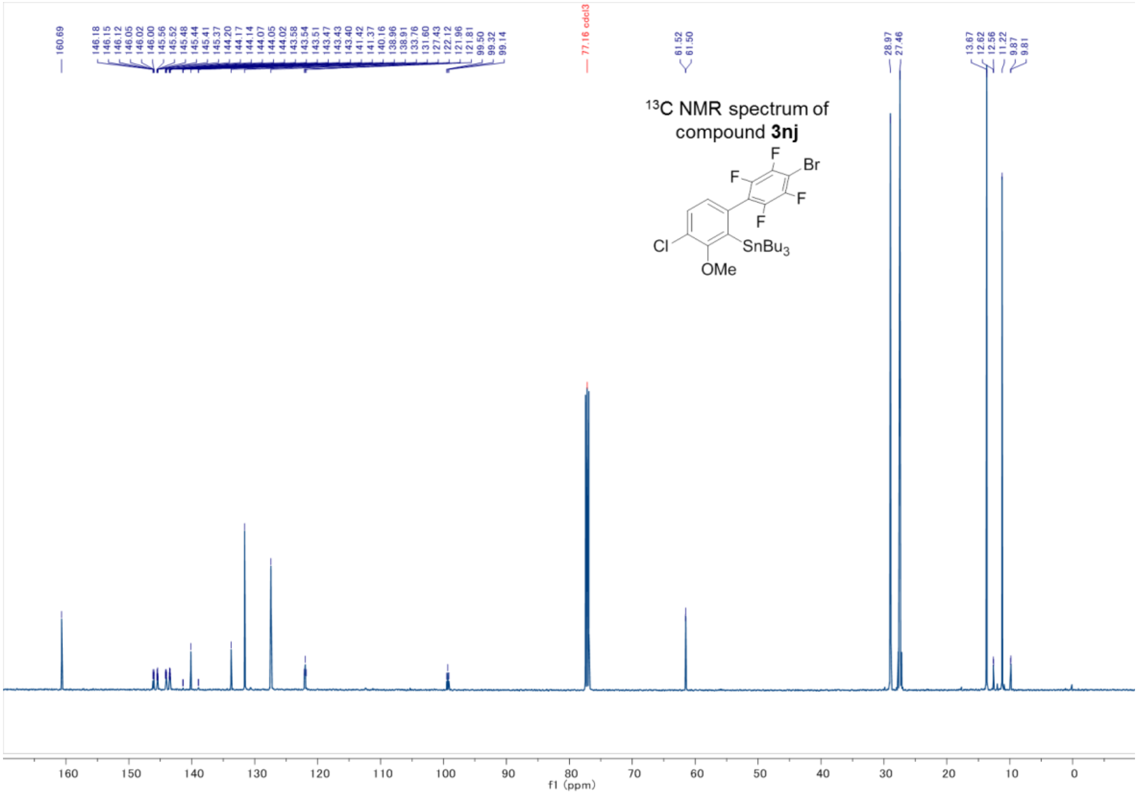

−141.68
−141.72
−141.73
−157.09
−157.13
−157.18
−163.63
−163.64
−163.68
−163.69
−163.72
−163.74
^{19}F NMR spectrum of compound **3ai**
F5
SnBu3
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

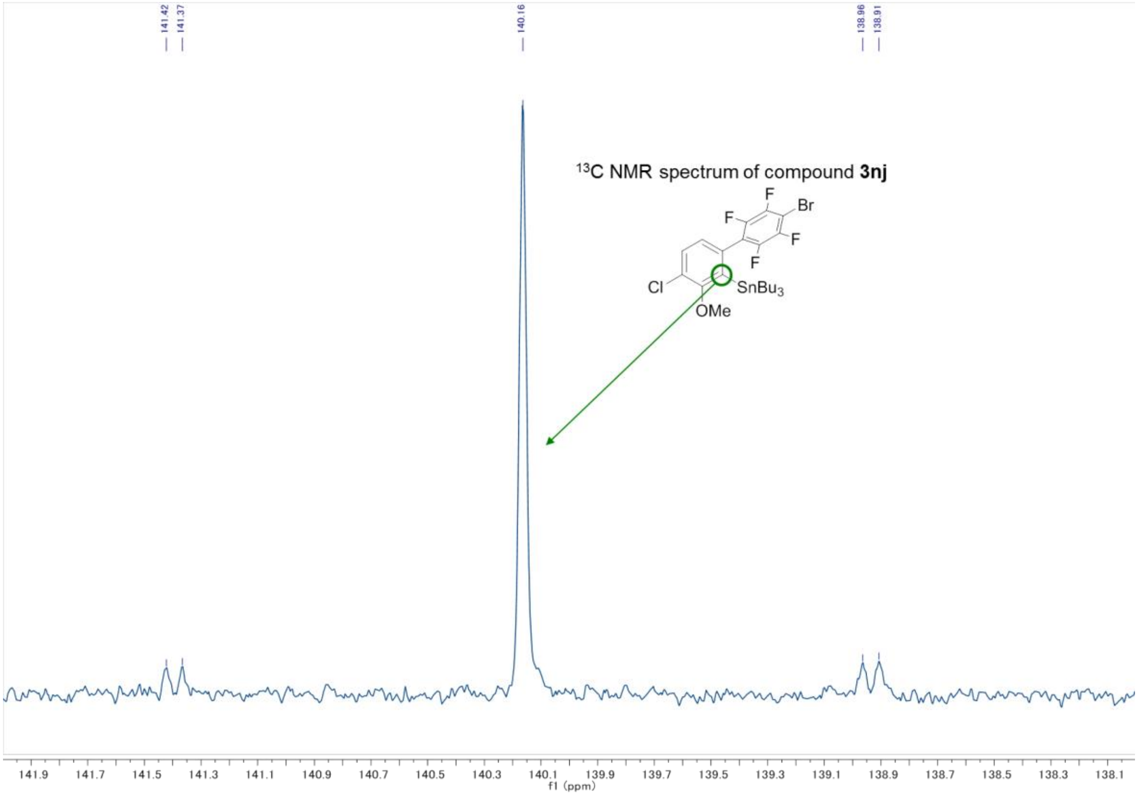


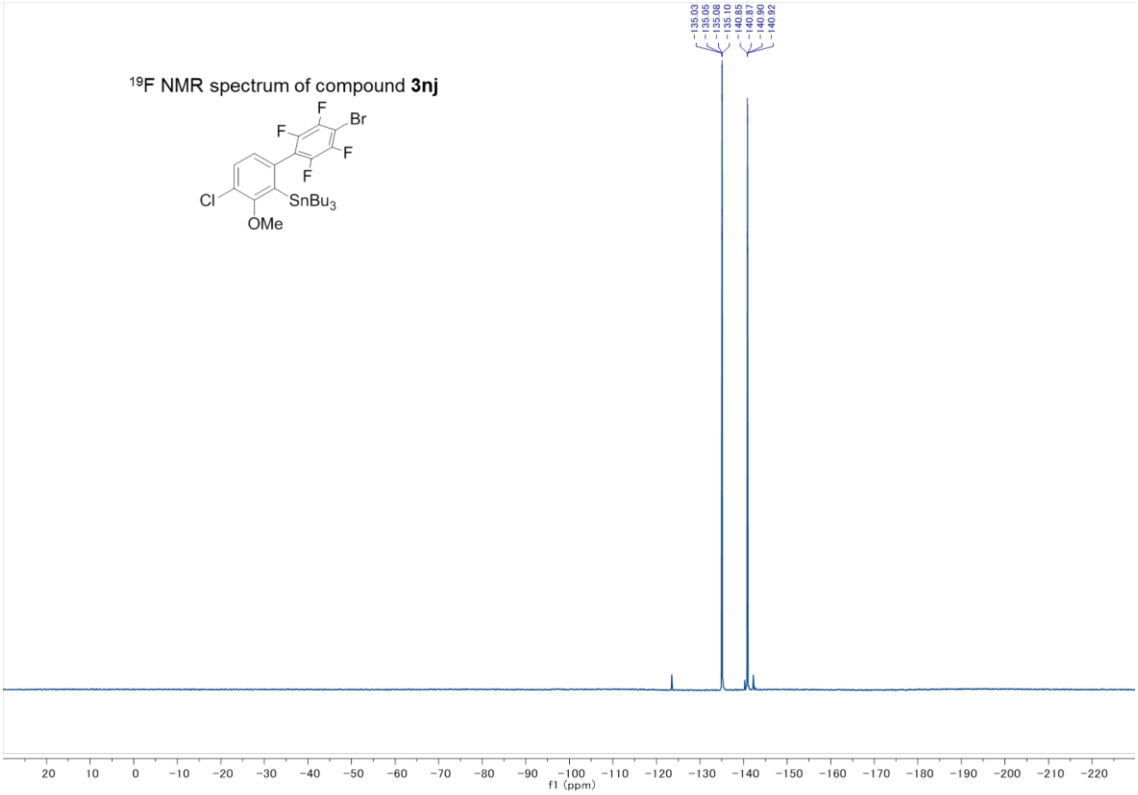
^{119}Sn NMR spectrum of compound **3ai**
F_5
SnBu$_3$
−46.37
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

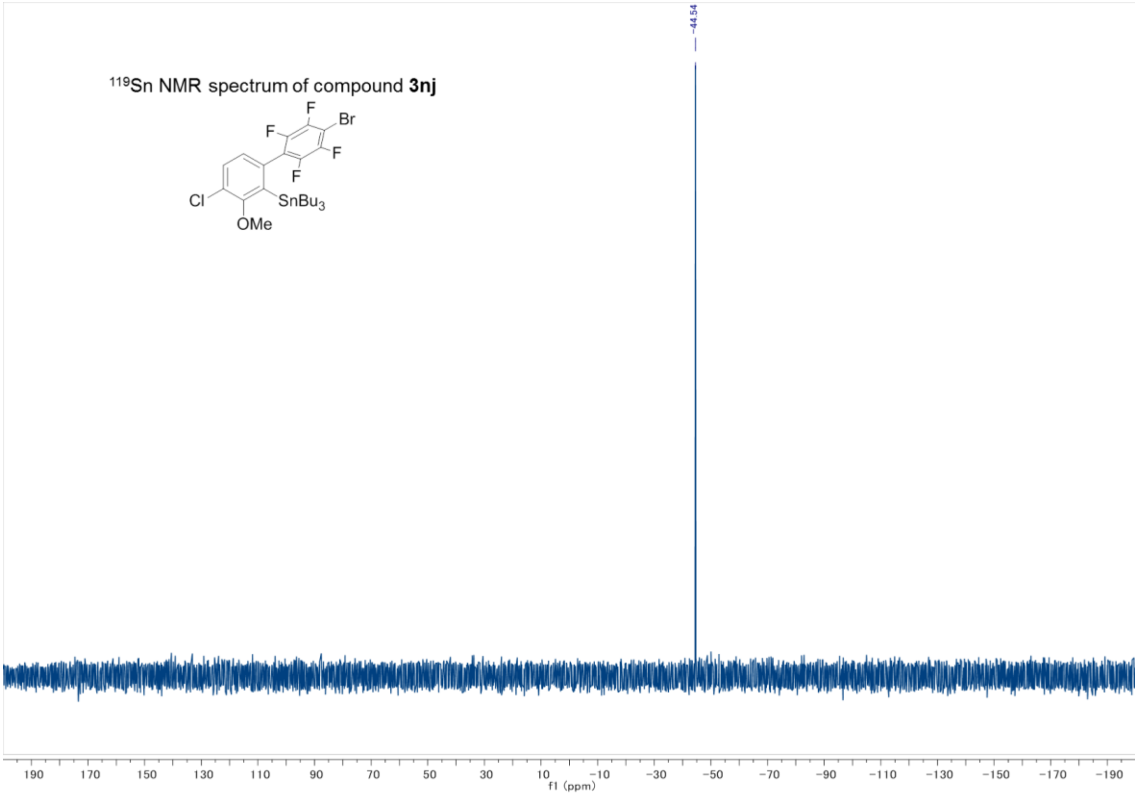


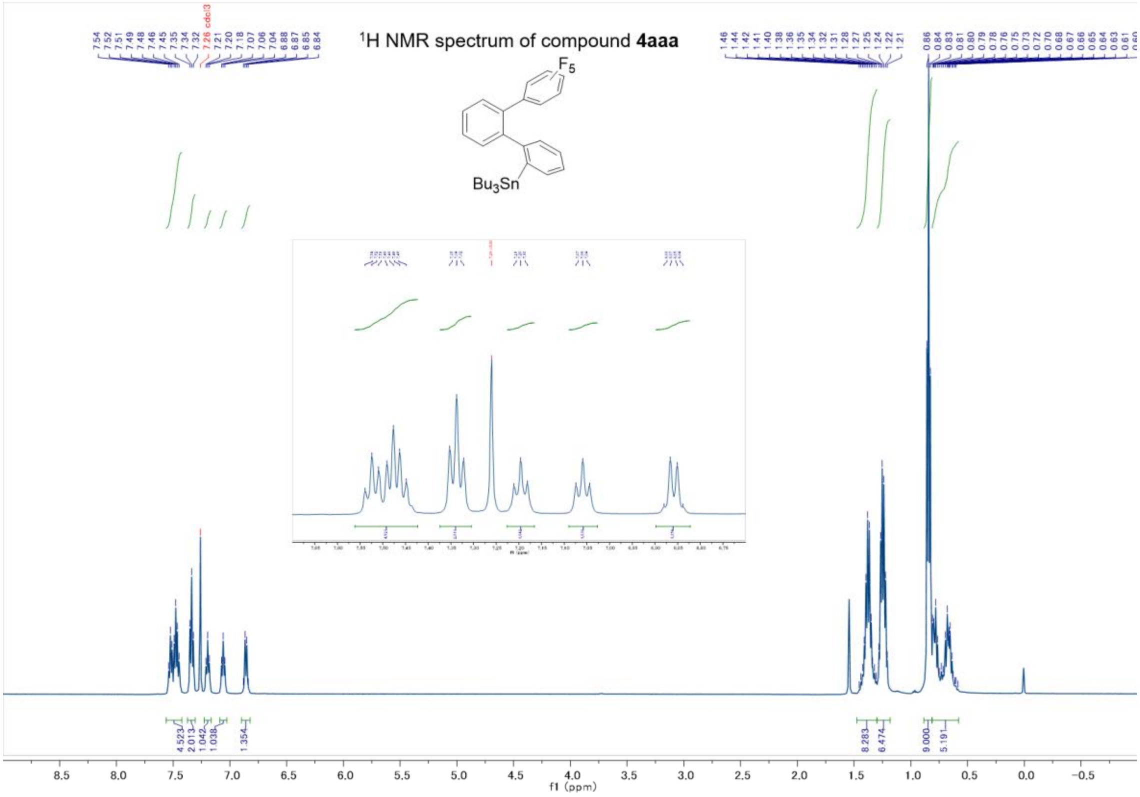
7.43
7.41
7.26 cdcl3
6.93
6.92
6.90
6.89
3.95
1.42 1.40 1.38 1.37 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.25 1.24 1.22 1.21 1.20 1.18 0.85 0.84 0.82 0.79 0.78 0.76 0.74 0.72 0.71 0.71 0.69
^{1}H NMR spectrum of compound **3nj**
H
F
F
Br
F
F
Cl
SnBu$_3$
OMe
$J_{Sn–Hmeta}$ = 11.5 Hz
0.910
1.123
2.435
10.913
8.166
9.000
7.896
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

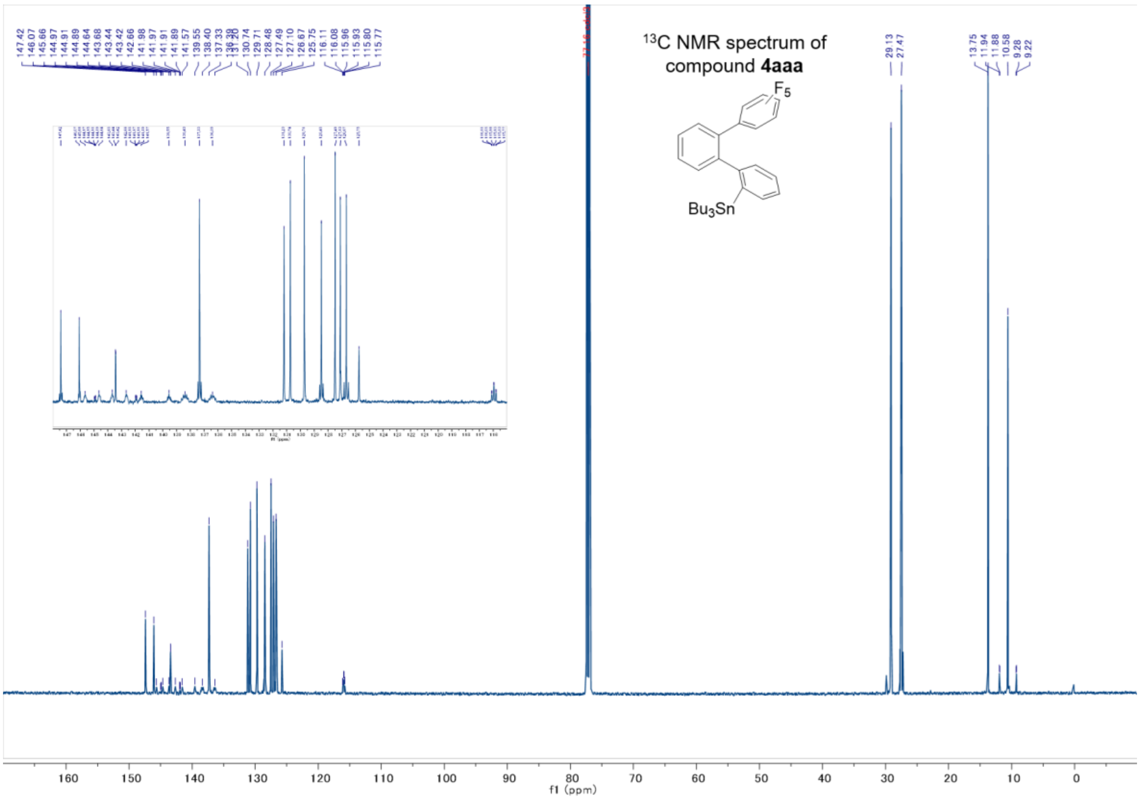

160.69
146.18
146.15
146.12
146.05
146.02
146.00
145.56
145.52
145.48
145.44
145.41
145.37
144.20
144.17
144.14
144.07
144.05
144.02
143.58
143.54
143.51
143.47
143.43
143.40
141.42
141.37
140.16
138.96
138.91
133.76
131.60
127.43
122.12
121.96
121.81
99.50
99.32
99.14
77.16 cdcl3
61.52
61.50
28.97
27.46
13.67
12.62
12.56
11.22
9.87
9.81
^{13}C NMR spectrum of compound **3nj**
F
Br
F
F
F
Cl
SnBu$_3$
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

