Supplementary Information

Cross-Electrophile Stannylation of Alkyl Triflates and Halides with Chlorostannanes Enabled by Cr(II)-Phenanthroline Catalysis

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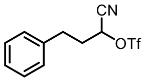
1. Methods and Materials

General. All reactions involving air- or moisture-sensitive compounds were carried out in a flame-dried and sealed Schlenk tube under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates pre-coated with silica gel (0.25 mm, 230–400 mesh) containing a fluorescent indicator (Merck). Visualization was achieved by exposure to UV light or by staining with phosphomolybdic acid hydrate or $KMnO_4$ solutions, followed by heating as necessary. Flash silica gel column chromatography was performed on silica gel 60 N (spherical and neutral, 140–325 mesh). NMR spectra were recorded on a Bruker AVANCE III HD spectrometer and reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ and referenced internally to tetramethylsilane as standard. ^{13}C NMR spectra were recorded at 100 MHz and referenced to the deuterated solvent resonance. ^{19}F NMR spectra were recorded at 376 MHz and not calibrated by an internal reference. ^{31}P NMR spectra were recorded at 162 MHz. Melting points were determined using a Hanon Instruments MP-300 apparatus. GC-MS spectra were recorded on an Agilent Technologies 7890B GC-system with an Agilent 5977B MSD and a HP–5MS column (0.25 mm × 30 m × 0.25 μm). High-resolution mass spectra (HRMS) were recorded on an Exactive Mass Spectrometer (X500R, USA) equipped with an ESI ionization source and a TOF mass analyzer. X-ray photoelectron spectroscopy (XPS) was performed on a AXIS SUPRA^{+} spectrometer. Cyclic voltammetry (CV) experiments were conducted using a CHI760E series electrochemical workstation (CH Instruments, Inc.).

Materials. Unless otherwise noted, all reagents and materials were purchased from commercial suppliers such as Tokyo Chemical Industry (TCI), Aldrich, Alfa Aesar, Adamas-beta, and Energy Chemical, and were used without further purification. $CrCl_2$ (99.99% purity) was purchased from Aldrich Inc. in China (product number: 450782) and used as received. Solvents were dried over sodium (for THF, toluene, hexane and DME) by refluxing overnight and freshly distilled prior to use, and other anhydrous solvents were purchased from Energy Chemical.

2. Methods of the Preparation of Alkyl Triflates and Alkyl Halides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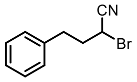
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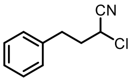
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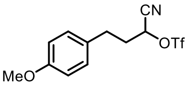
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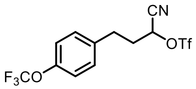
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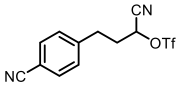
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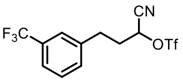
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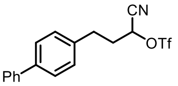
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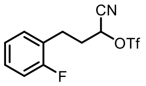
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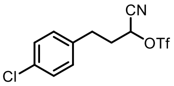
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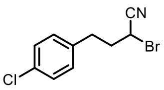
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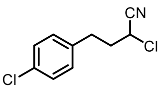
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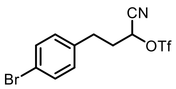
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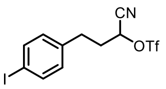
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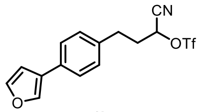
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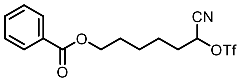
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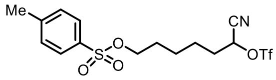
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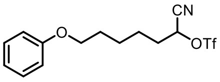
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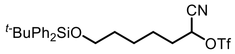
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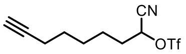
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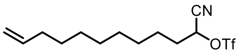
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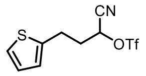
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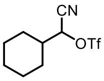
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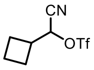
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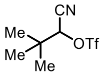
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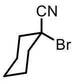
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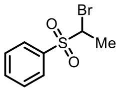
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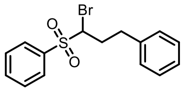
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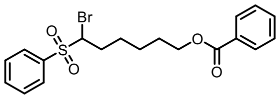
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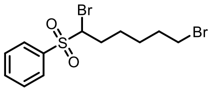
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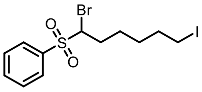
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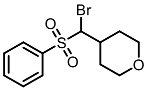
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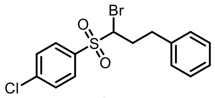
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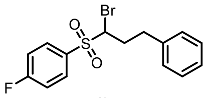
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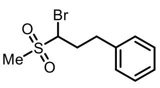
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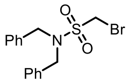
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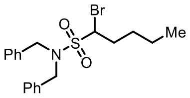
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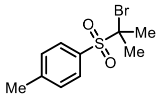
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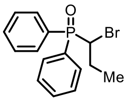
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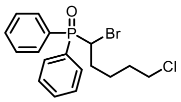
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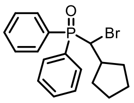
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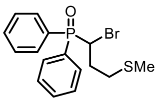
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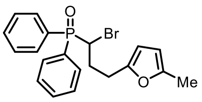
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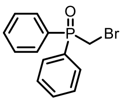
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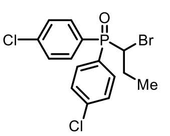
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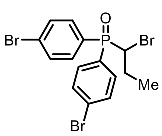
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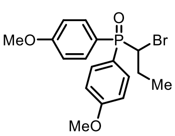
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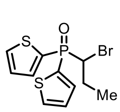
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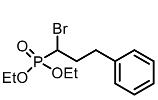
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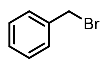
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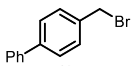
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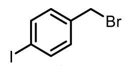
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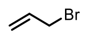
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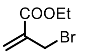
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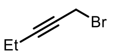
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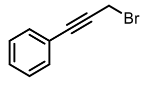
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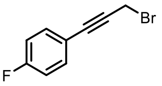
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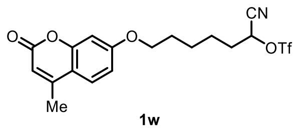
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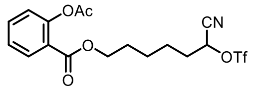
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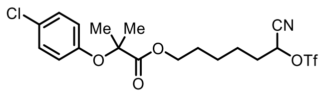
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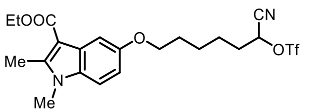
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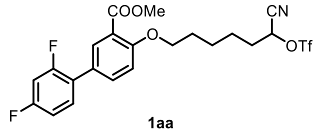
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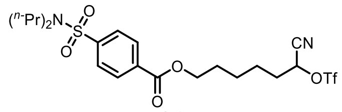
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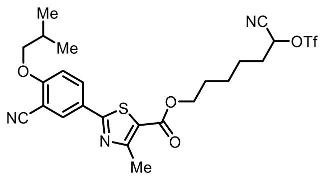
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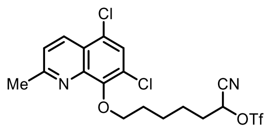
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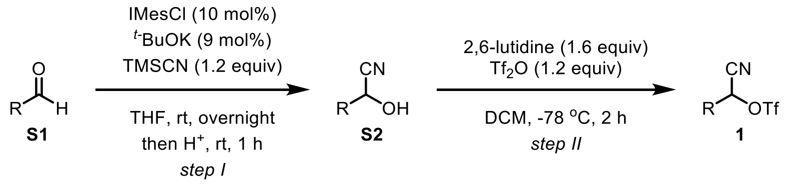
Figure S1. Substrates of alkyl triflates and alkyl halides.

General Procedure A in the preparation of **1a–1u**, **1w–1ad**:

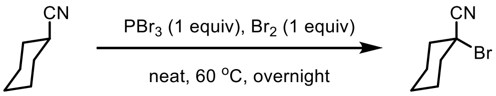


Step I: To an oven-dried 50 mL Schlenk flask equipped with a magnetic stir bar was added IMesCl (171 mg, 0.50 mmol). The flask was placed under vacuum and backfilled with N_2 (three cycles). A solution of the corresponding aldehyde **S1** (5.0 mmol) and TMSCN (595 mg, 6.0 mmol) in THF (10 mL) was then added by syringe, and the mixture was stirred for 5 min. KO^{t}-Bu (51 mg, 0.45 mmol) was added in one portion, and the reaction mixture was maintained with stirring at room temperature overnight. After TLC analysis indicated complete conversion, the mixture was quenched with an aqueous solution of HCl (1 M) and extracted with DCM (3×10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford cyanohydrins **S2**, which were used directly in the next step without further purification.[1]

Step II: To an oven-dried 50 mL Schlenk flask equipped with a magnetic stir bar were subsequently added the crude cyanohydrins **S2** and 2,6-lutidine (857 mg, 8.0 mmol) at

-78 °C under an atmosphere of N_2. DCM (10 mL) was added by syringe. Tf_2O (1.69 g, 6.0 mmol) was then added dropwise, and the reaction mixture was stirred at this temperature for 2 h. After the indicated reaction time, the mixture was quenched with water (10 mL) and extracted with DCM (3×10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The α-cyano triflates **1** (**1a**–**1u**, **1w**–**1ad**) were purified by flash column chromatography on silica gel.[2]

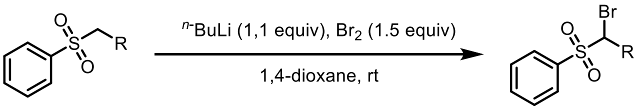
Procedure B in the preparation of **1v**:



1v

To ice-cooled PBr_3 (542 mg, 2 mmol) was added Br_2 (320 mg, 2 mmol) and cyclohexanecarbonitrile (218 mg, 2 mmol). After the addition, the ice bath was removed and the reaction was heated at 60 °C and stirred overnight. The mixture was poured into ice and extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the product **1v**.[3]

General Procedure C in the preparation of **4a** and **4f**:



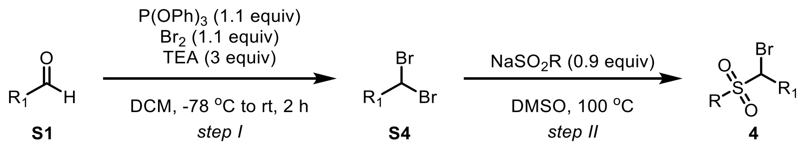
S3

4a or **4f**

An oven-dried microwave vial equipped with a magnetic stir bar was charged with the alkyl sulfone **S3** (2.0 mmol), capped and flushed with N_2. Anhydrous dioxane (10 mL) was added, followed by dropwise addition of $^{n-}$BuLi (2.2 mmol, 2.5 M in hexane). The resulting mixture was stirred at room temperature for 1.5 h. After this time, the deprotonated sulfone solution was transferred via syringe to a separate oven-dried microwave vial containing Br_2 (480 mg, 3 mmol) in dioxane (4 mL). The reaction mixture was stirred for 2 h and then quenched by slow addition of aqueous sat. Na_2SO_3

(10 mL) and extracted with DCM (2×30 mL). The combined organic fractions were washed with aqueous sat. Na_2SO_3 (2×30 mL), dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude product, which was purified by flash chromatography to afford the pure product **4a** or **4f**.[4]

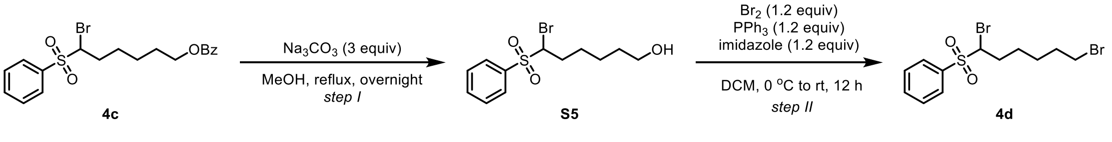
General Procedure D in the preparation of **4b**, **4c** and **4g**–**4i**:



Step I: To a stirred solution of triphenyl phosphite (1.71 g, 5.5 mmol) in anhydrous DCM (50 mL) at -78 °C under N_2 was added Br_2 (880 mg, 5.5 mmol) dropwise. Freshly distilled triethylamine (1.52 g, 15 mmol) and the corresponding aldehyde **S1** (5 mmol) were added at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Upon completion, the solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography on silica gel to afford the 1,1-dibromide **S4**.[5]

Step II: **S4** (3 mmol) was dissolved in DMSO (3 mL), followed by addition of sodium sulfinate (2.7 mmol). The reaction mixture was stirred at 100 °C. When the reaction was completed as determined by TLC analysis, it was quenched with water (30 mL) and extracted with DCM (2×30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired products **4b**, **4c** and **4g**–**4i**.[6]

Procedure E in the preparation of **4d**:

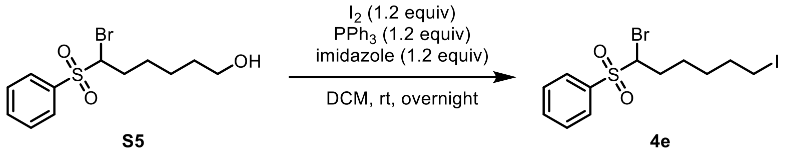


Step I: To a solution of **4c** (2.13 g, 5 mmol) in methanol (50 mL) was added Na_2CO_3

(1.59 g, 15 mmol). The mixture was heated overnight under reflux. After cooling to room temperature, the resulting mixture was filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product **S5**.

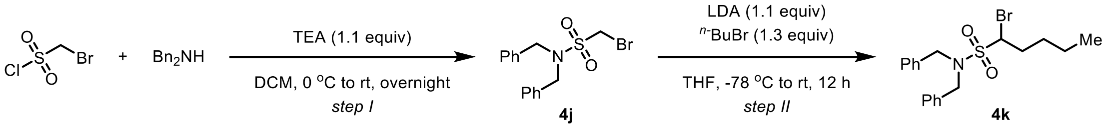
Step II: A flame-dried flask equipped with a stir bar was charged with PPh_3 (630 mg, 2.4 mmol) and imidazole (163 mg, 2.4 mmol) under an atmosphere of N_2, and anhydrous DCM (4 mL) was then added by syringe. The flask was cooled with an ice bath, and Br_2 (384 mg, 2.4 mmol) was added dropwise. After stirring for 10 min, a solution of **S5** (642 mg, 2 mmol) in DCM (4 mL) was added dropwise at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. Next, the reaction was warmed to room temperature and stirred for 12 h. Then the mixture was filtered through celite, followed by elution with DCM. The solution was washed with water, brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the product **4d**.[6]

Procedure F in the preparation of **4e**:



To the solution of **S5** (642 mg, 2 mmol) and PPh_3 (630 mg, 2.4 mmol) in DCM (8 mL) under an atmosphere of N_2 was added imidazole (163 mg, 2.4 mmol) and I_2 (610 mg, 2.4 mmol). The reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered through celite, followed by elution with DCM. The solution was washed with water, brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the product **4e**.[6]

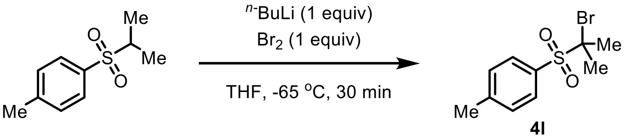
Procedure G in the preparation of **4j** and **4k**:



Step I: An oven-dried 50 mL flask equipped with a magnetic stir bar was charged with 1-bromomethanesulfonyl chloride (968 mg, 5 mmol), and DCM (5 mL) was added via syringe. A mixture of triethylamine (560 mg, 5.5 mmol) and Bn_2NH (1.09 g, 5.5 mmol) in DCM (5 mL) was then added dropwise at 0 °C. The resulting mixture was stirred at room temperature overnight. Upon completion, the volatiles were removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the product **4j**.[7]

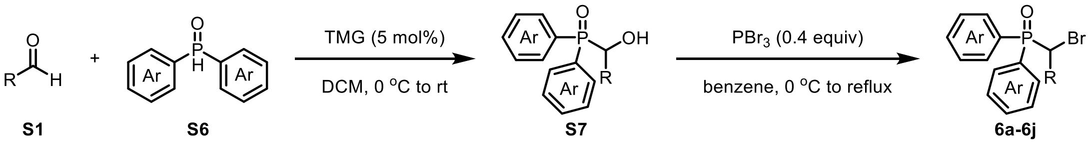
Step II: A solution of **4j** (1.42 g, 4 mmol) in THF (25 mL) was added over 15 min to the LDA solution (4.4 mmol, 2 M in THF/*n*-heptane/ethylbenzene) at -78 °C. The mixture was stirred for 30 min, and then a solution of $^{n-}$BuBr (713 mg, 5.2 mmol) in THF (9 mL) was added over 15 min. After stirring at -78 °C for 2 h, the reaction mixture was warmed slowly to room temperature. The reaction mixture was stirred at room temperature for 12 h, and then the reaction was quenched by the addition of saturated aqueous NH_4Cl (25 mL). The mixture was extracted with Et_2O (3×50 mL), and the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the product **4k**.[8]

Procedure H in the preparation of **4l**:



In a sealed flask, a solution of 1-(isopropylsulfonyl)-4-methylbenzene (516 mg, 2.6 mmol) in THF (5 mL) was maintained between -70 °C and -60 °C under N_2. $^{n-}$BuLi (2.6 mmol, 2.5 M in hexane) was then added by syringe, and the reaction was stirred for 1 h. A bromine-hexane solution (2.6 mmol of Br_2 and 4.45 mL hexane) was added, and the mixture was stirred for 30 min at -65 °C. Then saturated NH_4Cl (20 mL) was added to quench the reaction and the organic materials were extracted with Et_2O (3×20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding product **4l**.[9]

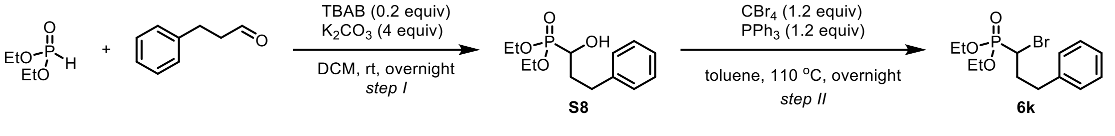
General Procedure I in the preparation of **6a**–**6j**:



Step I: To a solution of the corresponding aldehyde **S1** (10 mmol) and diarylphosphine oxide **S6** (5.0 mmol) in DCM (20.0 mL) at 0 °C was added 1,1,3,3-tetramethylguanidine (29 mg, 0.25 mmol) dropwise. The reaction mixture was stirred at room temperature for 0.5–6 h, and concentrated under reduced pressure. The residue **S7** was used for the next step without purification.

Step II: To a solution of the above residue **S7** in dry benzene (10 mL) was added dropwise PBr_3 (542 mg, 2 mmol) in 5 mL of dry benzene at 0 °C under a nitrogen atmosphere, and then the resulting mixture was refluxed for 1.5–3 h. The reaction mixture was diluted with chloroform (15 mL), quenched by slow addition of saturated aqueous solution of $NaHCO_3$ (30 mL) at 0 °C, and extracted with chloroform (2×30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the desired products **6a**–**6j**.[6]

Procedure J in the preparation **6k**:



Step I: A flask was charged with tetrabutylammonium bromide (194 mg, 0.6 mmol), K_2CO_3 (1.66 g, 12 mmol), and DCM (6 mL). The mixture was stirred at room temperature for 10 min, followed by the addition of diethyl phosphite (415 mg, 3.0

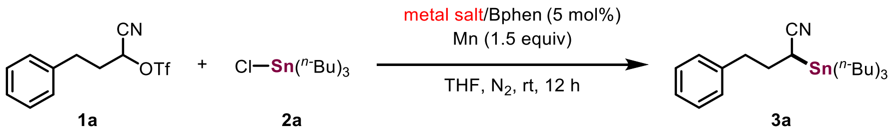
mmol). After stirring for 0.5 h, 3-phenylpropanal (443 mg, 3.3 mmol) was added. The resulting mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered, and the solid was rinsed with additional DCM. The combined filtrates were washed sequentially with water and saturated brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide the crude product **S8**.

Step II: The crude product **S8** and triphenylphosphine (945 mg, 3.6 mmol) were added to a Schlenk flask, and purged with N_2 (three cycles). Under a nitrogen atmosphere, toluene (8 mL) was added to the flask via syringe, and the mixture was stirred for 5 min at room temperature. A separate solution of carbon tetrabromide (1.20 g, 3.6 mmol) in toluene (4 mL) was prepared and then added dropwise to the Schlenk flask. The resulting mixture was stirred at room temperature for 0.5 h, during which it became turbid. The reaction was then placed at 110 °C overnight. After removing the toluene under reduced pressure, the crude residue was purified by flash column chromatography on silica gel to afford the desired product **6k**.[10]

Compounds **8a**–**8h** were commercially available and used as received.

3. Optimization of Reaction Conditions

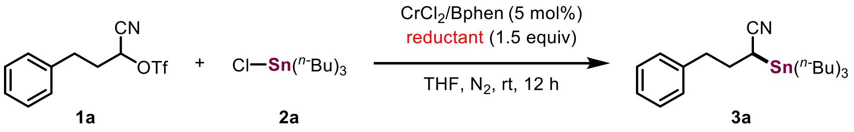
Table S1. Studying the Effect of Transition Metal Salts on the α-Stannylation of Cyano-Substituted Alkyl Triflate **1a**[a]



Entry	Metal salt	Yield (3a)
1	-	nd[b]
2	**$CrCl_2$**	**89%**
3	$MnCl_2$	nd[b]
4	$FeCl_2$	nd[b]
5	$CoCl_2$	nd[b]
6	$NiCl_2$	nd[b]
7	$CuCl_2$	nd[b]
8	$ZnCl_2$	nd[b]
9	$CrCl_3$•3THF	77%
10	$Cr(OAc)_3$	nd[b]
11	$Cr(acac)_3$	nd[b]
12	CrF_3	nd[b]
13	$CrCl_2$[c]	89%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), metal salt (0.01 mmol), Bphen (0.01 mmol), Mn (0.3 mmol), THF (2 mL), room temperature, 12 h. The yield was determined by isolation. [b]Not detected. [c]0.02 mmol $CrCl_2$, 0.02 mmol Bphen.

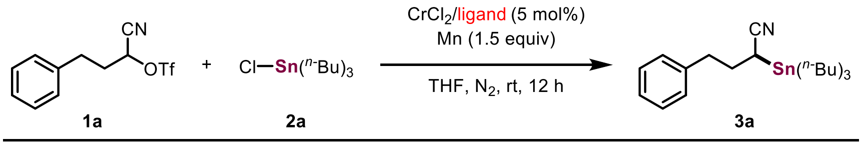
Table S2. Studying the Effect of Reductants on the α-Stannylation of Cyano-Substituted Alkyl Triflate **1a**[a]

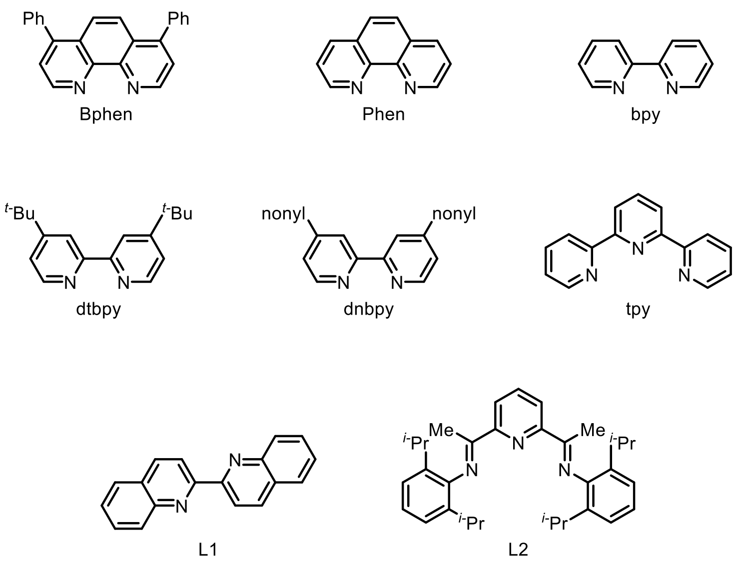


Entry	Reductant	Yield (**3a**)
1	-	nd[b]
2	**Mn**	**89%**
3	Zn	85%
4	Al	nd[b]
5	Mg	51%
6	Mn (1.0 equiv)	84%
7	Mn (2.0 equiv)	88%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $CrCl_2$ (0.01 mmol), Bphen (0.01 mmol), reductant (0.3 mmol), THF (2 mL), room temperature, 12 h. The yield was determined by isolation. [b]Not detected.

Table S3. Studying the Effect of Ligands on the α-Stannylation of Cyano-Substituted Alkyl Triflate **1a**[a]

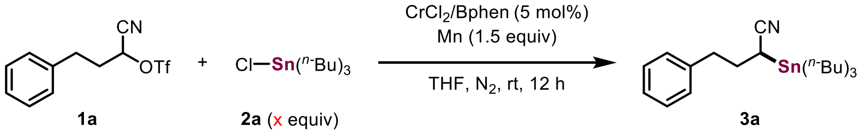




Entry	Ligand	Yield (**3a**)
1	-	nd[b]
2	**Bphen**	**89%**
3	Phen	44%
4	bpy	63%
5	dtbpy	81%
6	dnbpy	72%
7	tpy	49%
8	L1	51%
9	L2	18%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $CrCl_2$ (0.01 mmol), ligand (0.01 mmol), Mn (0.3 mmol), THF (2 mL), room temperature, 12 h. The yield was determined by isolation. [b]Not detected.

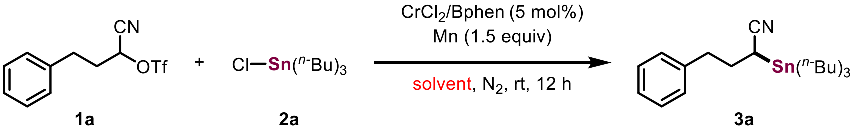
Table S4. Studying the Effect of Tributylchlorostannane **2a** Stoichiometry on the α-Stannylation of Cyano-Substituted Alkyl Triflate **1a**[a]



Entry	x	Yield (**3a**)
1	**1.2**	**89%**
2	1.5	88%
3	2	85%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (x equiv), $CrCl_2$ (0.01 mmol), Bphen (0.01 mmol), Mn (0.3 mmol), THF (2 mL), room temperature, 12 h. The yield was determined by isolation.

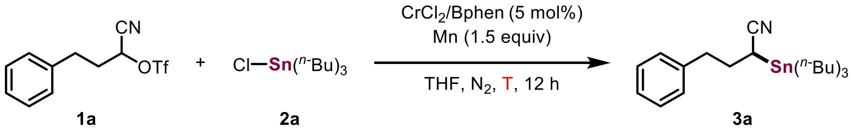
Table S5. Studying the Effect of Solvents on the α-Stannylation of Cyano-Substituted Alkyl Triflate **1a**[a]



Entry	Solvent	Yield (**3a**)
1	**THF**	**89%**
2	DME	76%
3	CH_3CN	72%
4	DMA	trace
5	EA	14%
6	Toluene	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $CrCl_2$ (0.01 mmol), Bphen (0.01 mmol), Mn (0.3 mmol), solvent (2 mL), room temperature, 12 h. The yield was determined by isolation.

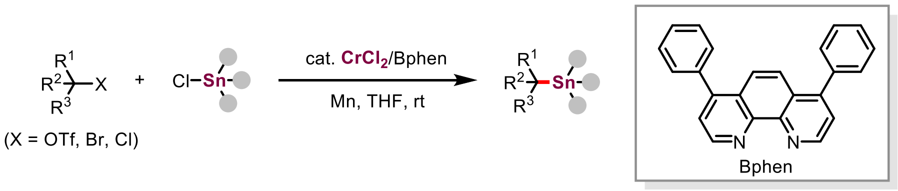
Table S6. Studying the Effect of Temperature on the α-Stannylation of Cyano-Substituted Alkyl Triflate **1a**[a]



Entry	T	Yield (**3a**)
1	**rt**	**89%**
2	40 °C	82%
3	60 °C	71%

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $CrCl_2$ (0.01 mmol), Bphen (0.01 mmol), Mn (0.3 mmol), THF (2 mL), T, 12 h. The yield was determined by isolation.

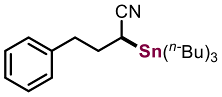
4. General Procedure of Cr-Catalyzed α-Cross-Electrophile Stannylation of Alkyl Triflates and Halides with Chlorostannanes



General procedure K: In a dried Schlenk tube under a nitrogen atmosphere, $CrCl_2$ (1.2 mg, 0.01 mmol), Bphen (3.3 mg, 0.01 mmol), and manganese powder (17 mg, 0.3 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, chlorostannanes (0.24 mmol) and alkyl triflate (or alkyl halide, 0.2 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatiles under reduced pressure, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding stannylation product.

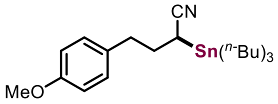
General procedure L: In a dried Schlenk tube under a nitrogen atmosphere, $CrCl_2$ (7.4 mg, 0.06 mmol), Bphen (19.9 mg, 0.06 mmol), and manganese powder (17 mg, 0.3 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, tributylchlorostannane (78 mg, 0.24 mmol) and alkyl bromide (0.2 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatiles under reduced pressure, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding stannylation product.

5. Characterization of the Stannylation Products



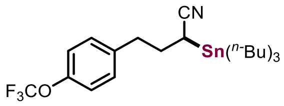
4-phenyl-2-(tributylstannyl)butanenitrile (3a)

The general procedure K was applied to 1-cyano-3-phenylpropyl trifluoromethanesulfonate (59 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (77 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.28 (m, 2H), 7.25–7.17 (m, 3H), 3.01–2.88 (m, 1H), 2.78–2.65 (m, 1H), 2.12–1.97 (m, 1H), 1.90–1.76 (m, 2H), 1.59–1.41 (m, 6H), 1.37–1.27 (m, 6H), 1.17–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 128.7, 128.7, 126.4, 124.6, 36.8, 31.0, 28.8, 27.4, 13.7, 10.2, 8.8. Spectroscopic data are in accordance with those described in the literature.[11]



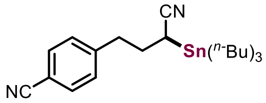
4-(4-methoxyphenyl)-2-(tributylstannyl)butanenitrile (3b)

The general procedure K was applied to 1-cyano-3-(4-methoxyphenyl)propyl trifluoromethanesulfonate (65 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (82 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.94–2.81 (m, 1H), 2.72–2.59 (m, 1H), 2.06–1.95 (m, 1H), 1.89–1.73 (m, 2H), 1.59–1.44 (m, 6H), 1.37–1.27 (m, 6H), 1.14–1.01 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 132.6, 129.6, 124.7, 114.1, 55.3, 35.8, 31.1, 28.8, 27.4, 13.7, 10.1, 8.6. HRMS (ESI$^+$): calcd for $C_{23}H_{40}NOSn$ $[M+H]^+$ 466.2126, found 466.2126.



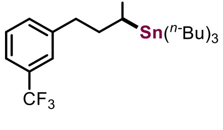
4-(4-(trifluoromethoxy)phenyl)-2-(tributylstannyl)butanenitrile (3c)

The general procedure K was applied to 1-cyano-3-(4-(trifluoromethoxy)phenyl)propyl trifluoromethanesulfonate (76 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (86 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.21 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 3.00–2.87 (m, 1H), 2.78–2.64 (m, 1H), 2.09–1.94 (m, 1H), 1.92–1.71 (m, 2H), 1.60–1.41 (m, 6H), 1.36–1.28 (m, 6H), 1.17–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 147.9 (q, J = 1.6 Hz), 139.3, 129.9, 124.4, 121.3, 120.6 (q, J = 256.8 Hz), 36.1, 30.9, 28.8, 27.4, 13.7, 10.2, 8.7; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -58.0. HRMS (ESI$^+$): calcd for $C_{23}H_{37}F_3NOSn$ [M+H]$^+$ 520.1844, found 520.1845.



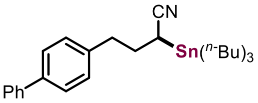
4-(3-cyano-3-(tributylstannyl)propyl)benzonitrile (3d)

The general procedure K was applied to 1-cyano-3-(4-cyanophenyl)propyl trifluoromethanesulfonate (64 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a colorless oil (77 mg, 84% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.59 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 3.04–2.93 (m, 1H), 2.83–2.72 (m, 1H), 2.10–1.94 (m, 1H), 1.89–1.71 (m, 2H), 1.61–1.41 (m, 6H), 1.35–1.25 (m, 6H), 1.15–0.99 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 146.1, 132.5, 129.4, 124.2, 119.0, 110.4, 36.8, 30.4, 28.8, 27.3, 13.7, 10.2, 8.7. HRMS (ESI$^+$): calcd for $C_{23}H_{37}N_2Sn$ [M+H]$^+$ 461.1973, found 461.1970.



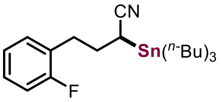
4-(3-(trifluoromethyl)phenyl)-2-(tributylstannyl)butanenitrile (3e)

The general procedure K was applied to 1-cyano-3-(3-(trifluoromethyl)phenyl)propyl trifluoromethanesulfonate (72 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (90 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.36 (m, 4H), 3.08–2.94 (m, 1H), 2.86–2.70 (m, 1H), 2.11–1.97 (m, 1H), 1.94–1.75 (m, 2H), 1.62–1.43 (m, 6H), 1.37–1.27 (m, 6H), 1.18–1.00 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 132.2 (d, J = 1.2 Hz), 131.1 (q, J = 32.0 Hz), 129.1, 125.2 (q, J = 3.8 Hz), 124.4, 124.3 (q, J = 272.2 Hz), 123.4 (q, J = 3.8 Hz), 36.6, 30.8, 28.8, 27.4, 13.7, 10.2, 8.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.6. HRMS (ESI$^+$): calcd for $C_{23}H_{37}F_3NSn$ [M+H]$^+$ 504.1895, found 504.1902.



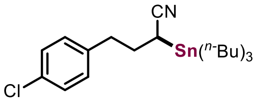
4-([1,1'-biphenyl]-4-yl)-2-(tributylstannyl)butanenitrile (3f)

The general procedure K was applied to 3-([1,1'-biphenyl]-4-yl)-1-cyanopropyl trifluoromethanesulfonate (74 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (86 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.52 (m, 4H), 7.48–7.40 (m, 2H), 7.38–7.32 (m, 1H), 7.31–7.25 (m, 2H), 3.08–2.94 (m, 1H), 2.84–2.70 (m, 1H), 2.16–2.01 (m, 1H), 1.96–1.80 (m, 2H), 1.62–1.49 (m, 6H), 1.39–1.29 (m, 6H), 1.18–1.03 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 139.7, 139.4, 129.1, 128.9, 127.4, 127.3, 127.1, 124.6, 36.4, 30.9, 28.9, 27.4, 13.7, 10.2, 8.8. HRMS (ESI$^+$): calcd for $C_{28}H_{42}NSn$ [M+H]$^+$ 512.2334, found 512.2334.



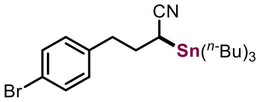
4-(2-fluorophenyl)-2-(tributylstannyl)butanenitrile (3g)

The general procedure K was applied to 1-cyano-3-(2-fluorophenyl)propyl trifluoromethanesulfonate (62 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (80 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.15 (m, 2H), 7.11–6.98 (m, 2H), 3.01–2.90 (m, 1H), 2.80–2.69 (m, 1H), 2.06–1.95 (m, 1H), 1.94–1.83 (m, 2H), 1.59–1.47 (m, 6H), 1.35–1.28 (m, 6H), 1.15–1.01 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3 (d, J = 245.1 Hz), 131.2 (d, J = 5.1 Hz), 128.3 (d, J = 8.1 Hz), 127.4 (d, J = 15.8 Hz), 124.6, 124.3 (d, J = 3.7 Hz), 115.5 (d, J = 21.9 Hz), 30.6 (d, J = 2.0 Hz), 29.4 (d, J = 1.5 Hz), 28.8, 27.4, 13.7, 10.2, 9.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -118.6. HRMS (ESI$^+$): calcd for $C_{22}H_{37}FNSn$ $[M+H]^+$ 454.1927, found 454.1934.



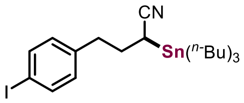
4-(4-chlorophenyl)-2-(tributylstannyl)butanenitrile (3h)

The general procedure K was applied to 3-(4-chlorophenyl)-1-cyanopropyl trifluoromethanesulfonate (66 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (81 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 2.96–2.84 (m, 1H), 2.75–2.63 (m, 1H), 2.07–1.95 (m, 1H), 1.88–1.72 (m, 2H), 1.60–1.41 (m, 6H), 1.37–1.27 (m, 6H), 1.17–0.98 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 132.2, 130.0, 128.8, 124.4, 36.0, 30.8, 28.9, 28.8, 28.7, 27.7, 27.4, 27.1, 13.7, 10.2, 8.6. HRMS (ESI$^+$): calcd for $C_{22}H_{37}ClNSn$ $[M+H]^+$ 470.1631, found 470.1632.



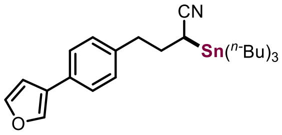
4-(4-bromophenyl)-2-(tributylstannyl)butanenitrile (3i)

The general procedure K was applied to 3-(4-bromophenyl)-1-cyanopropyl trifluoromethanesulfonate (74 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (88 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 2.96–2.82 (m, 1H), 2.74–2.61 (m, 1H), 2.07–1.94 (m, 1H), 1.86–1.72 (m, 2H), 1.59–1.42 (m, 6H), 1.36–1.27 (m, 6H), 1.15–1.00 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 131.7, 130.4, 124.4, 120.2, 36.1, 30.8, 28.8, 27.4, 13.7, 10.2, 8.6. HRMS (ESI$^+$): calcd for $C_{22}H_{37}BrNSn$ [M+H]$^+$ 514.1126, found 514.1119.



4-(4-iodophenyl)-2-(tributylstannyl)butanenitrile (3j)

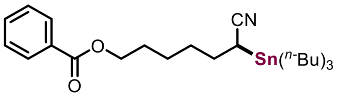
The general procedure K was applied to 1-cyano-3-(4-iodophenyl)propyl trifluoromethanesulfonate (84 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (98 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 2.95–2.81 (m, 1H), 2.72–2.56 (m, 1H), 2.05–1.93 (m, 1H), 1.85–1.71 (m, 2H), 1.60–1.41 (m, 6H), 1.36–1.26 (m, 6H), 1.16–0.97 (m, 6H), 0.89 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1, 137.7, 130.7, 124.4, 91.5, 36.2, 30.7, 28.8, 27.4, 13.7, 10.2, 8.6. HRMS (ESI$^+$): calcd for $C_{22}H_{37}INSn$ [M+H]$^+$ 562.0987, found 562.0988.



4-(4-(furan-3-yl)phenyl)-2-(tributylstannyl)butanenitrile (3k)

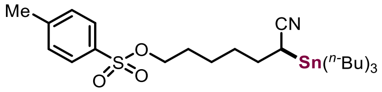
The general procedure K was applied to 1-cyano-3-(4-(furan-3-yl)phenyl)propyl trifluoromethanesulfonate (72 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24

mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (87 mg, 87% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.72 (s, 1H), 7.47 (t, J = 1.7 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 6.69 (dd, J = 1.9, 0.9 Hz, 1H), 3.01–2.89 (m, 1H), 2.79–2.67 (m, 1H), 2.13–1.98 (m, 1H), 1.97–1.78 (m, 2H), 1.63–1.41 (m, 6H), 1.37–1.29 (m, 6H), 1.18–0.99 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.7, 139.3, 138.4, 130.6, 129.1, 126.3, 126.2, 124.6, 108.9, 36.4, 30.9, 28.8, 27.4, 13.7, 10.2, 8.7. HRMS (ESI$^+$): calcd for $C_{26}H_{40}NOSn$ [M+H]$^+$ 502.2126, found 502.2123.



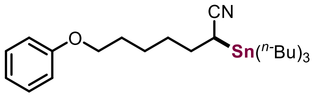
6-cyano-6-(tributylstannyl)hexyl benzoate (3l)

The general procedure K was applied to 6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl benzoate (76 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (88 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.10–7.96 (m, 2H), 7.59–7.51 (m, 1H), 7.48–7.37 (m, 2H), 4.32 (t, J = 6.5 Hz, 2H), 1.96–1.85 (m, 1H), 1.83–1.72 (m, 3H), 1.67–1.43 (m, 11H), 1.37–1.27 (m, 6H), 1.14–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.7, 133.0, 130.5, 129.6, 128.4, 124.8, 64.9, 30.7, 28.9, 28.8, 28.7, 27.4, 25.6, 13.7, 10.1, 9.4. HRMS (ESI$^+$): calcd for $C_{26}H_{44}NO_2Sn$ [M+H]$^+$ 522.2389, found 522.2384.



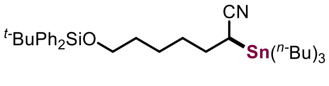
6-cyano-6-(tributylstannyl)hexyl 4-methylbenzenesulfonate (3m)

The general procedure K was applied to 6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl 4-methylbenzenesulfonate (86 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 15:1) to afford the title compound as a colorless oil (99 mg, 87% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.76 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 2.42 (s, 3H), 1.92–1.76 (m, 1H), 1.67–1.58 (m, 3H), 1.58–1.41 (m, 8H), 1.39–1.22 (m, 9H), 1.15–0.95 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.8, 133.1, 129.9, 127.9, 124.7, 70.4, 30.3, 28.8, 28.7, 27.3, 24.8, 21.7, 13.7, 10.1, 9.3. HRMS (ESI$^+$): calcd for $C_{26}H_{46}NO_3SSn$ [M+H]$^+$ 572.2215, found 572.2218.



7-phenoxy-2-(tributylstannyl)heptanenitrile (3n)

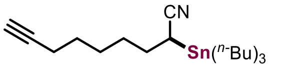
The general procedure K was applied to 1-cyano-6-phenoxyhexyl trifluoromethanesulfonate (70 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (89 mg, 90% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.31–7.23 (m, 2H), 6.97–6.85 (m, 3H), 3.96 (t, J = 6.3 Hz, 2H), 1.98–1.86 (m, 1H), 1.85–1.71 (m, 3H), 1.66–1.44 (m, 11H), 1.39–1.29 (m, 6H), 1.16–1.01 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.1, 129.5, 124.8, 120.6, 114.5, 67.6, 30.7, 29.2, 29.0, 28.9, 27.4, 25.6, 13.7, 10.1, 9.5. HRMS (ESI$^+$): calcd for $C_{25}H_{44}NOSn$ [M+H]$^+$ 494.2439, found 494.2428.



7-((*tert*-butyldiphenylsilyl)oxy)-2-(tributylstannyl)heptanenitrile (3o)

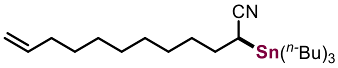
The general procedure K was applied to 6-((*tert*-butyldiphenylsilyl)oxy)-1-cyanohexyl trifluoromethanesulfonate (103 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (115 mg, 88% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.75–7.64 (m, 4H), 7.48–7.35 (m, 6H), 3.69 (t, J = 6.4

Hz, 2H), 1.98–1.80 (m, 1H), 1.77–1.68 (m, 1H), 1.64–1.52 (m, 9H), 1.47–1.27 (m, 10H), 1.19–1.02 (m, 15H), 0.94 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.6, 134.1, 129.6, 127.7, 124.9, 63.8, 32.4, 30.7, 29.0, 28.9, 27.4, 27.0, 25.3, 19.3, 13.7, 10.1, 9.5. HRMS (ESI$^+$): calcd for $C_{35}H_{58}NOSiSn$ [M+H]$^+$ 656.3304, found 656.3300.



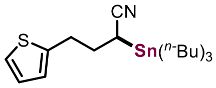
2-(tributylstannyl)non-8-ynenitrile (3p)

The general procedure K was applied to 1-cyanooct-7-yn-1-yl trifluoromethanesulfonate (57 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (72 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.19 (td, J = 6.9, 2.7 Hz, 2H), 1.99–1.78 (m, 2H), 1.75–1.64 (m, 1H), 1.64–1.38 (m, 13H), 1.37–1.27 (m, 6H), 1.17–0.96 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 124.8, 84.4, 68.5, 30.4, 28.9, 28.9, 28.3, 28.1, 27.4, 18.4, 13.7, 10.1, 9.5. HRMS (ESI$^+$): calcd for $C_{21}H_{40}NSn$ [M+H]$^+$ 426.2177, found 426.2180.



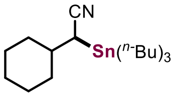
2-(tributylstannyl)dodec-11-enenitrile (3q)

The general procedure K was applied to 1-cyanoundec-10-en-1-yl trifluoromethanesulfonate (65 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (82 mg, 87% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.90–5.72 (m, 1H), 5.06–4.86 (m, 2H), 2.08–1.99 (m, 2H), 1.96–1.82 (m, 1H), 1.76–1.66 (m, 1H), 1.58–1.48 (m, 7H), 1.41–1.26 (m, 18H), 1.15–1.01 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.3, 125.0, 114.3, 33.9, 30.9, 29.5, 29.5, 29.2, 29.0, 28.9, 27.4, 13.8, 10.2, 9.6. HRMS (ESI$^+$): calcd for $C_{24}H_{48}NSn$ [M+H]$^+$ 470.2803, found 470.2803.



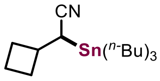
4-(thiophen-2-yl)-2-(tributylstannyl)butanenitrile (3r)

The general procedure K was applied to 1-cyano-3-(thiophen-2-yl)propyl trifluoromethanesulfonate (60 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (73 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.15 (dd, J = 5.1, 1.2 Hz, 1H), 6.98–6.90 (m, 1H), 6.88–6.79 (m, 1H), 3.18–3.06 (m, 1H), 3.04–2.90 (m, 1H), 2.16–2.02 (m, 1H), 1.97–1.82 (m, 2H), 1.59–1.43 (m, 6H), 1.36–1.29 (m, 6H), 1.16–1.01 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.0, 127.0, 125.3, 124.4, 123.7, 31.3, 30.8, 28.8, 27.4, 13.7, 10.2, 8.5. HRMS (ESI$^+$): calcd for $C_{20}H_{36}NSSn$ [M+H]$^+$ 442.1585, found 442.1590.



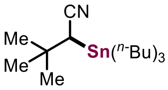
2-cyclohexyl-2-(tributylstannyl)acetonitrile (3s)

The general procedure K was applied to cyano(cyclohexyl)methyl trifluoromethanesulfonate (54 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (64 mg, 77% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.94–1.71 (m, 4H), 1.68–1.62 (m, 2H), 1.61–1.42 (m, 7H), 1.38–1.28 (m, 6H), 1.26–1.13 (m, 5H), 1.13–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 123.7, 37.5, 34.8, 33.4, 28.9, 27.4, 26.4, 26.4, 25.7, 18.6, 13.7, 10.8. HRMS (ESI$^+$): calcd for $C_{20}H_{40}NSn$ [M+H]$^+$ 414.2177, found 414.2180.



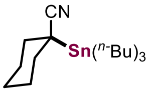
2-cyclobutyl-2-(tributylstannyl)acetonitrile (3t)

The general procedure K was applied to cyano(cyclobutyl)methyl trifluoromethanesulfonate (49 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (55 mg, 71% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.62–2.46 (m, 1H), 2.19–1.74 (m, 7H), 1.60–1.42 (m, 6H), 1.38–1.28 (m, 6H), 1.16–0.96 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 123.6, 35.2, 29.6, 29.3, 28.9, 27.4, 17.3, 17.1, 13.7, 10.4. HRMS (ESI$^+$): calcd for $C_{18}H_{36}NSn$ [M+H]$^+$ 386.1864, found 386.1866.



3,3-dimethyl-2-(tributylstannyl)butanenitrile (3u)

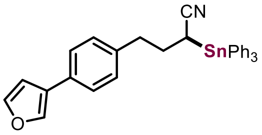
The general procedure K was applied to 1-cyano-2,2-dimethylpropyl trifluoromethanesulfonate (49 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (62 mg, 80% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.92 (s, 1H), 1.61–1.43 (m, 6H), 1.40–1.29 (m, 6H), 1.18–1.00 (m, 15H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 123.6, 33.5, 30.9, 28.9, 27.4, 27.3, 13.7, 11.7. HRMS (ESI$^+$): calcd for $C_{18}H_{38}NSn$ [M+H]$^+$ 388.2021, found 388.2011.



1-(tributylstannyl)cyclohexane-1-carbonitrile (3v)

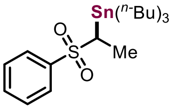
The general procedure K was applied to 1-bromocyclohexane-1-carbonitrile (38 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (65 mg, 82% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.03–1.93 (m, 2H), 1.76–1.65 (m, 3H), 1.63–1.47 (m, 10H), 1.38–1.25 (m, 7H), 1.10–

0.98 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 126.7, 33.1, 29.0, 27.5, 26.2, 24.3, 22.3, 13.7, 9.4. Spectroscopic data are in accordance with those described in the literature.[11]



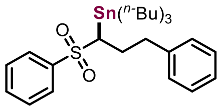
4-(4-(furan-3-yl)phenyl)-2-(triphenylstannyl)butanenitrile (3w)

The general procedure K was applied to 1-cyano-3-(4-(furan-3-yl)phenyl)propyl trifluoromethanesulfonate (72 mg, 0.2 mmol) and chlorotriphenylstannane (93 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a colorless oil (95 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.79–7.57 (m, 7H), 7.56–7.39 (m, 12H), 7.15 (d, J = 8.1 Hz, 2H), 6.73 (d, J = 1.7 Hz, 1H), 3.07–2.93 (m, 1H), 2.91–2.76 (m, 1H), 2.70–2.46 (m, 1H), 2.38–2.21 (m, 1H), 2.21–1.99 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.7, 138.7, 138.4, 137.1, 135.3, 130.6, 130.1, 129.2, 129.1, 126.2, 126.1, 123.3, 108.8, 35.8, 30.6, 11.6. HRMS (ESI$^+$): calcd for $C_{32}H_{28}NOSn$ [M+H]$^+$ 562.1187, found 562.1184.



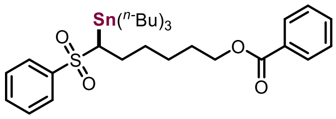
tributyl(1-(phenylsulfonyl)ethyl)stannane (5a)

The general procedure K was applied to ((1-bromoethyl)sulfonyl)benzene (50 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 15:1) to afford the title compound as a colorless oil (79 mg, 86% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.87–7.80 (m, 2H), 7.60–7.45 (m, 3H), 2.95–2.76 (m, 1H), 1.65–1.47 (m, 6H), 1.40–1.32 (m, 6H), 1.29–1.24 (m, 4H), 1.22–1.15 (m, 5H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.1, 132.6, 129.0, 127.9, 48.1, 29.0, 27.4, 13.8, 13.0, 11.1. Spectroscopic data are in accordance with those described in the literature.[12]



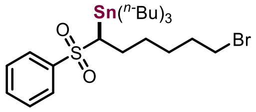
tributyl(3-phenyl-1-(phenylsulfonyl)propyl)stannane (5b)

The general procedure K was applied to (3-bromo-3-(phenylsulfonyl)propyl)benzene (68 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a colorless oil (97 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.79 (m, 2H), 7.63–7.46 (m, 3H), 7.24–7.10 (m, 3H), 6.90–6.79 (m, 2H), 3.02–2.84 (m, 1H), 2.57–2.43 (m, 1H), 2.31–2.17 (m, 1H), 2.14–1.96 (m, 2H), 1.67–1.51 (m, 6H), 1.42–1.33 (m, 6H), 1.29–1.19 (m, 6H), 0.94 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 140.4, 132.7, 129.1, 128.6, 128.2, 127.8, 126.3, 53.6, 35.0, 29.4, 29.0, 27.4, 13.8, 11.8. HRMS (ESI$^+$): calcd for $C_{27}H_{43}O_2SSn$ [M+H]$^+$ 551.2000, found 551.1998.



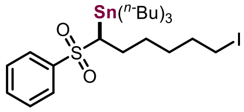
6-(phenylsulfonyl)-6-(tributylstannyl)hexyl benzoate (5c)

The general procedure K was applied to 6-bromo-6-(phenylsulfonyl)hexyl benzoate (85 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a colorless oil (114 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06–7.93 (m, 2H), 7.89–7.78 (m, 2H), 7.58–7.39 (m, 6H), 4.17 (t, J = 6.6 Hz, 2H), 2.99–2.79 (m, 1H), 1.75–1.52 (m, 10H), 1.40–1.32 (m, 6H), 1.29–1.11 (m, 9H), 1.05–0.88 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 141.0, 133.0, 132.6, 130.4, 129.6, 129.0, 128.4, 127.8, 64.6, 54.6, 29.0, 28.9, 28.4, 27.8, 27.4, 25.9, 13.8, 11.8. HRMS (ESI$^+$): calcd for $C_{31}H_{49}O_4SSn$ [M+H]$^+$ 637.2368, found 637.2372.



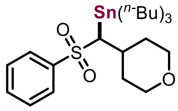
(6-bromo-1-(phenylsulfonyl)hexyl)tributylstannane (5d)

The general procedure K was applied to ((1,6-dibromohexyl)sulfonyl)benzene (77 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a colorless oil (106 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.74 (m, 2H), 7.62–7.45 (m, 3H), 3.25 (t, J = 6.7 Hz, 2H), 2.95–2.77 (m, 1H), 1.74–1.48 (m, 11H), 1.41–1.31 (m, 6H), 1.28–1.14 (m, 9H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 132.6, 129.1, 127.8, 54.5, 33.5, 32.2, 29.0, 28.3, 27.8, 27.7, 27.4, 13.8, 11.8. HRMS (ESI$^+$): calcd for $C_{24}H_{44}BrO_2SSn$ [M+H]$^+$ 595.1262, found 595.1244.



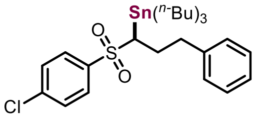
tributyl(6-iodo-1-(phenylsulfonyl)hexyl)stannane (5e)

The general procedure K was applied to ((1-bromo-6-iodohexyl)sulfonyl)benzene (86 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a colorless oil (92 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.78 (m, 2H), 7.62–7.45 (m, 3H), 3.03 (t, J = 6.9 Hz, 2H), 2.94–2.78 (m, 1H), 1.70–1.49 (m, 10H), 1.41–1.31 (m, 6H), 1.29–1.09 (m, 10H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 132.7, 129.1, 127.8, 54.5, 32.9, 30.1, 29.0, 28.1, 27.7, 27.4, 13.8, 11.8, 6.6. HRMS (ESI$^+$): calcd for $C_{24}H_{44}IO_2SSn$ [M+H]$^+$ 643.1123, found 643.1121.



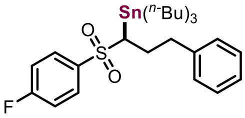
tributyl((phenylsulfonyl)(tetrahydro-*2H*-pyran-4-yl)methyl)stannane (5f)

The general procedure K was applied to 4-(bromo(phenylsulfonyl)methyl)tetrahydro-*2H*-pyran (64 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 6:1) to afford the title compound as a colorless oil (96 mg, 91% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.86–7.78 (m, 2H), 7.62–7.47 (m, 3H), 3.86 (ddd, J = 31.4, 11.5, 4.3 Hz, 2H), 3.30–3.06 (m, 2H), 3.01–2.82 (m, 1H), 2.17–2.04 (m, 1H), 1.94–1.79 (m, 1H), 1.68–1.49 (m, 6H), 1.47–1.31 (m, 8H), 1.30–1.15 (m, 6H), 1.12–1.03 (m, 1H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 141.4, 132.7, 129.1, 127.5, 68.1, 68.0, 61.5, 35.4, 33.6, 32.8, 29.0, 27.3, 13.8, 13.1. HRMS (ESI$^+$): calcd for $C_{24}H_{43}O_3SSn$ [M+H]$^+$ 531.1949, found 531.1946.



tributyl(1-((4-chlorophenyl)sulfonyl)-3-phenylpropyl)stannane (5g)

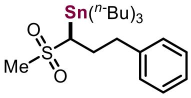
The general procedure K was applied to 1-((1-bromo-3-phenylpropyl)sulfonyl)-4-chlorobenzene (75 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (100 mg, 86% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.72 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.23–7.12 (m, 3H), 6.91–6.80 (m, 2H), 2.96–2.79 (m, 1H), 2.61–2.48 (m, 1H), 2.32–2.19 (m, 1H), 2.15–1.92 (m, 2H), 1.63–1.54 (m, 6H), 1.42–1.32 (m, 6H), 1.28–1.15 (m, 6H), 0.93 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.2, 139.5, 139.2, 129.4, 129.3, 128.7, 128.3, 126.4, 53.4, 35.0, 29.4, 29.0, 27.4, 13.8, 11.9. HRMS (ESI$^+$): calcd for $C_{27}H_{42}ClO_2SSn$ [M+H]$^+$ 585.1611, found 585.1616.



tributyl(1-((4-fluorophenyl)sulfonyl)-3-phenylpropyl)stannane (5h)

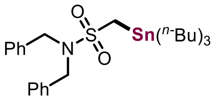
The general procedure K was applied to 1-((1-bromo-3-phenylpropyl)sulfonyl)-4-fluorobenzene (71 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA =

20:1) to afford the title compound as a colorless oil (100 mg, 88% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.88–7.73 (m, 2H), 7.24–7.09 (m, 5H), 6.93–6.81 (m, 2H), 2.98–2.79 (m, 1H), 2.60–2.49 (m, 1H), 2.32–2.20 (m, 1H), 2.13–1.92 (m, 2H), 1.66–1.50 (m, 6H), 1.43–1.33 (m, 6H), 1.28–1.16 (m, 6H), 0.93 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.2 (d, J = 254.4 Hz), 140.2, 137.0 (d, J = 3.1 Hz), 130.5 (d, J = 9.3 Hz), 128.6, 128.2, 126.4, 116.3 (d, J = 22.4 Hz), 53.5, 35.0, 29.4, 29.0, 27.4, 13.8, 11.8; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -105.7. HRMS (ESI$^+$): calcd for $C_{27}H_{42}FO_2SSn$ [M+H]$^+$ 569.1906, found 569.1908.



tributyl(1-(methylsulfonyl)-3-phenylpropyl)stannane (5i)

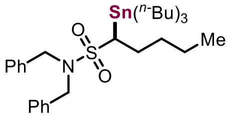
The general procedure K was applied to (3-bromo-3-(methylsulfonyl)propyl)benzene (55 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 5:1) to afford the title compound as a colorless oil (87 mg, 89% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.36–7.28 (m, 2H), 7.26–7.13 (m, 3H), 2.93–2.76 (m, 5H), 2.70–2.59 (m, 1H), 2.39–2.15 (m, 2H), 1.62–1.47 (m, 6H), 1.40–1.30 (m, 6H), 1.23–1.08 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.5, 128.8, 128.5, 126.6, 53.0, 40.8, 35.7, 30.2, 28.9, 27.4, 13.7, 11.6. HRMS (ESI$^+$): calcd for $C_{22}H_{41}O_2SSn$ [M+H]$^+$ 489.1844, found 489.1849.



***N,N*-dibenzyl-1-(tributylstannyl)methanesulfonamide (5j)**

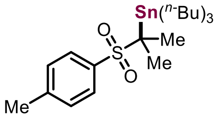
The general procedure K was applied to *N,N*-dibenzyl-1-bromomethanesulfonamide (71 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (98 mg, 87% yield). ^{1}H NMR (400 MHz, CDCl$_3$):

δ = 7.37–7.24 (m, 10H), 4.31 (s, 4H), 2.43 (s, 2H), 1.60–1.43 (m, 6H), 1.38–1.29 (m, 6H), 1.22–1.03 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.2, 129.0, 128.7, 127.9, 50.3, 35.2, 28.9, 27.3, 13.8, 11.1. HRMS (ESI$^+$): calcd for $C_{27}H_{44}NO_2SSn$ [M+H]$^+$ 566.2109, found 566.2105.



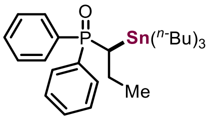
N,N-dibenzyl-1-(tributylstannyl)pentane-1-sulfonamide (5k)

The general procedure K was applied to *N,N*-dibenzyl-1-bromopentane-1-sulfonamide (82 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (109 mg, 88% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37–7.21 (m, 10H), 4.59 (d, *J* = 15.3 Hz, 2H), 4.14 (d, *J* = 15.3 Hz, 2H), 2.82–2.64 (m, 1H), 1.84–1.66 (m, 2H), 1.60–1.45 (m, 6H), 1.40–1.06 (m, 16H), 0.92 (t, *J* = 7.3 Hz, 9H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.9, 128.9, 128.6, 127.8, 52.9, 51.2, 31.4, 29.0, 27.6, 27.5, 22.9, 14.0, 13.8, 11.4. HRMS (ESI$^+$): calcd for $C_{31}H_{52}NO_2SSn$ [M+H]$^+$ 622.2735, found 622.2740.



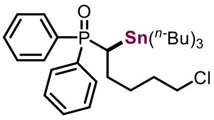
tributyl(2-tosylpropan-2-yl)stannane (5l)

The general procedure K was applied to 1-((2-bromopropan-2-yl)sulfonyl)-4-methylbenzene (55 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (89 mg, 91% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.65–1.50 (m, 6H), 1.39–1.32 (m, 6H), 1.29–1.14 (m, 12H), 0.91 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ =143.4, 132.4, 129.8, 129.2, 55.5, 29.1, 27.6, 22.3, 21.6, 13.8, 11.2. HRMS (ESI$^+$): calcd for $C_{22}H_{41}O_2SSn$ [M+H]$^+$ 489.1844, found 489.1849.



diphenyl(1-(tributylstannyl)propyl)phosphine oxide (7a)

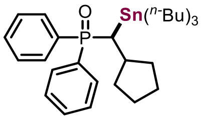
The general procedure K was applied to (1-bromopropyl)diphenylphosphine oxide (65 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 5:1) to afford the title compound as a white solid (93 mg, 87% yield); Melting point: 79–81 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.86–7.69 (m, 4H), 7.51–7.29 (m, 6H), 2.14–1.94 (m, 1H), 1.92–1.70 (m, 2H), 1.41–1.17 (m, 12H), 0.95 (t, J = 7.4 Hz, 3H), 0.91–0.62 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.1 (d, J = 96.3 Hz), 135.2 (d, J = 92.5 Hz), 131.2 (d, J = 2.6 Hz), 131.1 (d, J = 9.0 Hz), 130.8 (d, J = 2.8 Hz), 130.6 (d, J = 8.5 Hz), 128.6 (d, J = 8.4 Hz), 128.5 (d, J = 8.6 Hz), 29.0, 27.5 (d, J = 63.7 Hz), 27.4, 19.9 (d, J = 3.3 Hz), 16.5 (d, J = 12.8 Hz), 13.7, 10.9 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 35.9. HRMS (ESI$^+$): calcd for $C_{27}H_{44}OPSn$ [M+H]$^+$ 535.2146, found 535.2143.



(5-chloro-1-(tributylstannyl)pentyl)diphenylphosphine oxide (7b)

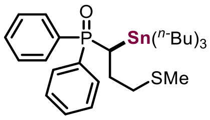
The general procedure K was applied to (1-bromo-5-chloropentyl)diphenylphosphine oxide (77 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 2:1) to afford the title compound as a white solid (107 mg, 90% yield); Melting point: 86–88 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.86–7.69 (m, 4H), 7.54–7.31 (m, 6H), 3.46–3.14 (m, 2H), 2.14–2.03 (m, 1H), 1.84–1.69 (m, 2H), 1.66–1.55 (m, 2H), 1.43–1.16 (m, 14H), 0.94–0.61 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.9 (d, J = 89.5 Hz), 135.0 (d, J = 85.2 Hz), 131.3 (d, J = 2.7 Hz), 131.0 (d, J = 9.0 Hz), 130.9 (d, J = 2.6 Hz), 130.6 (d, J = 8.6 Hz), 128.7 (d, J = 5.5 Hz), 128.6 (d, J = 5.6 Hz), 44.7, 33.1 (d, J = 63.1 Hz), 32.6, 29.0, 27.4, 26.0 (d, J = 3.3 Hz), 25.3 (d, J = 63.7 Hz), 13.7, 11.0 (d, J

= 1.5 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 35.7. HRMS (ESI$^+$): calcd for $C_{29}H_{47}ClOPSn$ [M+H]$^+$ 597.2070, found 597.2074.



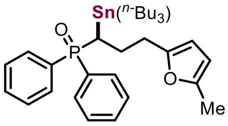
(cyclopentyl(tributylstannyl)methyl)diphenylphosphine oxide (7c)

The general procedure K was applied to (bromo(cyclopentyl)methyl)diphenylphosphine oxide (73 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 4:1) to afford the title compound as a white solid (99 mg, 86% yield); Melting point: 100–102 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.85–7.68 (m, 4H), 7.50–7.29 (m, 6H), 2.57–2.48 (m, 1H), 2.31–2.11 (m, 1H), 1.94–1.81 (m, 1H), 1.60–1.48 (m, 3H), 1.40–1.12 (m, 16H), 0.92–0.67 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.9 (d, J = 30.3 Hz), 135.9 (d, J = 26.3 Hz), 131.1 (d, J = 2.6 Hz), 131.1 (d, J = 9.1 Hz), 130.8 (d, J = 9.2 Hz), 130.6 (d, J = 8.6 Hz), 128.5 (d, J = 11.0 Hz), 128.4 (d, J = 11.6 Hz), 39.3 (d, J = 3.5 Hz), 35.4 (d, J = 12.1 Hz), 34.9 (d, J = 5.9 Hz), 32.4 (d, J = 61.9 Hz), 29.0, 27.4, 25.0, 24.5, 13.7, 12.2 (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 34.5. HRMS (ESI$^+$): calcd for $C_{30}H_{48}OPSn$ [M+H]$^+$ 575.2459, found 575.2463.



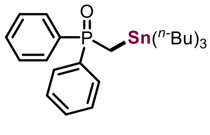
(3-(methylthio)-1-(tributylstannyl)propyl)diphenylphosphine oxide (7d)

The general procedure K was applied to (1-bromo-3-(methylthio)propyl)diphenylphosphine oxide (74 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 3:1) to afford the title compound as a colorless oil (108 mg, 93% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.87–7.74 (m, 4H), 7.47–7.32 (m, 6H), 2.53–2.37 (m, 2H), 2.33–2.20 (m, 1H), 2.11–1.93 (m, 2H), 1.81 (s, 3H), 1.40–1.15 (m, 12H), 0.91–0.66 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.8 (d, J = 83.6 Hz), 134.9 (d, J = 78.6 Hz), 131.3 (d, J = 2.6 Hz), 131.0 (d, J = 9.0 Hz), 130.9 (d, J = 2.7 Hz), 130.5 (d, J = 8.6 Hz), 128.6 (d, J = 8.4 Hz), 128.5 (d, J = 8.6 Hz), 35.4 (d, J = 11.9 Hz), 28.9, 27.4, 25.4 (d, J = 2.8 Hz), 23.9 (d, J = 64.1 Hz), 15.0, 13.6, 10.9 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 35.4. HRMS (ESI$^+$): calcd for $C_{28}H_{46}OPSSn$ [M+H]$^+$ 581.2023, found 581.2020.



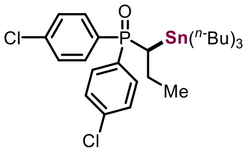
(3-(5-methylfuran-2-yl)-1-(tributylstannyl)propyl)diphenylphosphine oxide (7e)

The general procedure K was applied to (1-bromo-3-(5-methylfuran-2-yl)propyl)diphenylphosphine oxide (81 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 3:1) to afford the title compound as a colorless oil (104 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.79–7.64 (m, 4H), 7.48–7.31 (m, 6H), 5.83 (d, J = 4.1 Hz, 1H), 5.75 (d, J = 2.9 Hz, 1H), 2.64–2.54 (m, 1H), 2.47–2.36 (m, 1H), 2.26–2.16 (m, 4H), 2.15–1.99 (m, 2H), 1.39–1.18 (m, 12H), 0.90–0.72 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 152.9, 150.5, 135.9 (d, J = 96.1 Hz), 134.9 (d, J = 92.1 Hz), 131.2 (d, J = 2.6 Hz), 131.0 (d, J = 9.0 Hz), 130.8 (d, J = 2.7 Hz), 130.5 (d, J = 8.5 Hz), 128.6 (d, J = 9.1 Hz), 128.4 (d, J = 9.2 Hz), 106.4, 105.9, 29.3 (d, J = 12.2 Hz), 28.9, 27.4, 25.0 (d, J = 3.1 Hz), 24.2 (d, J = 64.2 Hz), 13.7, 13.6, 10.9 (d, J = 1.2 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 35.9. HRMS (ESI$^+$): calcd for $C_{32}H_{48}O_2PSn$ [M+H]$^+$ 615.2408, found 615.2396.



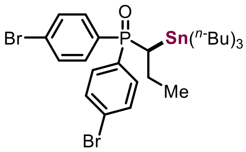
diphenyl((tributylstannyl)methyl)phosphine oxide (7f)

The general procedure K was applied to (bromomethyl)diphenylphosphine oxide (59 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 3:1) to afford the title compound as a white solid (91 mg, 90% yield); Melting point: 75–77 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.81–7.65 (m, 4H), 7.47–7.32 (m, 6H), 1.75–1.56 (m, 2H), 1.41–1.28 (m, 6H), 1.25–1.16 (m, 6H), 0.92–0.76 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 137.1 (d, J = 98.1 Hz), 131.0 (d, J = 2.7 Hz), 130.4 (d, J = 9.5 Hz), 128.4 (d, J = 11.6 Hz), 28.9, 27.3, 13.7, 10.8 (d, J = 1.7 Hz), 9.6 (d, J = 67.0 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 33.6. HRMS (ESI$^+$): calcd for $C_{25}H_{40}OPSn$ [M+H]$^+$ 507.1833, found 507.1821.



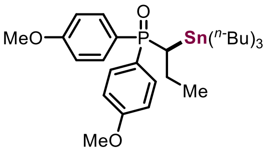
bis(4-chlorophenyl)(1-(tributylstannyl)propyl)phosphine oxide (7g)

The general procedure K was applied to (1-bromopropyl)bis(4-chlorophenyl)phosphine oxide (78 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 7:1) to afford the title compound as a white solid (111 mg, 92% yield); Melting point: 82–84 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.75–7.59 (m, 4H), 7.39 (td, J = 8.6, 2.1 Hz, 4H), 2.05–1.87 (m, 1H), 1.86–1.66 (m, 2H), 1.39–1.15 (m, 12H), 0.94 (t, J = 7.4 Hz, 3H), 0.88–0.69 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.0 (d, J = 3.2 Hz), 137.5 (d, J = 3.3 Hz), 134.3 (d, J = 96.9 Hz), 133.3 (d, J = 93.0 Hz), 132.4 (d, J = 9.8 Hz), 131.9 (d, J = 9.3 Hz), 129.0 (d, J = 5.2 Hz), 128.9 (d, J = 5.4 Hz), 29.0, 27.4, 26.8, 19.8 (d, J = 3.4 Hz), 16.5 (d, J = 12.9 Hz), 13.7, 11.1 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 35.1. HRMS (ESI$^+$): calcd for $C_{27}H_{42}Cl_2OPSn$ [M+H]$^+$ 603.1367, found 603.1356.