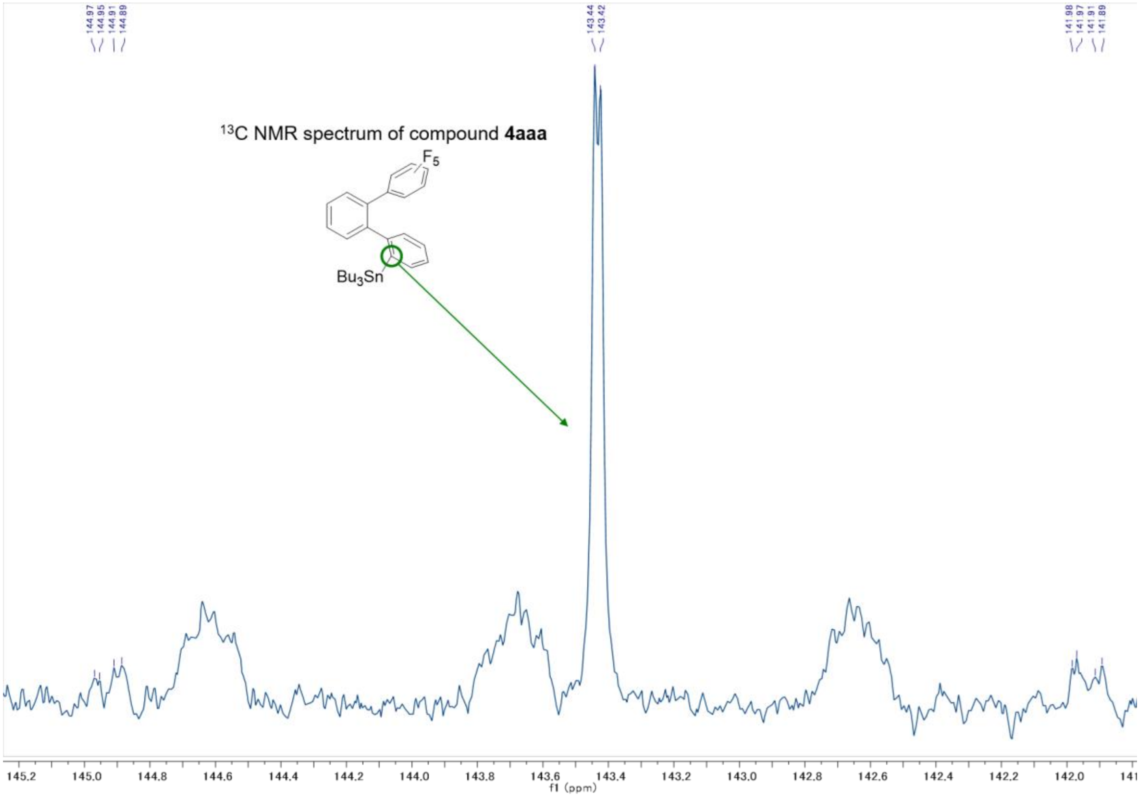

141.42
141.37
140.16
138.96
138.91
^{13}C NMR spectrum of compound **3nj**
F
Br
F
F
F
Cl
SnBu$_3$
OMe
141.9
141.7
141.5
141.3
141.1
140.9
140.7
140.5
140.3
140.1
139.9
139.7
139.5
139.3
139.1
138.9
138.7
138.5
138.3
138.1
f1 (ppm)

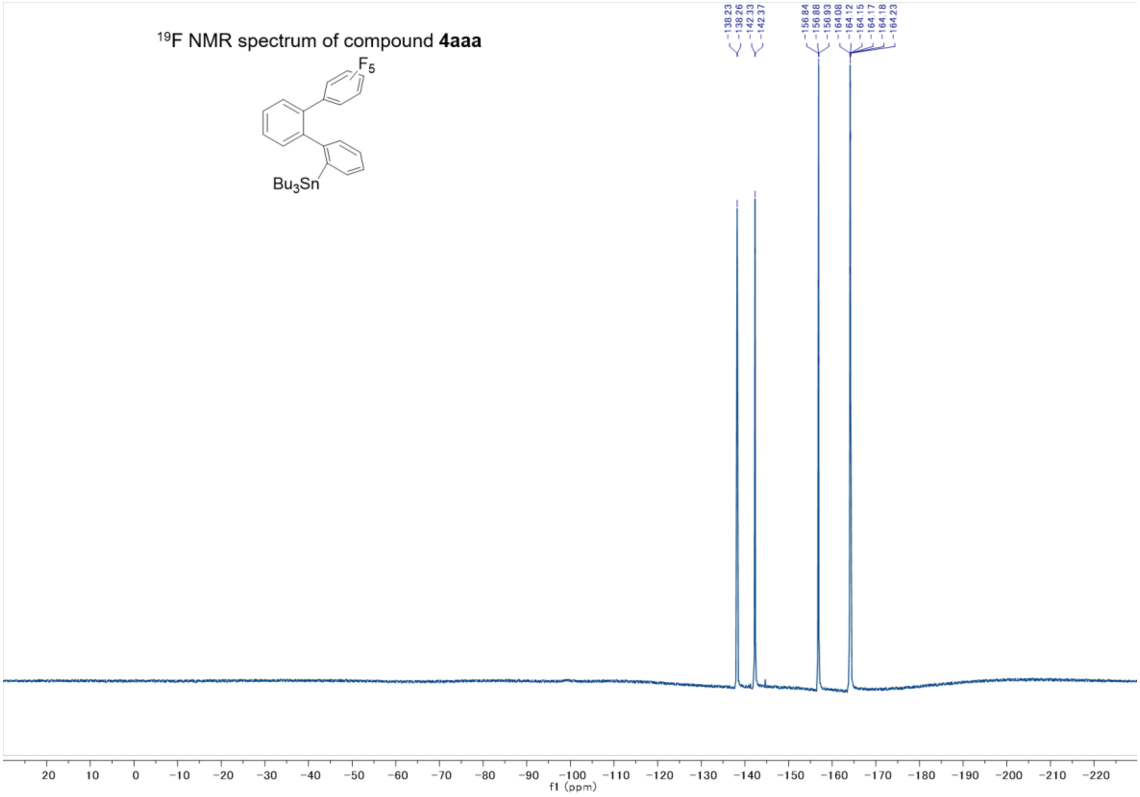

^{19}F NMR spectrum of compound **3nj**

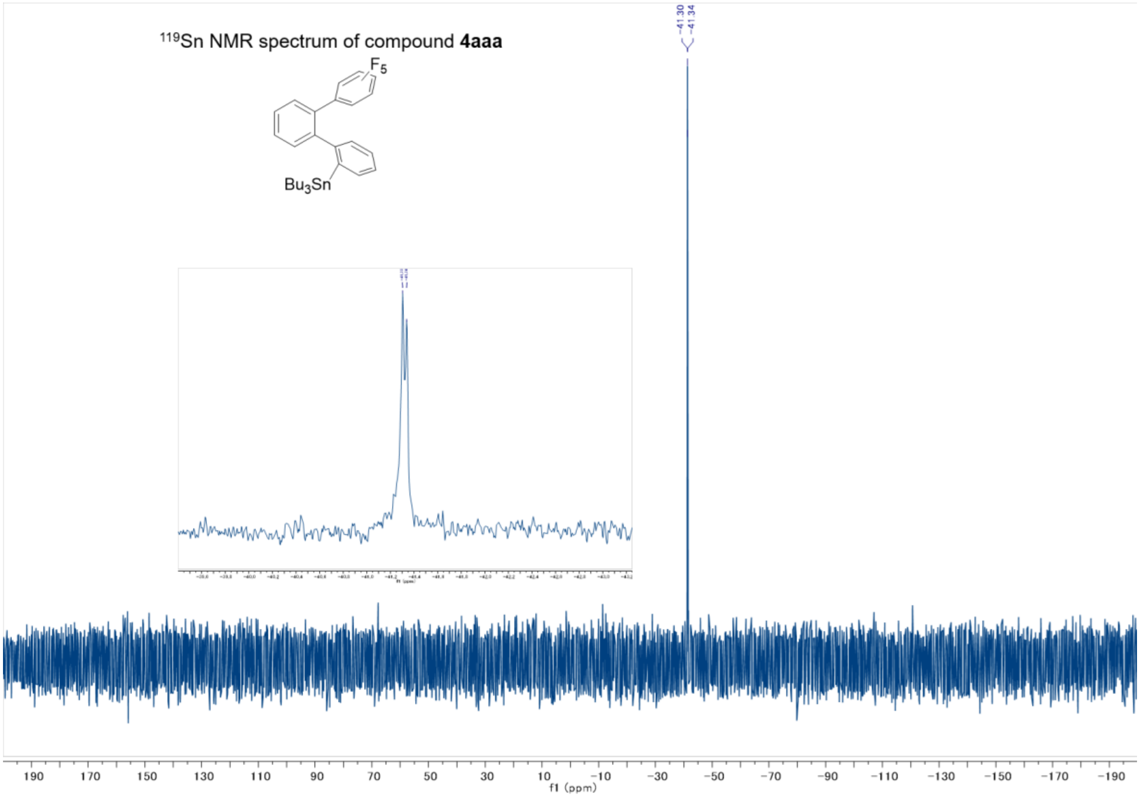

^{119}Sn NMR spectrum of compound **3nj**

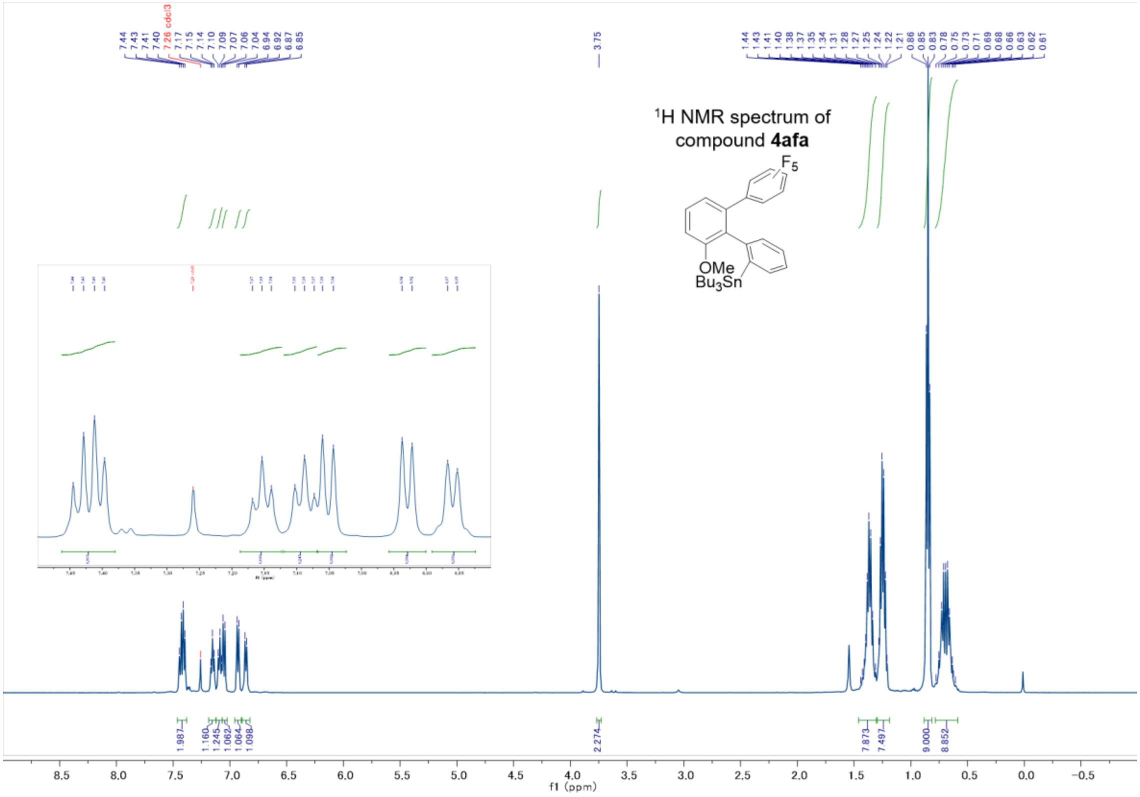

^{1}H NMR spectrum of compound **4aaa**
F5
Bu3Sn
7.54
7.52
7.51
7.49
7.48
7.46
7.45
7.35
7.34
7.32
7.26 cdcl3
7.21
7.20
7.18
7.07
7.06
7.04
6.88
6.87
6.85
6.84
1.46
1.44
1.42
1.41
1.40
1.38
1.36
1.35
1.34
1.32
1.31
1.28
1.27
1.25
1.24
1.22
1.21
0.86
0.84
0.83
0.81
0.80
0.79
0.78
0.76
0.75
0.73
0.72
0.70
0.68
0.67
0.66
0.65
0.64
0.63
0.61
0.60
4.523
2.013
1.042
1.038
1.354
8.283
6.474
9.000
5.191
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

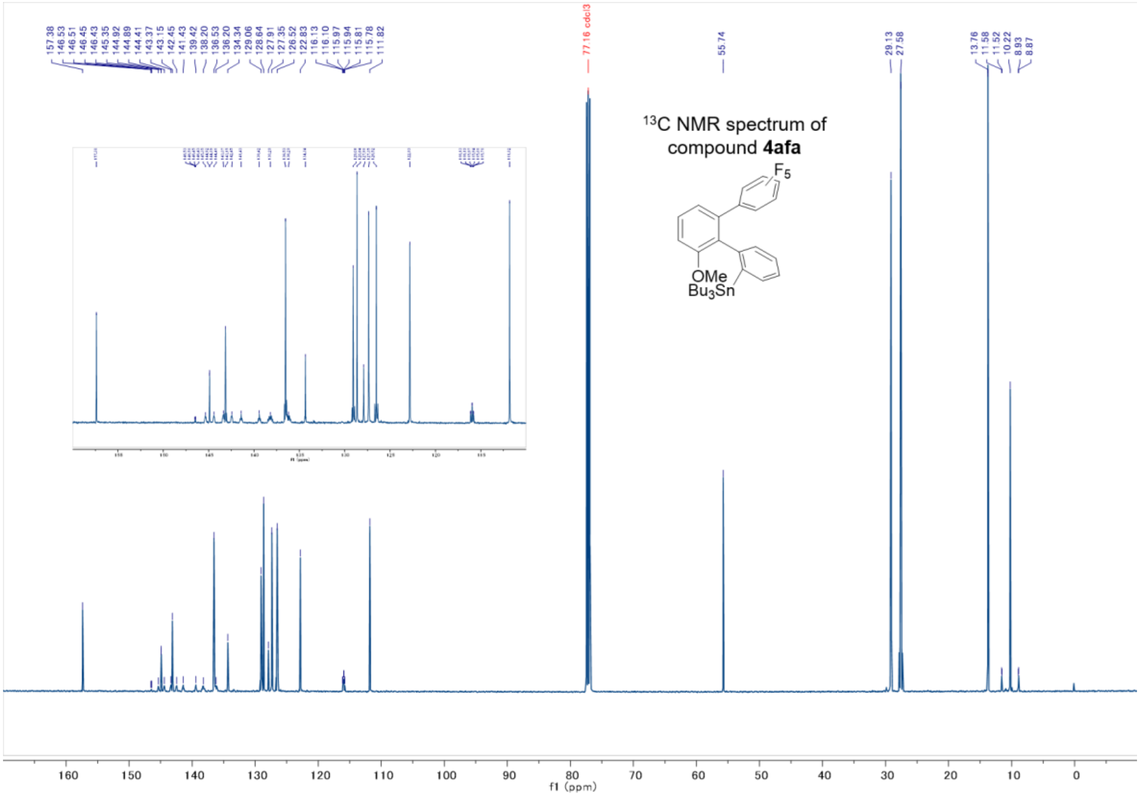

^{13}C NMR spectrum of compound **4aaa**
F5
Bu3Sn
147.42
146.07
145.66
144.97
144.91
144.89
144.64
143.68
143.44
143.42
142.66
141.98
141.97
141.91
141.89
141.57
139.55
138.40
137.33
137.30
137.20
130.74
129.71
128.48
127.49
127.10
126.67
125.75
116.11
116.08
115.96
115.93
115.80
115.77
29.13
27.47
13.75
11.94
11.88
10.58
9.28
9.22
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

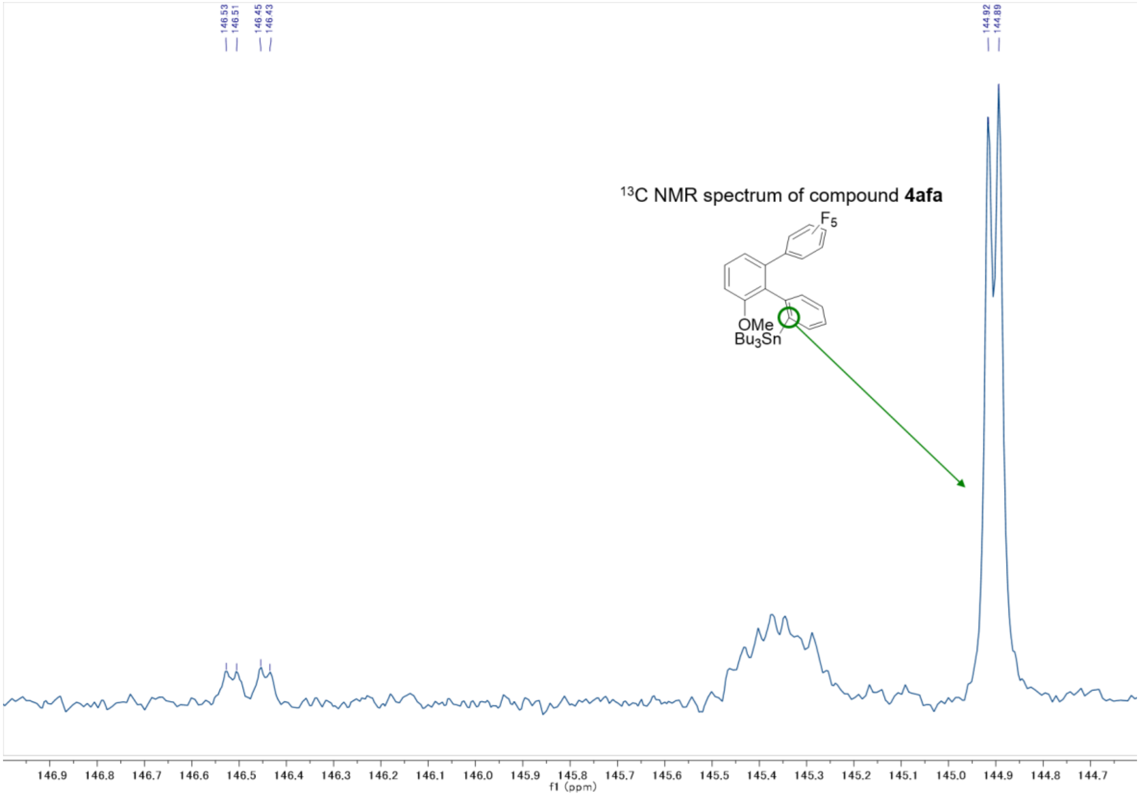

^{13}C NMR spectrum of compound **4aaa**

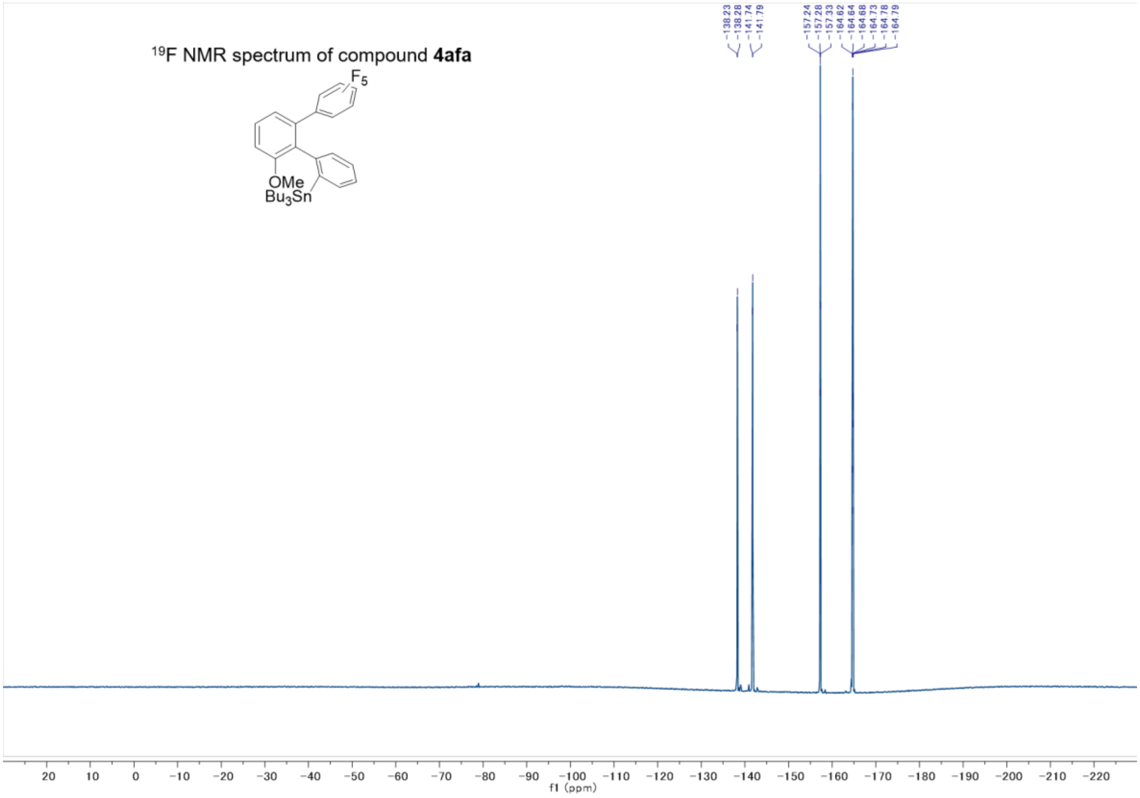

^{19}F NMR spectrum of compound **4aaa**


^{119}Sn NMR spectrum of compound **4aaa**
F5
Bu3Sn
-41.30
-41.34
190
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
f1 (ppm)