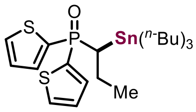
bis(4-bromophenyl)(1-(tributylstannyl)propyl)phosphine oxide (7h)

The general procedure K was applied to bis(4-bromophenyl)(1-bromopropyl)phosphine oxide (96 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 6:1) to afford the title compound as a white solid (126 mg, 91% yield); Melting point: 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.47 (m, 8H), 2.04–1.88 (m, 1H), 1.86–1.67 (m, 2H), 1.39–1.16 (m, 12H), 0.94 (t, J = 7.4 Hz, 3H), 0.90–0.69 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.7 (d, J = 96.4 Hz), 133.7 (d, J = 92.5 Hz), 132.5 (d, J = 9.6 Hz), 132.0 (d, J = 7.2 Hz), 131.9 (d, J = 3.7 Hz), 131.8 (d, J = 5.9 Hz), 126.5 (d, J = 3.3 Hz), 126.1 (d, J = 3.4 Hz), 29.0, 27.4, 27.0 (d, J = 64.4 Hz), 19.8 (d, J = 3.4 Hz), 16.5 (d, J = 12.9 Hz), 13.7, 11.1 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.4. HRMS (ESI$^+$): calcd for $C_{27}H_{42}Br_2OPSn$ [M+H]$^+$ 691.0357, found 691.0359.



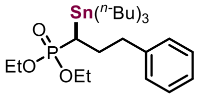
bis(4-methoxyphenyl)(1-(tributylstannyl)propyl)phosphine oxide (7i)

The general procedure K was applied to (1-bromopropyl)bis(4-methoxyphenyl)phosphine oxide (77 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 2:1) to afford the title compound as a white solid (101 mg, 85% yield); Melting point: 95–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.54 (m, 4H), 7.02–6.75 (m, 4H), 3.77 (d, J = 3.6 Hz, 6H), 2.03–1.90 (m, 1H), 1.87–1.64 (m, 2H), 1.40–1.26 (m, 6H), 1.25–1.17 (m, 6H), 0.93 (t, J = 7.4 Hz, 3H), 0.89–0.70 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9 (d, J = 2.8 Hz), 161.6 (d, J = 2.9 Hz), 132.7 (d, J = 10.2 Hz), 132.2 (d, J = 9.7 Hz), 127.7 (d, J = 102.1 Hz), 126.6 (d, J = 98.5 Hz), 114.1 (d, J = 5.9 Hz), 113.9 (d, J = 6.0 Hz), 55.3 (d, J = 4.9 Hz), 29.0, 28.2 (d, J = 64.5 Hz), 27.4, 20.0 (d, J = 3.4 Hz), 16.5 (d, J = 12.7 Hz), 13.7, 10.9 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.0. HRMS (ESI$^+$): calcd for $C_{29}H_{48}O_3PSn$ [M+H]$^+$ 595.2358, found 595.2344.



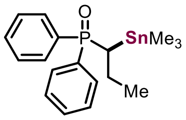
di(thiophen-2-yl)(1-(tributylstannyl)propyl)phosphine oxide (7j)

The general procedure K was applied to (1-bromopropyl)di(thiophen-2-yl)phosphine oxide (67 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 3.5:1) to afford the title compound as a colorless oil (89 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.60 (m, 2H), 7.60–7.51 (m, 2H), 7.17–7.09 (m, 2H), 1.97–1.78 (m, 3H), 1.46–1.34 (m, 6H), 1.28–1.22 (m, 6H), 0.99–0.82 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4 (d, J = 100.3 Hz), 136.3 (d, J = 97.3 Hz), 134.9 (d, J = 9.1 Hz), 134.7 (d, J = 8.8 Hz), 132.4 (d, J = 4.6 Hz), 132.4 (d, J = 4.6 Hz), 128.3 (d, J = 13.2 Hz), 128.1 (d, J = 13.3 Hz), 32.9 (d, J = 71.4 Hz), 29.1, 27.5, 20.1 (d, J = 3.2 Hz), 16.4 (d, J = 13.4 Hz), 13.7, 11.0 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.0. HRMS (ESI$^+$): calcd for $C_{23}H_{40}OPS_2Sn$ [M+H]$^+$ 547.1275, found 547.1267.



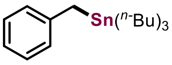
diethyl (3-phenyl-1-(tributylstannyl)propyl)phosphonate (7k)

The general procedure K was applied to diethyl (1-bromo-3-phenylpropyl)phosphonate (67 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 3:1) to afford the title compound as a colorless oil (93 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.26 (m, 2H), 7.24–7.16 (m, 3H), 4.19–3.96 (m, 4H), 2.92–2.62 (m, 2H), 2.30–2.13 (m, 1H), 2.03–1.83 (m, 1H), 1.58–1.41 (m, 7H), 1.38–1.27 (m, 12H), 1.10–0.95 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 128.6, 128.5, 126.0, 61.2 (d, J = 6.7 Hz), 61.1 (d, J = 7.0 Hz), 37.7 (d, J = 8.7 Hz), 29.1, 28.8 (d, J = 4.8 Hz), 27.5, 20.2 (d, J = 132.1 Hz), 16.7 (d, J = 2.7 Hz), 16.6 (d, J = 2.9 Hz), 13.8, 10.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.4. HRMS (ESI$^+$): calcd for $C_{25}H_{48}O_3PSn$ [M+H]$^+$ 547.2358, found 547.2359.



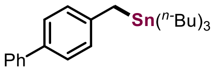
diphenyl(1-(trimethylstannyl)propyl)phosphine oxide (7l)

The general procedure K was applied to (1-bromopropyl)diphenylphosphine oxide (65 mg, 0.2 mmol) and chlorotrimethylstannane (48 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 2:1) to afford the title compound as a colorless oil (71 mg, 87% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.83–7.67 (m, 4H), 7.52–7.32 (m, 6H), 2.05–1.93 (m, 1H), 1.90–1.71 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.8 (d, J = 96.4 Hz), 134.7 (d, J = 92.9 Hz), 131.3 (d, J = 2.7 Hz), 131.0 (d, J = 9.0 Hz), 130.9 (d, J = 2.7 Hz), 130.5 (d, J = 8.6 Hz), 128.6 (d, J = 9.9 Hz), 128.5 (d, J = 10.1 Hz), 28.3 (d, J = 63.4 Hz), 19.7 (d, J = 3.4 Hz), 16.3 (d, J = 13.6 Hz), -7.6 (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, CDCl$_3$): δ = 36.1. HRMS (ESI$^+$): calcd for $C_{18}H_{26}OPSn$ [M+H]$^+$ 409.0738, found 409.0730.



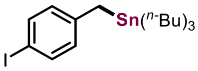
benzyltributylstannane (9a)

The general procedure L was applied to (bromomethyl)benzene (34 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (59 mg, 78% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.17 (t, J = 7.6 Hz, 2H), 7.08–6.89 (m, 3H), 2.31 (s, 2H), 1.50–1.37 (m, 6H), 1.31–1.23 (m, 6H), 0.92–0.72 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.9, 128.4, 127.1, 123.0, 29.2, 27.5, 18.3, 13.8, 9.4. Spectroscopic data are in accordance with those described in the literature.[13]



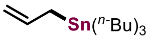
([1,1'-biphenyl]-4-ylmethyl)tributylstannane (9b)

The general procedure L was applied to 4-(bromomethyl)-1,1'-biphenyl (49 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (69 mg, 75% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.63–7.56 (m, 2H), 7.48–7.39 (m, 4H), 7.31 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 8.2 Hz, 2H), 2.38 (s, 2H), 1.54–1.38 (m, 6H), 1.34–1.25 (m, 6H), 0.96–0.79 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.2, 141.5, 135.9, 128.8, 127.5, 127.1, 126.8, 126.7, 29.2, 27.5, 18.1, 13.8, 9.5. Spectroscopic data are in accordance with those described in the literature.[14]



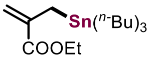
tributyl(4-iodobenzyl)stannane (9c)

The general procedure L was applied to 1-(bromomethyl)-4-iodobenzene (59 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (86 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (d, J = 8.3 Hz, 2H), 6.75 (d, J = 8.3 Hz, 2H), 2.25 (s, 2H), 1.50–1.35 (m, 6H), 1.31–1.23 (m, 6H), 0.93–0.79 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.8, 137.3, 129.2, 86.7, 29.1, 27.5, 18.1, 13.8, 9.5.



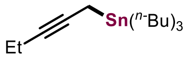
allyltributylstannane (9d)

The general procedure L was applied to allyl bromide (24 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (50 mg, 76% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.05–5.83 (m, 1H), 4.87–4.71 (m, 1H), 4.64 (dd, J = 9.9, 2.1 Hz, 1H), 1.78 (d, J = 8.5 Hz, 2H), 1.56–1.42 (m, 6H), 1.36–1.25 (m, 6H), 0.97–0.78 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.3, 109.3, 29.3, 27.5, 16.3, 13.9, 9.3. Spectroscopic data are in accordance with those described in the literature.[15]



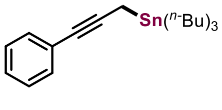
ethyl 2-((tributylstannyl)methyl)acrylate (9e)

The general procedure L was applied to ethyl 2-(bromomethyl)acrylate (39 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the title compound as a colorless oil (42 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (d, J = 1.6 Hz, 1H), 5.35–5.20 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.97 (d, J = 1.1 Hz, 2H), 1.53–1.40 (m, 6H), 1.34–1.24 (m, 9H), 0.94–0.78 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 141.5, 118.6, 60.8, 29.1, 27.5, 15.0, 14.4, 13.9, 9.9. Spectroscopic data are in accordance with those described in the literature.[16]



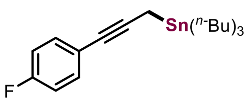
tributyl(pent-2-yn-1-yl)stannane (9f)

The general procedure L was applied to 1-bromopent-2-yne (29 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (41 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22–2.07 (m, 2H), 1.60–1.44 (m, 8H), 1.37–1.26 (m, 6H), 1.09 (t, J = 7.5 Hz, 3H), 1.05–0.84 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.6, 79.5, 29.1, 27.4, 14.9, 13.9, 12.9, 9.9, -4.2.



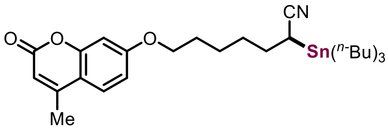
tributyl(3-phenylprop-2-yn-1-yl)stannane (9g)

The general procedure L was applied to (3-bromoprop-1-yn-1-yl)benzene (39 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (61 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, J = 8.2, 1.6 Hz, 2H), 7.29–7.18 (m, 3H), 1.79 (s, 2H), 1.66–1.51 (m, 6H), 1.41–1.30 (m, 6H), 1.12–0.97 (m, 6H), 0.92 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.3, 128.2, 126.7, 125.5, 91.8, 78.9, 29.1, 27.4, 13.9, 10.2, -3.0.



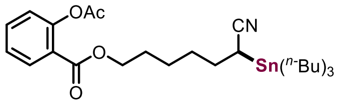
tributyl(3-(4-fluorophenyl)prop-2-yn-1-yl)stannane (9h)

The general procedure L was applied to 1-(3-bromoprop-1-yn-1-yl)-4-fluorobenzene (43 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE) to afford the title compound as a colorless oil (60 mg, 71% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.28 (dd, *J* = 8.6, 5.6 Hz, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 1.75 (s, 2H), 1.64–1.47 (m, 6H), 1.39–1.28 (m, 6H), 1.11–0.94 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 161.7 (d, *J* = 247.0 Hz), 132.9 (d, *J* = 8.1 Hz), 121.5 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 21.8 Hz), 91.4 (d, *J* = 1.4 Hz), 77.7, 29.1, 27.4, 13.9, 10.2, -3.1; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -113.8.



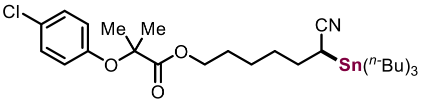
7-((4-methyl-2-oxo-*2H*-chromen-7-yl)oxy)-2-(tributylstannyl)heptanenitrile (10)

The general procedure K was applied to 1-cyano-6-((4-methyl-2-oxo-*2H*-chromen-7-yl)oxy)hexyl trifluoromethanesulfonate (87 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 4:1) to afford the title compound as a colorless oil (78 mg, 68% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.48 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 6.12 (d, *J* = 1.4 Hz, 1H), 4.01 (t, *J* = 6.3 Hz, 2H), 2.38 (d, *J* = 1.3 Hz, 3H), 1.91–1.78 (m, 3H), 1.73–1.44 (m, 13H), 1.37–1.29 (m, 6H), 1.16–0.99 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 162.2, 161.5, 155.4, 152.7, 125.6, 124.8, 113.6, 112.7, 112.0, 101.5, 68.4, 30.7, 29.0, 28.9, 28.9, 27.4, 25.5, 18.8, 13.7, 10.2, 9.5. HRMS (ESI$^+$): calcd for $C_{29}H_{46}NO_3Sn$ $[M+H]^+$ 576.2494, found 576.2487.



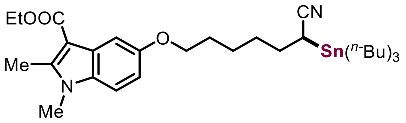
6-cyano-6-(tributylstannyl)hexyl 2-acetoxybenzoate (11)

The general procedure K was applied to 6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl 2-acetoxybenzoate (88 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a colorless oil (100 mg, 86% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.01 (dd, J = 7.8, 1.7 Hz, 1H), 7.54 (td, J = 7.7, 1.7 Hz, 1H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.09 (dd, J = 8.1, 1.1 Hz, 1H), 4.26 (t, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.97–1.81 (m, 1H), 1.79–1.68 (m, 3H), 1.64–1.42 (m, 11H), 1.37–1.29 (m, 6H), 1.14–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 169.7, 164.5, 150.8, 133.9, 131.8, 126.1, 124.8, 123.9, 123.5, 65.1, 30.7, 28.9, 28.8, 28.6, 27.3, 25.5, 21.1, 13.7, 10.1, 9.4. HRMS (ESI$^+$): calcd for $C_{28}H_{46}NO_4Sn$ [M+H]$^+$ 580.2443, found 580.2430.



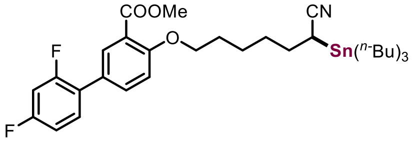
6-cyano-6-(tributylstannyl)hexyl 2-(4-chlorophenoxy)-2-methylpropanoate (12)

The general procedure K was applied to 6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl 2-(4-chlorophenoxy)-2-methylpropanoate (94 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 15:1) to afford the title compound as a colorless oil (110 mg, 90% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.17 (d, J = 8.9 Hz, 2H), 6.76 (d, J = 8.9 Hz, 2H), 4.13 (t, J = 6.5 Hz, 2H), 1.92–1.74 (m, 1H), 1.63–1.47 (m, 16H), 1.43–1.16 (m, 10H), 1.14–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 174.1, 154.2, 129.2, 127.1, 124.7, 120.3, 79.5, 65.5, 30.5, 28.8, 28.4, 27.3, 25.4, 25.4, 25.3, 13.7, 10.1, 9.4. HRMS (ESI$^+$): calcd for $C_{29}H_{49}ClNO_3Sn$ [M+H]$^+$ 614.2417, found 614.2413.



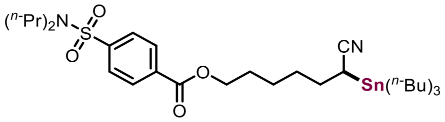
ethyl 5-((6-cyano-6-(tributylstannyl)hexyl)oxy)-1,2-dimethyl-*1H*-indole-3-carboxylate (13)

The general procedure K was applied to ethyl 5-((6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl)oxy)-1,2-dimethyl-*1H*-indole-3-carboxylate (98 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 5:1) to afford the title compound as a yellow oil (104 mg, 82% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.63 (d, J = 2.5 Hz, 1H), 7.11 (d, J = 8.8 Hz, 1H), 6.84 (dd, J = 8.8, 2.5 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 3.57 (s, 3H), 2.67 (s, 3H), 1.92–1.69 (m, 4H), 1.69–1.47 (m, 11H), 1.43 (t, J = 7.1 Hz, 3H), 1.39–1.27 (m, 6H), 1.16–0.98 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.1, 155.0, 145.2, 131.6, 127.4, 124.8, 112.0, 109.6, 104.6, 103.5, 68.3, 59.2, 30.7, 29.6, 29.3, 28.9, 28.8, 27.3, 25.6, 14.7, 13.6, 12.0, 10.1, 9.4. HRMS (ESI$^+$): calcd for $C_{32}H_{53}N_2O_3Sn$ [M+H]$^+$ 633.3073, found 633.3079.



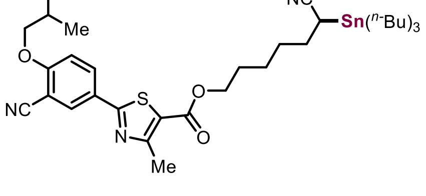
methyl 4-((6-cyano-6-(tributylstannyl)hexyl)oxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate (14)

The general procedure K was applied to methyl 4-((6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl)oxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate (104 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 8:1) to afford the title compound as a colorless oil (114 mg, 86% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.91 (dd, J = 2.5, 1.2 Hz, 1H), 7.57 (dt, J = 8.7, 2.1 Hz, 1H), 7.37 (td, J = 8.7, 6.4 Hz, 1H), 7.01 (d, J = 8.7 Hz, 1H), 6.96–6.82 (m, 2H), 4.08 (t, J = 6.3 Hz, 2H), 3.89 (s, 3H), 1.96–1.80 (m, 3H), 1.77–1.46 (m, 12H), 1.38–1.28 (m, 6H), 1.17–0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.6, 163.5 (d, J = 11.8 Hz), 161.0 (d, J = 11.8 Hz), 158.5 (d, J = 11.9 Hz), 158.2, 133.8 (d, J = 3.5 Hz), 132.1 (d, J = 2.5 Hz), 131.2 (dd, J = 9.4, 4.8 Hz), 126.9 (d, J = 1.3 Hz), 124.8, 124.1 (dd, J = 13.6, 3.8 Hz), 120.5, 113.3, 111.7 (dd, J = 21.1, 3.8 Hz), 104.4 (dd, J = 26.8, 25.3 Hz), 68.8, 52.1, 30.6, 29.0, 28.9, 28.8, 27.3, 25.4, 13.7, 10.1, 9.5; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -111.5 (d, J = 7.5 Hz), -113.7 (d, J = 7.5 Hz). HRMS (ESI$^+$): calcd for $C_{33}H_{48}F_2NO_3Sn$ [M+H]$^+$ 664.2619, found 664.2615.



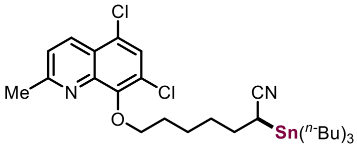
6-cyano-6-(tributylstannyl)hexyl 4-(*N,N*-dipropylsulfamoyl)benzoate (15)

The general procedure K was applied to 6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl 4-(*N,N*-dipropylsulfamoyl)benzoate (109 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 8:1) to afford the title compound as a colorless oil (116 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.14 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 4.34 (t, J = 6.5 Hz, 2H), 3.15–3.00 (m, 4H), 1.90–1.73 (m, 3H), 1.72–1.42 (m, 16H), 1.37–1.27 (m, 6H), 1.16–0.98 (m, 6H), 0.96–0.78 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.4, 144.3, 133.8, 130.3, 127.1, 124.8, 65.6, 50.0, 30.7, 28.9, 28.8, 28.6, 27.4, 25.6, 22.0, 13.7, 11.2, 10.2, 9.5. HRMS (ESI$^+$): calcd for $C_{32}H_{57}N_2O_4SSn$ [M+H]$^+$ 685.3056, found 685.3057.



6-cyano-6-(tributylstannyl)hexyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (16)

In a dried Schlenk tube under a nitrogen atmosphere, $CrCl_2$ (2.5 mg, 0.02 mmol), Bphen (6.6 mg, 0.02 mmol), and manganese powder (17 mg, 0.3 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, tributylchlorostannane (78 mg, 0.24 mmol) and 6-cyano-6-(((trifluoromethyl)sulfonyl)oxy)hexyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (115 mg, 0.2 mmol) were added sequentially. The reaction mixture was stirred at 80 °C for 5 h. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 8:1) to afford the title compound as a white solid (96 mg, 67% yield); Melting point: 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 2.3 Hz, 1H), 8.07 (dd, J = 8.8, 2.3 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H), 4.28 (t, J = 6.5 Hz, 2H), 3.88 (d, J = 6.5 Hz, 2H), 2.74 (s, 3H), 2.26–2.10 (m, J = 6.7 Hz, 1H), 1.91–1.83 (m, 1H), 1.79–1.70 (m, 3H), 1.66–1.41 (m, 11H), 1.36–1.27 (m, 6H), 1.14–1.00 (m, 12H), 0.89 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 162.6, 162.1, 161.2, 132.7, 132.1, 126.1, 124.8, 121.9, 115.4, 112.7, 103.0, 75.8, 65.3, 30.6, 28.9, 28.8, 28.6, 28.2, 27.3, 25.5, 19.1, 17.6, 13.7, 10.2, 9.4. HRMS (ESI$^+$): calcd for $C_{35}H_{54}N_3O_3SSn$ [M+H]$^+$ 716.2902, found 716.2908.

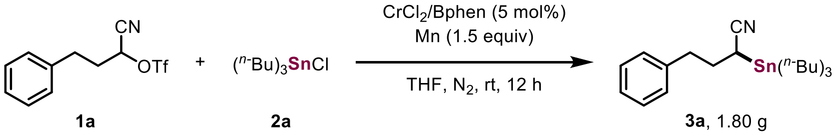


7-((5,7-dichloro-2-methylquinolin-8-yl)oxy)-2-(tributylstannyl)heptanenitrile (17)

The general procedure K was applied to 1-cyano-6-((5,7-dichloro-2-methylquinolin-8-yl)oxy)hexyl trifluoromethanesulfonate (97 mg, 0.2 mmol) and tributylchlorostannane (78 mg, 0.24 mmol). The crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a colorless oil (115 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.7 Hz, 1H), 7.52 (s, 1H), 7.35 (d, J = 8.6 Hz, 1H), 4.35 (t, J = 6.4 Hz, 2H), 2.76 (s, 3H), 1.98–1.83 (m, 3H), 1.82–1.44 (m, 12H), 1.37–1.27 (m, 6H), 1.16–0.98 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 150.5, 143.4, 133.3, 126.9, 126.6, 125.8, 124.9, 124.6, 122.9, 75.1, 30.7, 30.1, 29.0, 28.8, 27.4, 25.6, 25.5, 13.7, 10.1, 9.5. HRMS (ESI$^+$): calcd for $C_{29}H_{45}Cl_2N_2OSn$ [M+H]$^+$ 627.1925, found 627.1920.

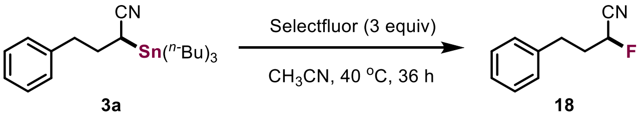
6. Scalability and Synthetic Applications

6.1 Scale-up Cross-Electrophile Coupling



In a 100 mL dried Schlenk flask under a nitrogen atmosphere, $CrCl_2$ (31 mg, 0.25 mmol), Bphen (83 mg, 0.25 mmol), and manganese powder (412 mg, 7.5 mmol) were placed, followed by the addition of anhydrous THF (50 mL) via syringe. After stirring the mixture at room temperature for 30 s, tributylchlorostannane (**2a**, 1.95 g, 6 mmol) and 1-cyano-3-phenylpropyl trifluoromethanesulfonate (**1a**, 1.47 g, 5 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatiles under reduced pressure, the crude residue was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the corresponding stannylation product **3a** as a colorless oil (1.80 g, 83% yield).

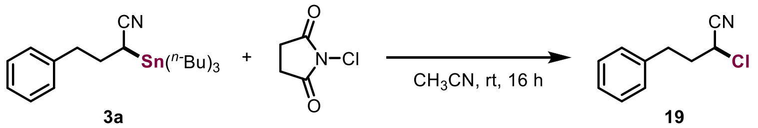
6.2 Late-Stage Functionalization of 3a



3a (87 mg, 0.2 mmol) and Selectfluor (213 mg, 0.6 mmol) were added to a Schlenk tube equipped with a stir bar. The tube was purged with N_2, and anhydrous CH_3CN (2 mL) was added via syringe. The reaction mixture was stirred at 40 °C for 36 h. The reaction was quenched with water and extracted with EA three times. The combined organic phase was washed sequentially with water and brine, dried over Na_2SO_4, and filtered. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (21 mg, 65% yield).

2-fluoro-4-phenylbutanenitrile (18)

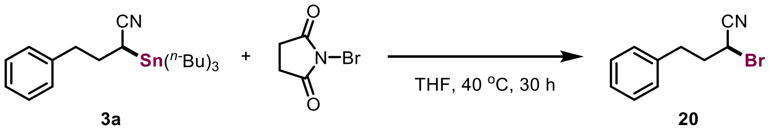
^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.38–7.30$ (m, 2H), 7.29–7.17 (m, 3H), 5.19–4.94 (m, 1H), 2.97–2.72 (m, 2H), 2.45–2.16 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.8, 129.0, 128.6, 127.0, 116.0 (d, J = 30.5 Hz), 78.8 (d, J = 181.6 Hz), 35.3 (d, J = 21.7 Hz), 30.1 (d, J = 4.3 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -189.5. Spectroscopic data are in accordance with those described in the literature.[17]



3a (87 mg, 0.2 mmol) and *N*-chlorosuccinimide (NCS, 81 mg, 0.6 mmol) were added to a Schlenk tube equipped with a stir bar. The tube was purged with N$_2$, and anhydrous CH$_3$CN (2 mL) was added via syringe. The reaction mixture was stirred at room temperature for 16 h. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (34 mg, 94% yield).

2-chloro-4-phenylbutanenitrile (19)

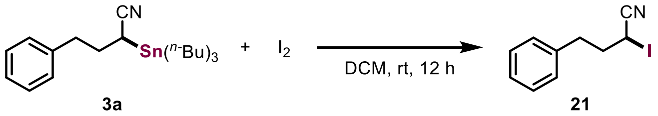
^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.39–7.31$ (m, 2H), 7.30–7.24 (m, 1H), 7.24–7.19 (m, 2H), 4.34 (t, J = 7.0 Hz, 1H), 3.00–2.81 (m, 2H), 2.46–2.27 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.5, 129.0, 128.6, 127.0, 117.1, 41.7, 37.9, 31.7. Spectroscopic data are in accordance with those described in the literature.[18]



3a (87 mg, 0.2 mmol) and *N*-bromosuccinimide (NBS, 107 mg, 0.6 mmol) were added to a Schlenk tube equipped with a stir bar. The tube was purged with N$_2$, and anhydrous THF (2 mL) was added via syringe. The reaction mixture was stirred at 40 °C for 30 h. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (44 mg, 99% yield).

2-bromo-4-phenylbutanenitrile (20)

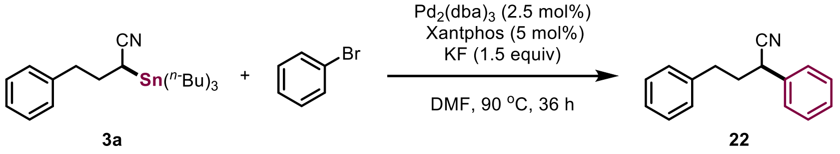
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 2H), 7.30–7.24 (m, 1H), 7.24–7.18 (m, 2H), 4.19 (t, J = 7.1 Hz, 1H), 2.91 (t, J = 7.4 Hz, 2H), 2.41 (qd, J = 7.2, 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 129.0, 128.6, 127.0, 117.3, 38.1, 32.9, 26.4. Spectroscopic data are in accordance with those described in the literature.[19]



3a (87 mg, 0.2 mmol) and I_2 (102 mg, 0.4 mmol) were added to a Schlenk tube equipped with a stir bar. The tube was purged with N_2, and anhydrous DCM (2 mL) was added via syringe. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a yellow oil (52 mg, 95% yield).

2-iodo-4-phenylbutanenitrile (21)

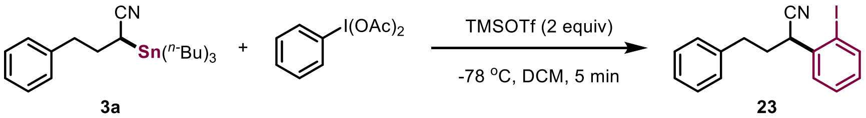
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 2H), 7.30–7.24 (m, 1H), 7.21 (d, J = 7.0 Hz, 2H), 4.10 (t, J = 7.3 Hz, 1H), 2.97–2.71 (m, 2H), 2.40–2.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 129.0, 128.6, 127.0, 119.1, 39.2, 34.9, -5.1. HRMS (ESI$^+$): calcd for $C_{10}H_{11}IN$ [M+H]$^+$ 271.9931, found 271.9930.



To a solution of bromobenzene (31 mg, 0.2 mmol) in DMF (0.2 mL) were added $Pd_2(dba)_3$ (5 mg, 0.005 mmol), Xantphos (6 mg, 0.01 mmol), **3a** (104 mg, 0.24 mmol), and KF (17 mg, 0.3 mmol). The flask was sealed and the mixture was stirred at 90 °C for 36 h. The reaction was then quenched by water after the reaction was cooled to room temperature. The mixture was extracted with EA three times. The combined organic layers were washed sequentially with water and brine, dried over Na_2SO_4, and filtered. After the solvents were removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a colorless oil (36 mg, 82% yield).

2,4-diphenylbutanenitrile (22)

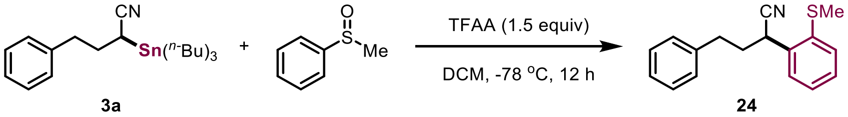
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46–7.38 (m, 2H), 7.38–7.30 (m, 5H), 7.29–7.19 (m, 3H), 3.77 (dd, J = 9.0, 6.1 Hz, 1H), 2.96–2.75 (m, 2H), 2.36–2.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.9, 135.7, 129.2, 128.8, 128.5, 128.2, 127.4, 126.6, 120.7, 37.4, 36.6, 33.1. Spectroscopic data are in accordance with those described in the literature.[20]



Followed a reported procedure,[11] to a solution of [bis(acetoxy)iodo]benzene (64 mg, 0.2 mmol) in DCM (2 mL) was added TMSOTf (89 mg, 0.4 mmol) at room temperature. After stirring for 5 min, the reaction mixture was cooled to -78 °C. **3a** (261 mg, 0.6 mmol) was added to the mixture at this temperature. The mixture was then stirred for an additional 5 min. After that, the mixture was filtered through a short silica gel column and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a yellow oil (51 mg, 74% yield).

2-(2-iodophenyl)-4-phenylbutanenitrile (23)

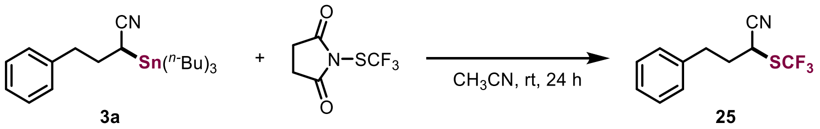
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.62 (dd, J = 7.8, 1.7 Hz, 1H), 7.42 (td, J = 7.5, 1.3 Hz, 1H), 7.37–7.31 (m, 2H), 7.31–7.22 (m, 3H), 7.02 (td, J = 7.7, 1.7 Hz, 1H), 4.14 (dd, J = 9.9, 5.1 Hz, 1H), 3.05–2.94 (m, 1H), 2.94–2.81 (m, 1H), 2.30–1.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.1, 139.6, 138.6, 129.9, 129.2, 128.7, 128.3, 126.6, 120.3, 98.8, 41.4, 36.5, 33.4. Spectroscopic data are in accordance with those described in the literature.[11]



Followed a reported procedure,[21] to a mixture of (methylsulfinyl)benzene (28 mg, 0.2 mmol) and **3a** (130 mg, 0.3 mmol) in DCM (1 mL) was added TFAA (63 mg, 0.3 mmol) at -78 °C. After stirring at -78 °C for 12 h, the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$. The mixture was then extracted with DCM. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the title compound as a colorless oil (50 mg, 93% yield).

2-(2-(methylthio)phenyl)-4-phenylbutanenitrile (24)

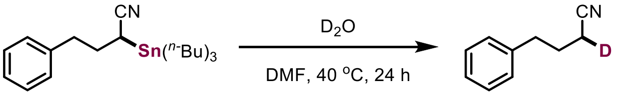
^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.4 Hz, 1H), 7.35–7.28 (m, 4H), 7.28–7.20 (m, 4H), 4.43–4.29 (m, 1H), 3.00–2.90 (m, 1H), 2.89–2.78 (m, 1H), 2.46 (s, 3H), 2.25–2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 136.5, 134.8, 128.9, 128.6, 128.6, 128.2, 127.8, 126.5, 126.4, 120.8, 36.2, 34.3, 33.5, 17.0. HRMS (ESI$^+$): calcd for $C_{17}H_{18}NS$ $[M+H]^+$ 268.1154, found 268.1149.



3a (87 mg, 0.2 mmol) and 1-((trifluoromethyl)thio)pyrrolidine-2,5-dione (120 mg, 0.6 mmol) were added to a Schlenk tube equipped with a stir bar. The tube was purged with N_2, and anhydrous CH_3CN (2 mL) was added via syringe. The reaction mixture was stirred at room temperature for 24 h. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (39 mg, 80% yield).

4-phenyl-2-((trifluoromethyl)thio)butanenitrile (25)

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 2H), 7.31–7.25 (m, 1H), 7.25–7.18 (m, 2H), 3.85 (dd, J = 8.1, 6.7 Hz, 1H), 3.04–2.79 (m, 2H), 2.38–2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 129.4 (q, J = 309.1 Hz), 129.1, 128.6, 127.2, 117.4, 34.1, 32.6, 30.8 (q, J = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -40.2. Spectroscopic data are in accordance with those described in the literature.[22]



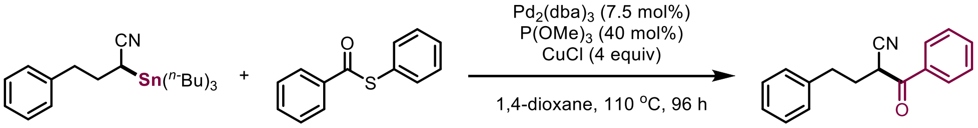
3a

26

3a (87 mg, 0.2 mmol) was added to a Schlenk tube equipped with a stir bar. The tube was purged with N_2, and anhydrous DMF (2 mL) and deuterium oxide (D_2O, 1.5 mL) were then added sequentially via syringe. The reaction mixture was stirred vigorously at 40 °C for 24 h. Then the mixture was extracted with Et_2O three times. The combined organic phase was washed sequentially with water and brine, dried over Na_2SO_4, and filtered. After the solvents were removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 15:1) to afford the title compound as a colorless oil (29 mg, 99% yield, 100% D).

4-phenylbutanenitrile-2-*d* (26)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 2H), 7.28–7.15 (m, 3H), 2.79 (t, J = 7.4 Hz, 2H), 2.42–2.20 (m, 1H), 1.98 (q, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 128.8, 128.5, 126.6, 119.6, 34.4, 26.9, 16.5–16.0 (m). Spectroscopic data are in accordance with those described in the literature.[18]



3a

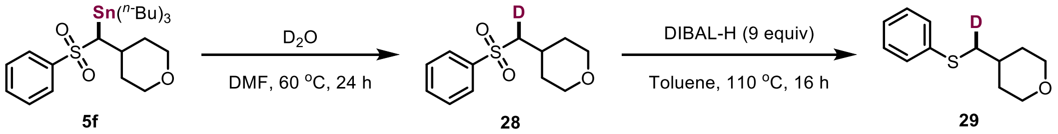
27

Followed a reported procedure,[23] $Pd_2(dba)_3$ (14 mg, 0.015 mmol), $P(OMe)_3$ (10 mg, 0.08 mmol), and CuCl (80 mg, 0.8 mmol) were added to a solution of **3a** (261 mg, 0.6 mmol) and phenyl thiobenzoate (48 mg, 0.2 mmol) in anhydrous 1,4-dioxane (4 mL). The reaction vessel was evacuated and backfilled with N_2 (three cycles) and the mixture was heated at 110 °C for 96 h. After cooling to room temperature, the mixture was directly filtered through a short pad of silica gel (eluting with EA), and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a colorless oil (31 mg, 62% yield).

2-benzoyl-4-phenylbutanenitrile (27)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.87–7.76 (m, 2H), 7.67–7.57 (m, 1H), 7.53–7.44 (m, 2H), 7.38–7.30 (m, 2H), 7.30–7.19 (m, 3H), 4.26 (t, J = 7.3 Hz, 1H), 3.03–2.91 (m, 1H), 2.91–2.80 (m, 1H), 2.39–2.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 190.7, 139.3, 134.6, 134.0, 129.2, 129.0, 128.8, 128.7, 127.0, 117.3, 39.0, 33.0, 31.5. Spectroscopic data are in accordance with those described in the literature.[24]

6.3 The Synthesis of α-Deuterated Thio Ether and Phosphine by Sequential Deuteration and Reduction



5f (106 mg, 0.2 mmol) was added to a Schlenk tube equipped with a stir bar. The tube was purged with N$_2$, and anhydrous DMF (2 mL) and deuterium oxide (D$_2$O, 1.5 mL) were then added sequentially via syringe. The reaction mixture was stirred vigorously at 60 °C for 24 h. Then the mixture was extracted with Et$_2$O three times. The combined organic phase was washed with water and brine, dried over Na$_2$SO$_4$, and filtered. After the solvents were removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 2:1) to afford the title compound as a colorless oil (48 mg, 99% yield, 100% D).

4-((phenylsulfonyl)methyl-*d*)tetrahydro-2*H*-pyran (28)

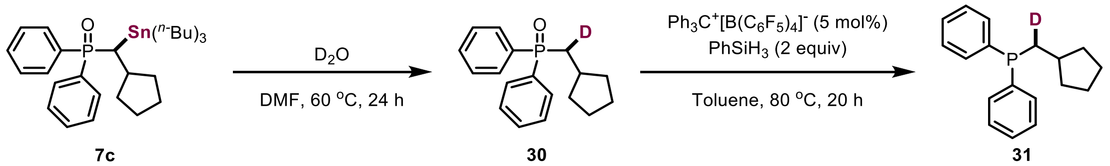
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.98–7.81 (m, 2H), 7.71–7.60 (m, 1H), 7.60–7.47 (m, 2H), 3.89 (ddd, J = 11.6, 4.6, 2.0 Hz, 2H), 3.37 (td, J = 11.8, 2.2 Hz, 2H), 2.99 (d, J = 6.6 Hz, 1H), 2.31–2.17 (m, 1H), 1.82–1.73 (m, 2H), 1.47–1.35 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.2, 133.8, 129.5, 127.8, 67.4, 62.2–61.6 (m), 32.8, 32.8, 30.2. HRMS (ESI$^+$): calcd for $C_{12}H_{16}DO_3S$ [M+H]$^+$ 242.0956, found 242.0951.

28 (48 mg, 0.198 mmol) was added to a Schlenk tube equipped with a stir bar. The tube was purged with N$_2$, and anhydrous toluene (4 mL) and DIBAL-H (1.8 mL, 1 M in hexane) were then added sequentially via syringe. The resulting mixture was stirred at

110 °C for 16 h. After cooling to room temperature, the reaction was carefully quenched by slow addition of water. The mixture was then diluted with EA, and the layers were separated. The aqueous layer was further extracted with EA and the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. After the solvents were removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford the title compound as a colorless oil (34 mg, 82% yield, 100% D).

4-((phenylthio)methyl-*d*)tetrahydro-2*H*-pyran (29)

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39–7.23$ (m, 4H), 7.22–7.08 (m, 1H), 4.09–3.84 (m, 2H), 3.35 (td, $J = 11.8, 1.9$ Hz, 2H), 2.91–2.77 (m, 1H), 1.87–1.68 (m, 3H), 1.42–1.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.9$, 129.2, 129.0, 126.0, 67.9, 40.5–39.9 (m), 34.9, 32.7. HRMS (ESI$^+$): calcd for $C_{12}H_{16}DOS$ $[M+H]^+$ 210.1057, found 210.1055.



7c **30** **31**

7c (115 mg, 0.2 mmol) was added to a Schlenk tube equipped with a stir bar. The tube was purged with N_2, and anhydrous DMF (2 mL) and deuterium oxide (D_2O, 1.5 mL) were then added sequentially via syringe. The reaction mixture was stirred vigorously at 60 °C for 24 h. Then the mixture was extracted with Et_2O three times. The combined organic phase was washed with water and brine, dried over Na_2SO_4, and filtered. After the solvents were removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 1:1) to afford the title compound as a white solid (55 mg, 96% yield, 100% D); Melting point: 128–130 °C.

(cyclopentylmethyl-*d*)diphenylphosphine oxide (30)

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90–7.65$ (m, 4H), 7.64–7.31 (m, 6H), 2.41–2.28 (m, 1H), 2.25–2.12 (m, 1H), 1.86–1.71 (m, 2H), 1.63–1.38 (m, 4H), 1.23–1.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.0$ (d, $J = 96.9$ Hz), 131.6 (d, $J = 2.7$ Hz), 130.9 (d, J

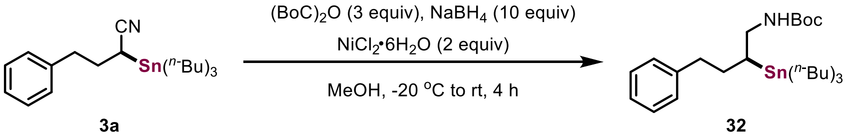
= 9.2 Hz), 128.7 (d, J = 11.4 Hz), 36.1–34.8 (m), 34.5 (d, J = 8.4 Hz), 34.1 (d, J = 4.3 Hz), 24.8; ^{31}P NMR (162 MHz, CDCl$_3$): δ = 30.8. HRMS (ESI$^+$): calcd for $C_{18}H_{21}DOP$ [M+H]$^+$ 286.1466, found 286.1460.

Followed a reported procedure,[25] **30** (55 mg, 0.192 mmol) and $Ph_3C^+[B(C_6F_5)_4]^-$ (9 mg, 0.01 mmol) were added to a Schlenk tube equipped with a stir bar. The tube was purged with N_2, and anhydrous toluene (0.4 mL) was added via syringe. Phenylsilane (42 mg, 0.384 mmol) was then added at room temperature, and the reaction mixture was stirred at 80 °C for 20 h. The reaction was carefully quenched with a 1:1 (v/v) mixture of methanol and triethylamine (1 mL). The volatiles were removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the title compound as a colorless oil (48 mg, 92% yield, 100% D).

(cyclopentylmethyl-*d*)diphenylphosphane (31)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.62–7.40 (m, 4H), 7.40–7.27 (m, 6H), 2.14 (d, J = 6.1 Hz, 1H), 1.95–1.77 (m, 3H), 1.72–1.60 (m, 2H), 1.57–1.46 (m, 2H), 1.35–1.22 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.4 (dd, J = 13.2, 1.7 Hz), 132.9 (dd, J = 18.5, 1.6 Hz), 128.5, 128.4 (d, J = 6.6 Hz), 37.4 (d, J = 12.5 Hz), 35.2–34.6 (m), 34.4 (d, J = 8.8 Hz), 25.1; ^{31}P NMR (162 MHz, CDCl$_3$): δ = -18.8. HRMS (ESI$^+$): calcd for $C_{18}H_{21}DP$ [M+H]$^+$ 270.1516, found 270.1510.

6.4 Functionalization of the α-Cyano Group of Alkyltin Reagent 3a



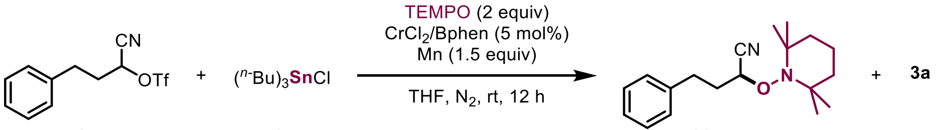
3a (87 mg, 0.2 mmol) was added to a Schlenk tube equipped with a stir bar, and anhydrous MeOH (2 mL) was then added via syringe. The solution was transferred to -20 °C, and then $NiCl_2(H_2O)_6$ (95 mg, 0.4 mmol), $(Boc)_2O$ (131 mg, 0.6 mmol), and $NaBH_4$ (76 mg, 2.0 mmol) were added sequentially to this cooled solution. The resulting mixture was warmed to room temperature and stirred for 4 h. The solvent was then removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the title compound as a colorless oil (51 mg, 47% yield).

***tert*-butyl (4-phenyl-2-(tributylstannyl)butyl)carbamate (32)**

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.32–7.25 (m, 2H), 7.23–7.11 (m, 3H), 4.47 (s, 1H), 3.52–3.27 (m, 2H), 2.73–2.50 (m, 2H), 2.08–1.77 (m, 2H), 1.53–1.40 (m, 15H), 1.39–1.25 (m, 7H), 0.99–0.80 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 156.0, 142.5, 128.5, 128.4, 125.9, 79.1, 43.8, 36.3, 33.4, 29.4, 28.6, 27.7, 27.6, 13.8, 9.0. HRMS (ESI$^+$): calcd for $C_{27}H_{50}NO_2Sn$ [M+H]$^+$ 540.2858, found 540.2860.

7. Mechanistic Studies

7.1 Radical Scavenger Experiment



1a **2a** **33** (46%) (nd)

In a dried Schlenk tube under a nitrogen atmosphere, CrCl$_2$ (1.2 mg, 0.01 mmol), Bphen (3.3 mg, 0.01 mmol), and manganese powder (17 mg, 0.3 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, TEMPO (63 mg, 0.4 mmol), **2a** (78 mg, 0.24 mmol), and **1a** (59 mg, 0.2 mmol) were sequentially added. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatiles under reduced pressure, the crude mixture was purified by flash column chromatography on silica gel (PE/EA = 30:1) to afford the corresponding radical trapped product **33** as a yellow oil (28 mg, 46% yield), and the stannylation product **3a** was not detected.

4-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (33)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.35–7.28 (m, 2H), 7.25–7.18 (m, 3H), 4.66–4.45 (m, 1H), 2.99–2.87 (m, 1H), 2.86–2.75 (m, 1H), 2.30–2.08 (m, 2H), 1.59–1.41 (m, 5H), 1.38–1.29 (m, 4H), 1.11 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 128.8, 128.5, 126.5, 119.6, 73.7, 61.0, 60.0, 40.1, 40.0, 34.7, 34.2, 33.6, 31.1, 20.6, 20.4, 17.1. Spectroscopic data are in accordance with those described in the literature.[19]

7.2 Cyclic Voltammetry Experiment

Linear sweep voltammetry was performed with an electrochemical analyzer. The voltammetric cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. All measurements were carried out under a nitrogen atmosphere. The analyte solution (0.1 M) was prepared in anhydrous CH_3CN, employing tetrabutylammonium perchlorate ($[^{n}\text{-}Bu_4N]^+[ClO_4]^-$, 0.1 M) as the supporting electrolyte.

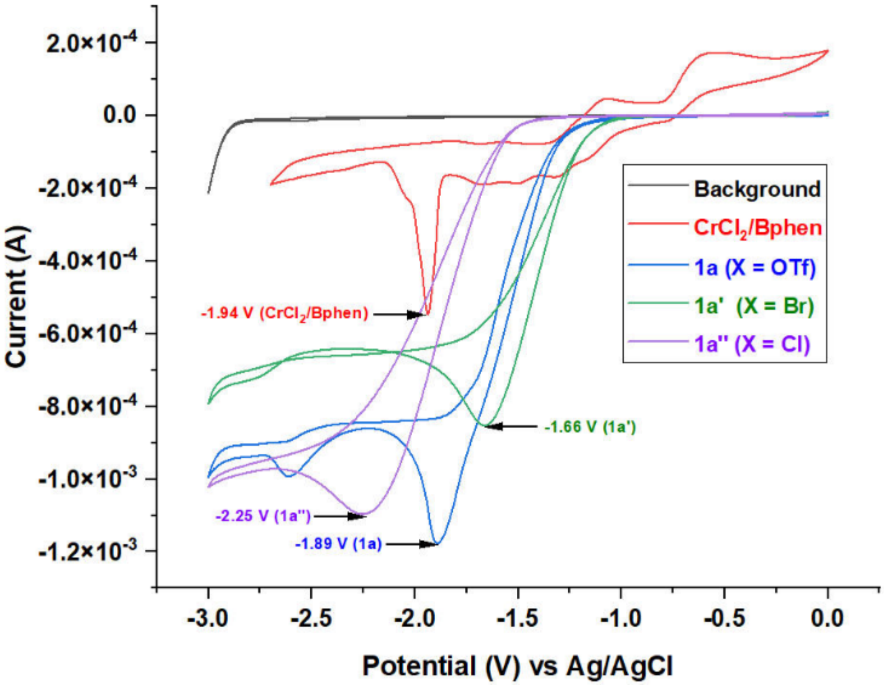
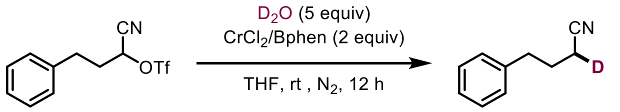


Figure S2. Measurements of the reduction potentials.

7.3 Deuterium-Labeling Experiment



1a

26 (83% yield)
(96% D incorporation)

In a dried Schlenk tube under a nitrogen atmosphere, $CrCl_2$ (49 mg, 0.4 mmol) and Bphen (133 mg, 0.4 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, **1a** (59 mg, 0.2 mmol) and D_2O (20 mg, 1.0 mmol) were sequentially added. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatiles under reduced pressure, the crude residue was purified by flash column chromatography on silica gel (PE/EA = 15:1) to afford the corresponding deuterated product **26** as a colorless oil (24 mg, 83% yield, 96% D).

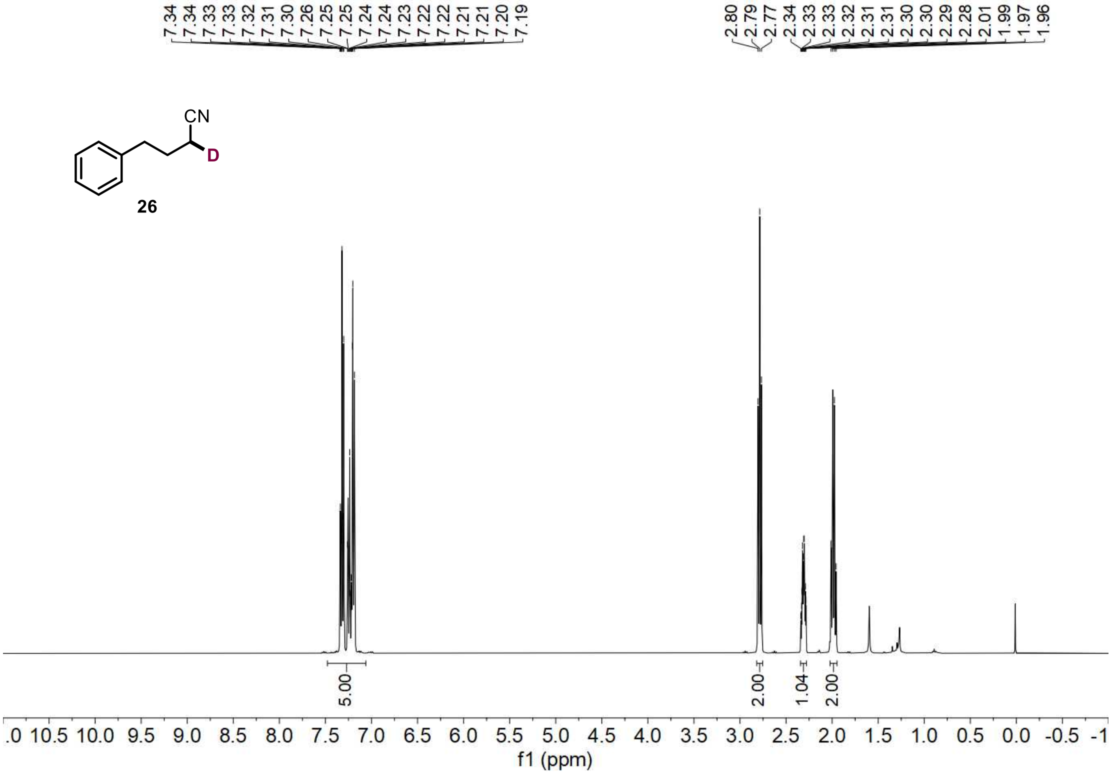
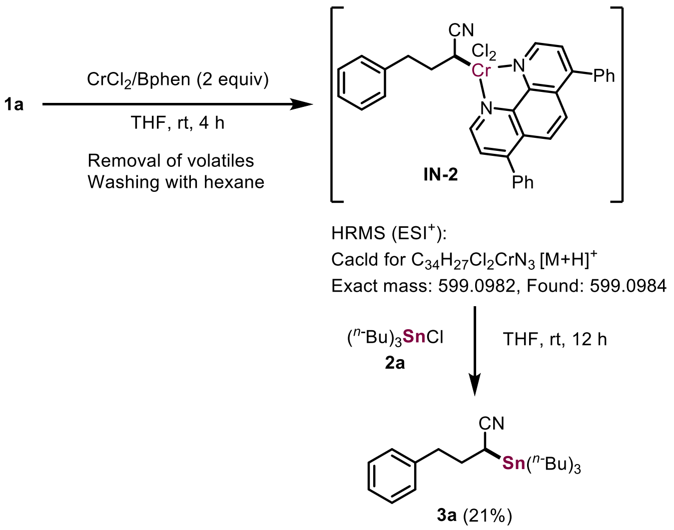


Figure S3. ^{1}H NMR spectrum of deuterated product **26**.

7.4 Detection of Alkylated Chromate by HRMS and Further Reaction with Chlorostannane



In a dried Schlenk tube under a nitrogen atmosphere, $CrCl_2$ (49 mg, 0.4 mmol) and Bphen (133 mg, 0.4 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, **1a** (59 mg, 0.2 mmol) was added. Stirring was continued at room temperature for 4 h. The solvent was then removed under reduced pressure, and the residue was washed with hexane (3×5 mL). The resulting residue was analyzed by high-resolution mass spectrometry (HRMS), which confirmed the formation of the alkylated chromate intermediate **IN-2**. The residue was then treated with a solution of **2a** (78 mg, 0.24 mmol) in THF (2 mL) and stirred at room temperature for an additional 12 h. After removal of the volatiles under reduced pressure, the crude product was purified by flash column chromatography on silica gel (PE/EA = 40:1) to afford the stannylation product **3a** as a colorless oil (18 mg, 21% yield).

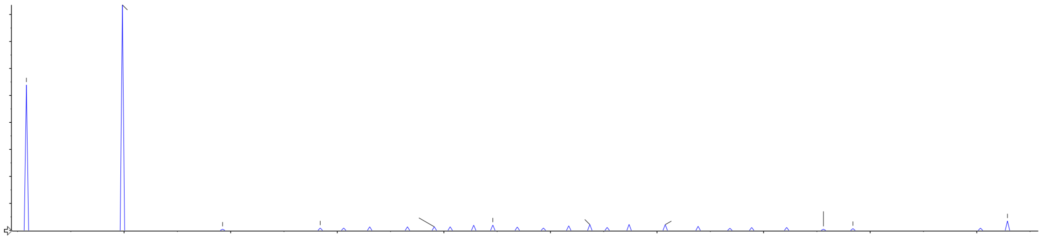
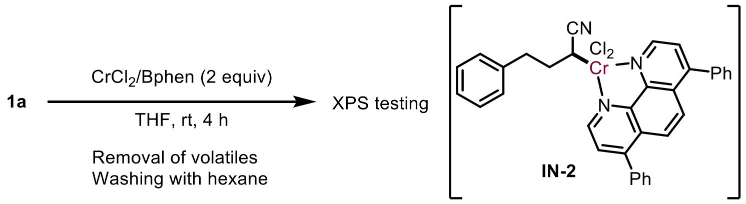


Figure S4. Image for HRMS analysis of alkylated chromate species **IN-2**.

7.5 XPS Analysis of the Alkylated Chromate Species IN-2



In a dried Schlenk tube under a nitrogen atmosphere, $CrCl_2$ (49 mg, 0.4 mmol) and Bphen (133 mg, 0.4 mmol) were placed, followed by the addition of anhydrous THF (2 mL) via syringe. After stirring the mixture at room temperature for 30 s, **1a** (59 mg, 0.2 mmol) was added. Stirring was continued at room temperature for 4 h. The solvent was then removed under reduced pressure, and the residue was washed with hexane (3×5 mL) for XPS analysis. X-ray photoelectron spectroscopy (XPS) analysis of the resulting residue confirmed the formation of a Cr(III) species. The characteristic peaks at binding energies of 577.18 eV and 586.34 eV are assigned to the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ core levels, respectively, consistent with reported values for Cr(III) complexes.[26,27]

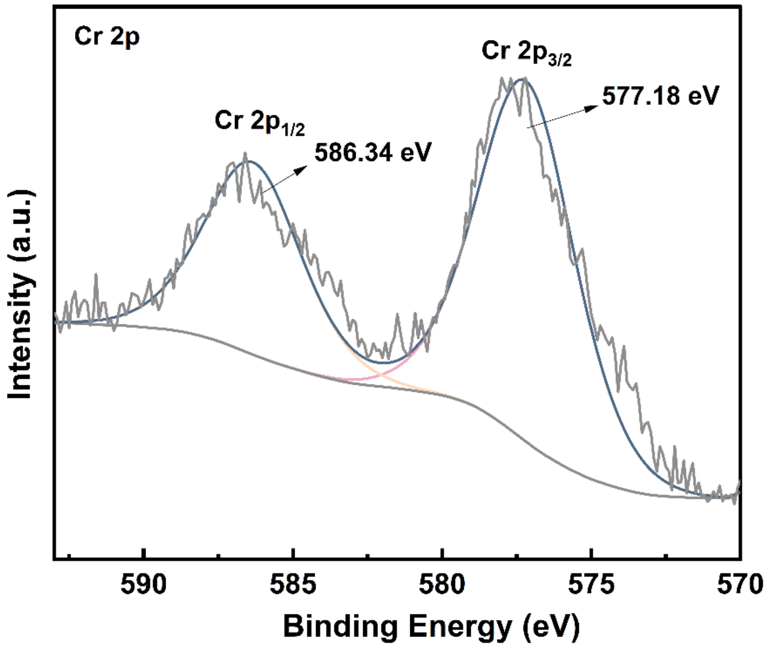


Figure S5. Image for XPS analysis of the alkylated chromate species **IN-2**.

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9. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR Spectra

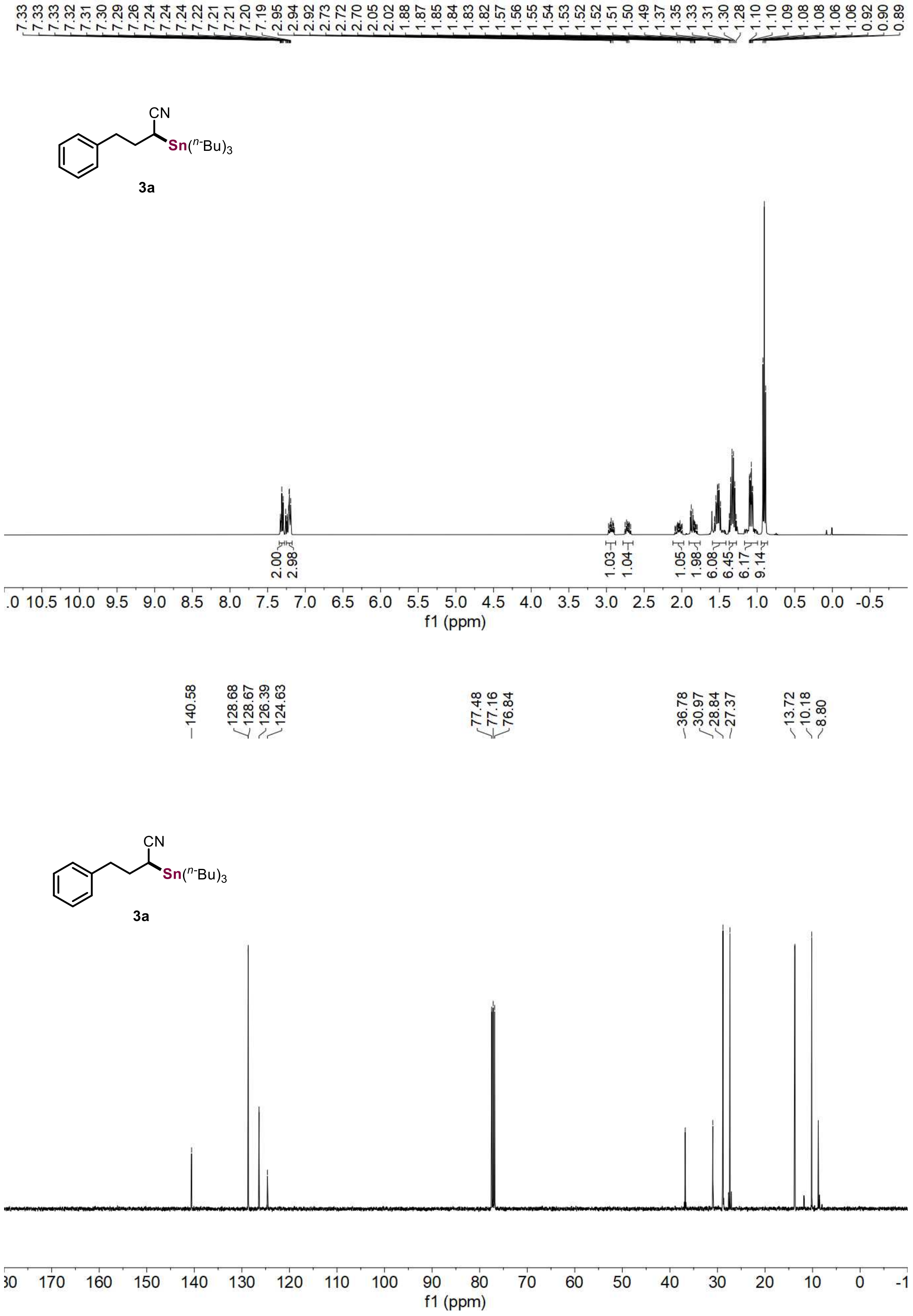


Figure S6. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3a**.

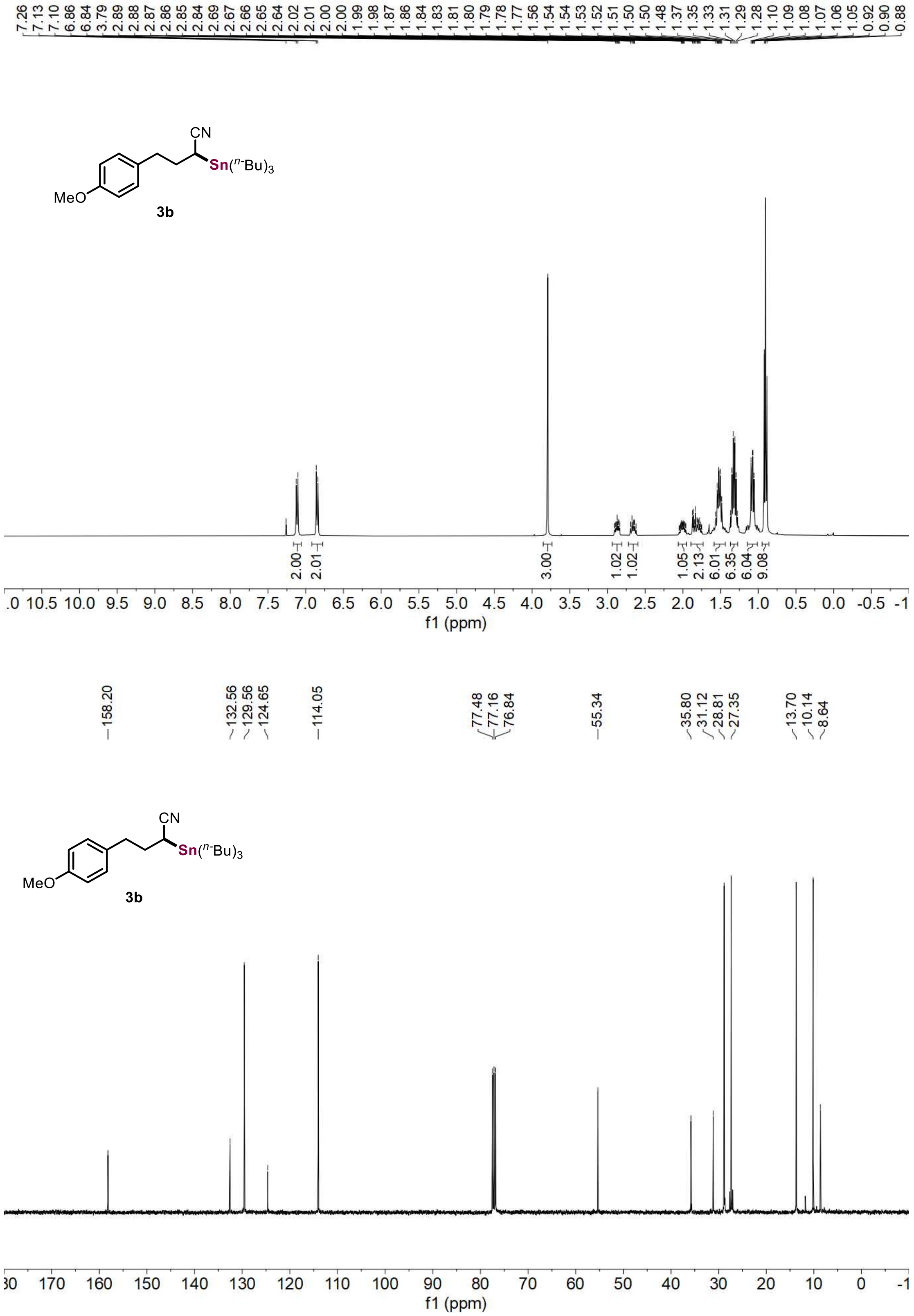
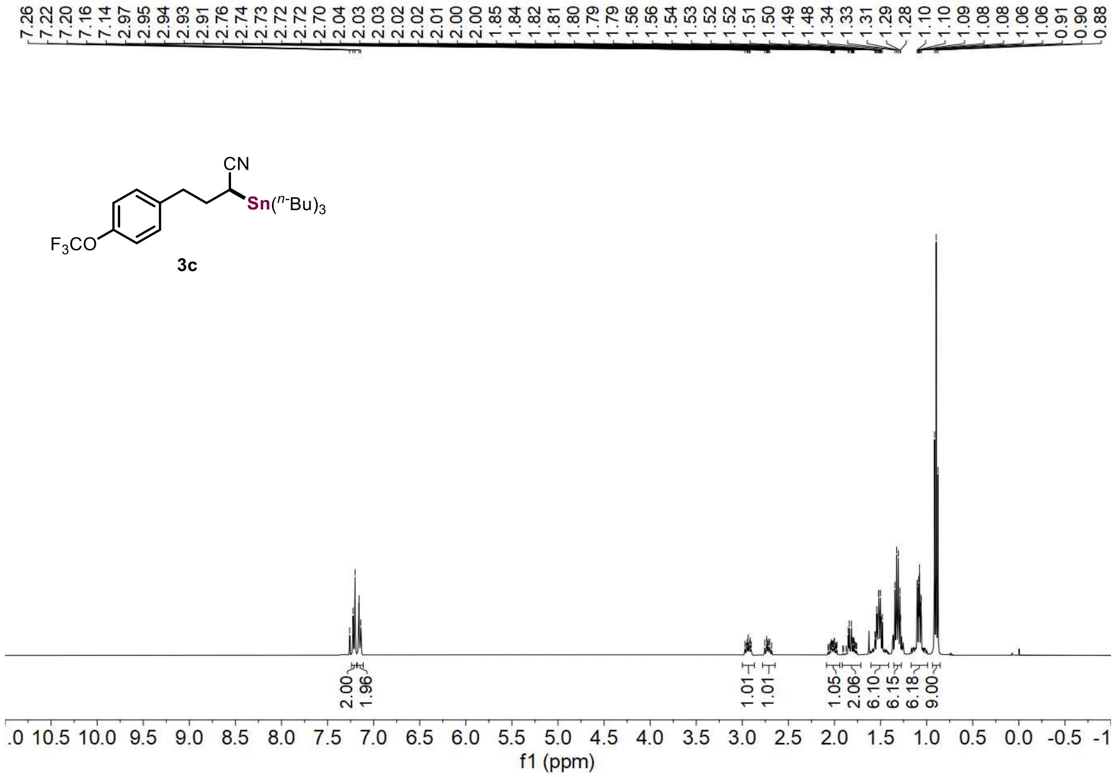


Figure S7. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **3b**.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7.22
7.20
7.16
7.14
2.97
2.95
2.94
2.93
2.91
2.76
2.74
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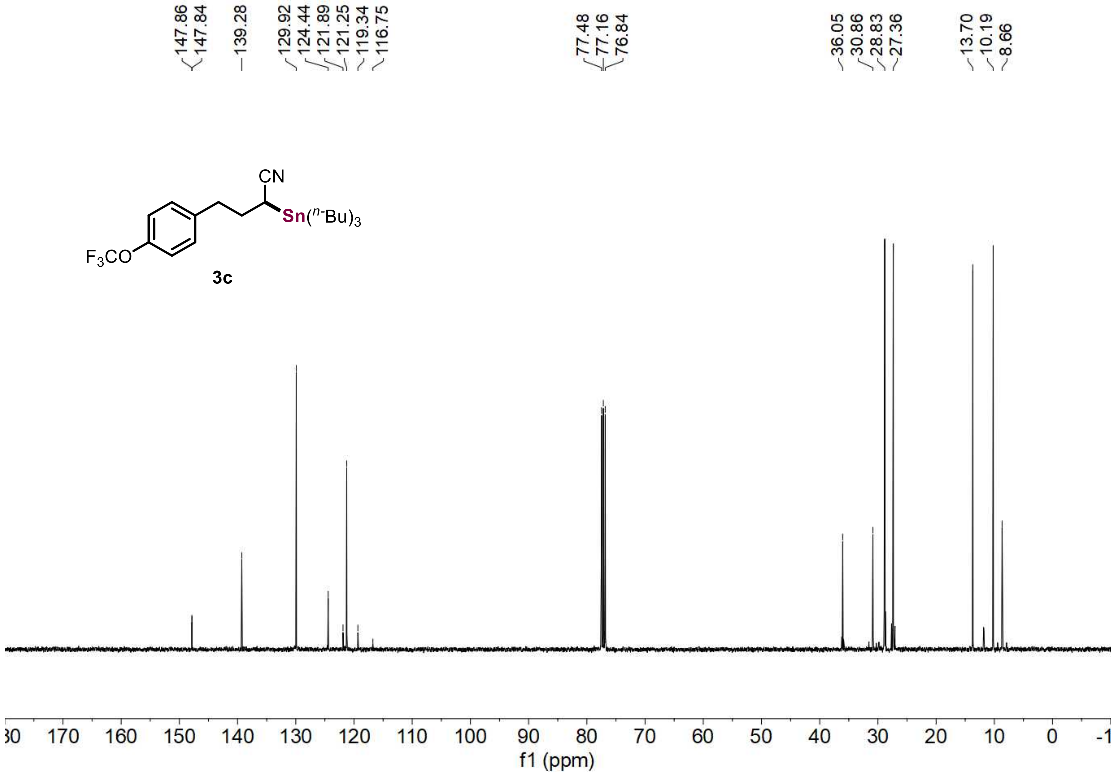
2.72
2.72
2.70
2.04
2.03
2.03
2.02
2.02
2.01
2.00
2.00
1.85
1.84
1.82
1.81
1.80
1.79
1.79
1.56
1.56
1.54
1.53
1.52
1.52
1.51
1.50
1.49
1.48
1.34
1.33
1.31
1.29
1.28
1.10
1.10
1.09
1.08
1.08
1.06
1.06
0.91
0.90
0.88
CN
Sn(^{n}-Bu)$_3$
F$_3$CO
3c
2.00
1.96
1.01
1.01
1.05
2.06
6.10
6.15
6.18
9.00
.0 10.5 10.0 9.5 9.0 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 -1
f1 (ppm)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147.84
139.28
129.92
124.44
121.89
121.25
119.34
116.75
77.48
77.16
76.84
36.05
30.86
28.83
27.36
13.70
10.19
8.66
CN
Sn(^{n}-Bu)$_3$
F$_3$CO
3c
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