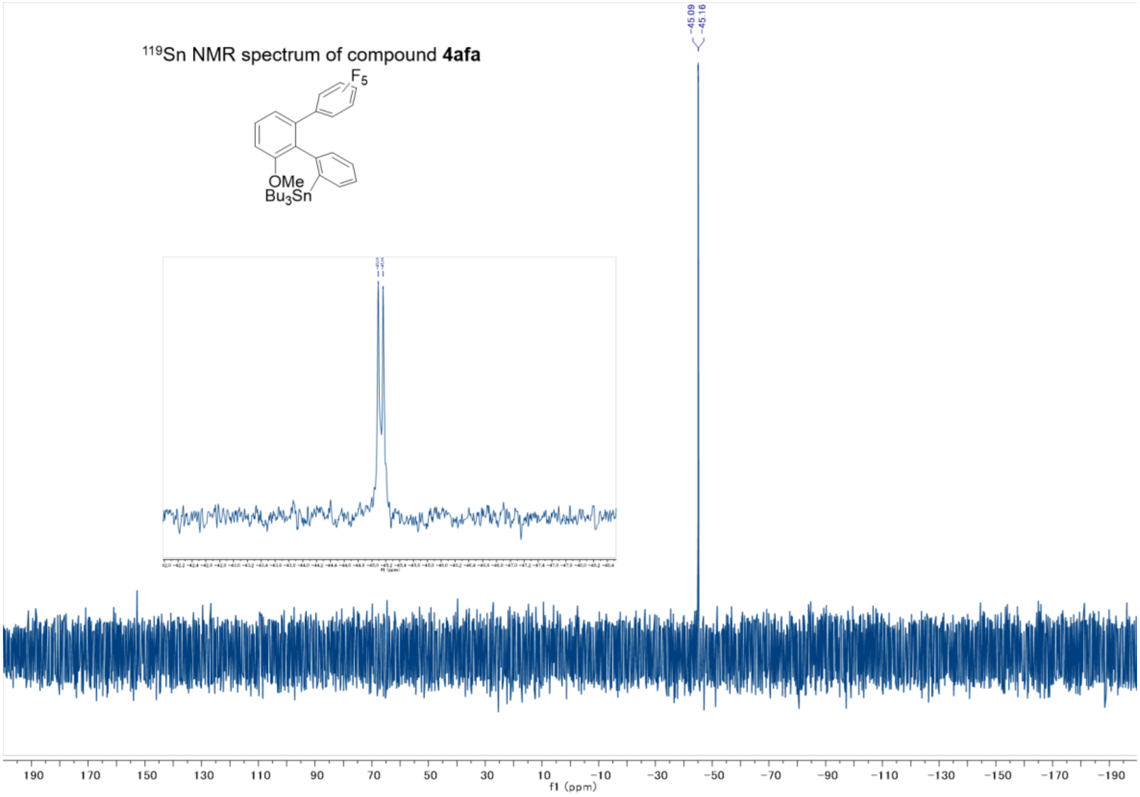

^{1}H NMR spectrum of compound **4afa**
F5
OMe
Bu3Sn
7.44
7.43
7.41
7.40
7.26 cdcl3
7.17
7.15
7.14
7.10
7.09
7.07
7.06
7.04
6.94
6.92
6.87
6.85
3.75
1.44
1.43
1.41
1.40
1.38
1.37
1.35
1.34
1.31
1.28
1.27
1.25
1.24
1.22
1.21
0.86
0.85
0.83
0.78
0.75
0.73
0.71
0.69
0.68
0.66
0.63
0.62
0.61
1.987
1.160
1.245
1.062
1.064
1.098
2.274
7.873
7.497
9.000
8.852
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


^{13}C NMR spectrum of compound **4afa**

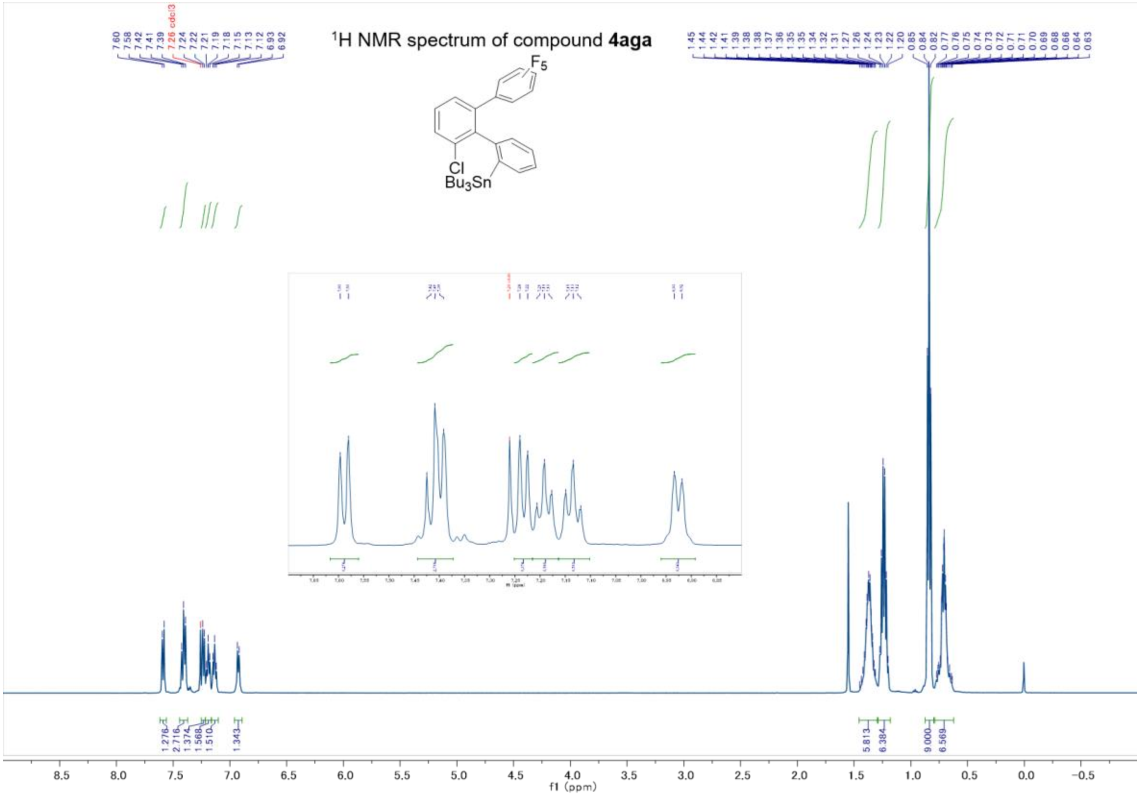

^{13}C NMR spectrum of compound **4afa**



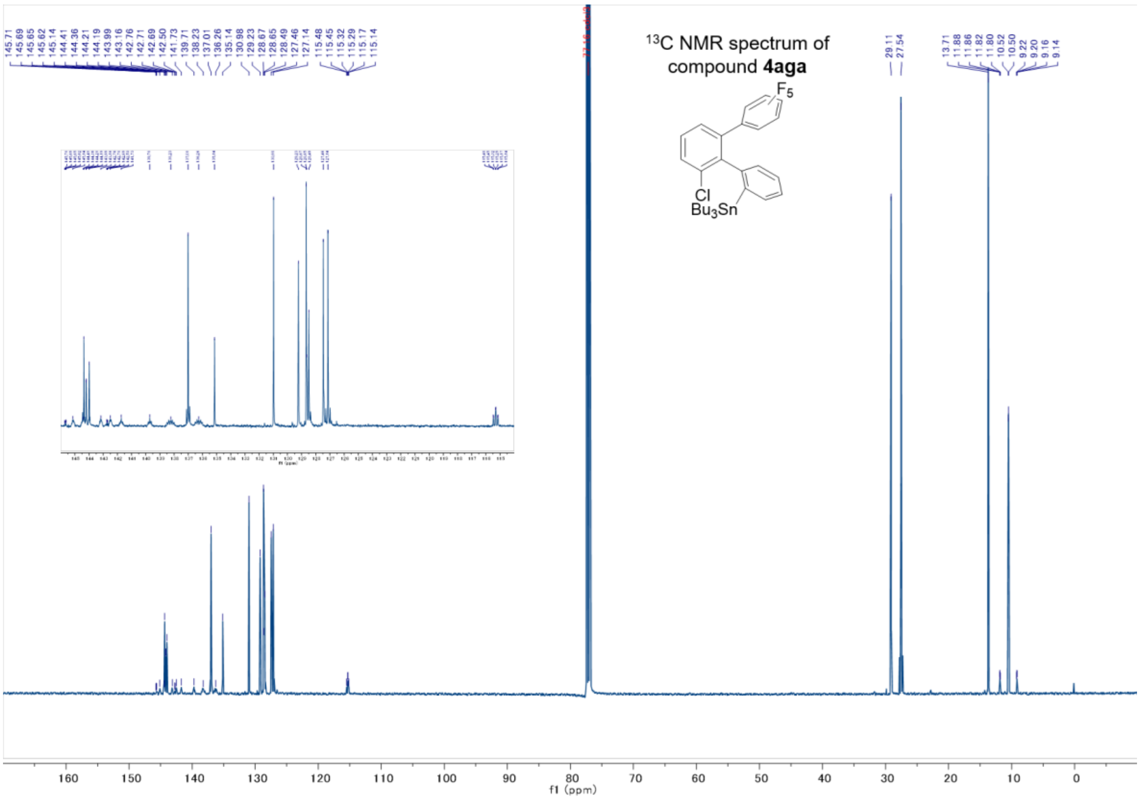
^{19}F NMR spectrum of compound **4afa**
F5
OMe
Bu3Sn
−138.23
−138.28
−141.74
−141.79
−157.24
−157.28
−157.33
−164.62
−164.64
−164.68
−164.73
−164.78
−164.79
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)



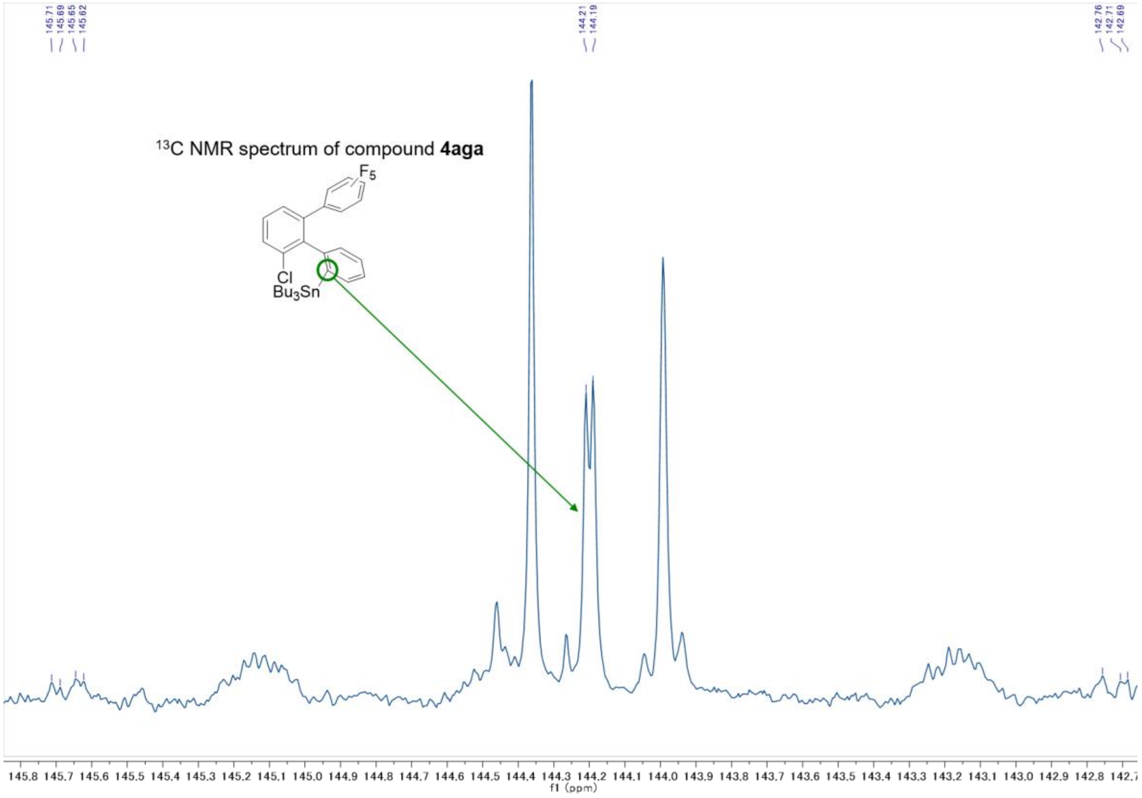
^{119}Sn NMR spectrum of compound **4afa**
F5
OMe
Bu3Sn
−45.09
−45.16
190
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
f1 (ppm)



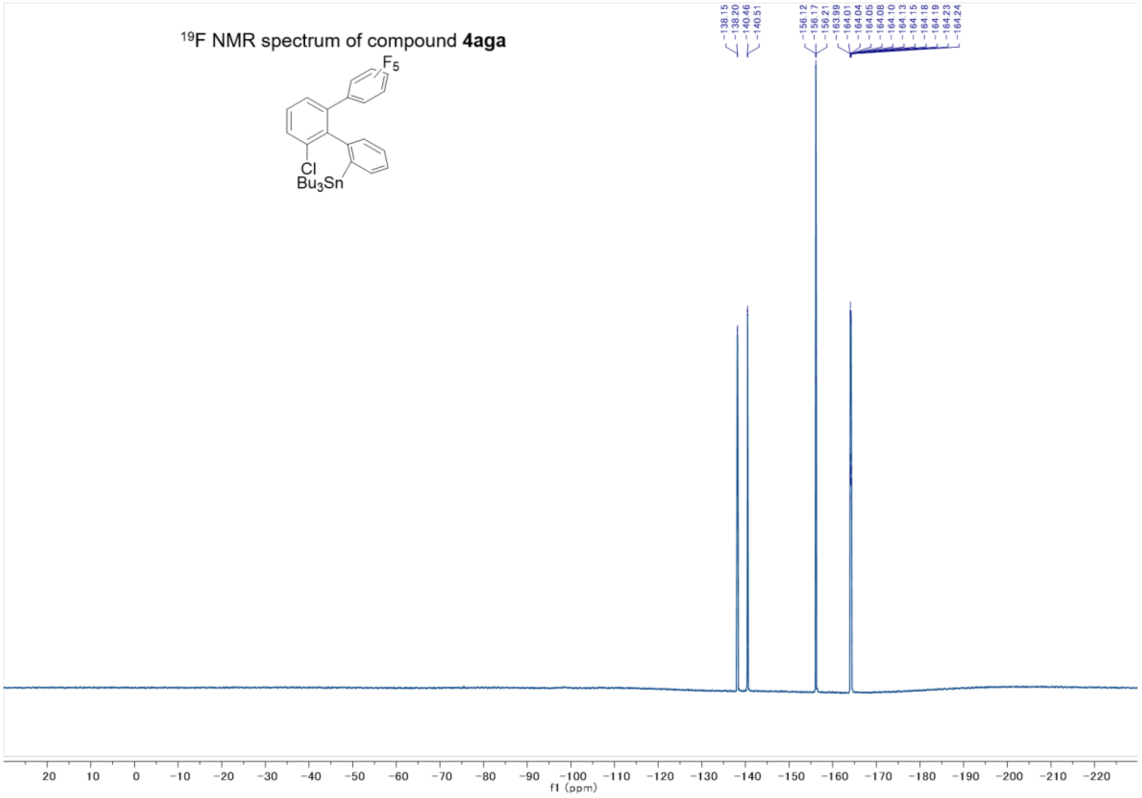
^{1}H NMR spectrum of compound **4aga**



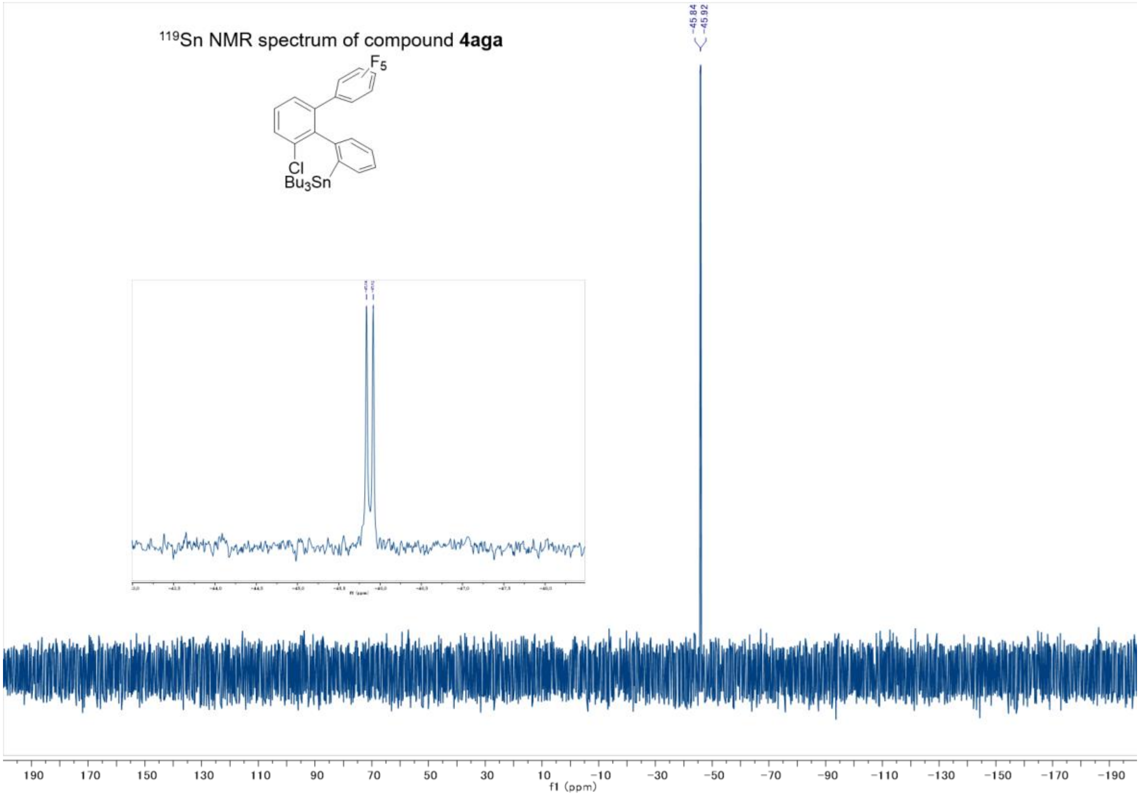
^{13}C NMR spectrum of compound **4aga**