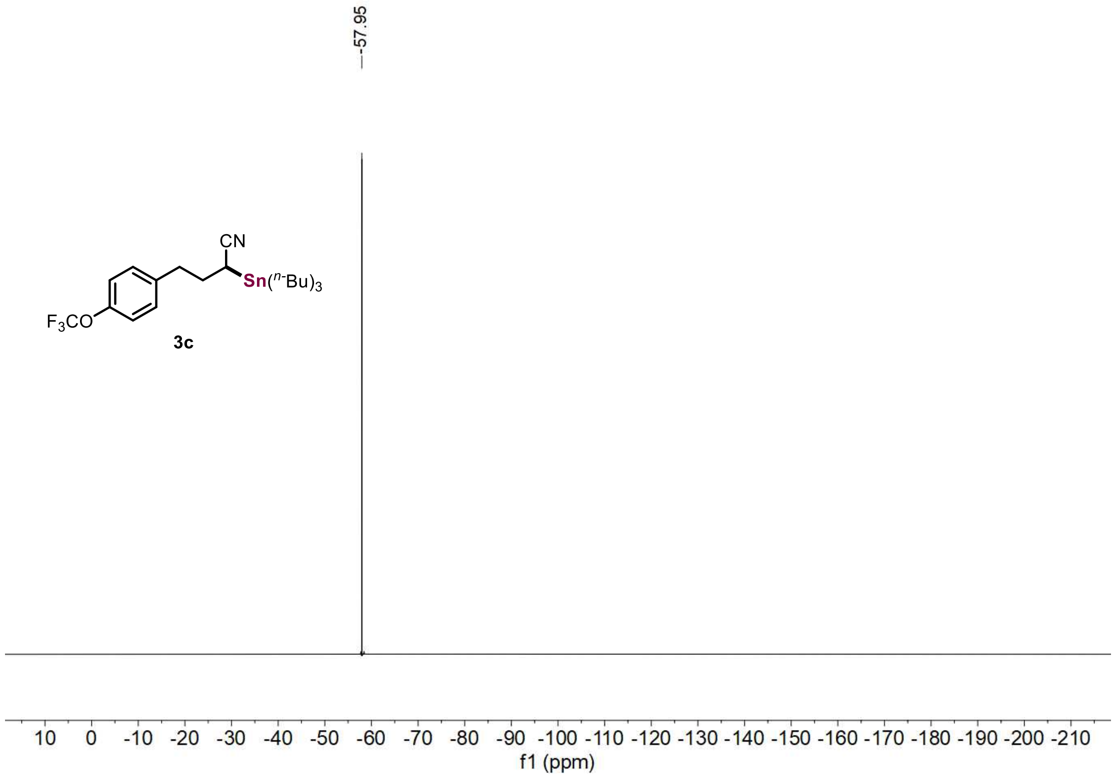
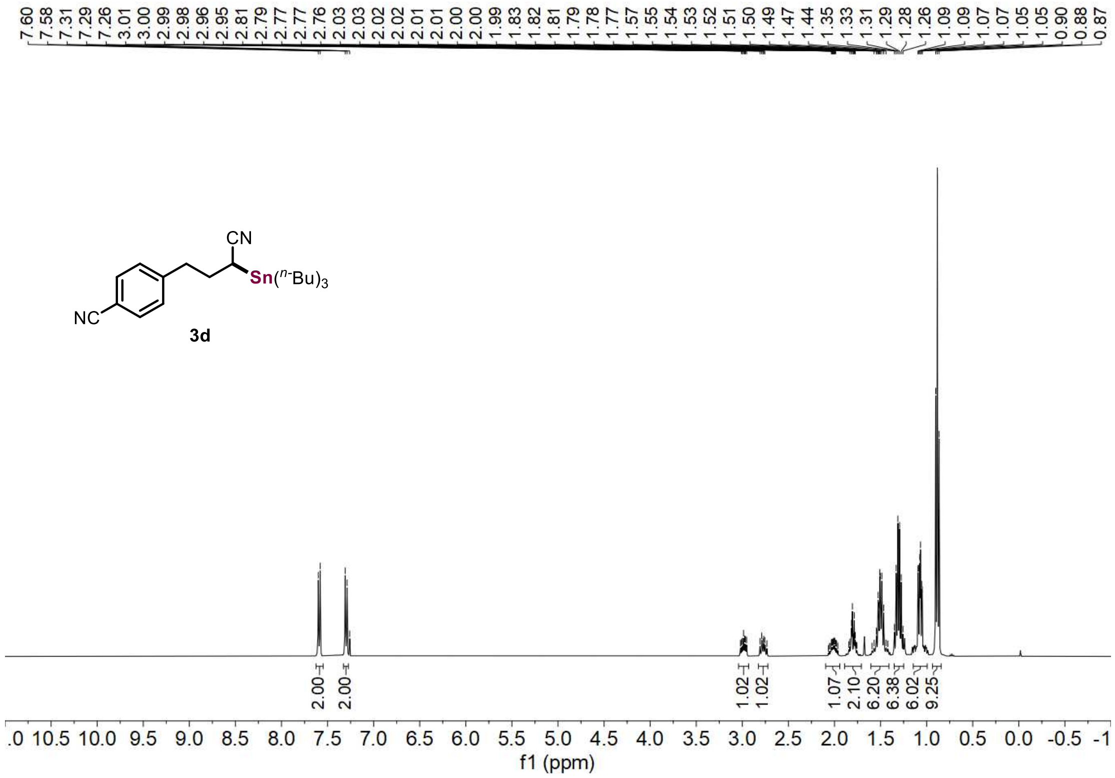


Figure S8. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{19}F (376 MHz, CDCl$_3$) NMR spectra for compound **3c**.



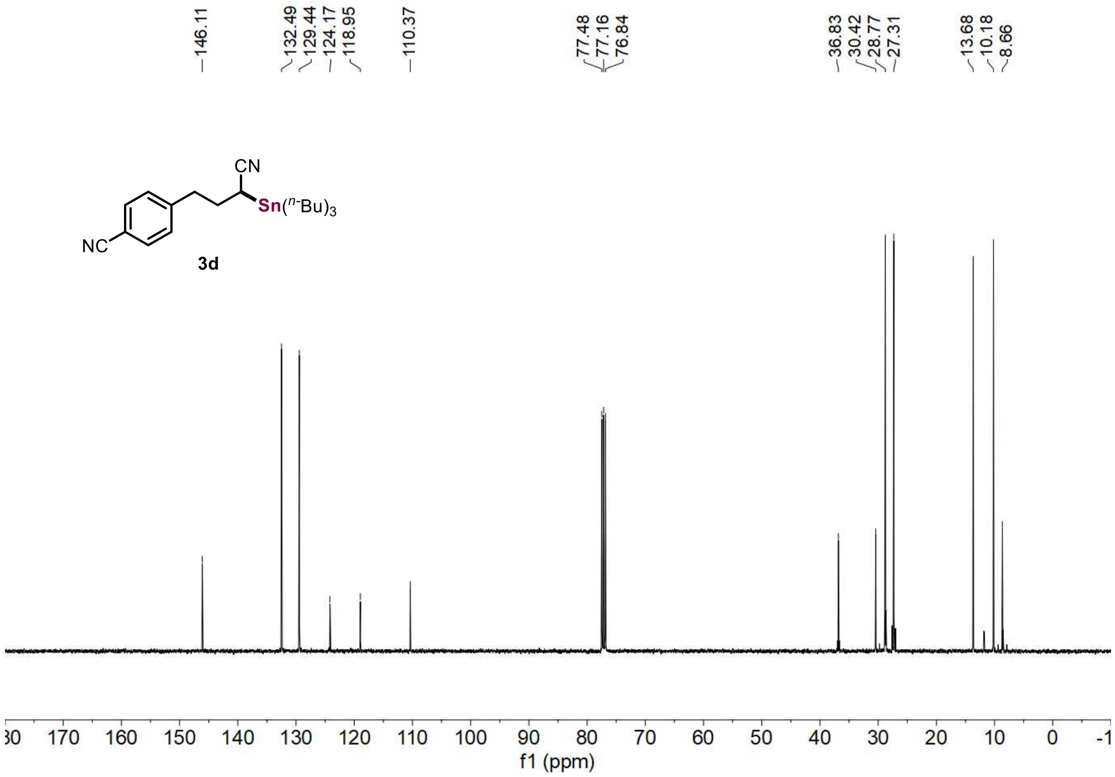
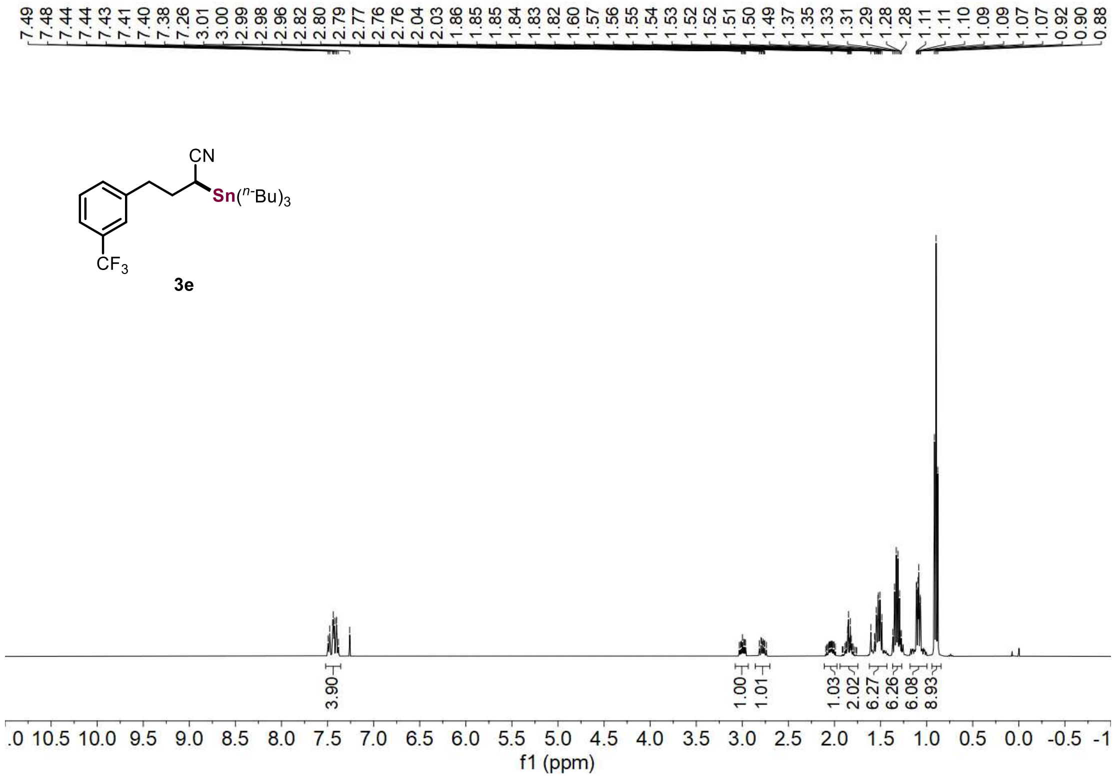


Figure S9. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3d**.



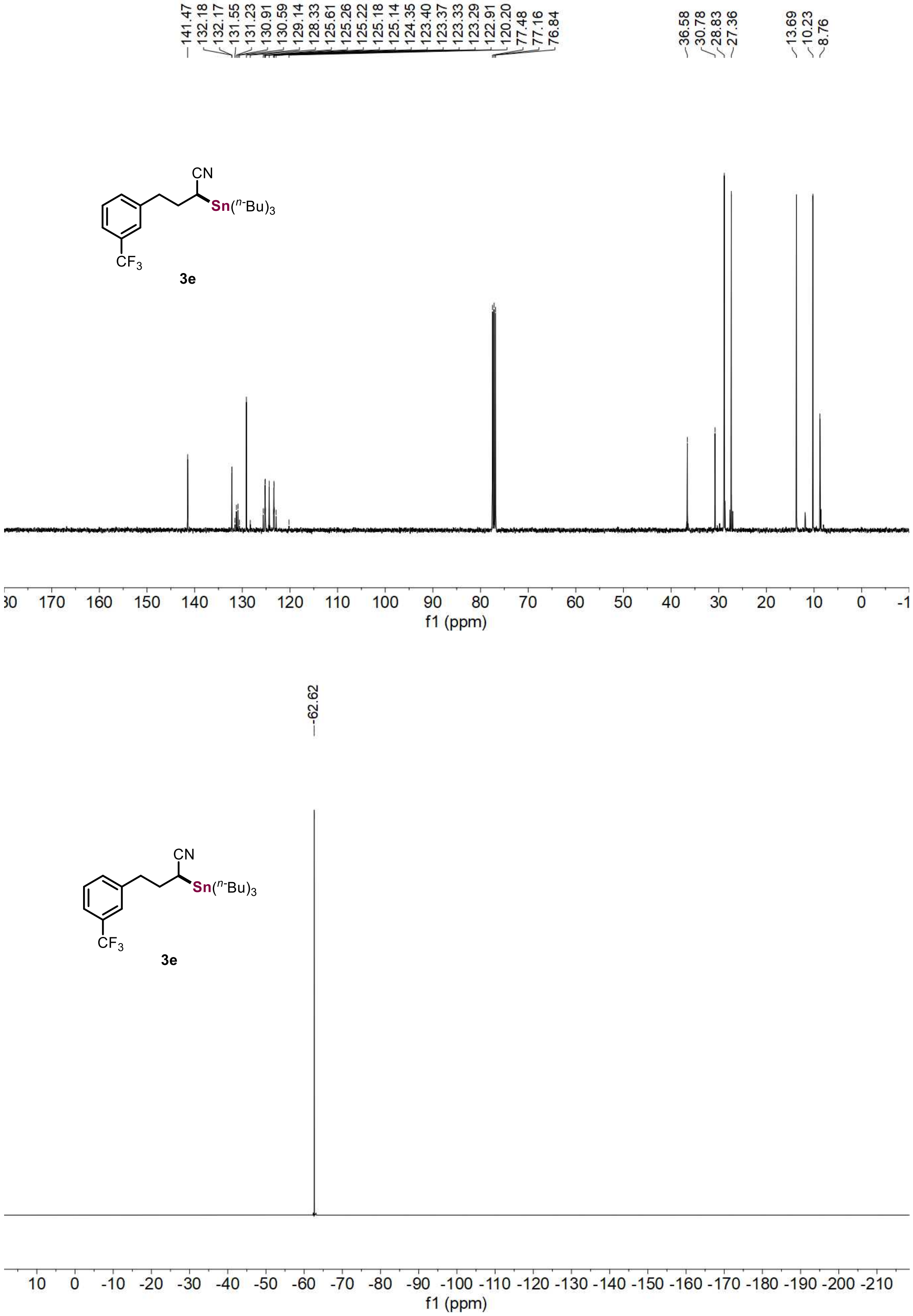


Figure S10. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{19}F (376 MHz, CDCl$_3$) NMR spectra for compound **3e**.

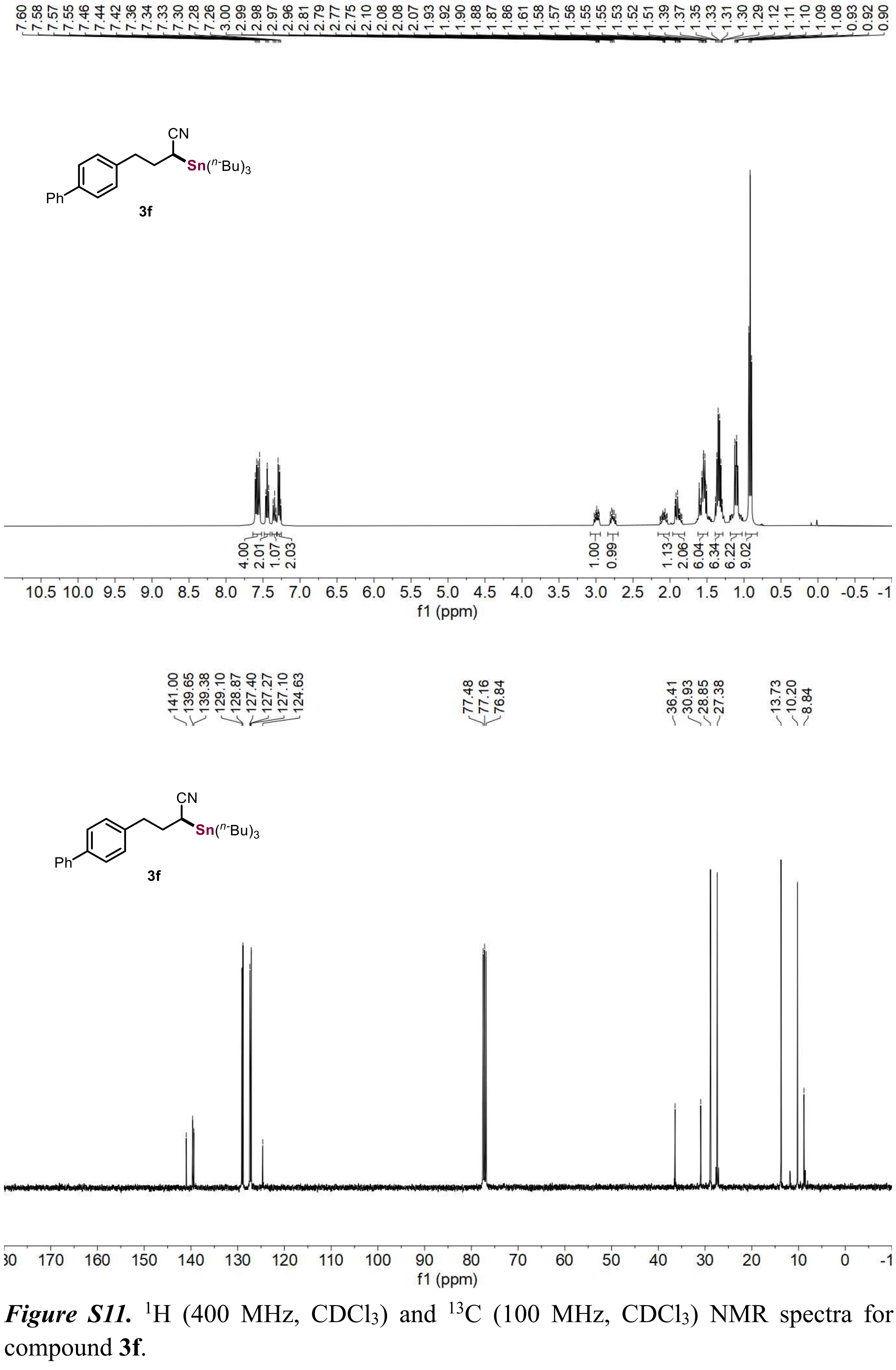
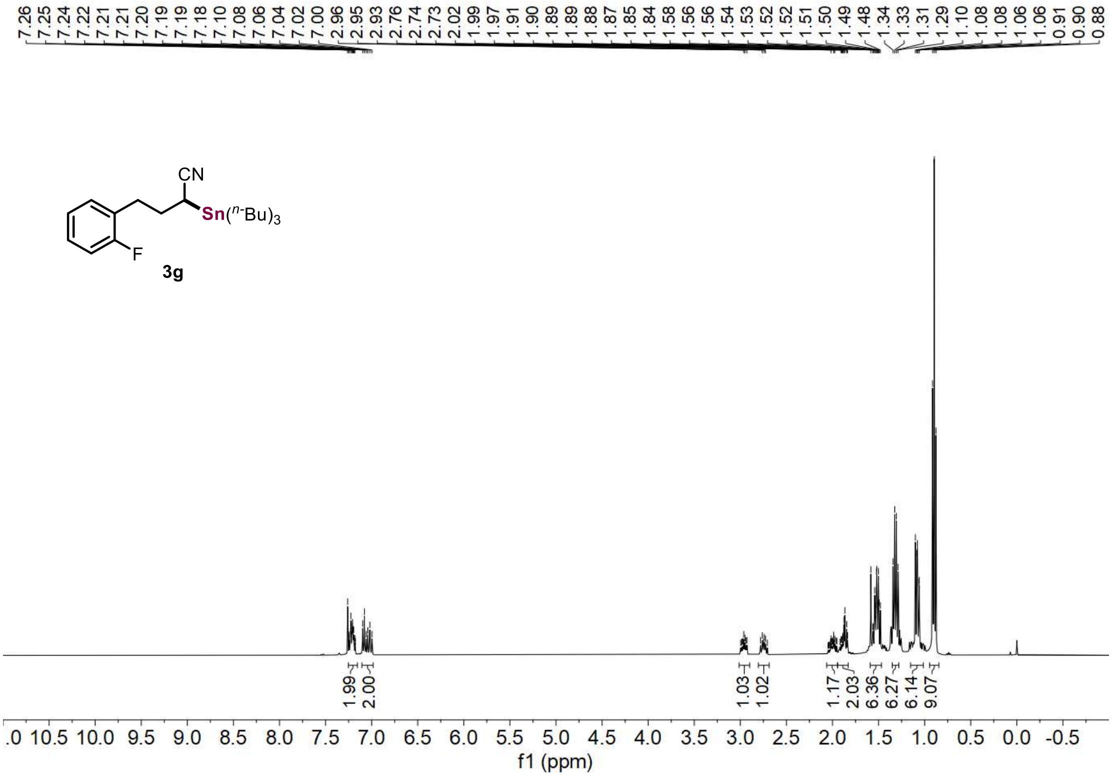


Figure S11. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **3f**.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7.22
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7.21
7.20
7.19
7.19
7.18
7.10
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7.04
7.02
7.00
2.96
2.95
2.93
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2.74
2.73
2.02
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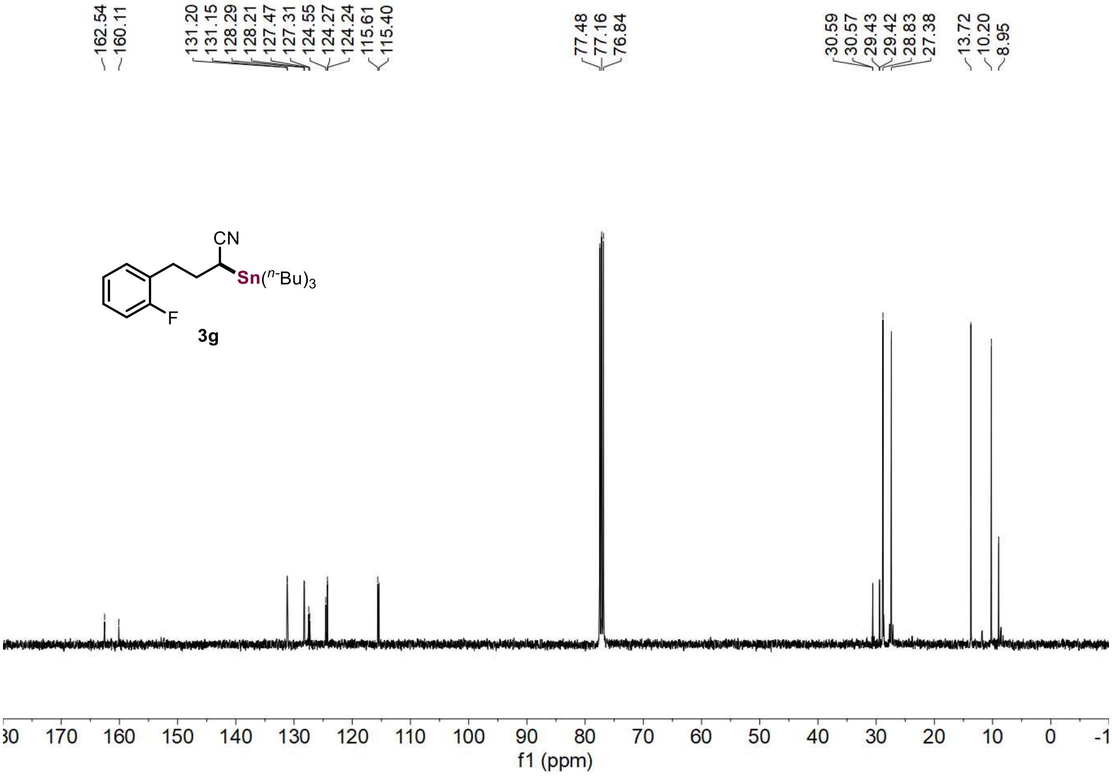
1.52
1.51
1.50
1.49
1.48
1.34
1.34
1.33
1.31
1.29
1.10
1.08
1.08
1.06
1.06
0.91
0.90
0.88
CN
Sn(n-Bu)3
F
3g
1.99
2.00
1.03
1.02
1.17
2.03
6.36
6.27
6.14
9.07
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.54
160.11
131.20
131.15
128.29
128.21
127.47
127.31
124.55
124.27
124.24
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115.40
77.48
77.16
76.84
30.59
30.57
29.43
29.42
28.83
27.38
13.72
10.20
8.95
CN
Sn(n-Bu)3
F
3g
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

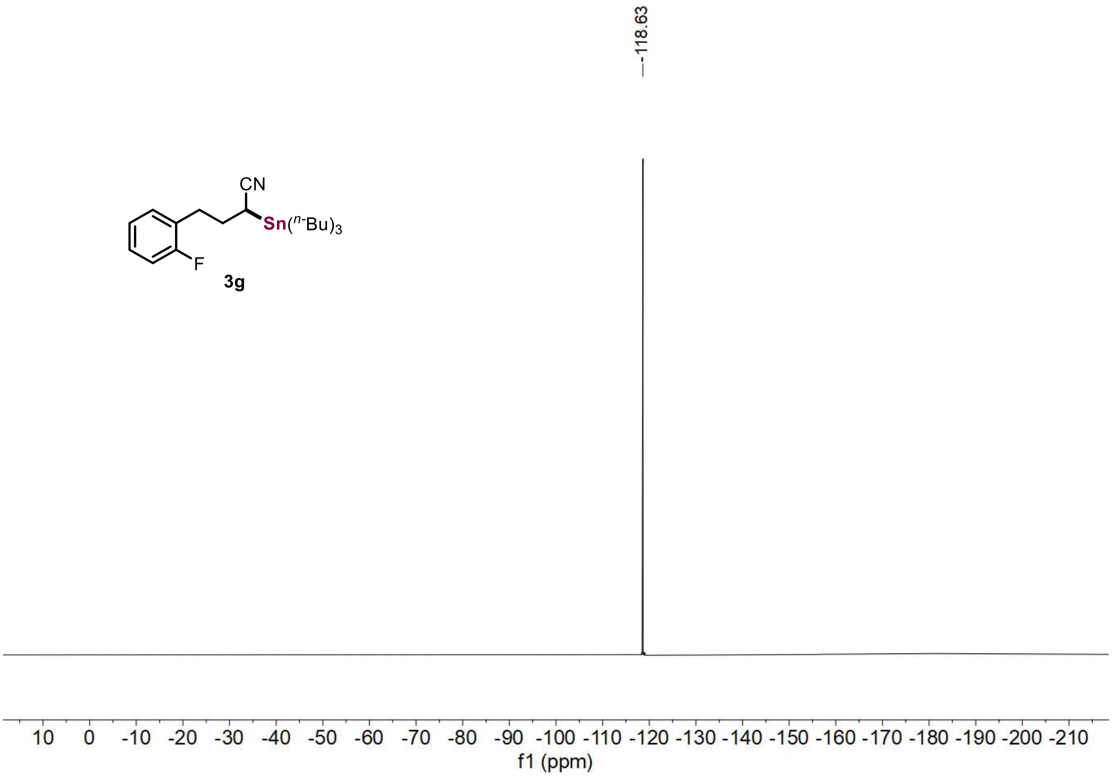
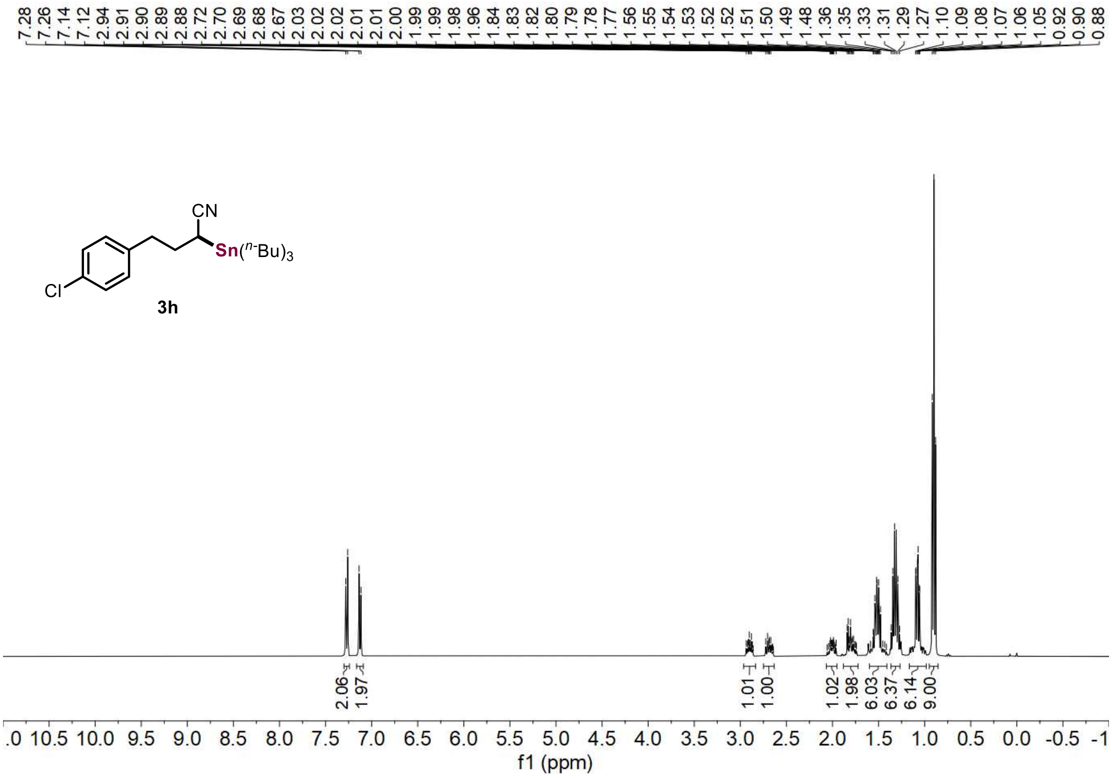


Figure S12. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{19}F (376 MHz, CDCl$_3$) NMR spectra for compound **3g**.



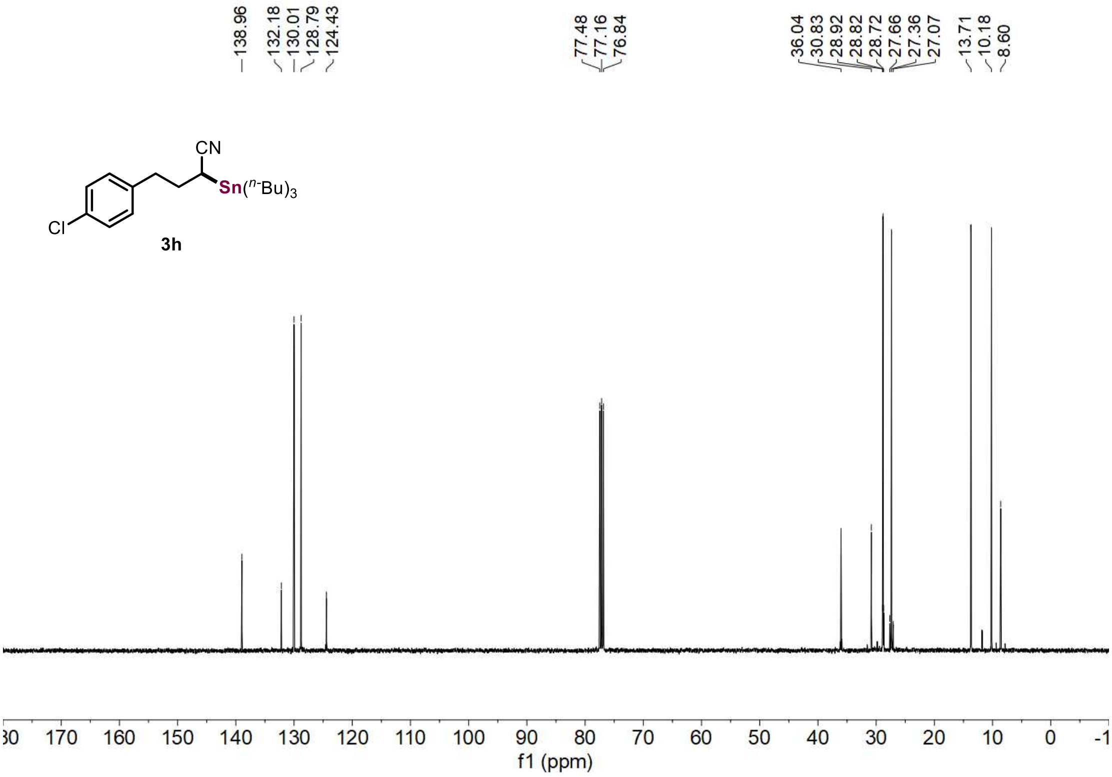
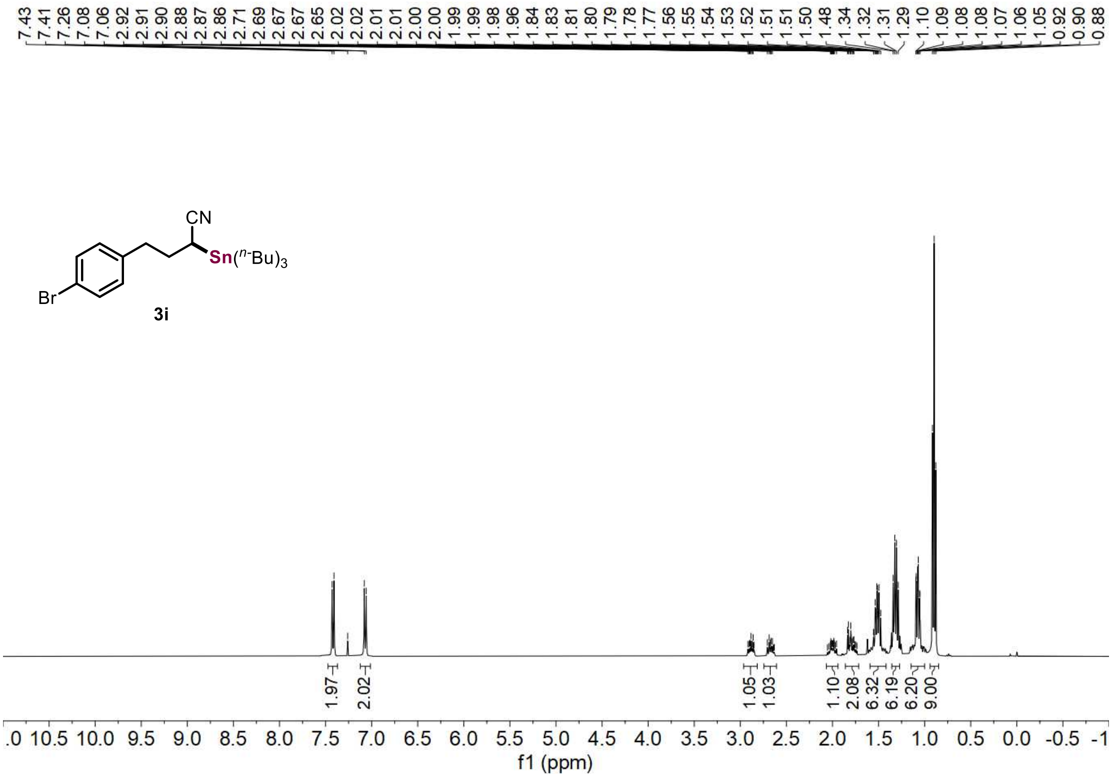


Figure S13. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3h**.



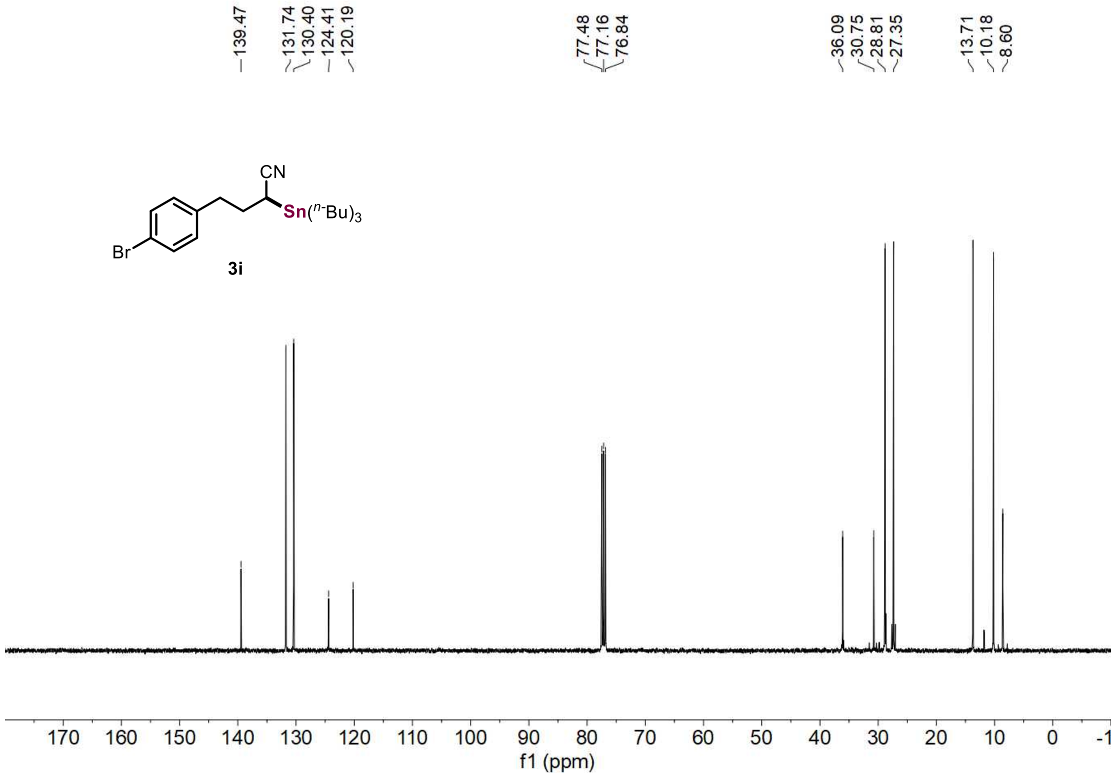
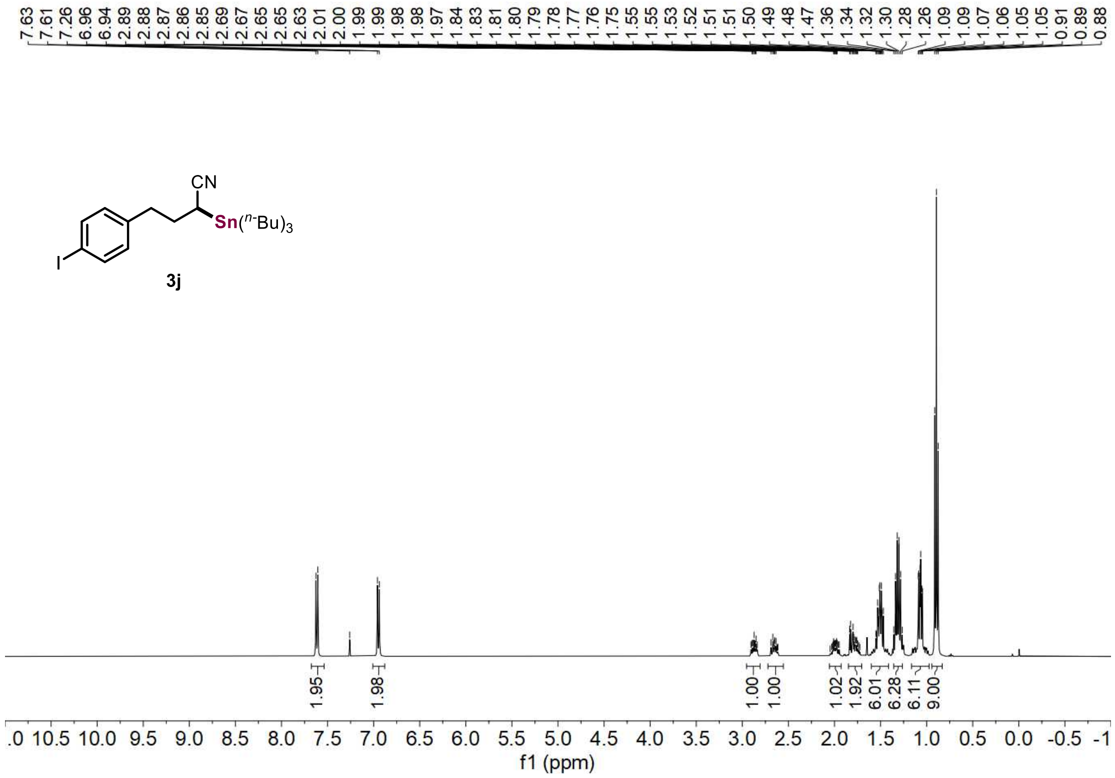


Figure S14. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3i**.



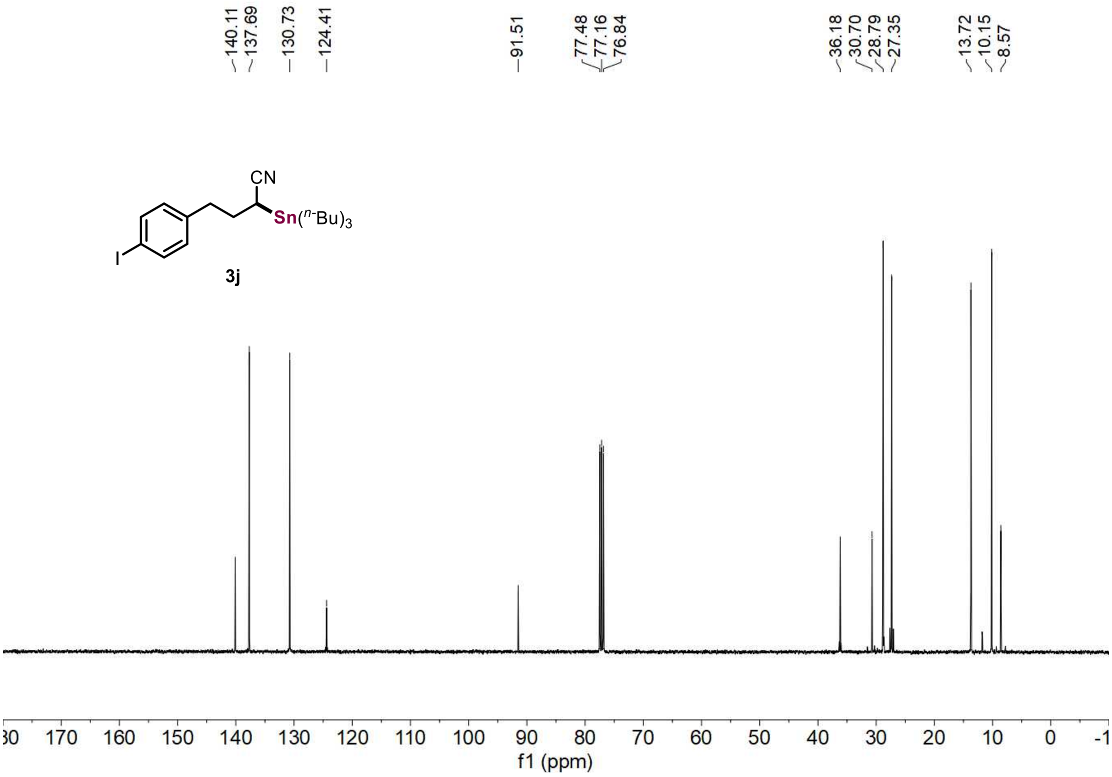
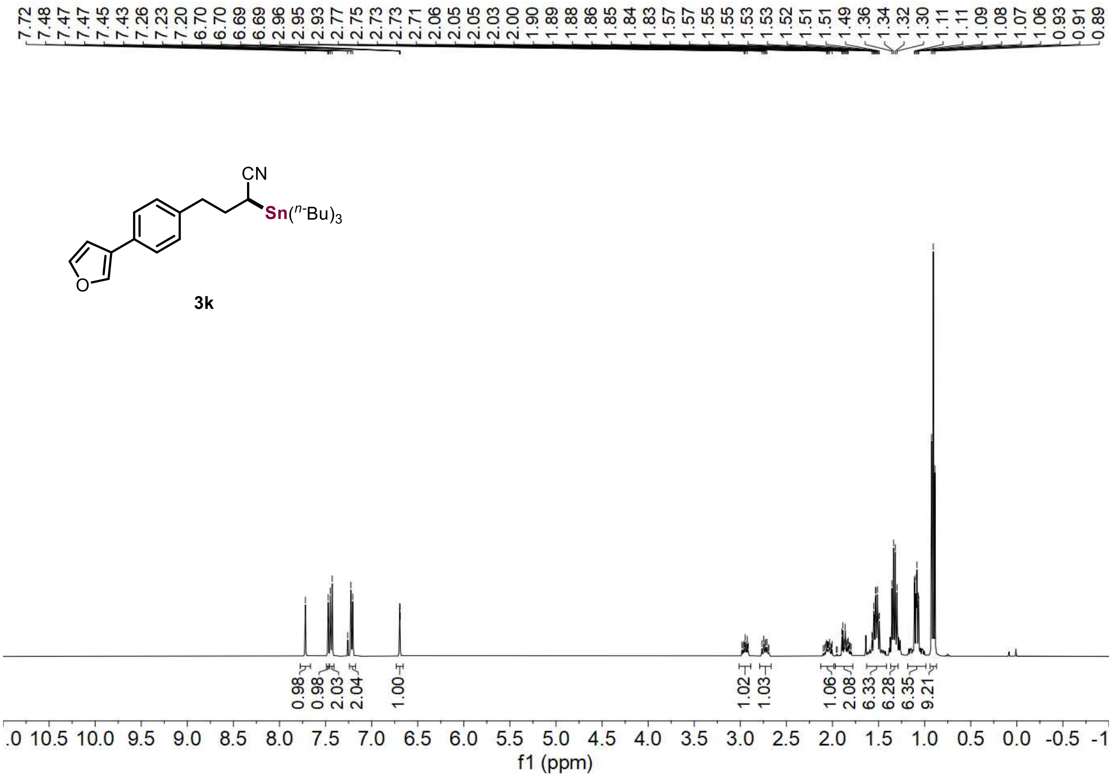


Figure S15. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3j**.



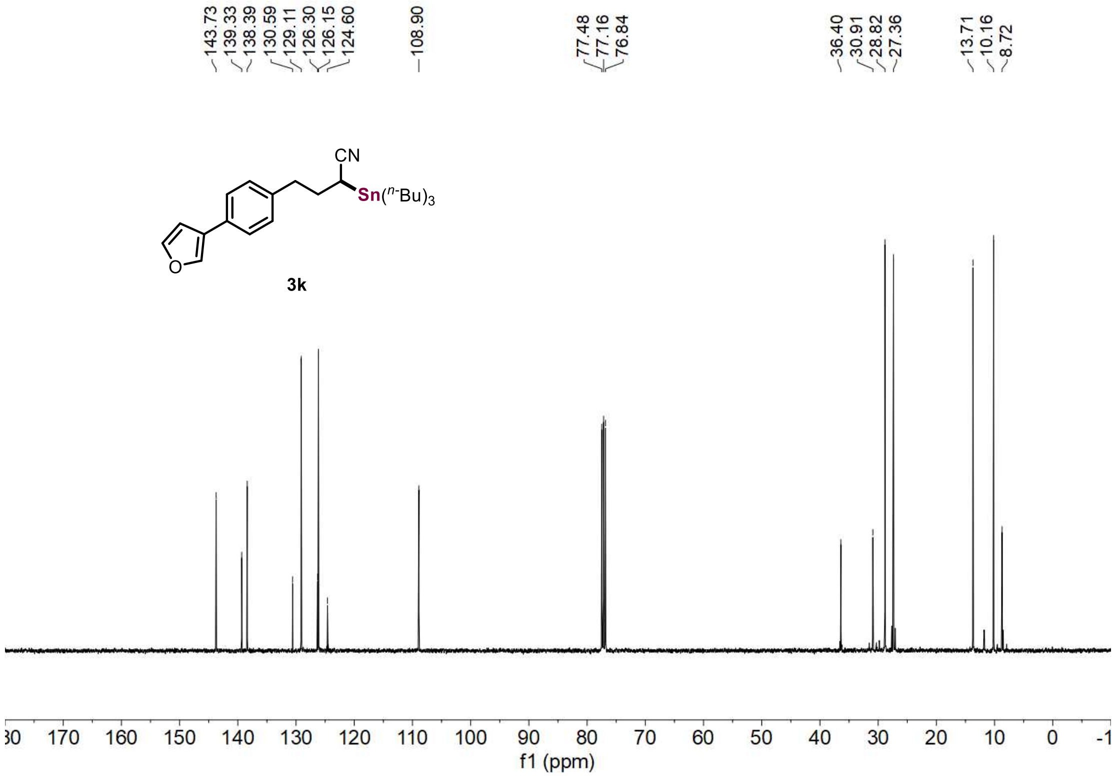
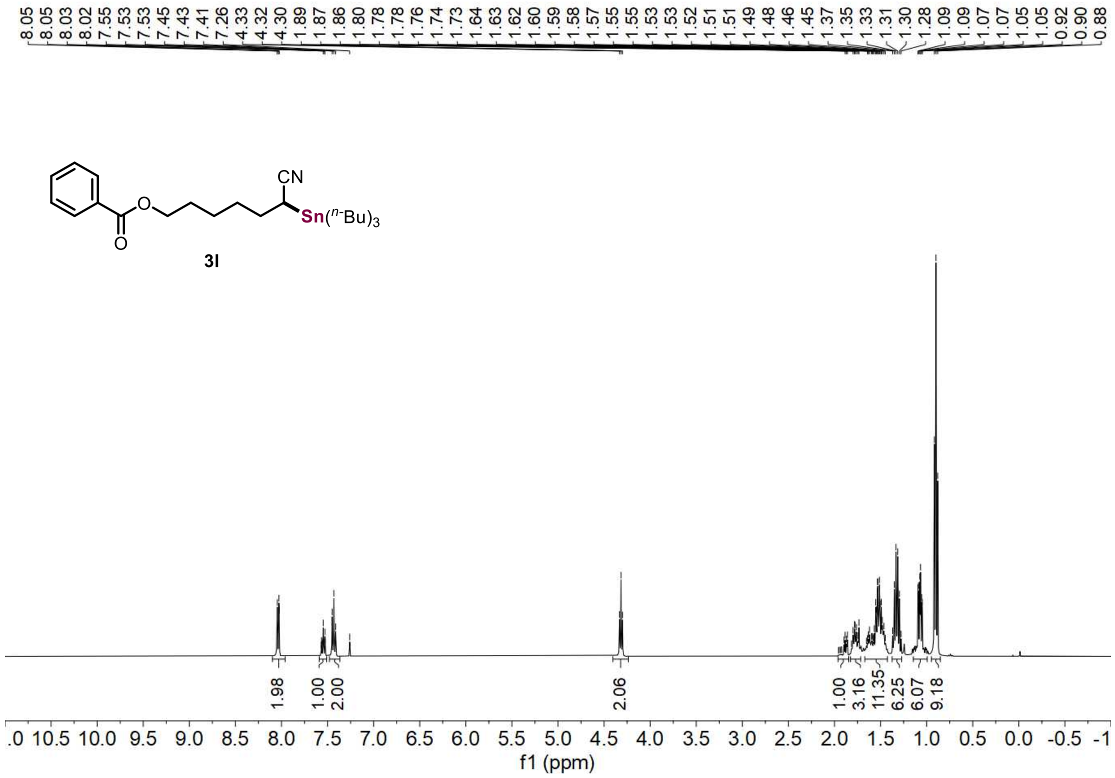


Figure S16. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3k**.



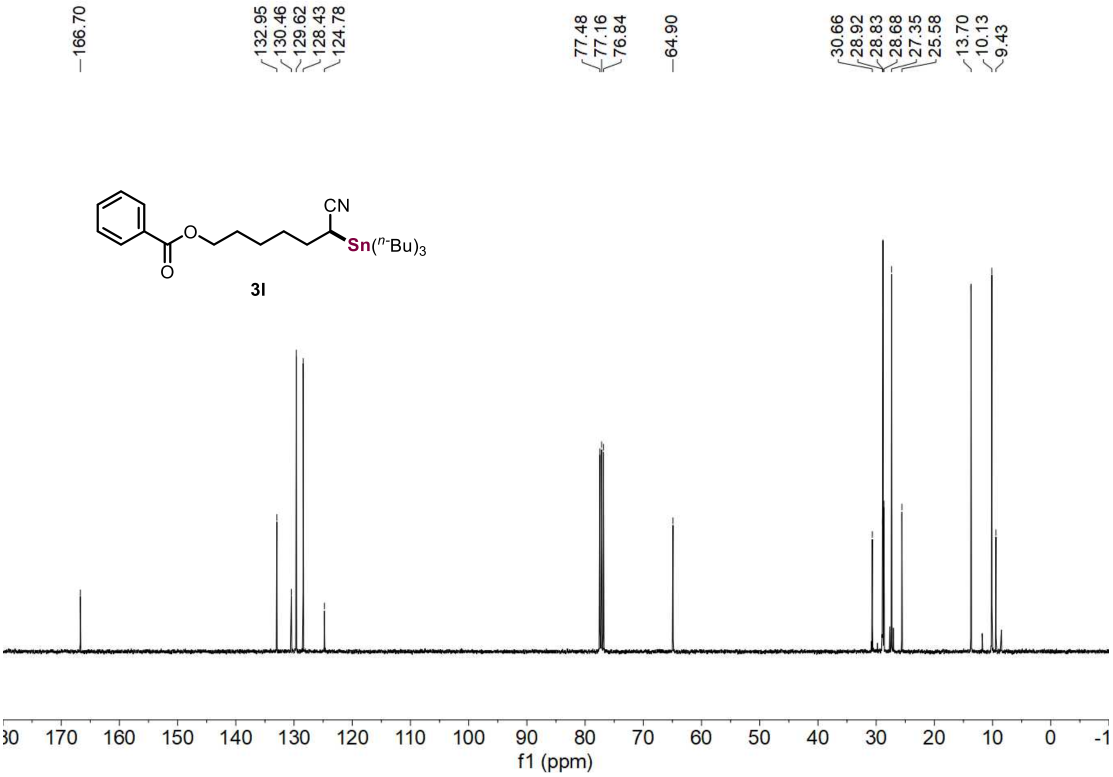
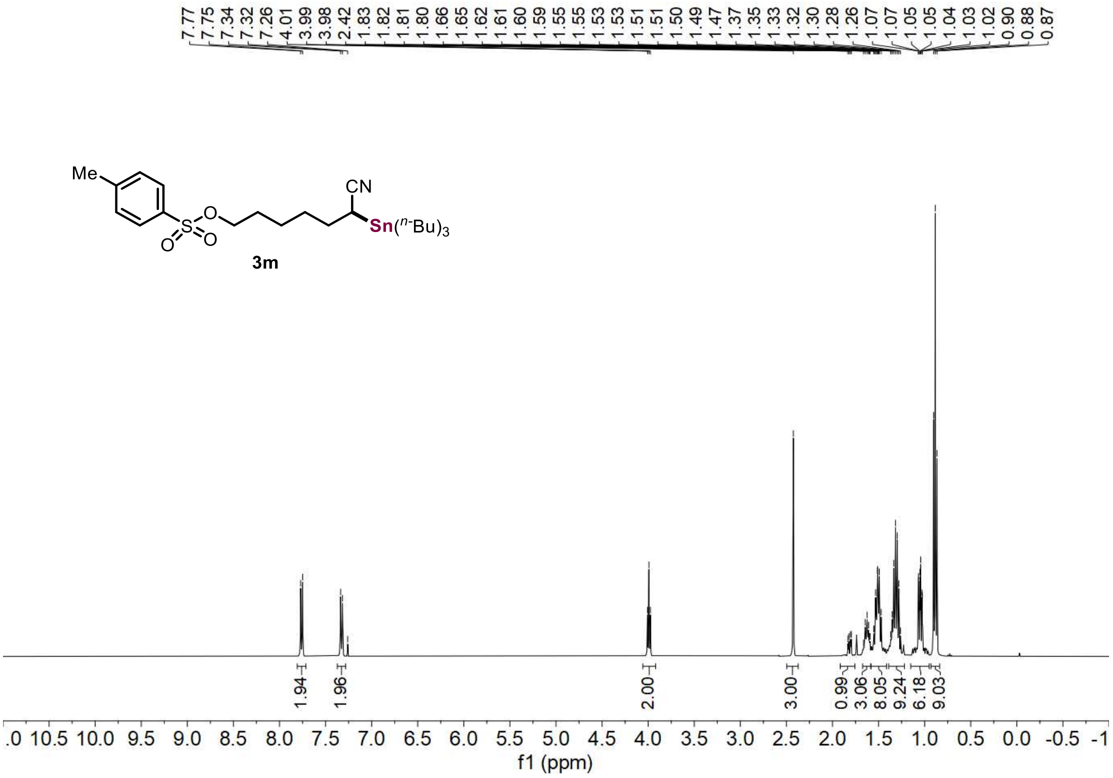


Figure S17. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3l**.



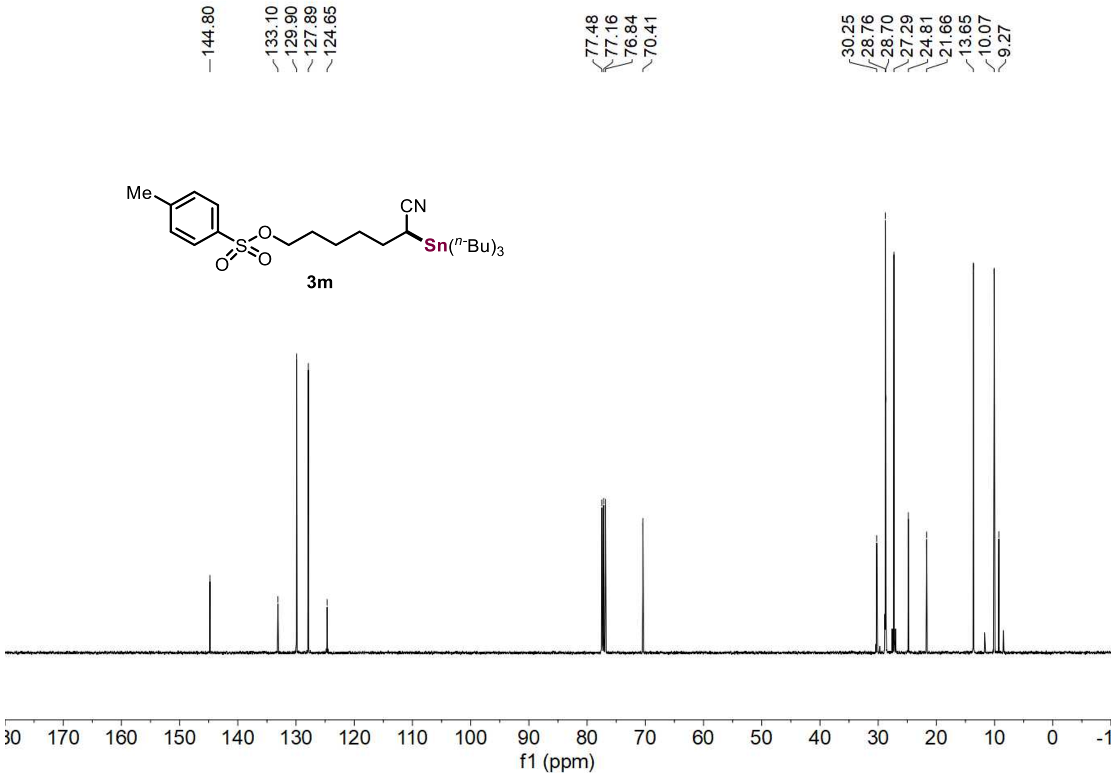
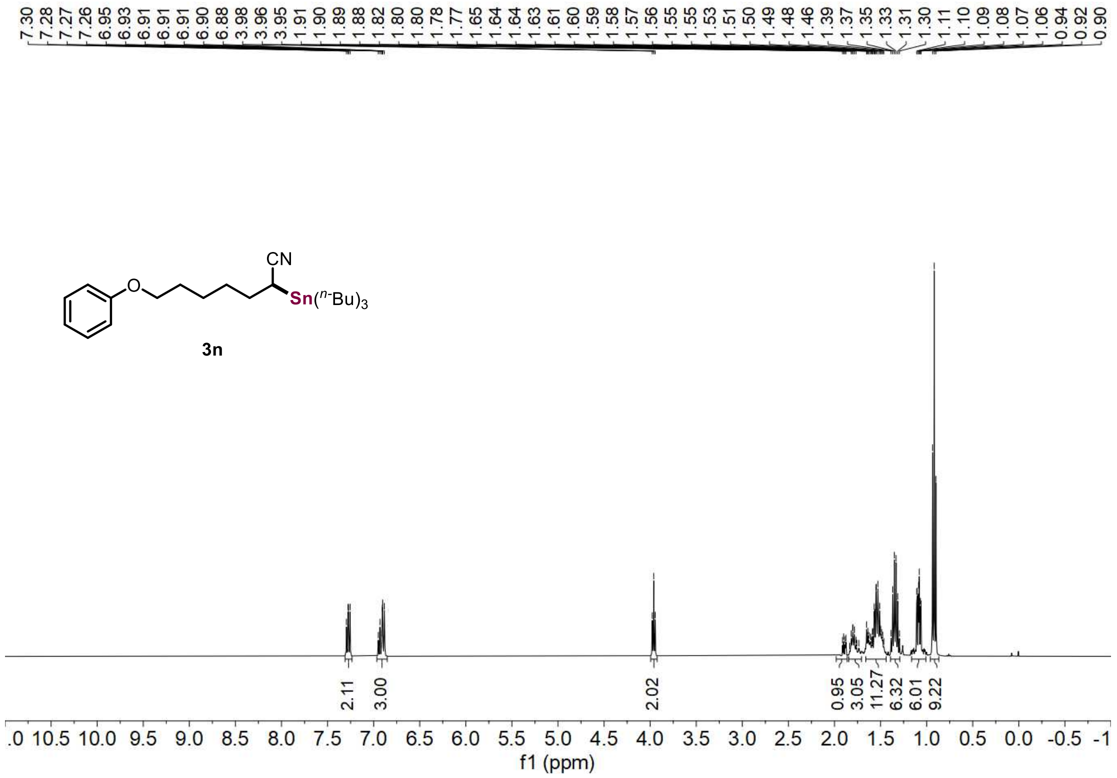


Figure S18. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3m**.



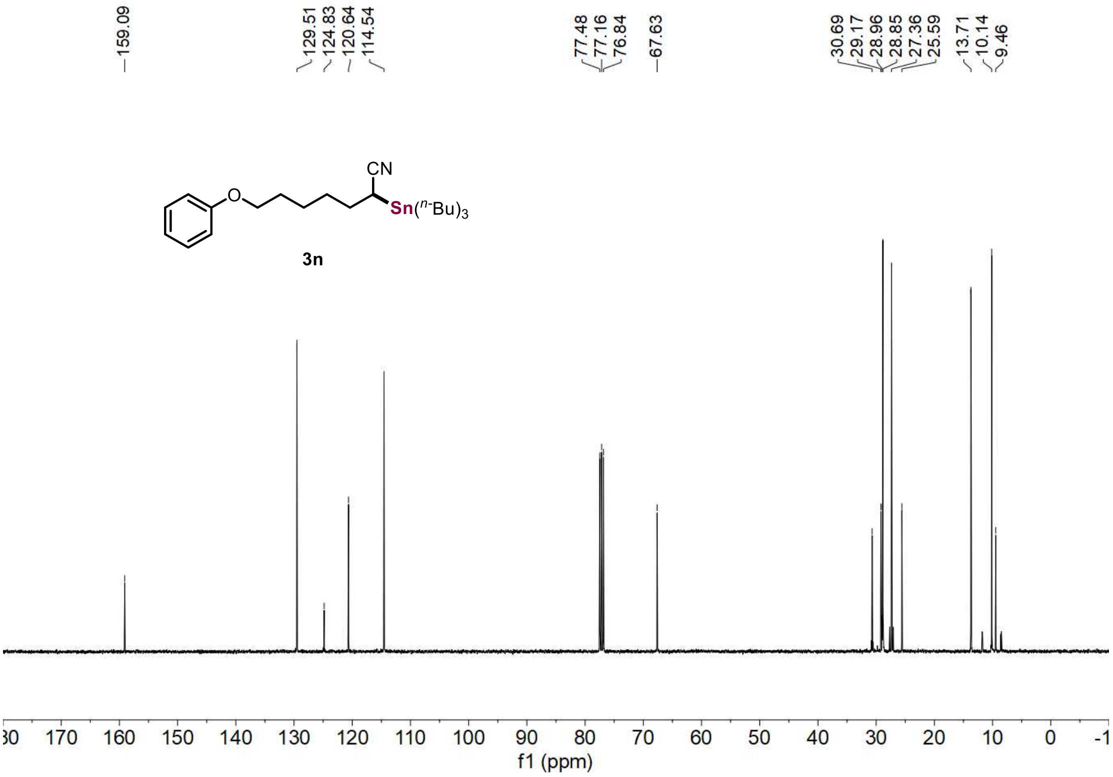
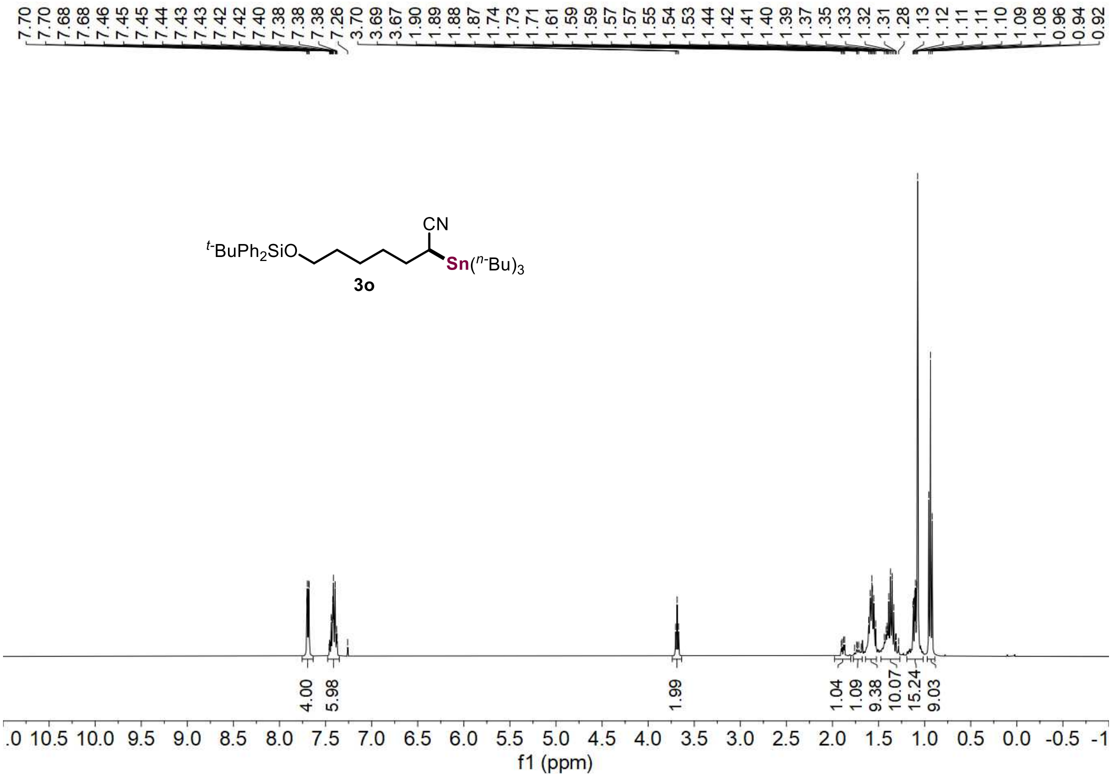


Figure S19. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3n**.