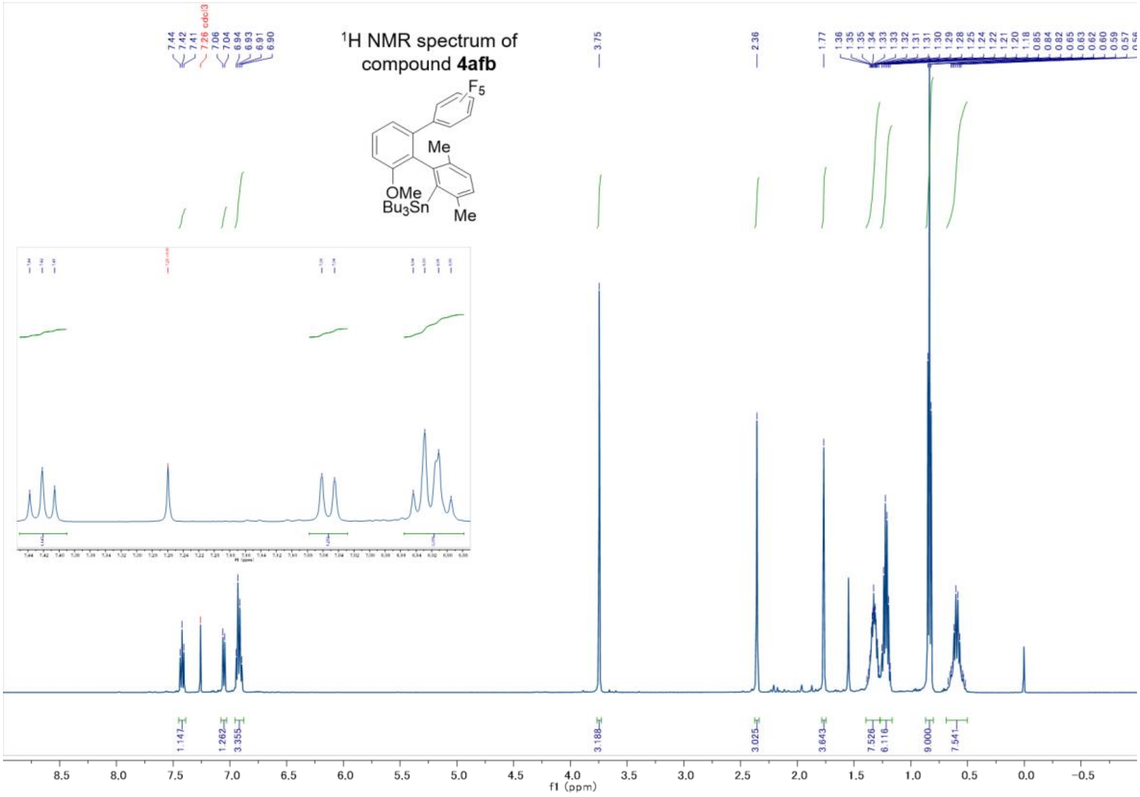
^{13}C NMR spectrum of compound **4aga**



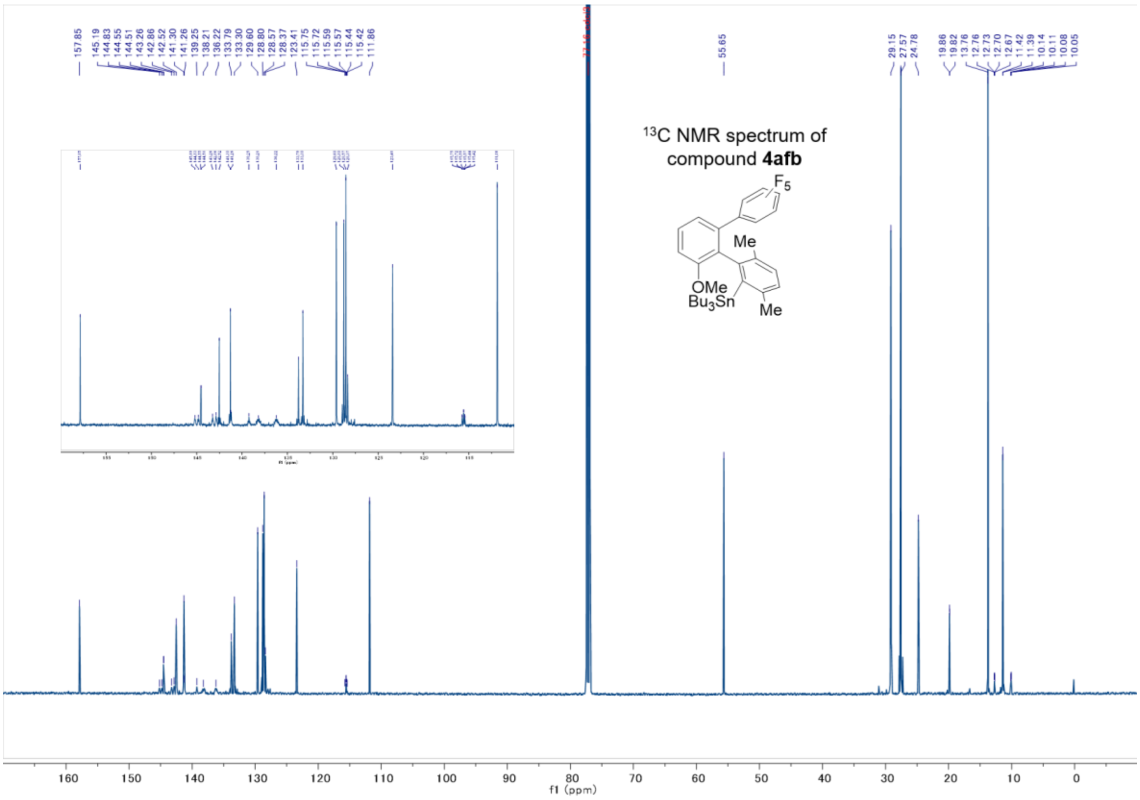
^{19}F NMR spectrum of compound **4aga**

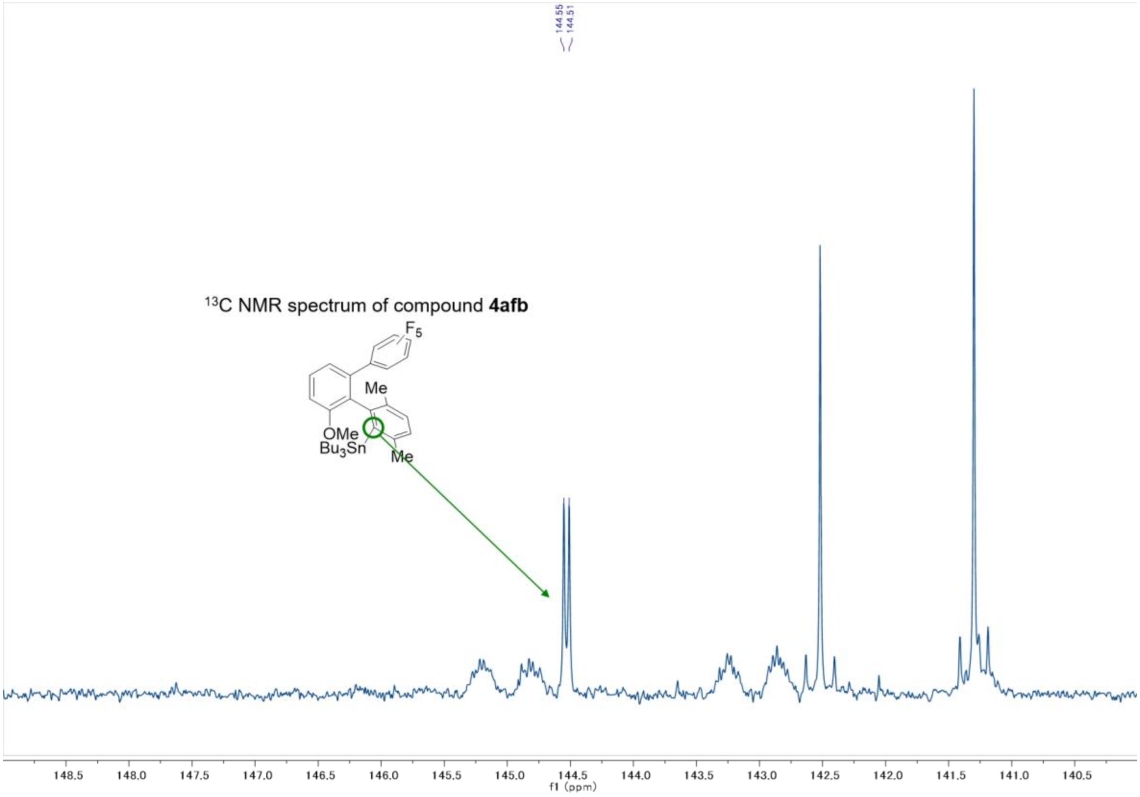


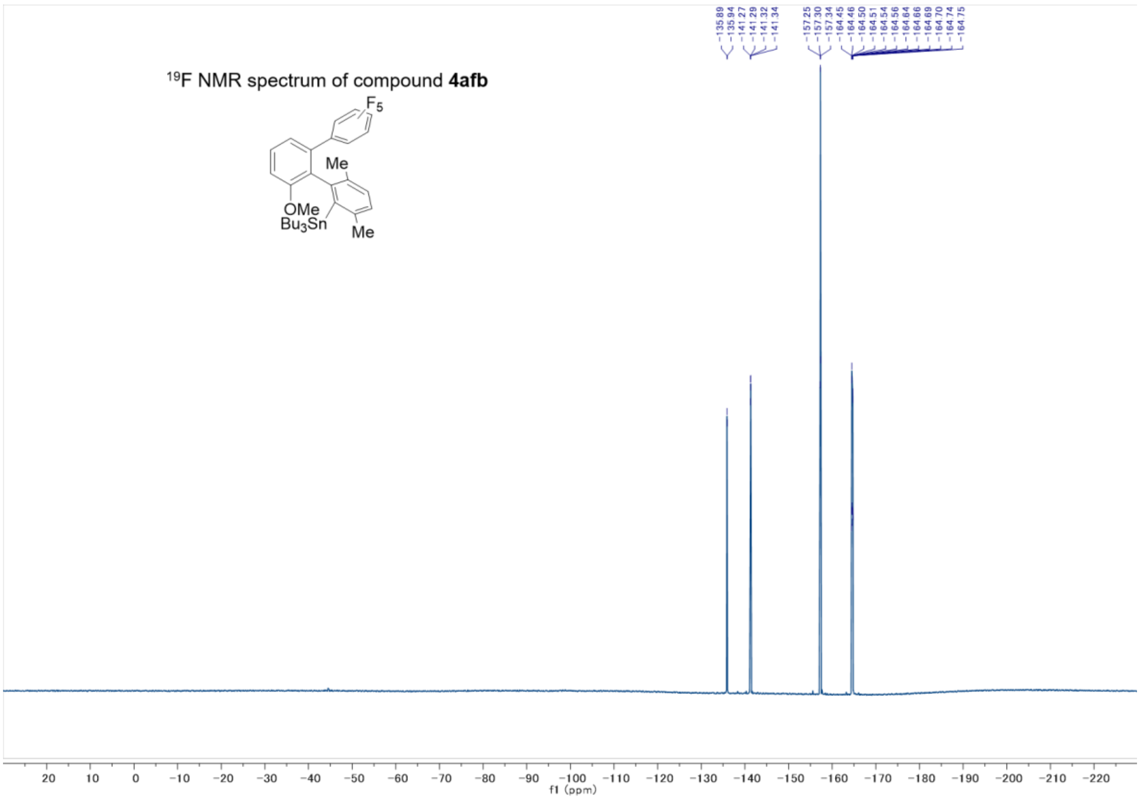
^{119}Sn NMR spectrum of compound **4aga**

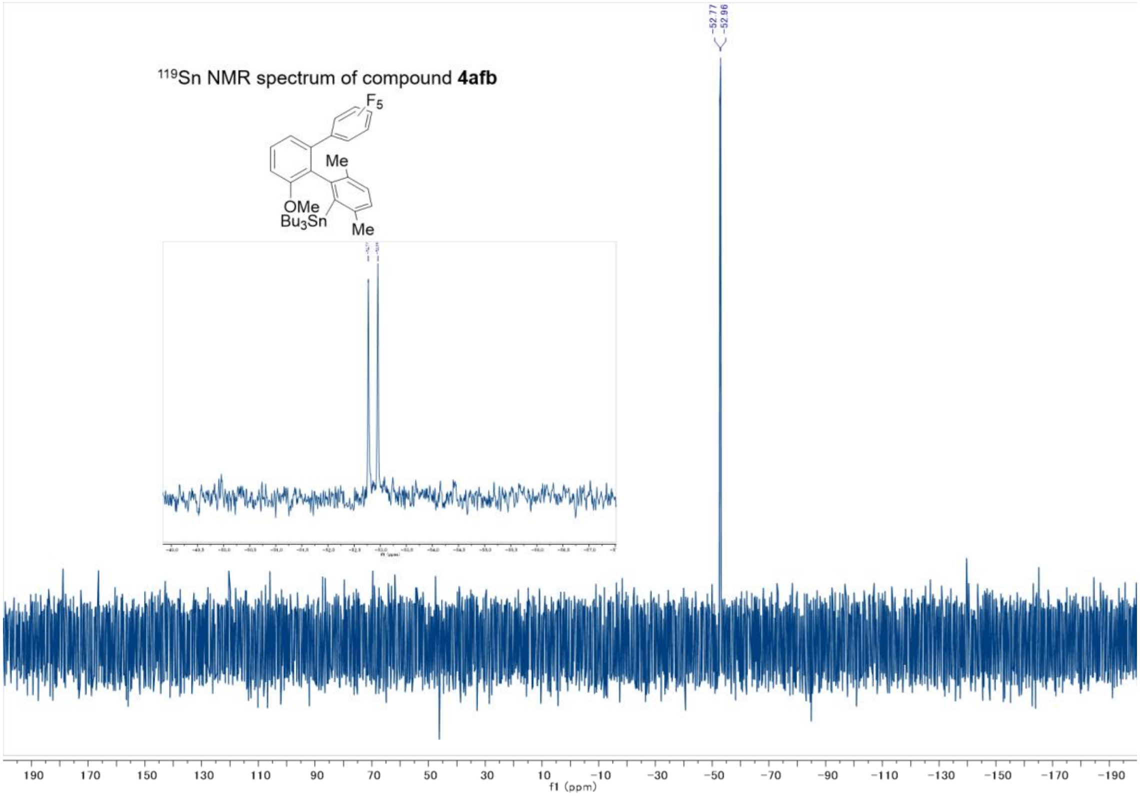


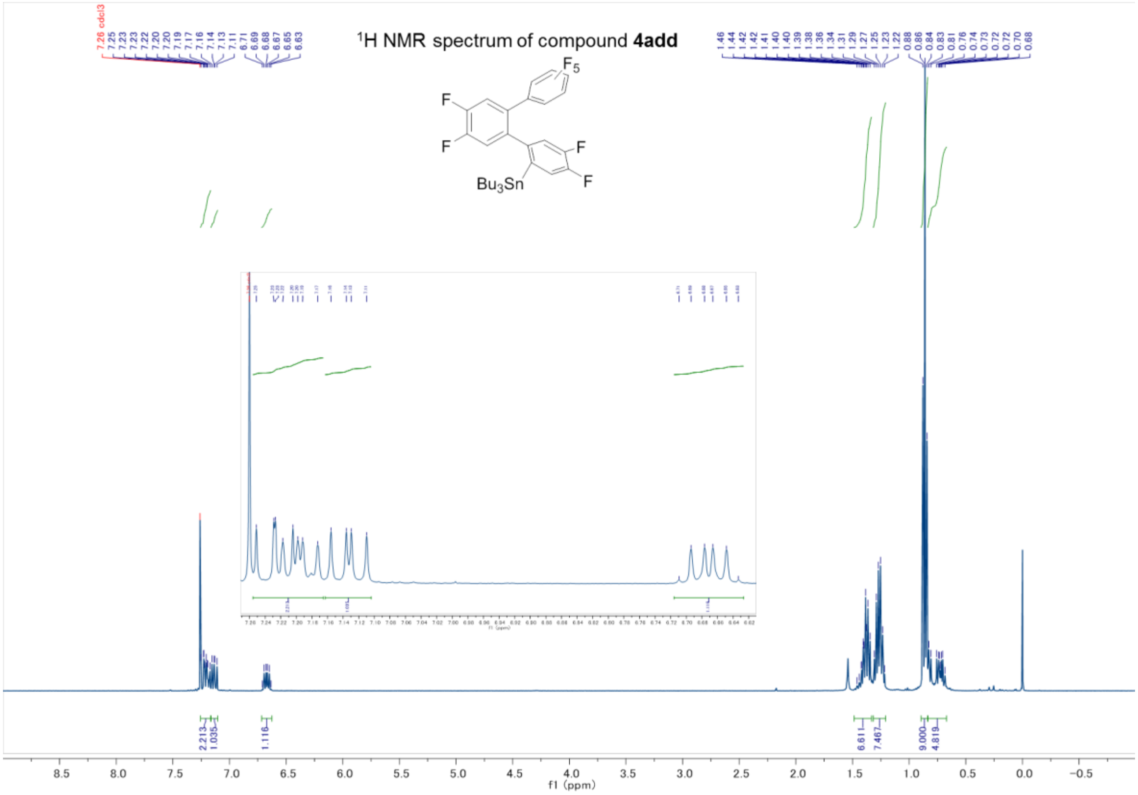
^{1}H NMR spectrum of compound **4afb**

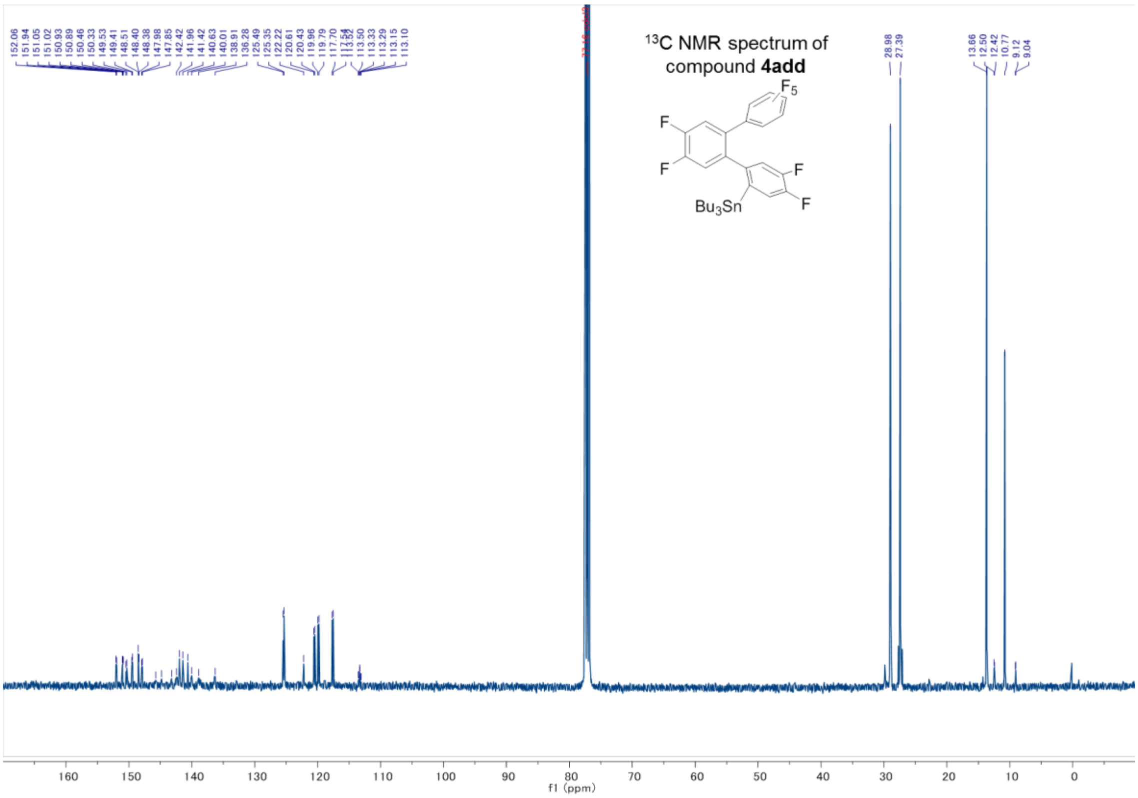

157.85
145.19
144.83
144.55
144.51
143.26
142.86
142.52
141.30
141.26
139.25
138.21
136.22
133.79
133.30
129.60
128.80
128.57
128.37
123.41
115.75
115.72
115.59
115.57
115.44
115.42
111.86
55.65
29.15
27.57
24.78
19.86
19.82
13.76
12.76
12.73
12.70
12.67
11.42
11.39
10.14
10.11
10.08
10.05
^{13}C NMR spectrum of compound **4afb**
F5
Me
OMe
Bu3Sn
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

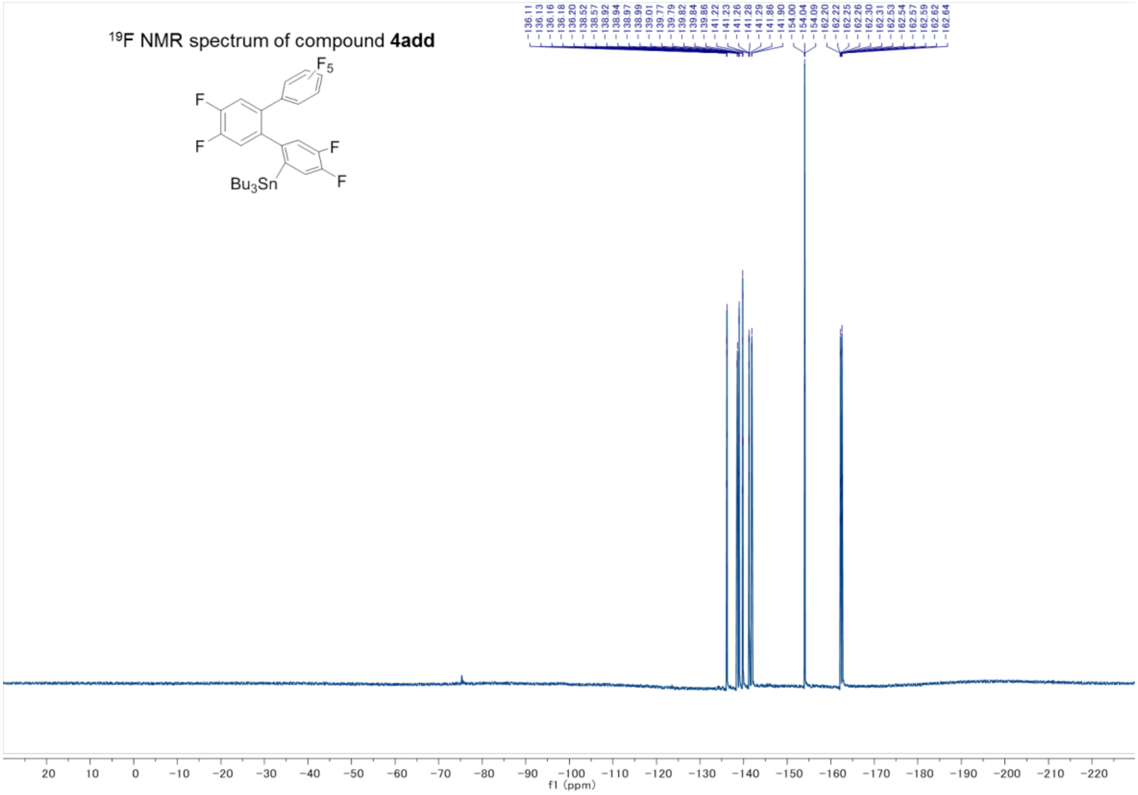

144.55
144.51
^{13}C NMR spectrum of compound **4afb**
F5
Me
OMe
Bu3Sn
Me
148.5
148.0
147.5
147.0
146.5
146.0
145.5
145.0
144.5
144.0
143.5
143.0
142.5
142.0
141.5
141.0
140.5
f1 (ppm)


-135.89
-135.94
-141.27
-141.29
-141.32
-141.34
-157.25
-157.30
-157.34
-164.45
-164.46
-164.50
-164.51
-164.54
-164.56
-164.64
-164.66
-164.69
-164.70
-164.74
-164.75
^{19}F NMR spectrum of compound **4afb**
F5
Me
OMe
Bu3Sn
Me
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

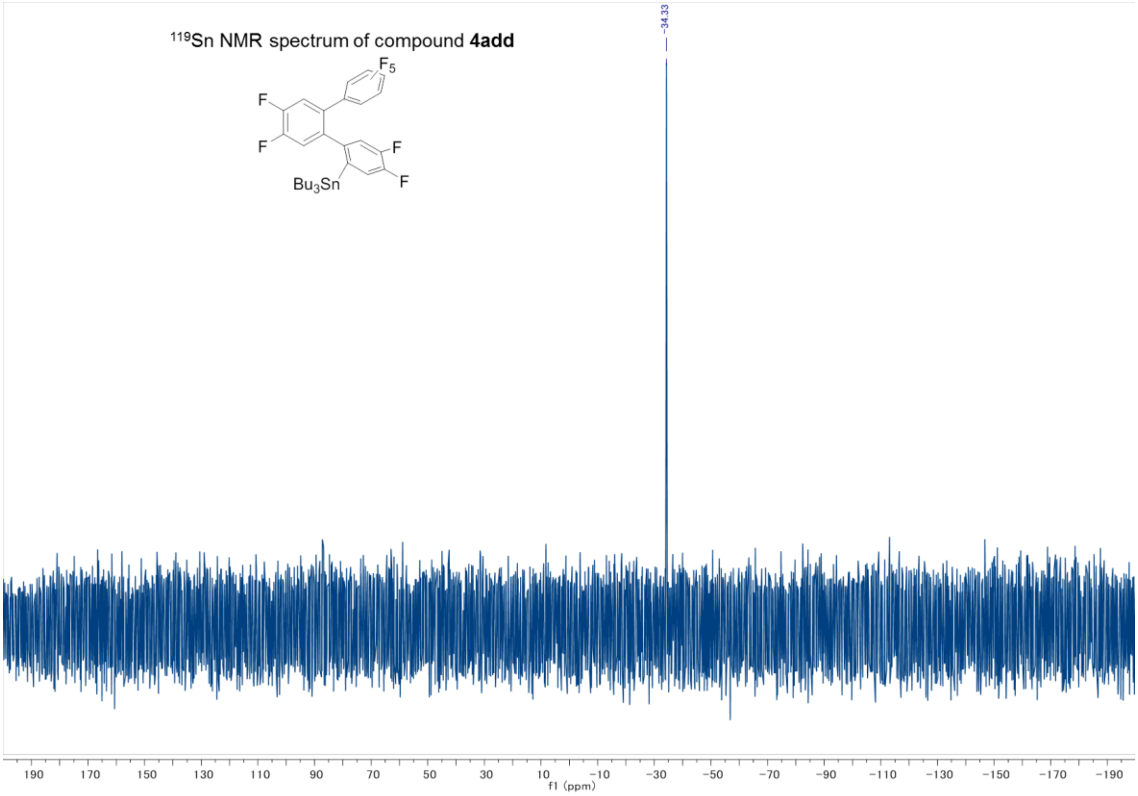

-52.77
-52.96
^{119}Sn NMR spectrum of compound **4afb**
F5
Me
OMe
Bu3Sn
Me
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)


¹H NMR spectrum of compound **4add**
F
F
F5
F
F
Bu3Sn
7.26 cdcl3
7.25 7.23 7.23 7.22 7.20 7.20 7.19 7.17 7.16 7.14 7.13 7.11 6.71 6.69 6.68 6.67 6.65 6.63
1.46 1.44 1.42 1.42 1.41 1.40 1.40 1.39 1.38 1.36 1.34 1.31 1.29 1.27 1.25 1.23 1.22 0.88 0.86 0.84 0.83 0.81 0.76 0.74 0.73 0.72 0.72 0.70 0.68
2.213 1.035 1.116 6.611 7.467 9.000 4.819
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

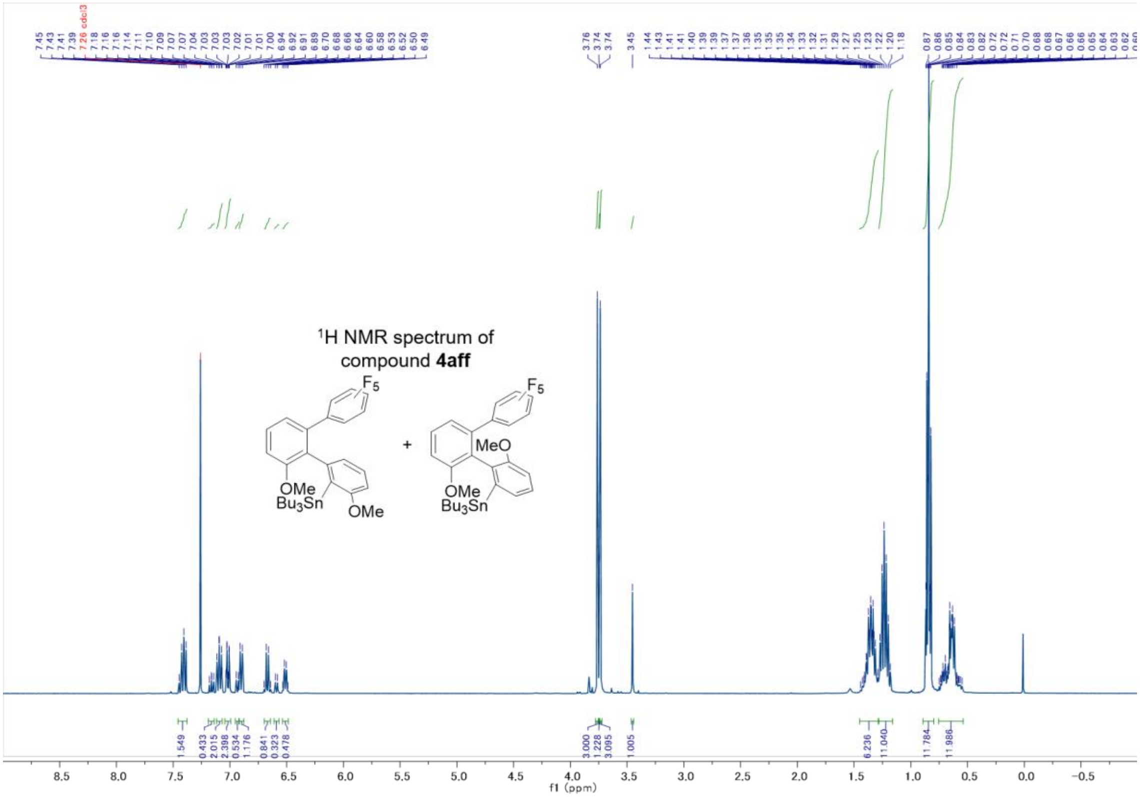

¹³C NMR spectrum of compound **4add**
F
F
F5
F
F
Bu3Sn
152.06 151.94 151.05 151.02 150.93 150.89 150.46 150.33 149.53 149.41 148.51 148.40 148.38 147.98 147.85 142.42 141.96 141.42 140.63 140.01 138.91 136.28 125.49 125.35 122.22 120.61 120.43 119.96 119.79 117.70 117.54 113.52 113.50 113.33 113.29 113.15 113.10
28.98 27.39
13.66 12.50 12.42 10.77 9.12 9.04
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

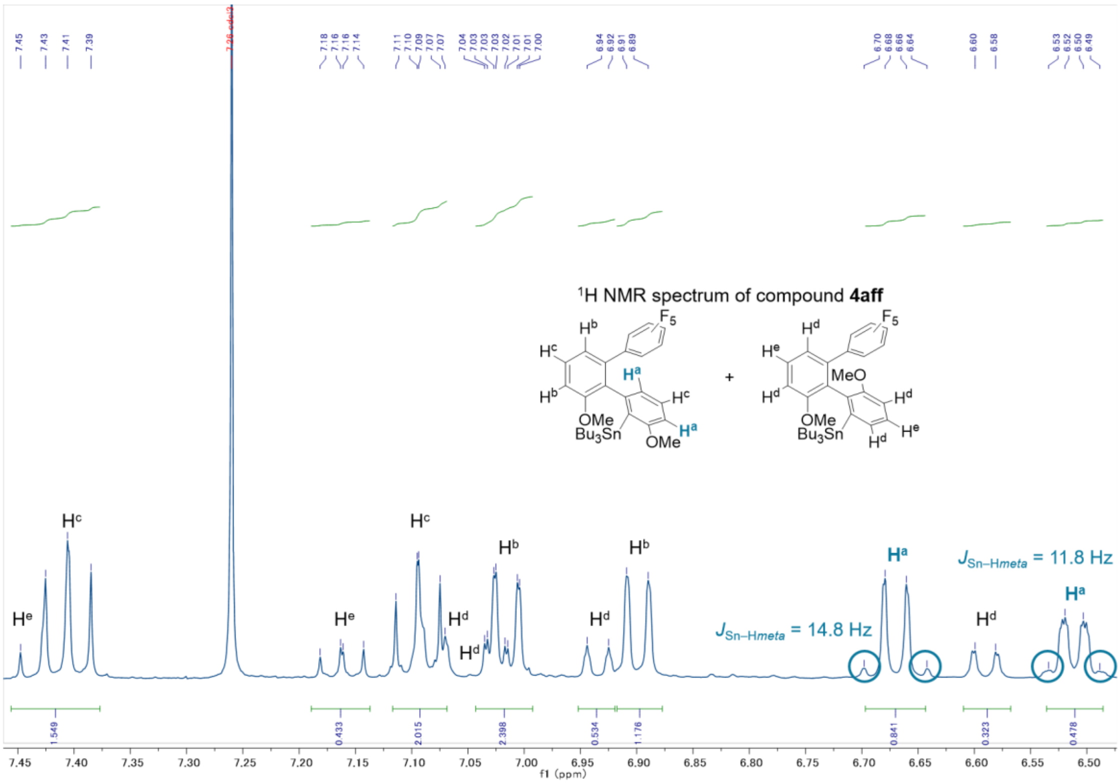


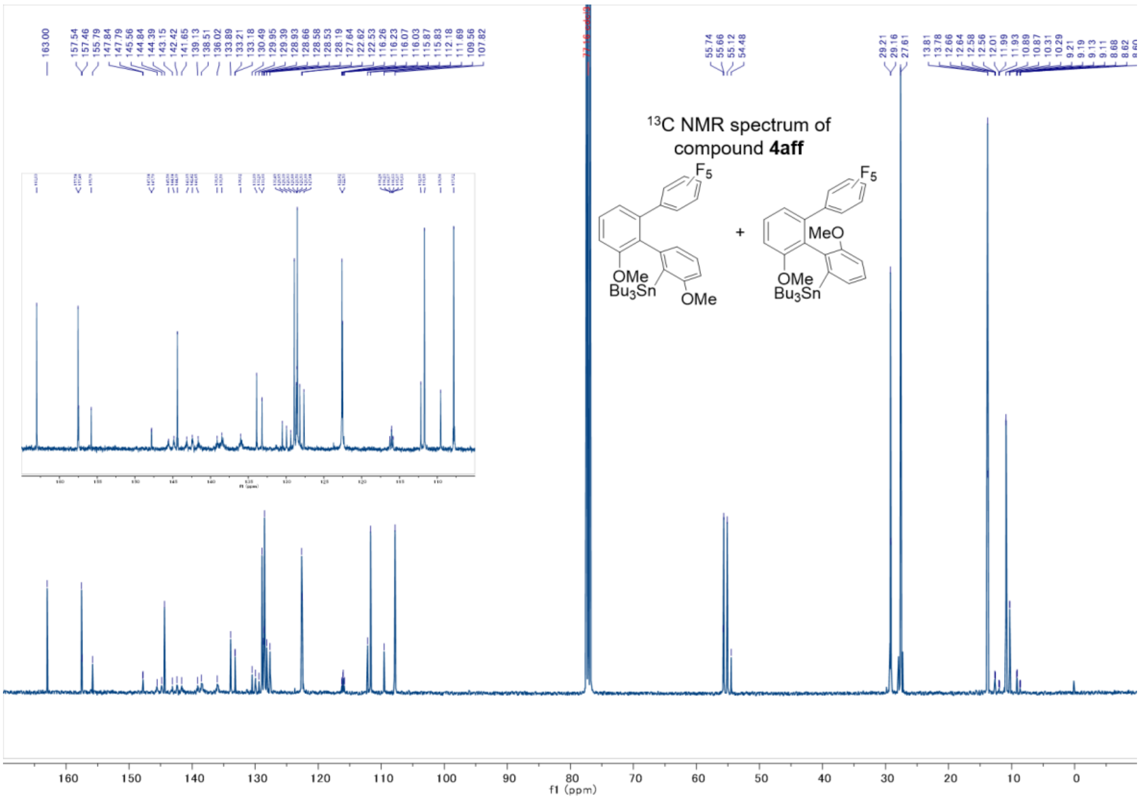
^{19}F NMR spectrum of compound **4add**