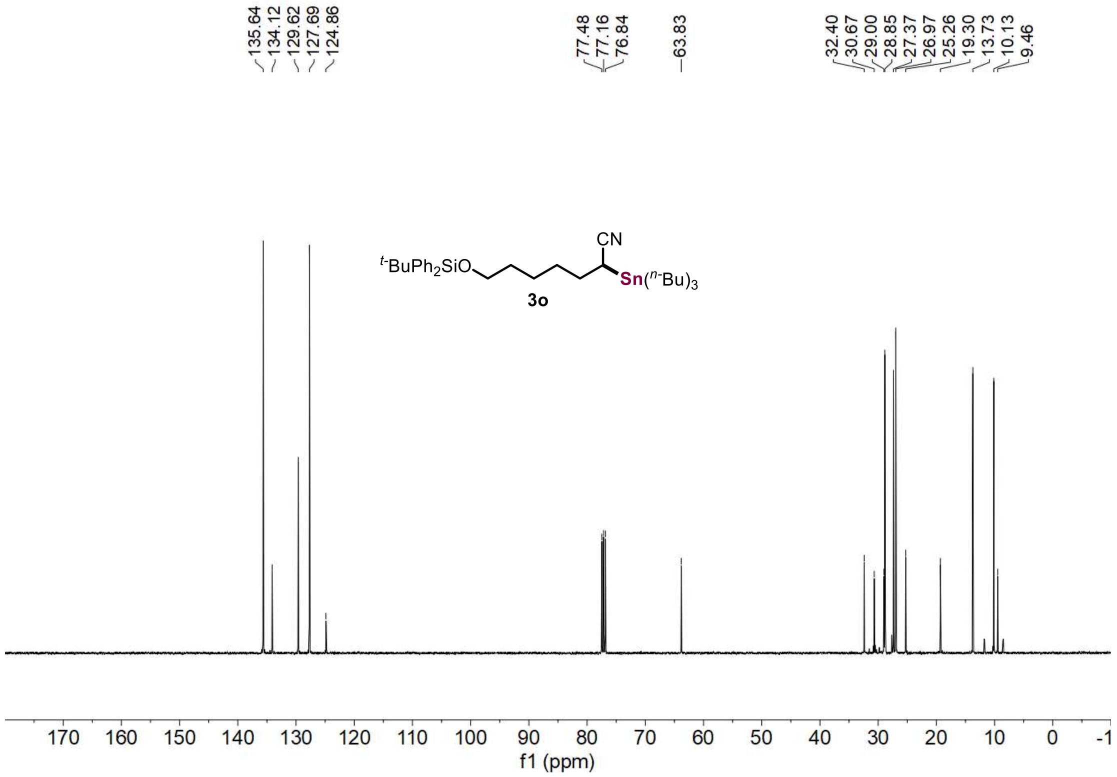
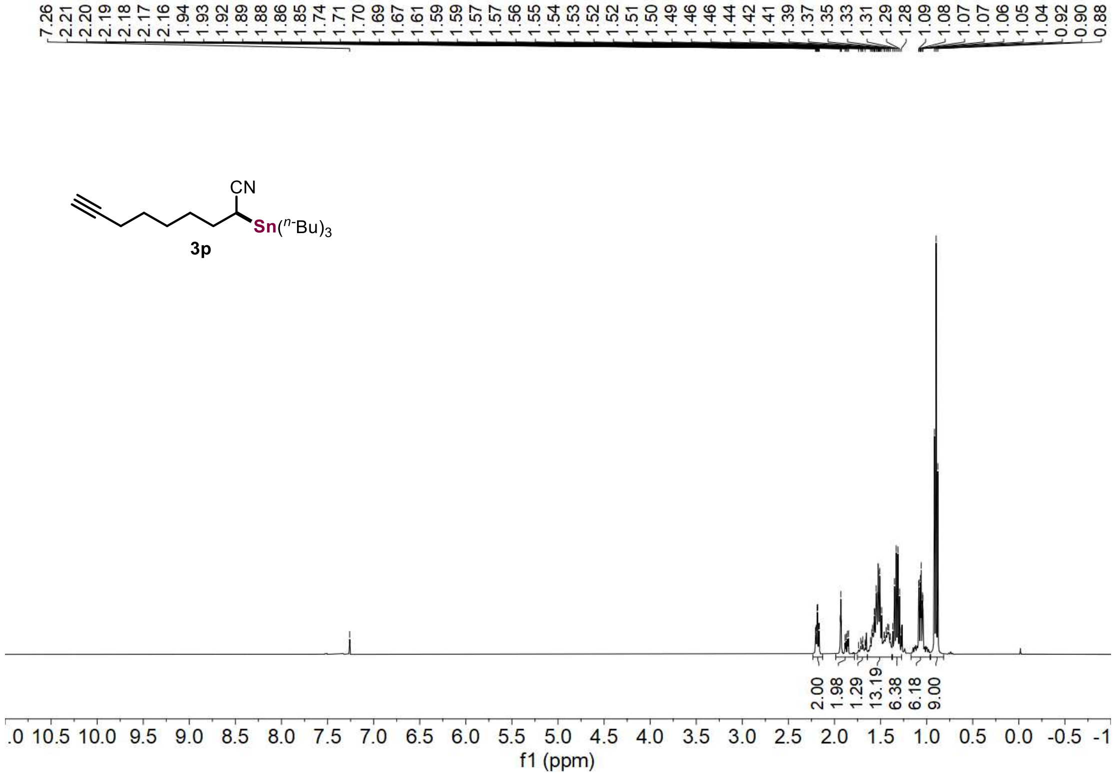


Figure S20. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **3o**.



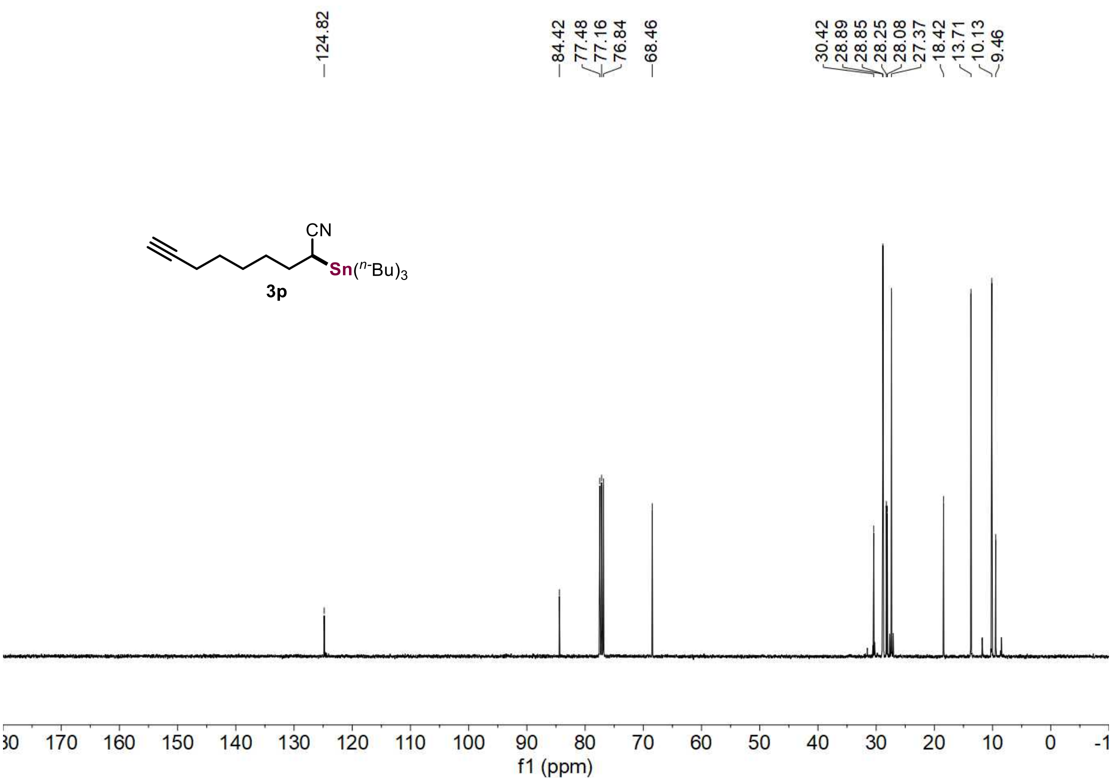
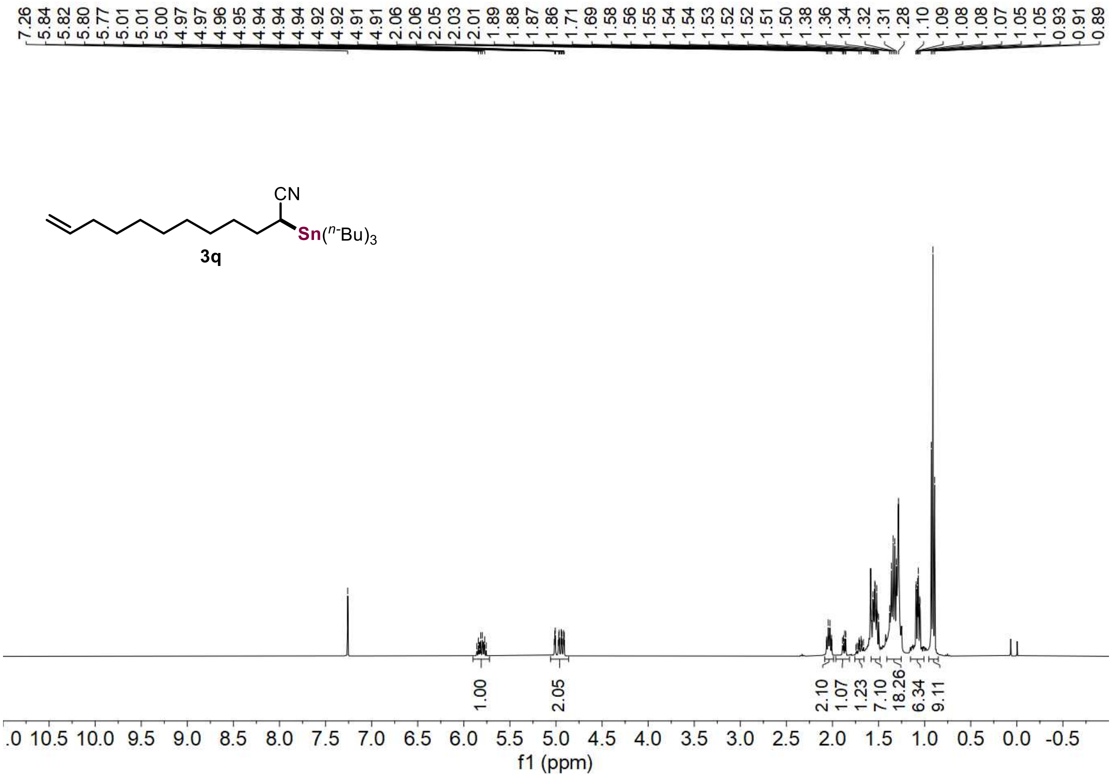


Figure S21. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3p**.



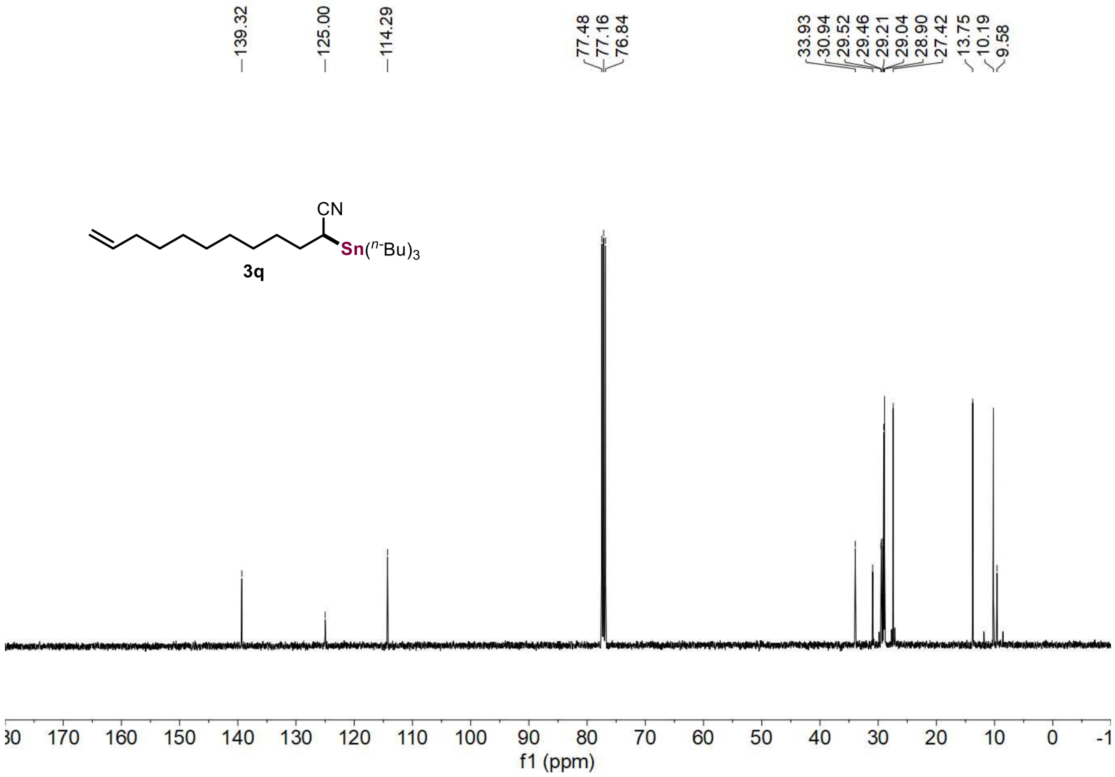
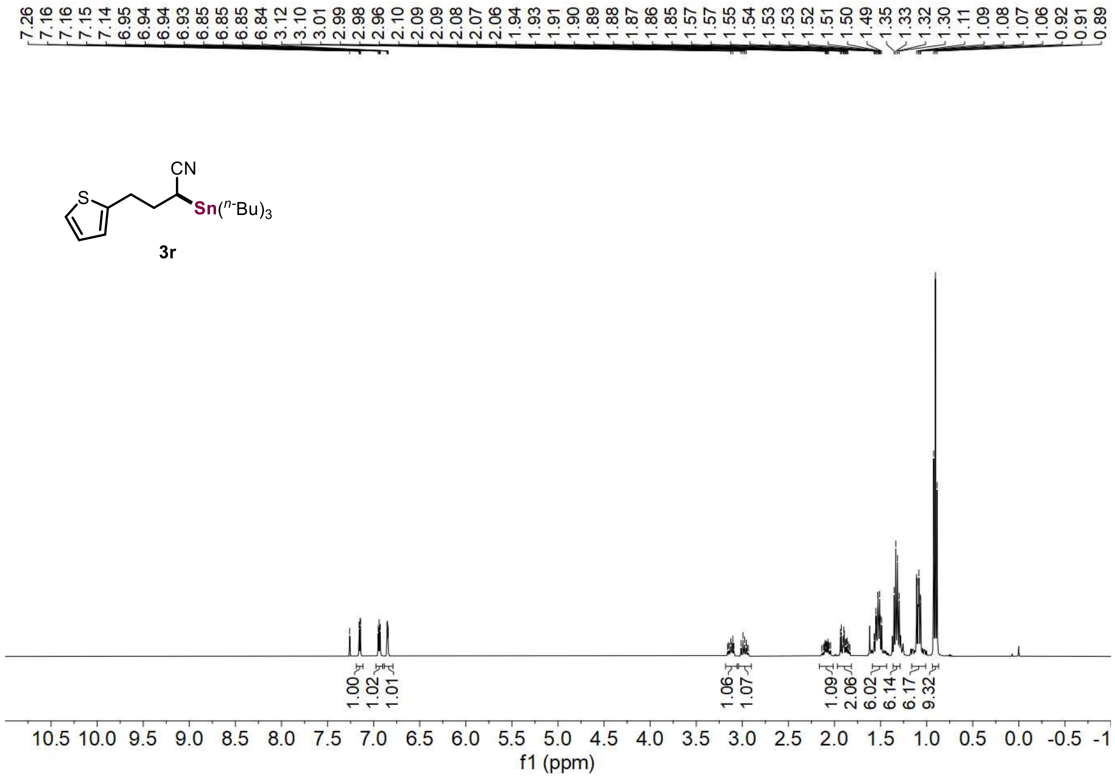


Figure S22. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3q**.



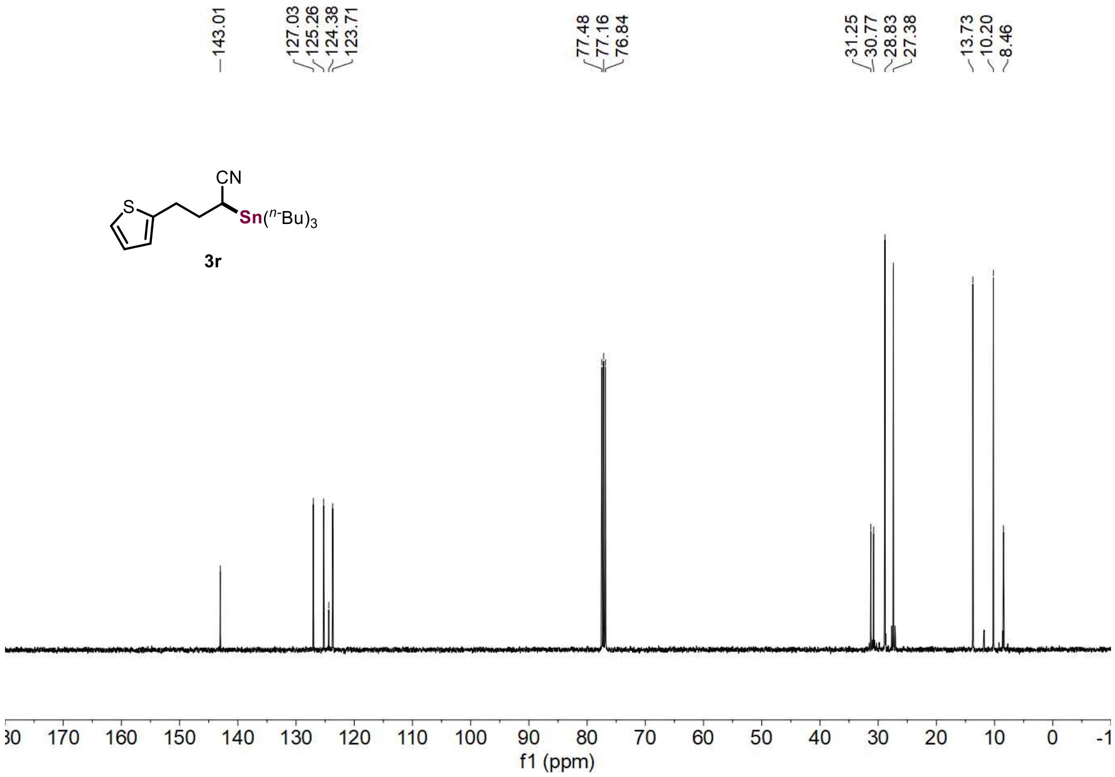
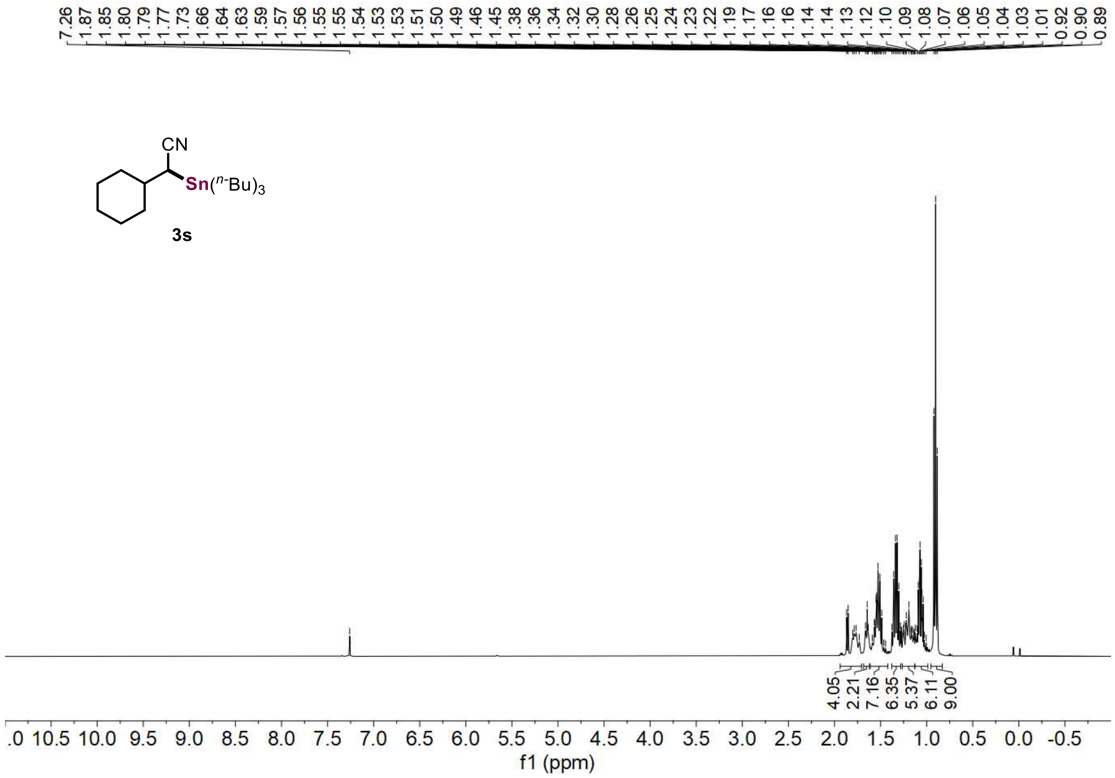


Figure S23. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3r**.



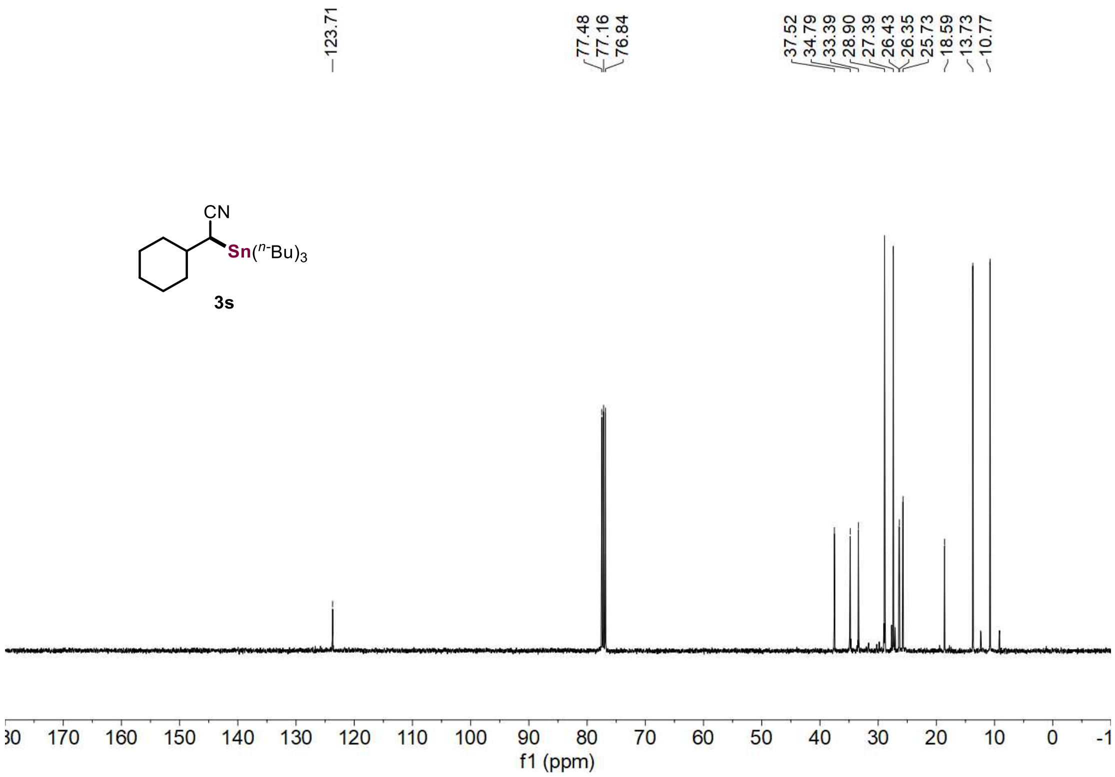
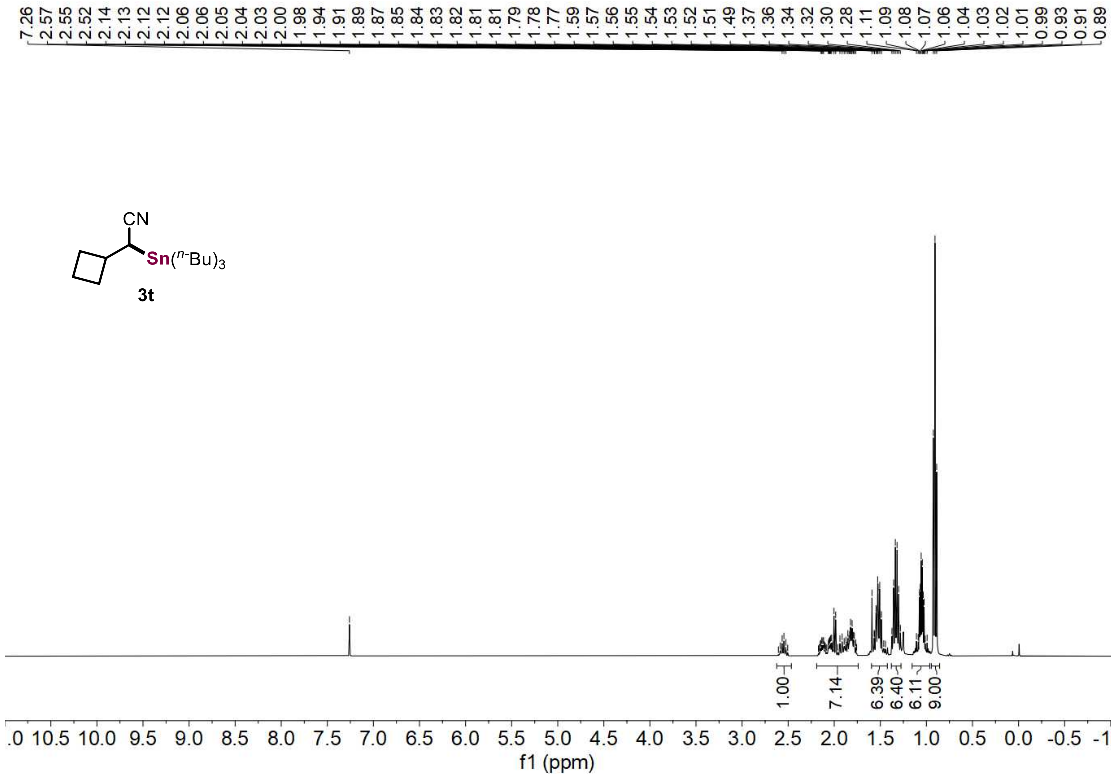


Figure S24. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3s**.



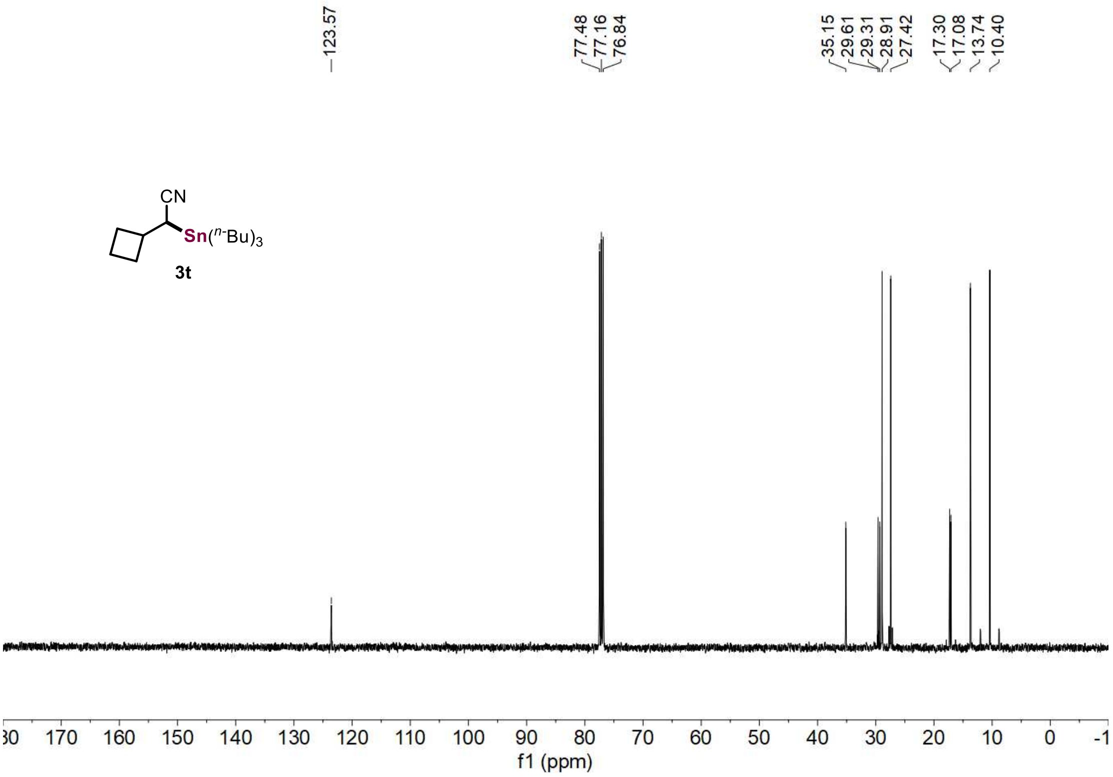
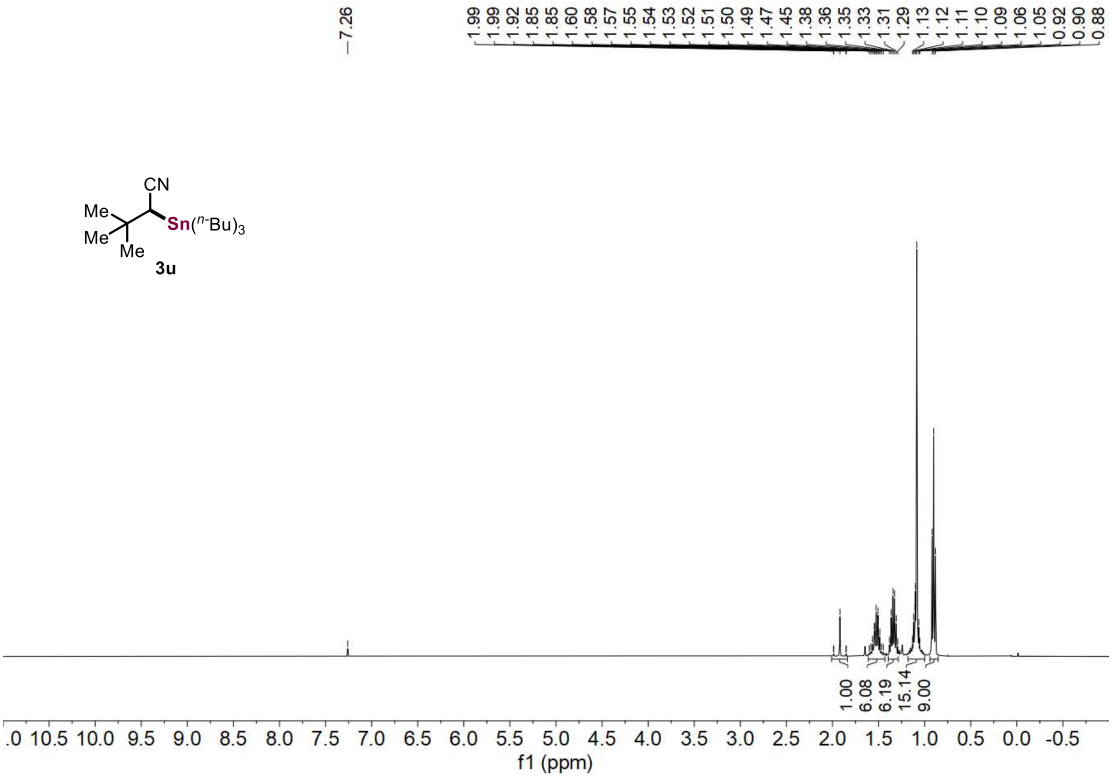


Figure S25. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3t**.



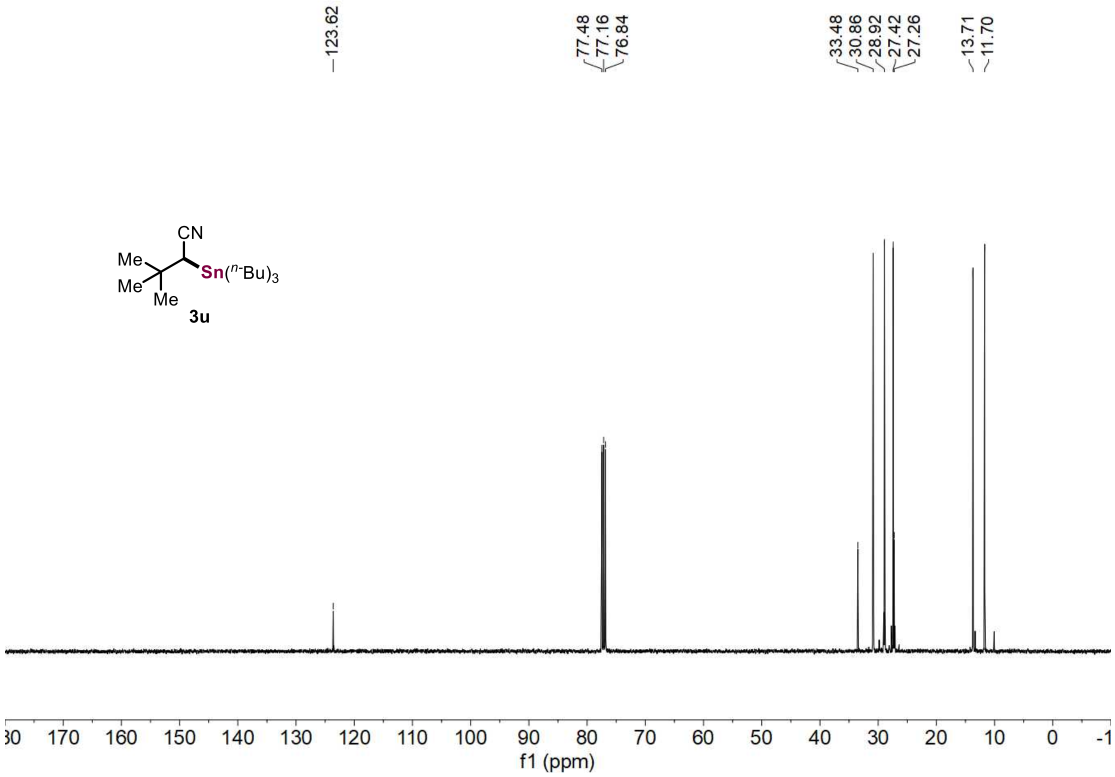
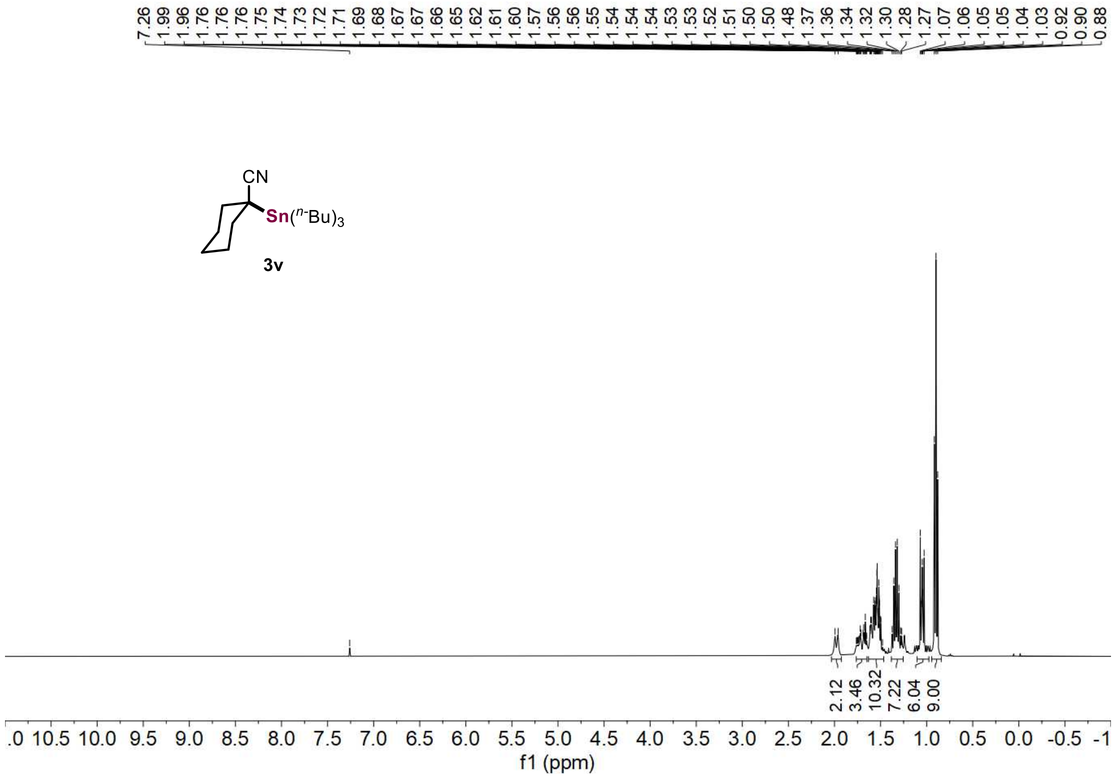


Figure S26. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3u**.