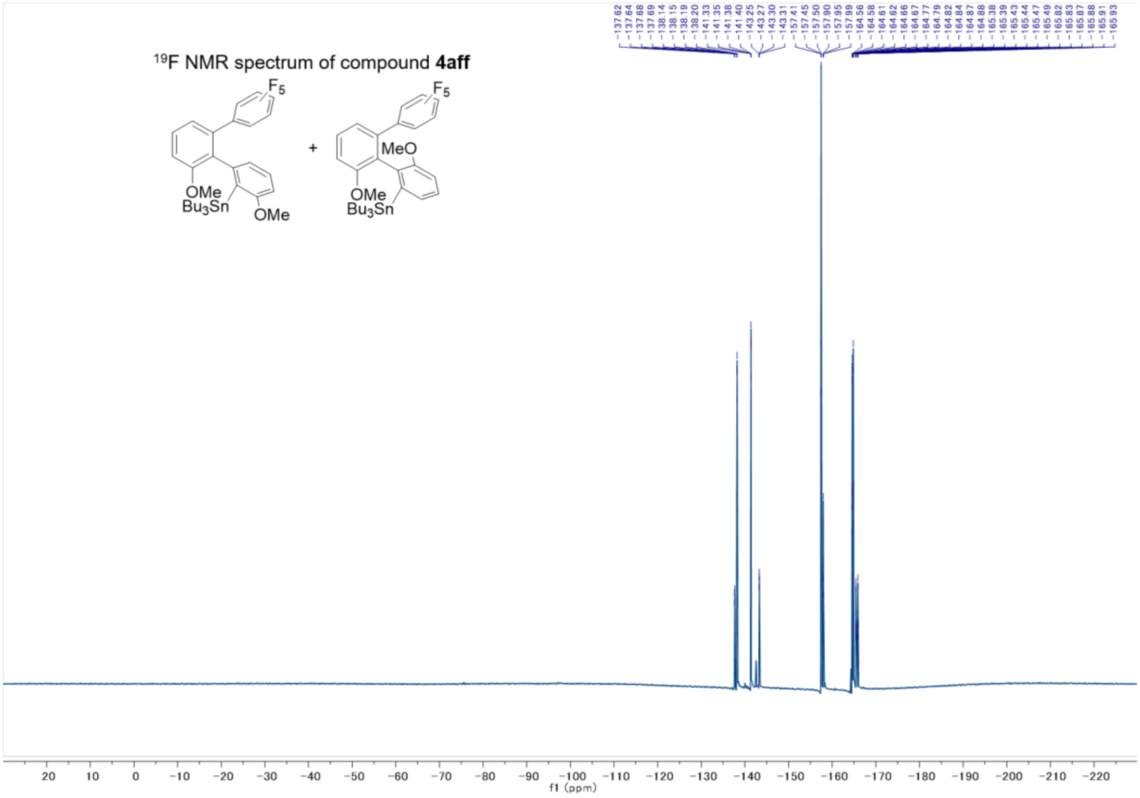


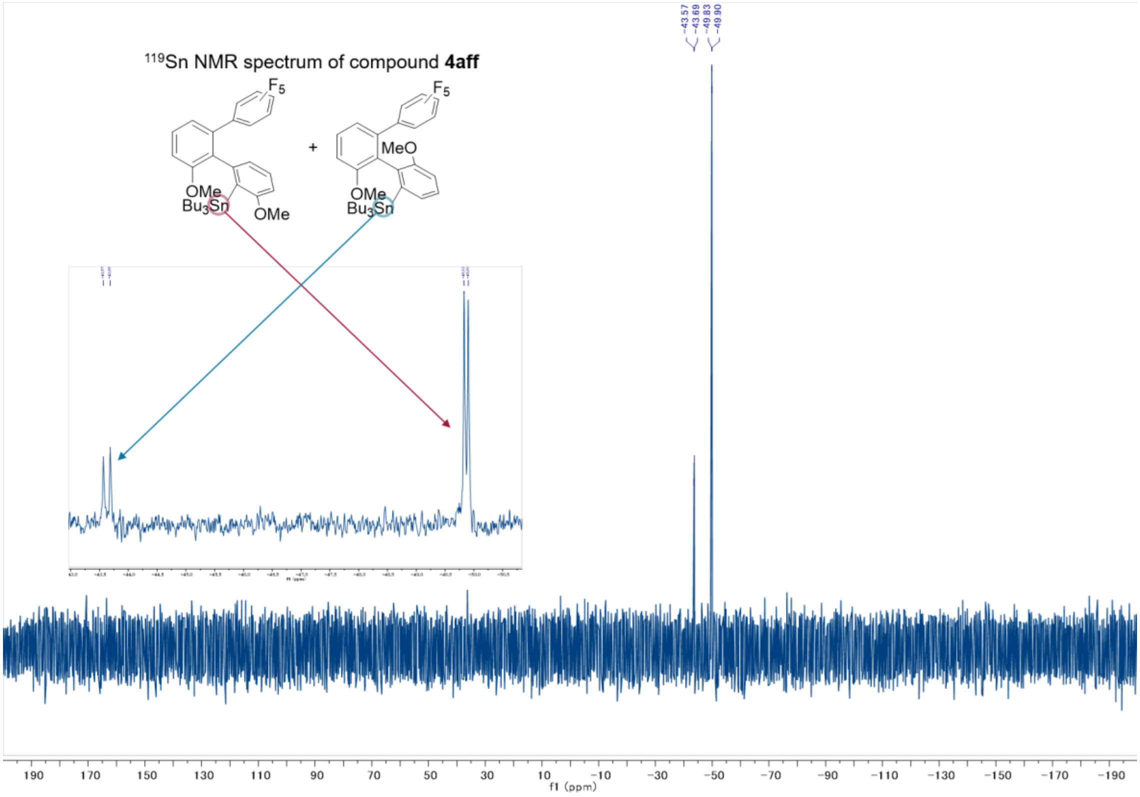
^{119}Sn NMR spectrum of compound **4add**


1H NMR spectrum of compound 4aff
F5
OMe
Bu3Sn
OMe
+
F5
MeO
OMe
Bu3Sn
1.549
0.433
2.015
2.398
0.534
1.176
0.841
0.323
0.478
3.000
1.228
3.095
1.005
6.236
11.040
11.784
11.986
f1 (ppm)

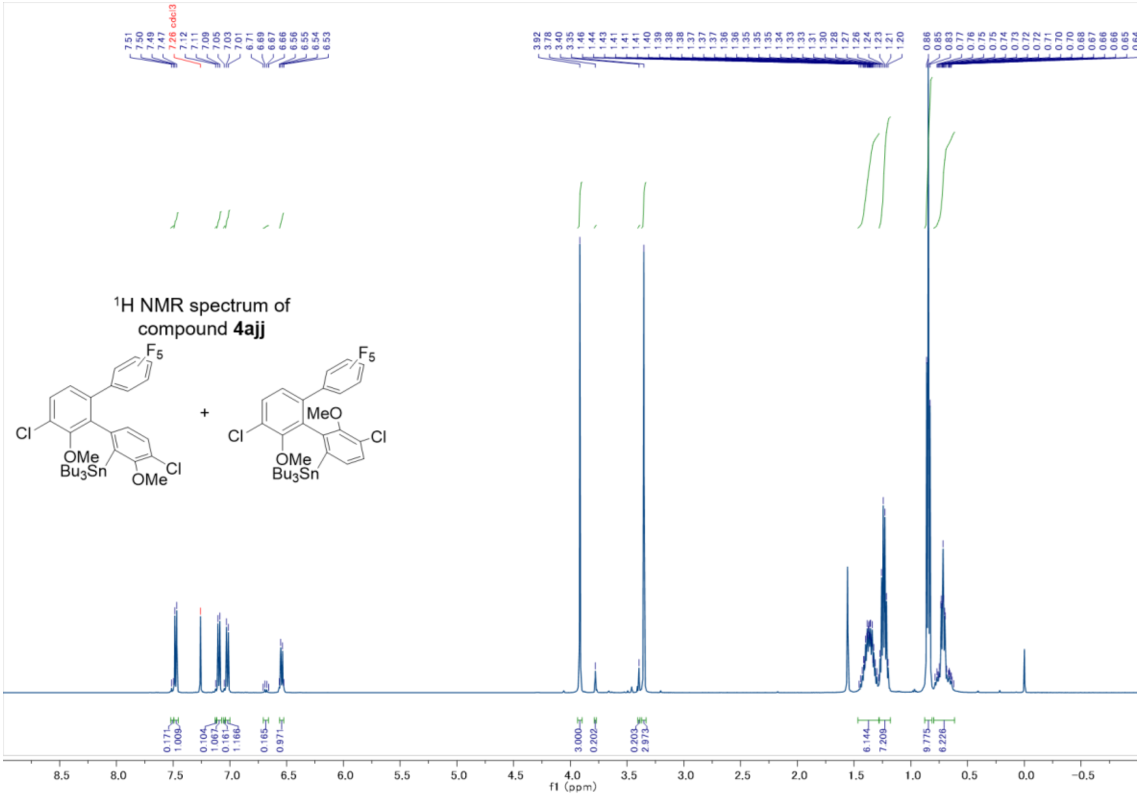

1H NMR spectrum of compound 4aff
Hb
Hc
Hb
Ha
Hc
Ha
F5
OMe
Bu3Sn
OMe
+
Hd
He
Hd
F5
MeO
Hd
He
Hd
OMe
Bu3Sn
He
Hc
He
Hc
Hd
Hd
Hb
Hd
Hb
Ha
JSn–Hmeta = 14.8 Hz
Hd
JSn–Hmeta = 11.8 Hz
Ha
1.549
0.433
2.015
2.398
0.534
1.176
0.841
0.323
0.478
f1 (ppm)


13C NMR spectrum of compound 4aff
163.00
157.54
157.46
155.79
147.84
147.79
145.56
144.84
144.39
143.15
142.42
141.65
139.13
138.51
136.02
133.89
133.21
133.18
130.49
129.95
129.39
128.93
128.66
128.58
128.53
128.19
127.64
122.62
122.53
116.26
116.23
116.07
116.03
115.87
115.83
112.18
111.89
109.56
107.82
55.74
55.66
55.12
54.48
29.21
29.16
27.61
13.81
13.78
12.66
12.64
12.58
12.56
12.01
11.99
11.93
10.89
10.87
10.31
10.29
9.21
9.19
9.13
9.11
8.68
8.62
F5
OMe
Bu3Sn
OMe
+
MeO
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

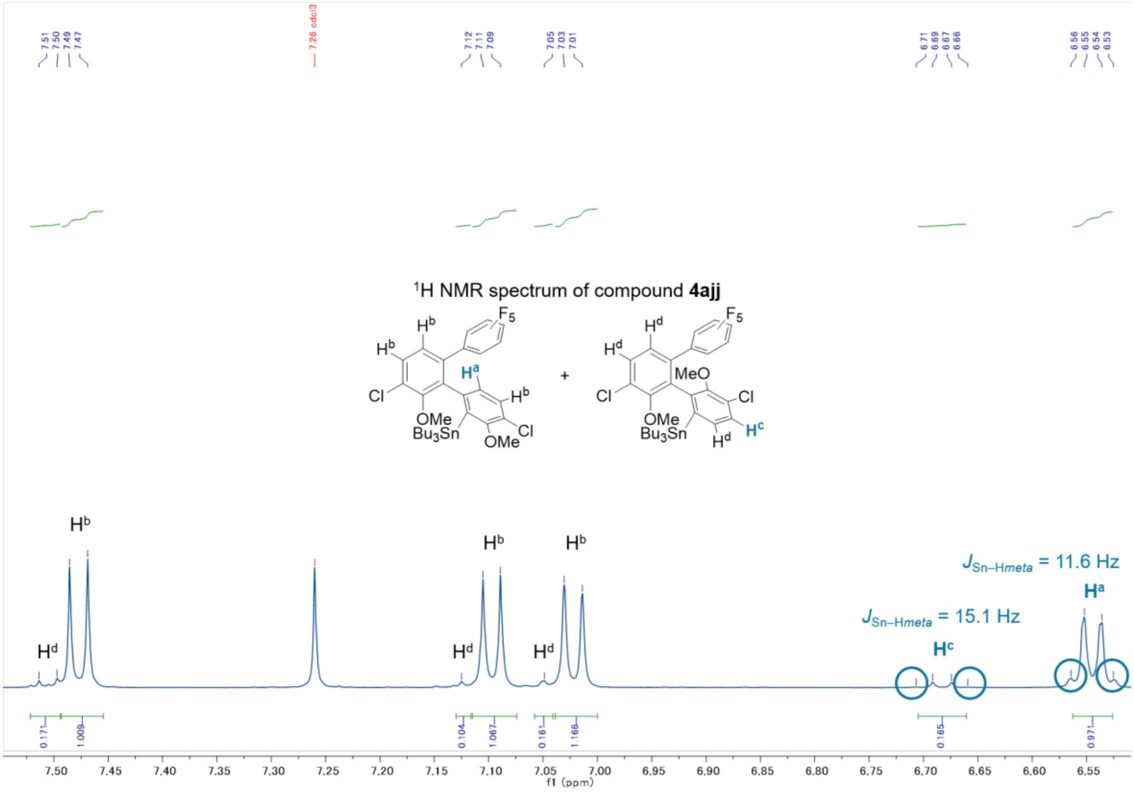

19F NMR spectrum of compound 4aff
-137.62
-137.64
-137.68
-137.69
-138.14
-138.15
-138.19
-138.20
-141.33
-141.35
-141.38
-141.40
-143.25
-143.27
-143.30
-143.31
-157.41
-157.45
-157.50
-157.90
-157.95
-157.99
-164.56
-164.58
-164.61
-164.62
-164.66
-164.67
-164.77
-164.79
-164.82
-164.84
-164.87
-164.88
-165.38
-165.39
-165.43
-165.44
-165.47
-165.49
-165.82
-165.83
-165.87
-165.88
-165.91
-165.93
F5
OMe
Bu3Sn
OMe
+
MeO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

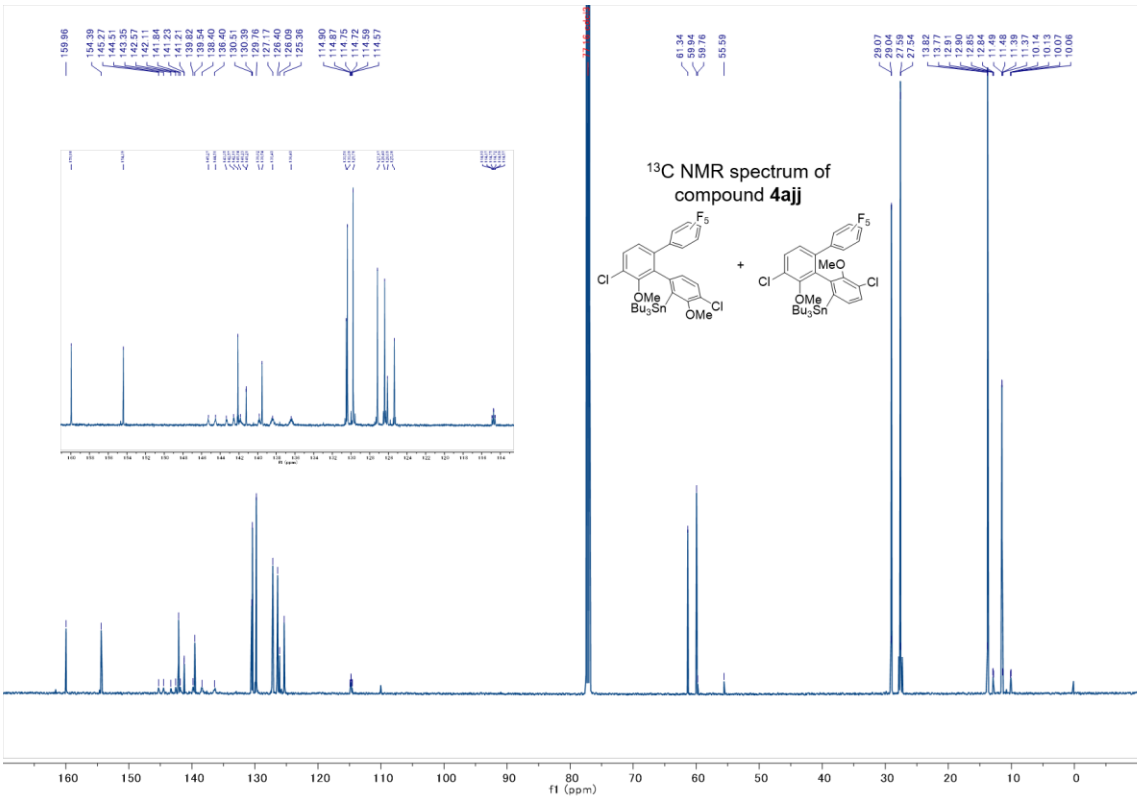


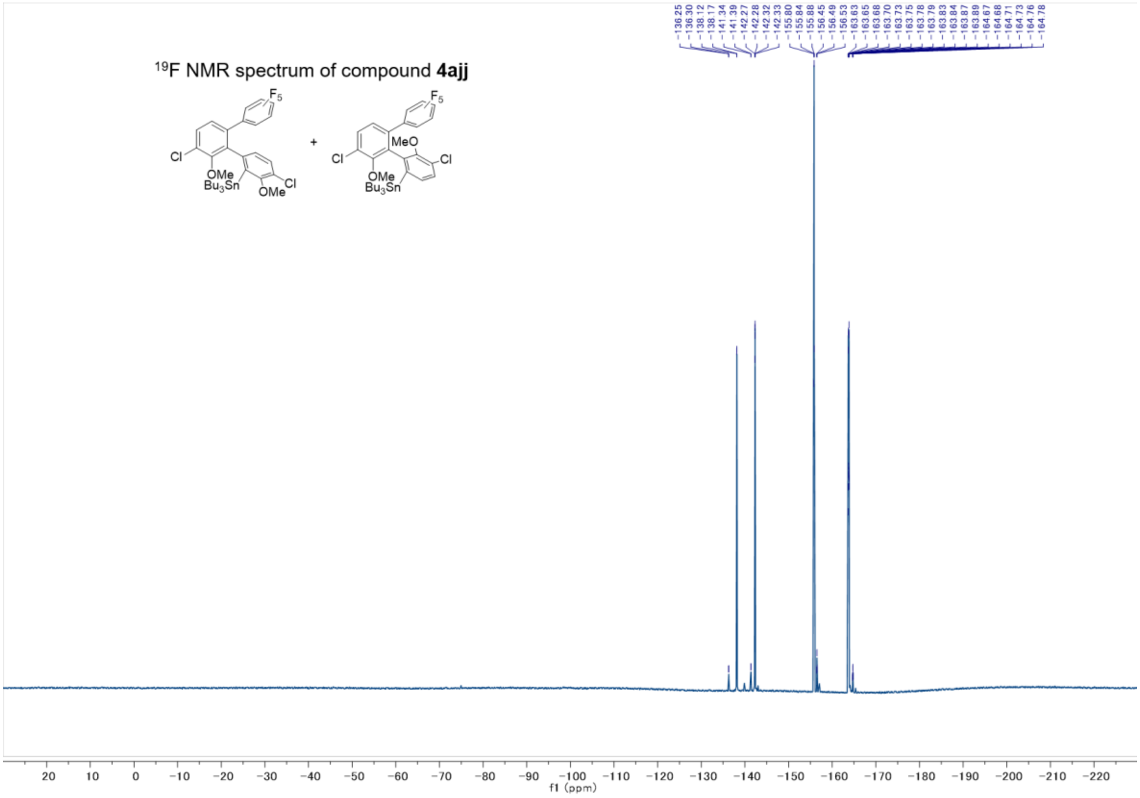
^{119}Sn NMR spectrum of compound **4aff**
F5
OMe
Bu3Sn
OMe
+
F5
MeO
OMe
Bu3Sn
-43.57
-43.89
-49.83
-49.90
190
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

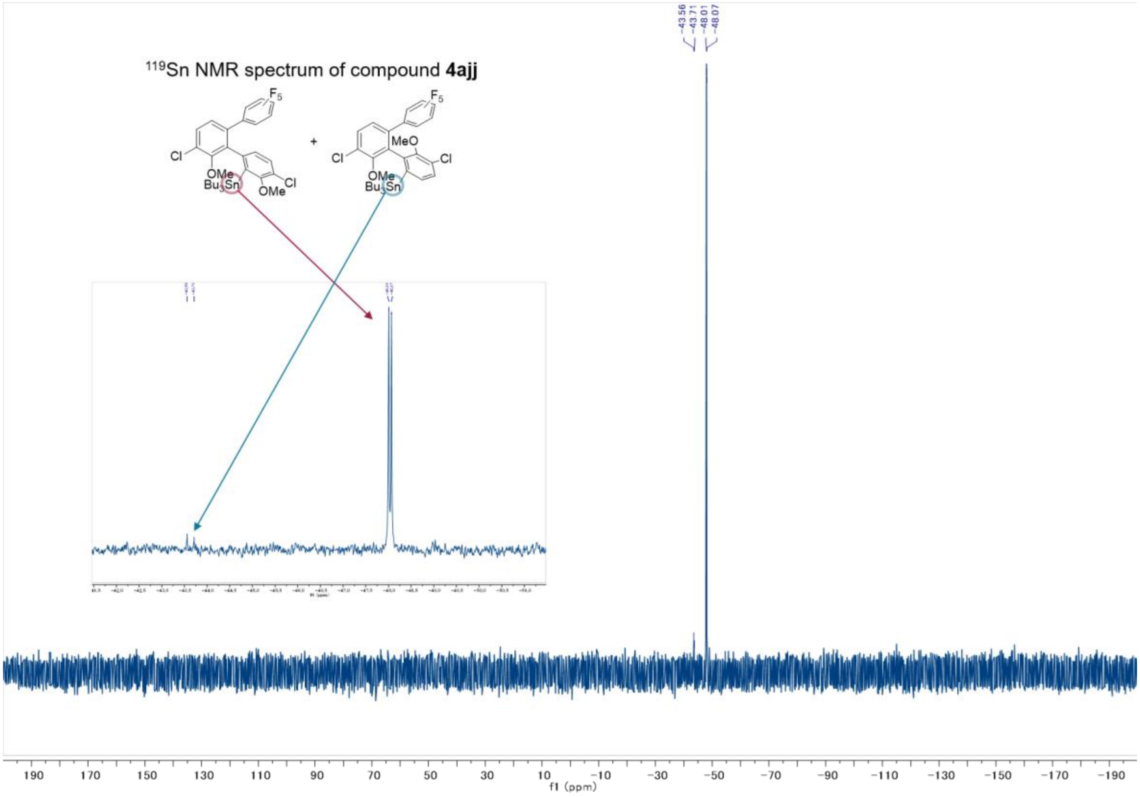


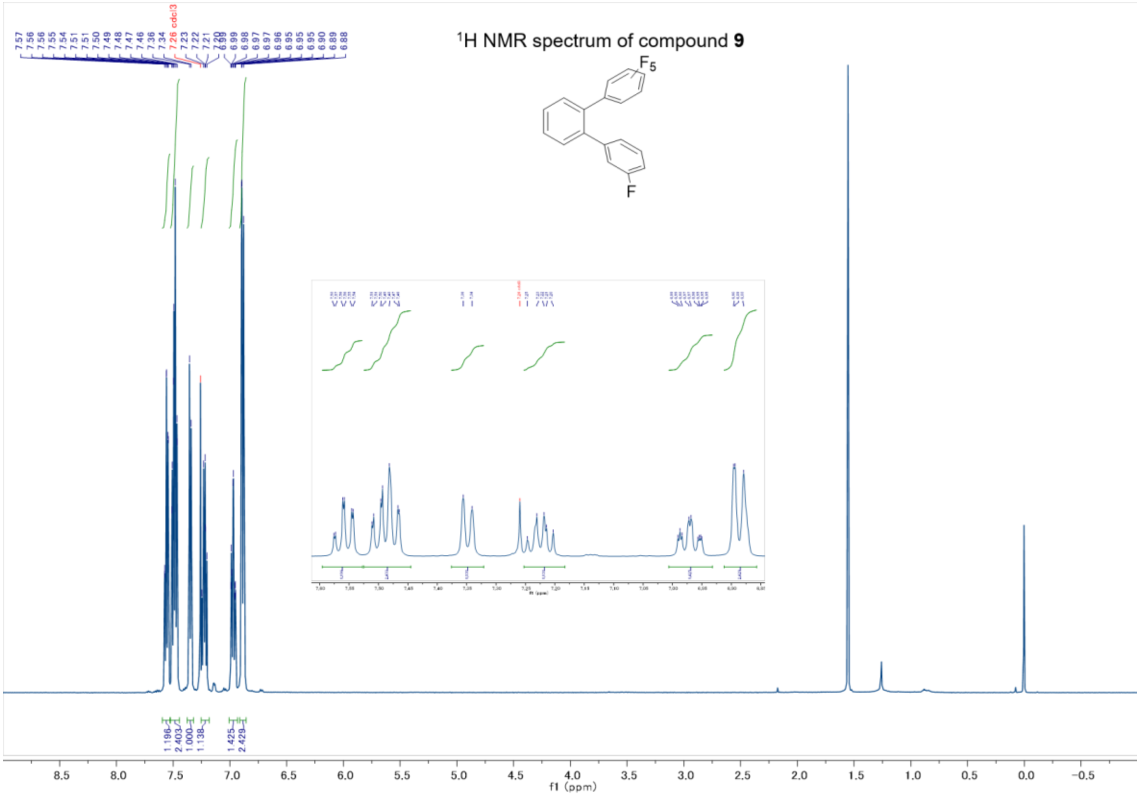
^{1}H NMR spectrum of compound **4ajj**
F5
Cl
OMe
Bu3Sn
OMe
Cl
+
F5
Cl
MeO
Cl
OMe
Bu3Sn
7.51
7.50
7.49
7.47
7.26 cdcl3
7.12
7.11
7.09
7.05
7.03
7.01
6.71
6.69
6.67
6.66
6.56
6.55
6.54
6.53
3.92
3.78
3.40
3.35
1.46
1.44
1.43
1.41
1.41
1.40
1.39
1.38
1.38
1.37
1.37
1.37
1.36
1.36
1.35
1.35
1.35
1.34
1.33
1.33
1.31
1.30
1.28
1.27
1.26
1.24
1.23
1.21
1.20
0.86
0.85
0.83
0.77
0.76
0.75
0.75
0.74
0.73
0.72
0.72
0.71
0.70
0.70
0.68
0.67
0.66
0.66
0.65
0.171
1.009
0.104
0.067
0.161
1.166
0.165
0.971
3.000
0.202
0.203
2.973
6.144
7.209
9.775
6.226
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


7.51
7.50
7.49
7.47
7.26 cdcl3
7.12
7.11
7.09
7.05
7.03
7.01
6.71
6.69
6.67
6.66
6.56
6.55
6.54
6.53
^{1}H NMR spectrum of compound **4ajj**
H^b
H^b
F$_5$
H^a
H^b
Cl
OMe
Bu$_3$Sn
OMe
Cl
+
H^d
H^d
F$_5$
MeO
Cl
Cl
OMe
Bu$_3$Sn
H^c
H^d
H^d
H^b
H^d
H^b
H^d
H^b
$J_{Sn-Hmeta}$ = 11.6 Hz
H^a
$J_{Sn-Hmeta}$ = 15.1 Hz
H^c
0.171
1.009
0.104
1.067
0.161
1.166
0.165
0.971
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
6.70
6.65
6.60
6.55
f1 (ppm)

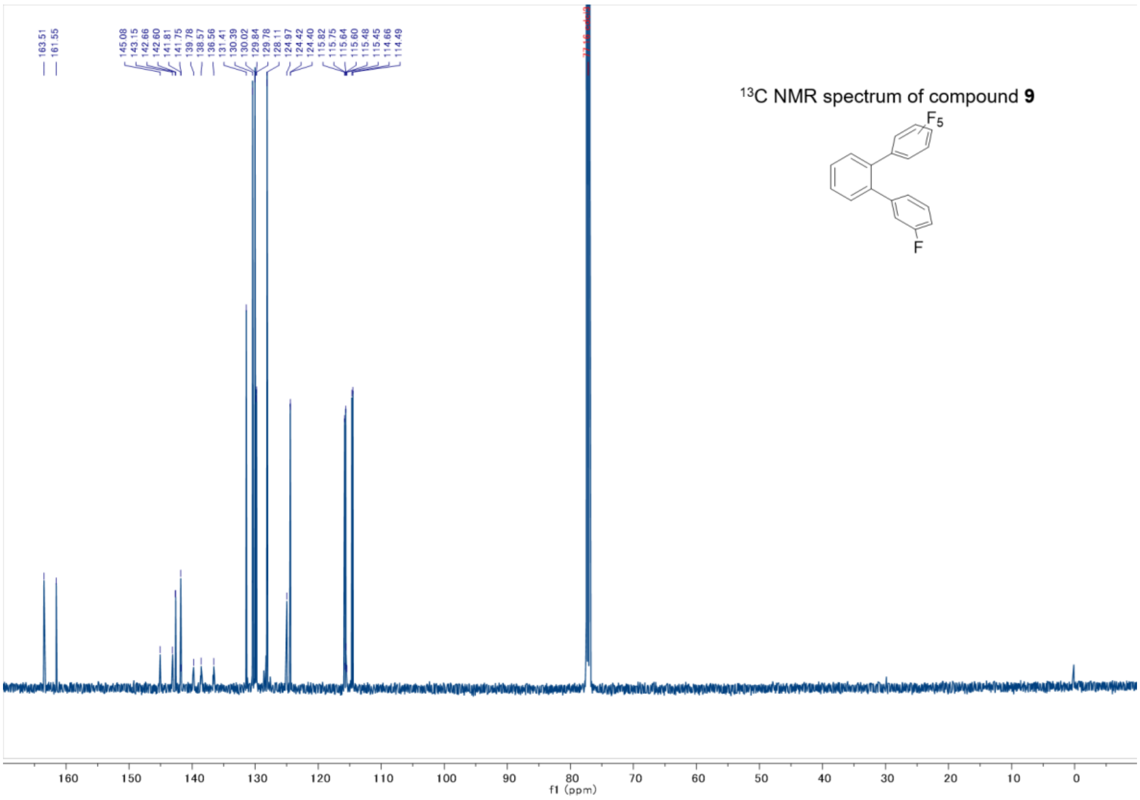

159.96
154.39
145.27
144.51
143.35
142.57
142.11
141.84
141.23
141.21
139.82
139.54
138.40
136.40
130.51
130.39
129.76
127.17
126.40
126.09
125.36
114.90
114.87
114.75
114.72
114.59
114.57
77.16 cdcl3
61.34
59.94
59.76
55.59
29.07
29.04
27.59
27.54
13.82
13.77
12.91
12.90
12.85
12.84
11.49
11.48
11.39
11.37
10.14
10.13
10.07
10.06
^{13}C NMR spectrum of compound **4ajj**
F$_5$
Cl
OMe
Bu$_3$Sn
OMe
Cl
+
F$_5$
MeO
Cl
Cl
OMe
Bu$_3$Sn
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


^{19}F NMR spectrum of compound **4ajj**
F5
Cl
OMe
Bu3Sn
OMe
Cl
+
F5
MeO
Cl
Cl
OMe
Bu3Sn
-136.25
-136.30
-138.12
-138.17
-141.34
-141.39
-142.27
-142.28
-142.32
-142.33
-155.80
-155.84
-155.88
-156.45
-156.49
-156.53
-163.63
-163.65
-163.68
-163.70
-163.73
-163.75
-163.78
-163.79
-163.83
-163.84
-163.87
-163.89
-164.67
-164.68
-164.71
-164.73
-164.76
-164.78
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

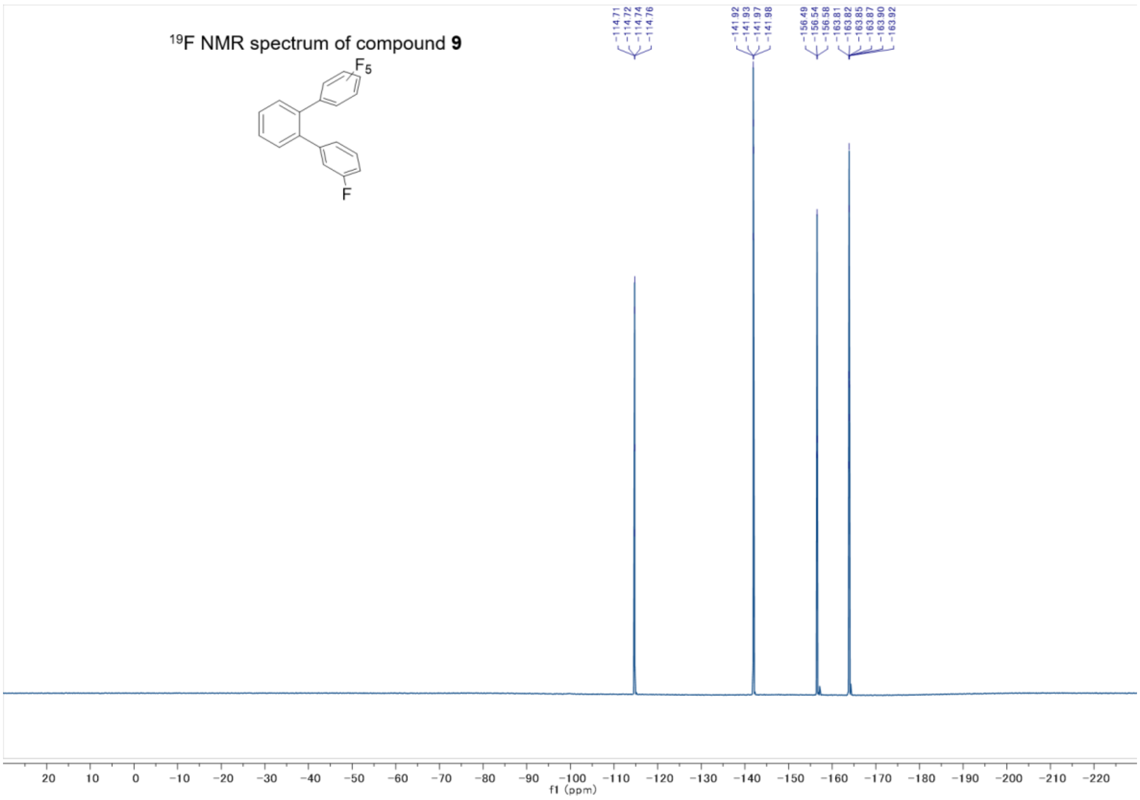

^{119}Sn NMR spectrum of compound **4ajj**
F5
Cl
OMe
Bu3Sn
OMe
Cl
+
F5
MeO
Cl
Cl
OMe
Bu3Sn
-43.56
-43.71
-48.01
-48.07
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

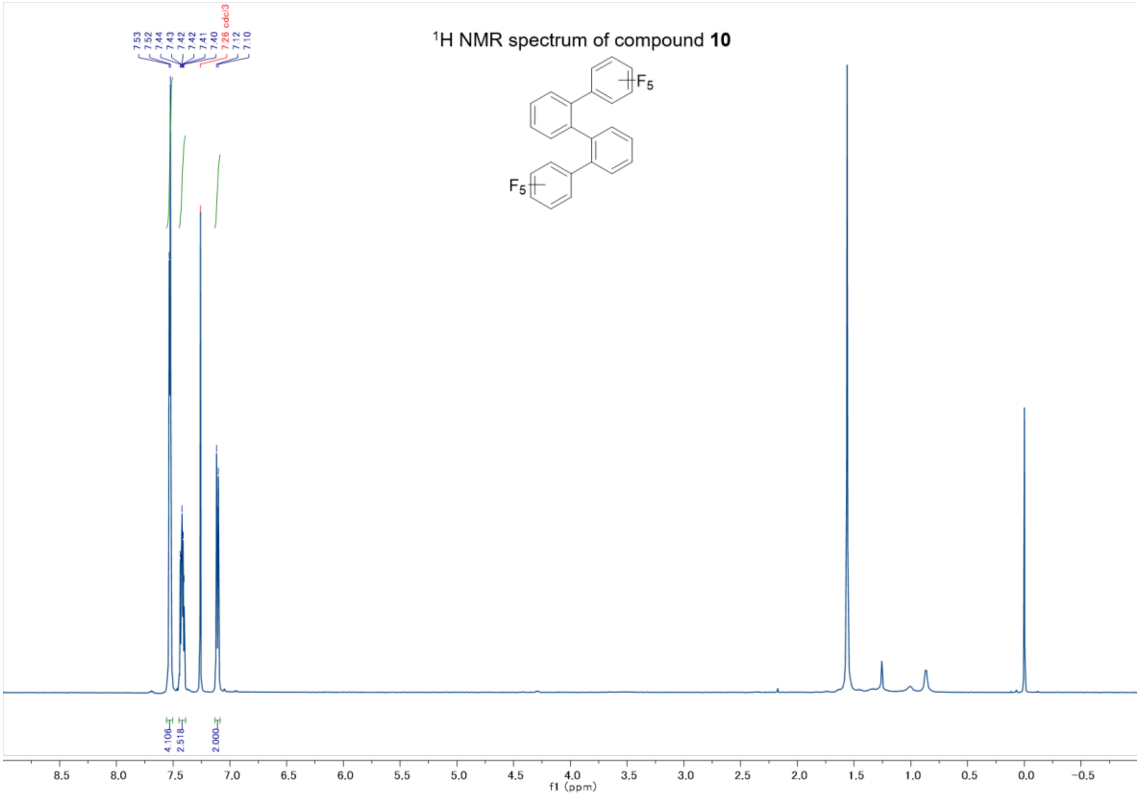


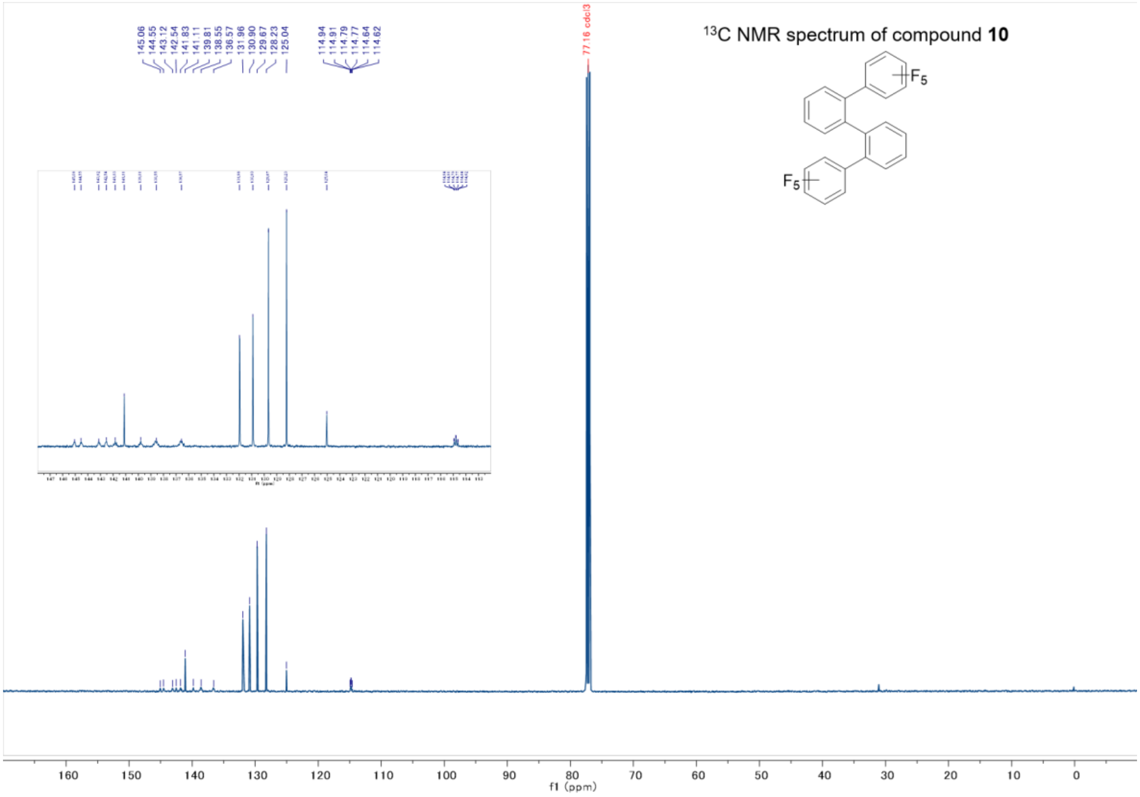
^{1}H NMR spectrum of compound **9**

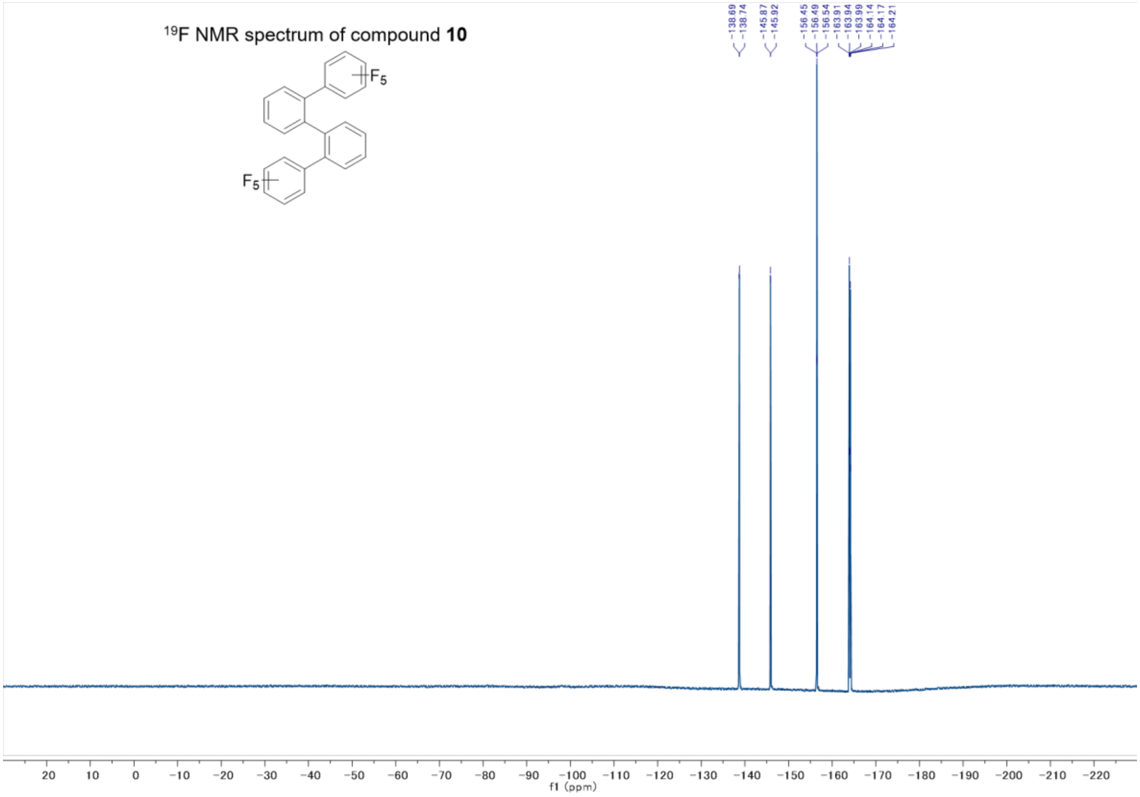


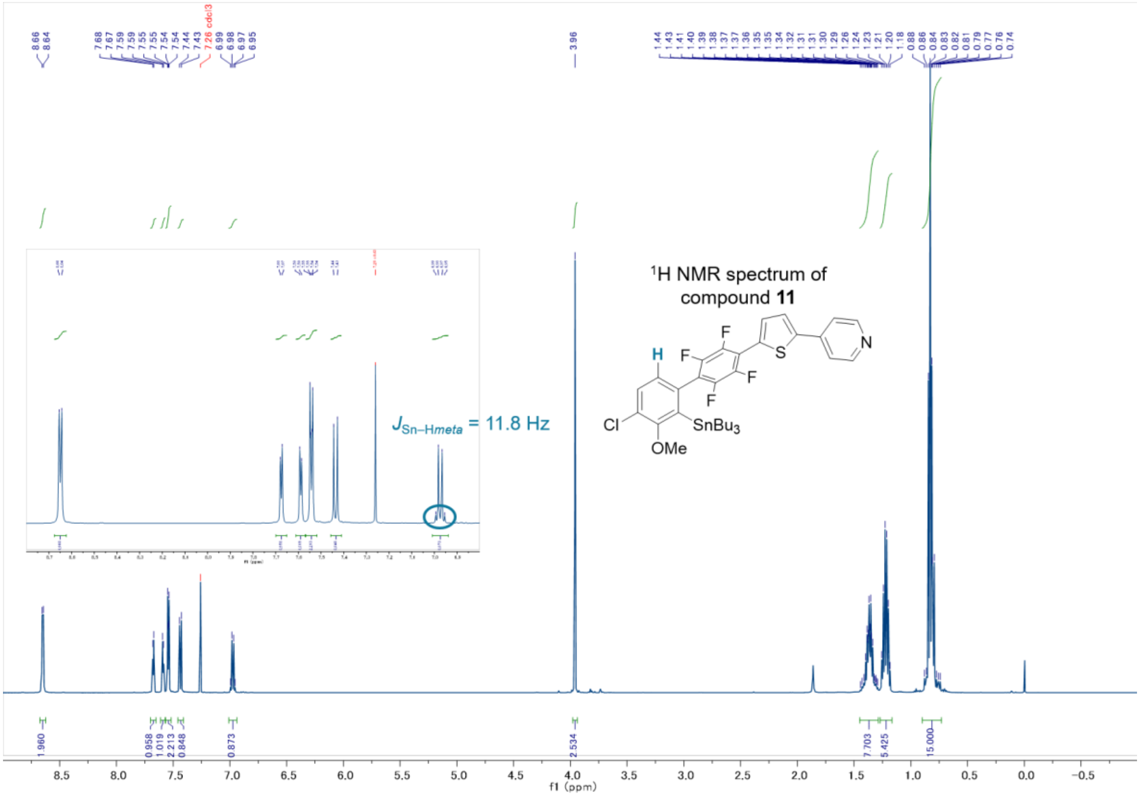
^{13}C NMR spectrum of compound **9**

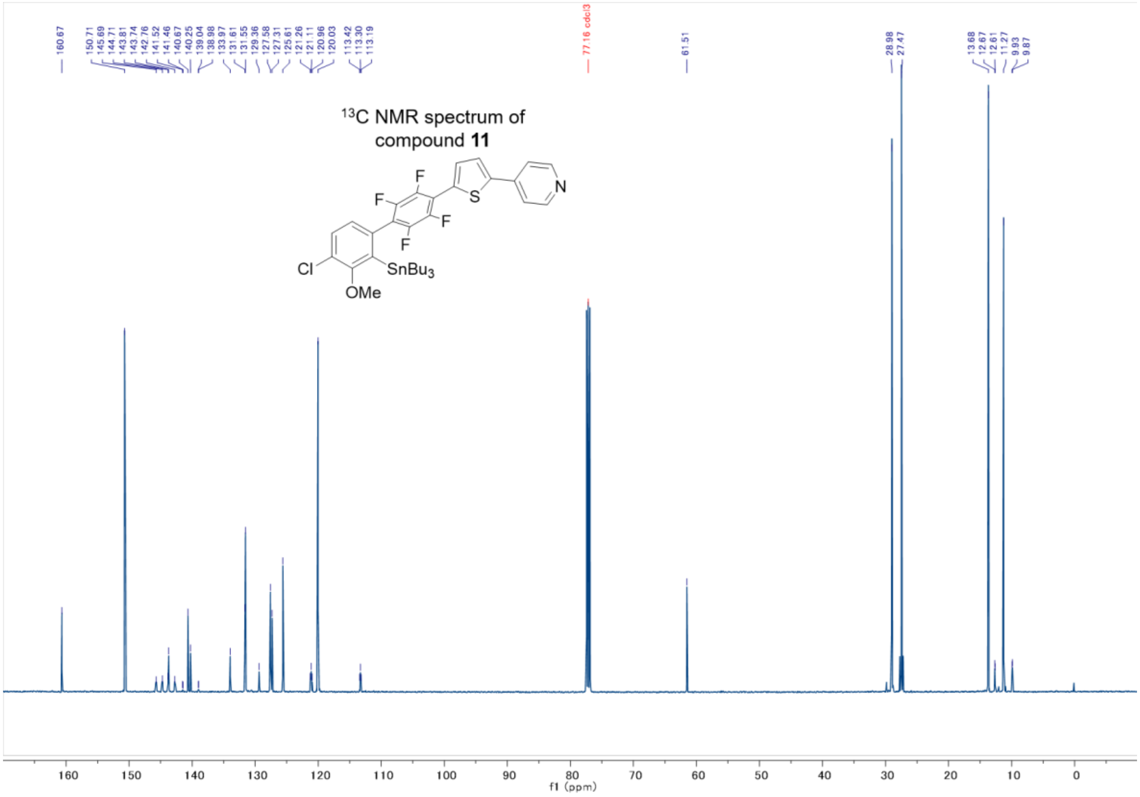

^{19}F NMR spectrum of compound **9**
F5
F
-114.71
-114.72
-114.74
-114.76
-141.92
-141.93
-141.97
-141.98
-156.49
-156.54
-156.58
-163.81
-163.82
-163.85
-163.87
-163.90
-163.92
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

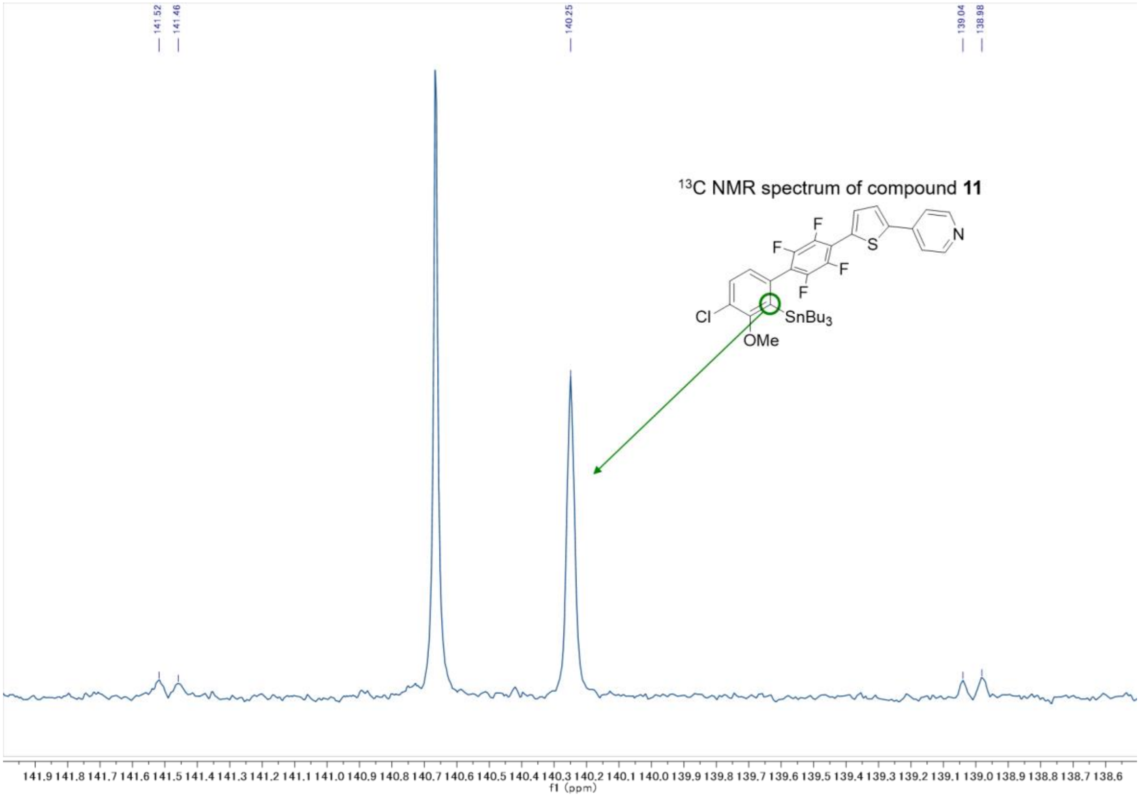

^{1}H NMR spectrum of compound **10**
F5
F5
7.53
7.52
7.44
7.43
7.42
7.42
7.41
7.40
7.26 cdcl3
7.12
7.10
4.106
2.518
2.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


145.06
144.55
143.12
142.54
141.83
141.11
139.81
138.55
136.57
131.96
130.90
129.67
128.23
125.04
114.94
114.91
114.79
114.77
114.64
114.62
77.16 cdcl3
^{13}C NMR spectrum of compound **10**
F5
F5
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

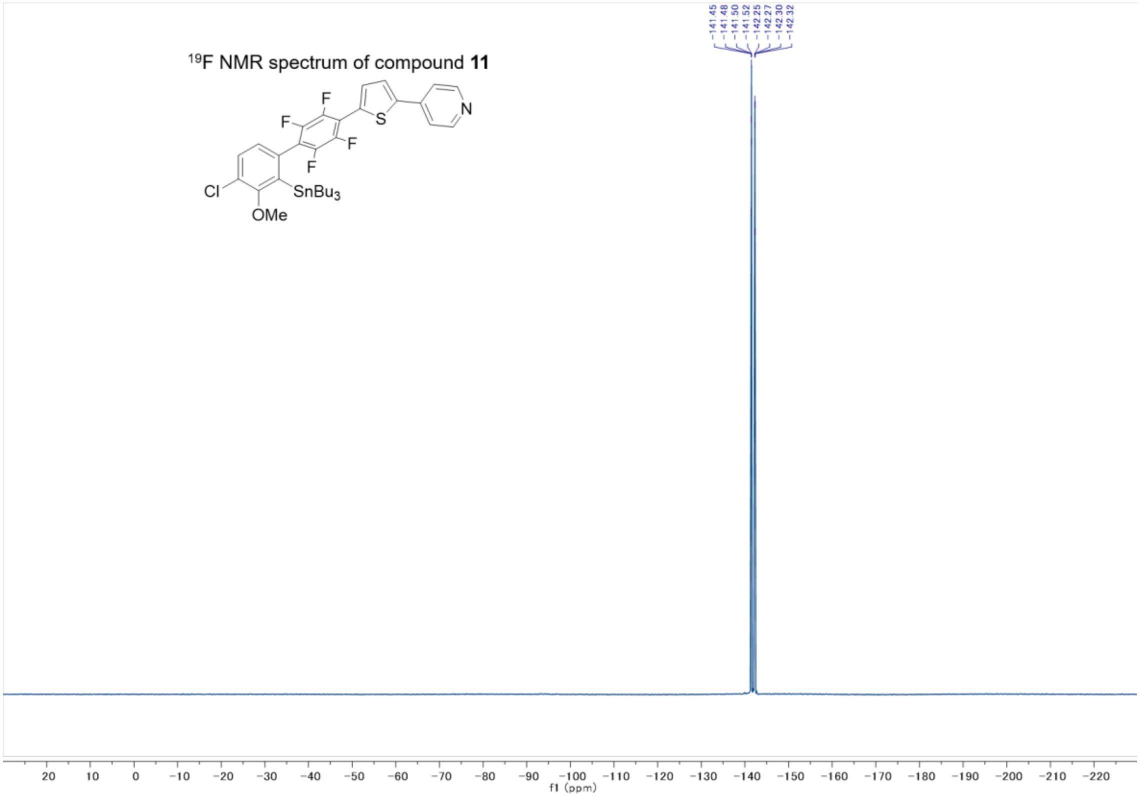

^{19}F NMR spectrum of compound **10**
F5
F5
-138.69
-138.74
-145.87
-145.92
-156.45
-156.49
-156.54
-163.91
-163.94
-163.99
-164.14
-164.17
-164.21
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


8.66
8.64
7.68
7.67
7.59
7.59
7.55
7.55
7.54
7.54
7.44
7.43
7.26 cdcl3
6.99
6.98
6.97
6.95
3.96
1.44
1.43
1.41
1.40
1.39
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.32
1.31
1.31
1.30
1.29
1.26
1.24
1.23
1.21
1.20
1.18
0.88
0.86
0.84
0.83
0.82
0.81
0.79
0.77
0.76
0.74
^{1}H NMR spectrum of compound **11**
H
F
F
F
F
S
N
Cl
SnBu$_3$
OMe
$J_{\mathrm{Sn-H}meta}$ = 11.8 Hz
1.960
0.958
1.019
2.213
0.848
0.873
2.534
7.703
5.425
15.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

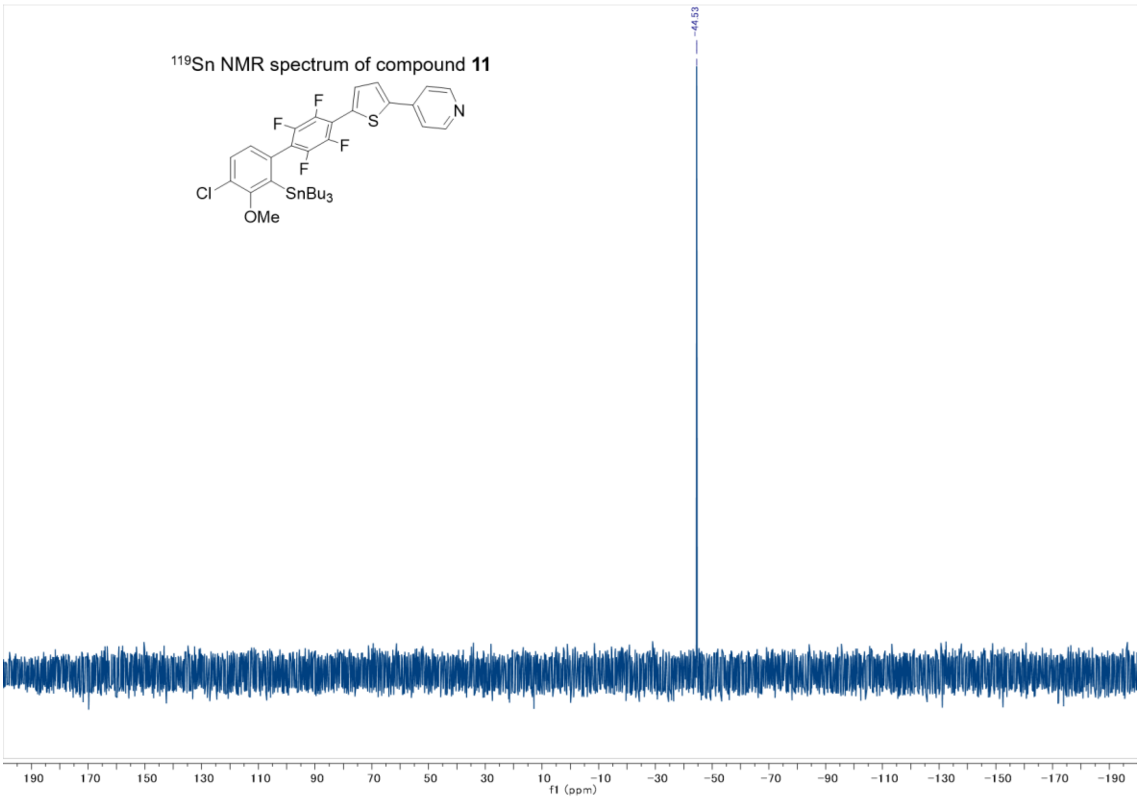

160.67
150.71
145.69
144.71
143.81
143.74
142.76
141.52
141.46
140.67
140.25
139.04
138.98
133.97
131.61
131.55
129.36
127.58
127.31
125.61
121.26
121.11
120.96
120.03
113.42
113.30
113.19
77.16 cdcl3
61.51
28.98
27.47
13.68
12.67
12.61
11.27
9.93
9.87
^{13}C NMR spectrum of compound **11**
F
F
F
F
S
N
Cl
SnBu$_3$
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{13}C NMR spectrum of compound **11**



^{19}F NMR spectrum of compound **11**



^{119}Sn NMR spectrum of compound **11**