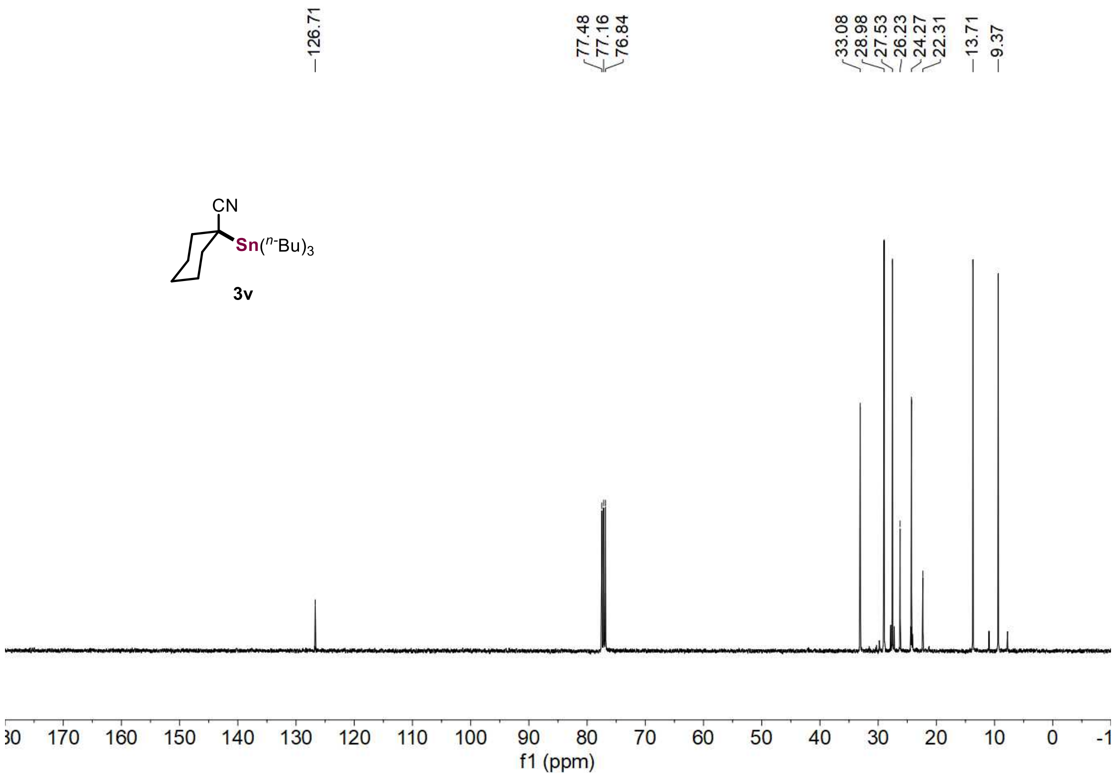
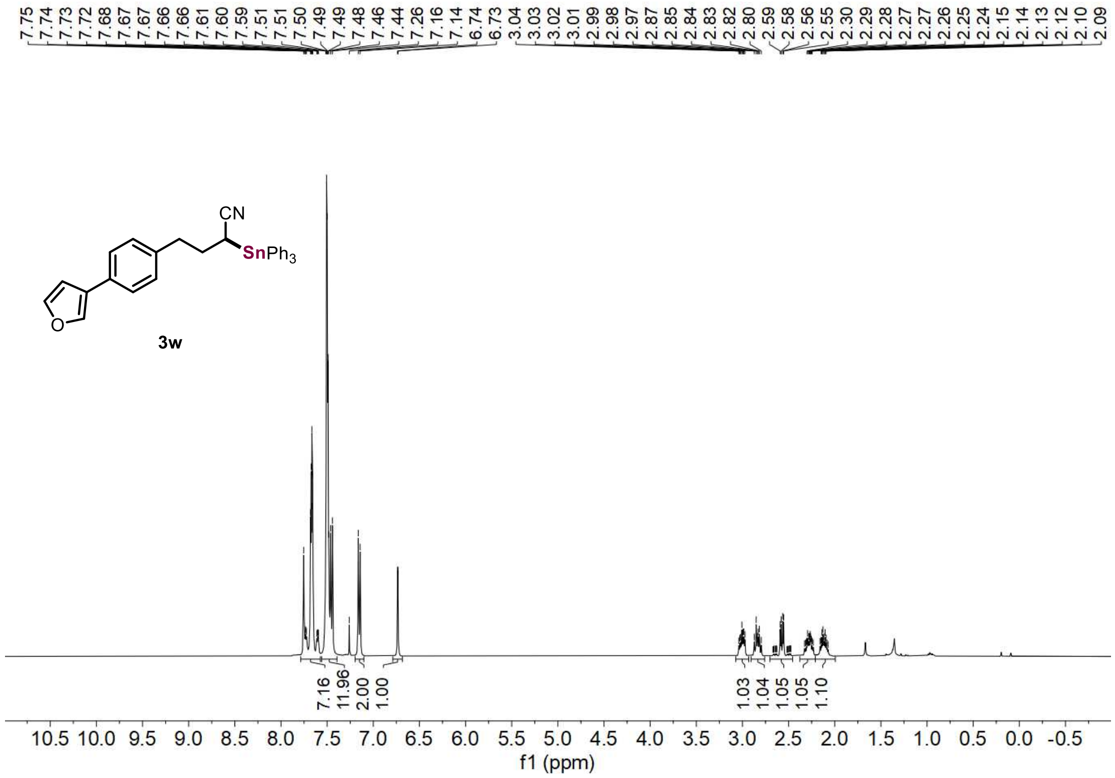


Figure S27. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3v**.



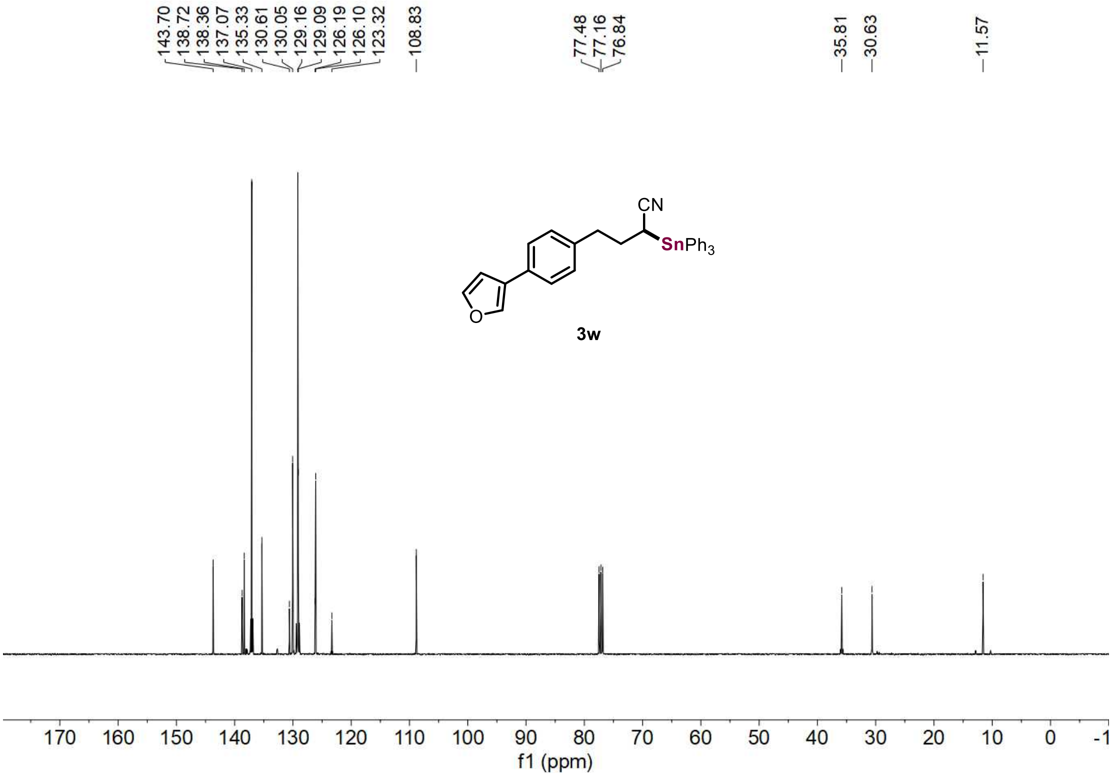
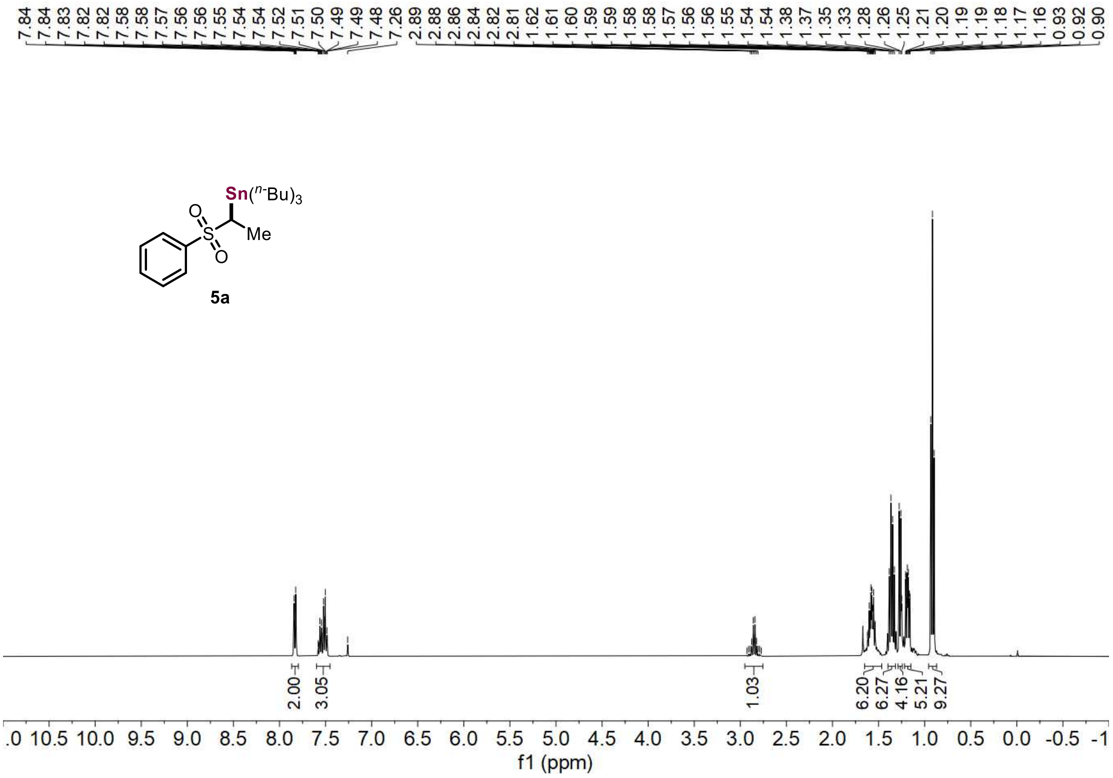


Figure S28. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **3w**.



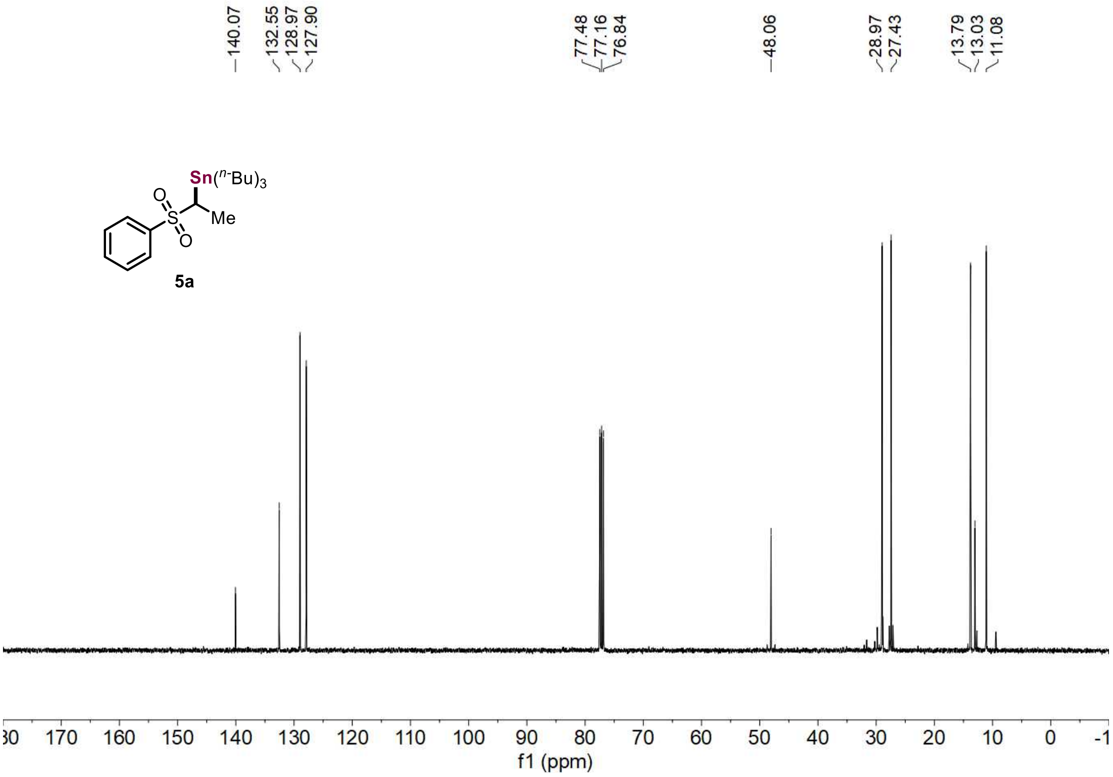
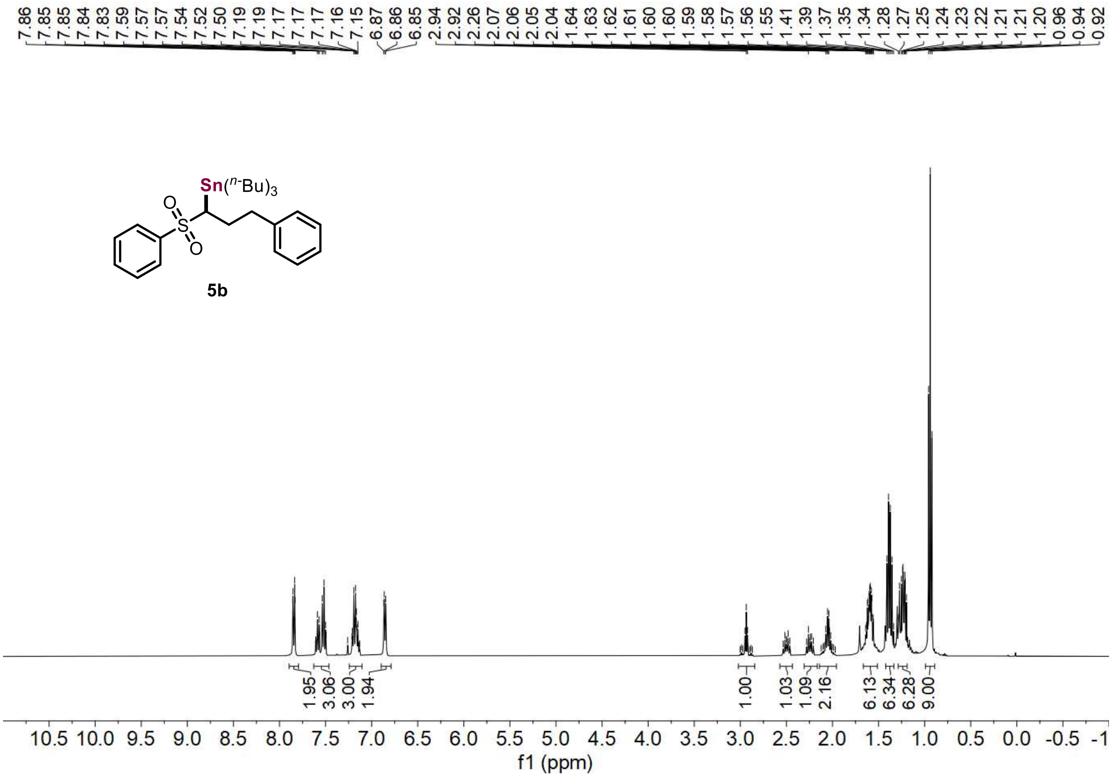


Figure S29. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5a**.



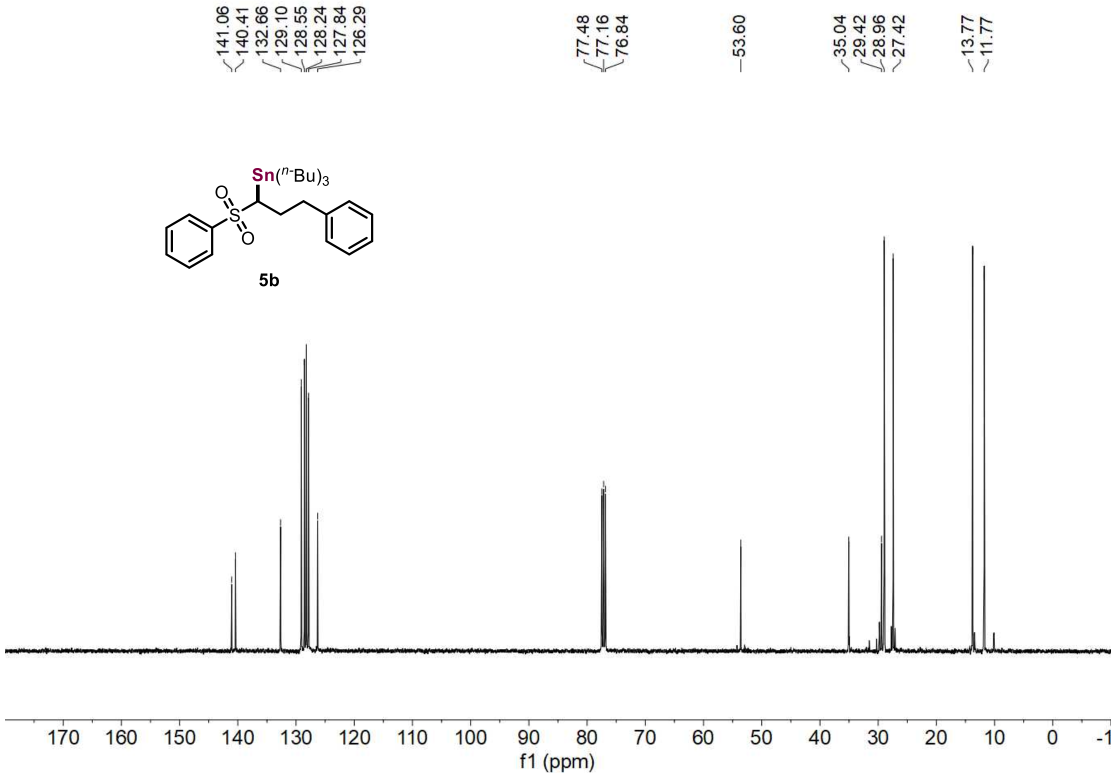
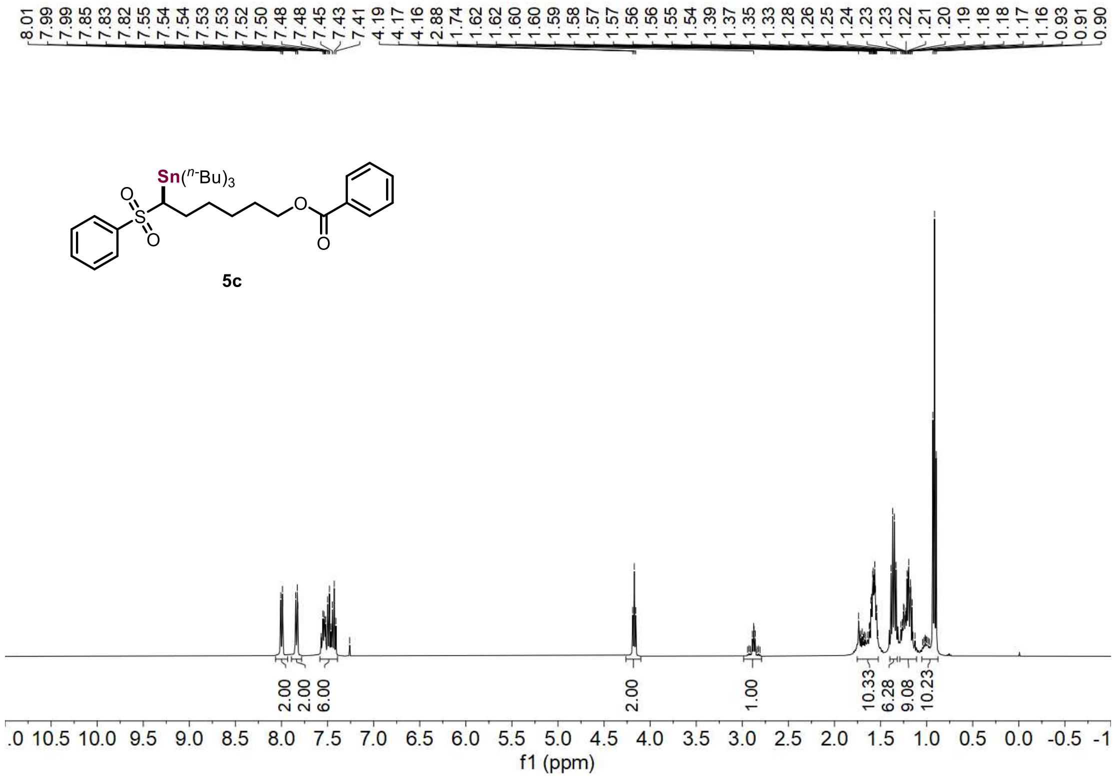


Figure S30. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5b**.



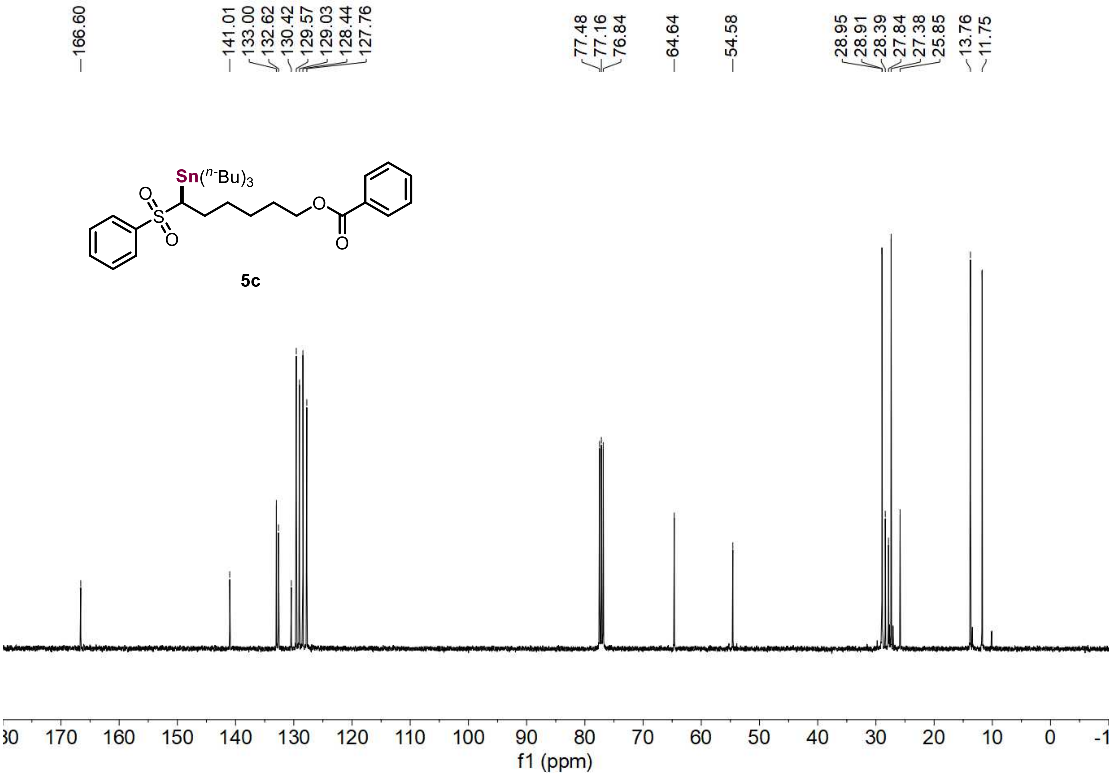
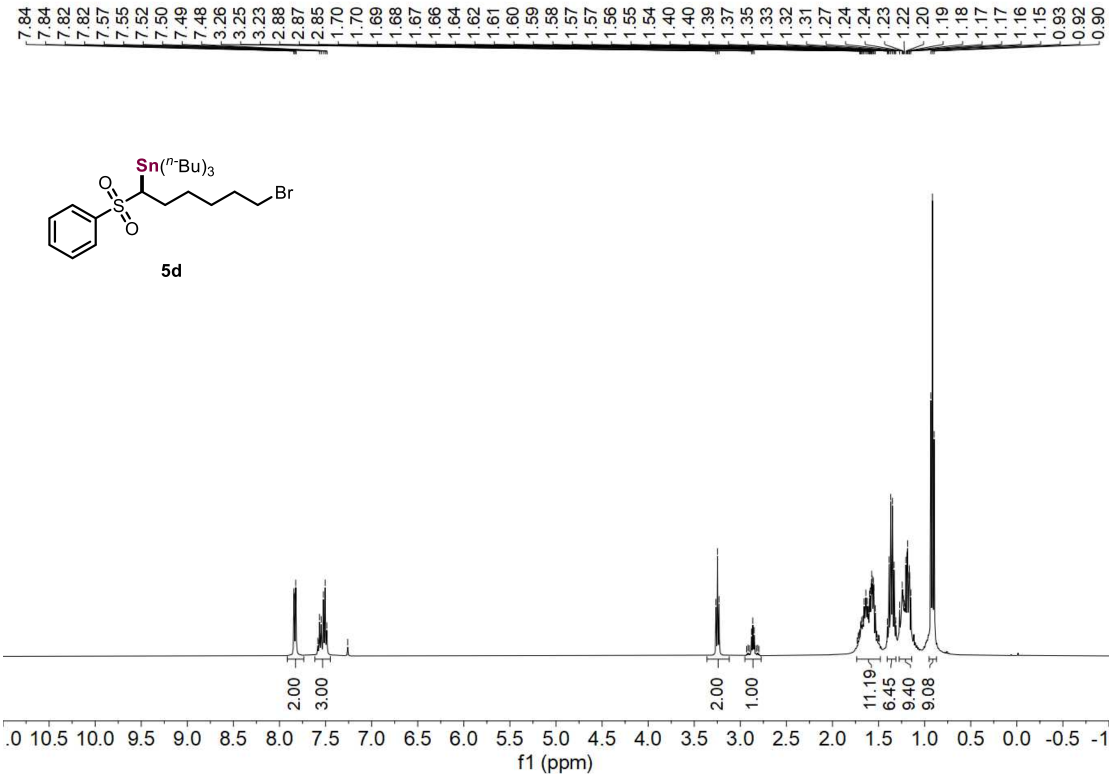


Figure S31. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5c**.



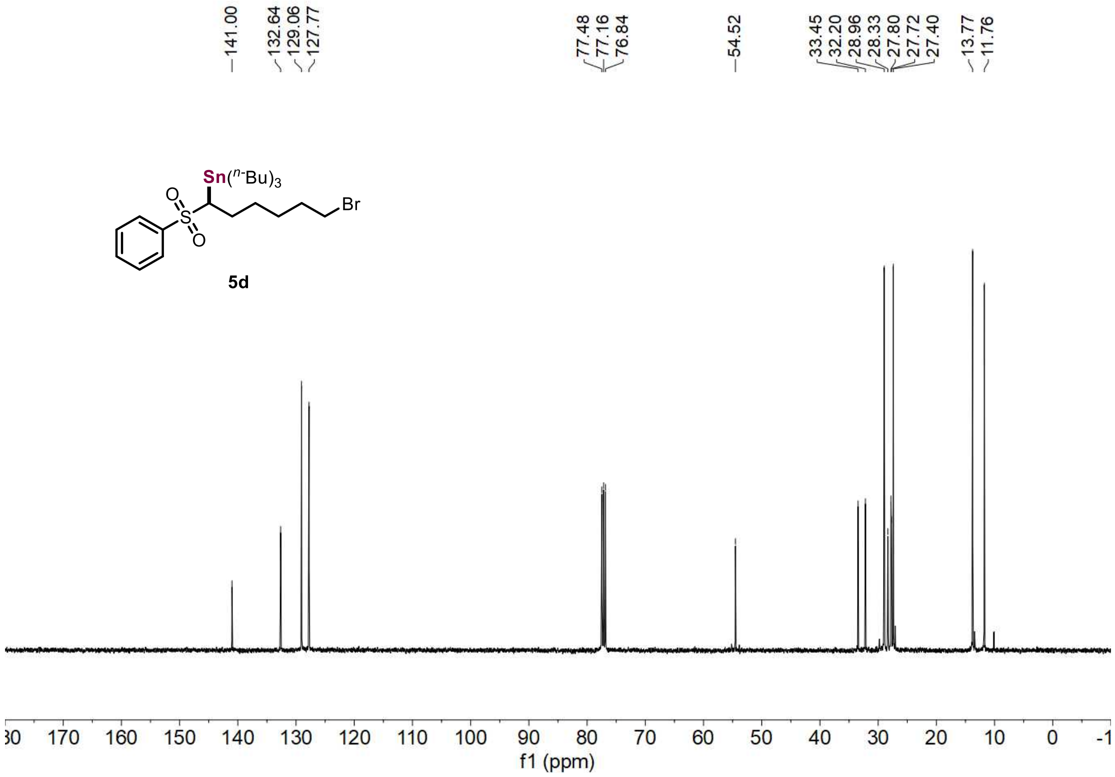
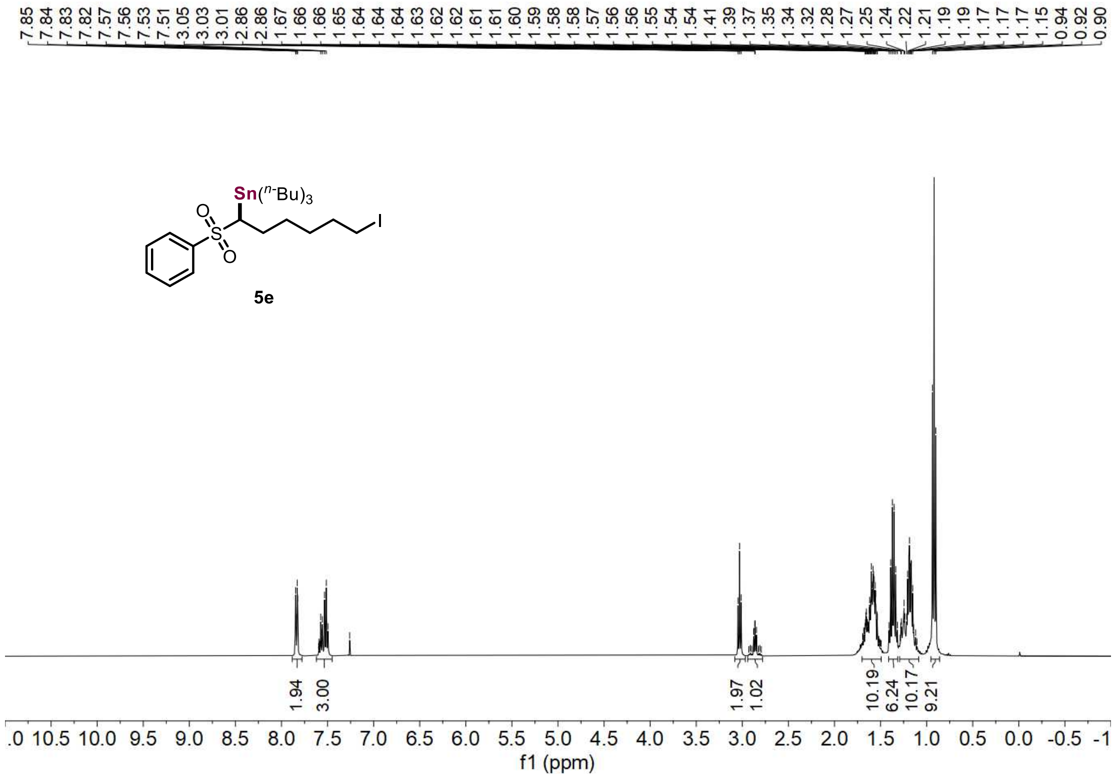


Figure S32. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **5d**.



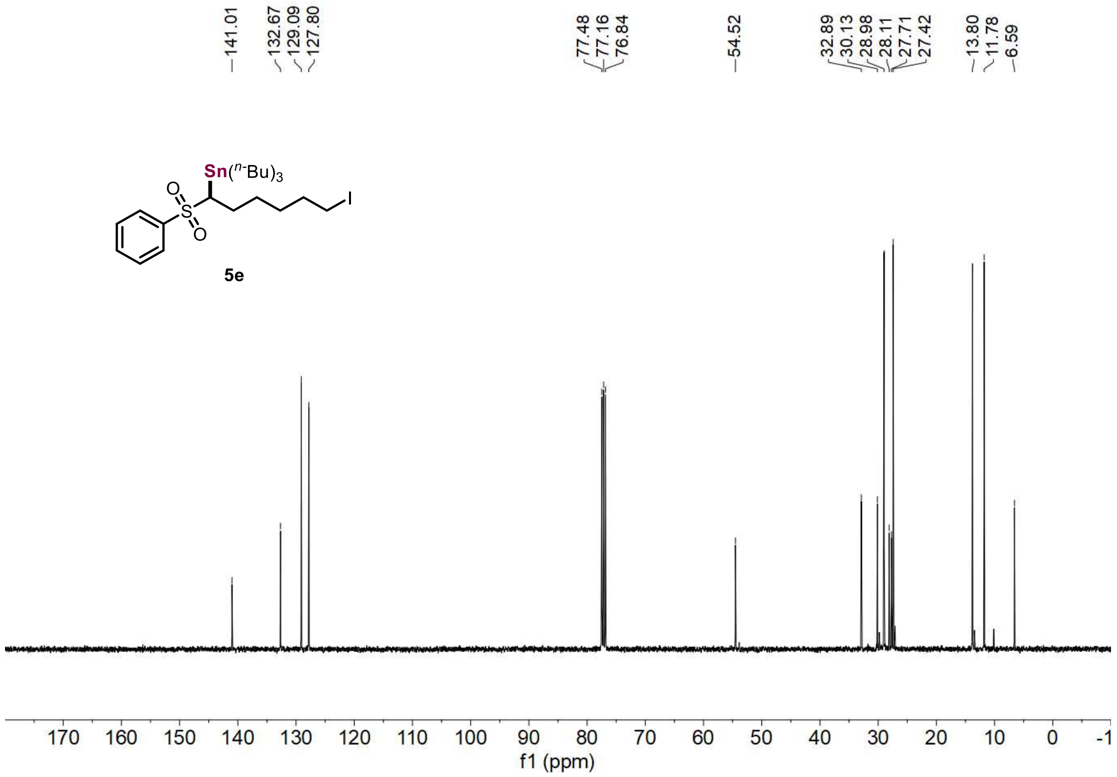
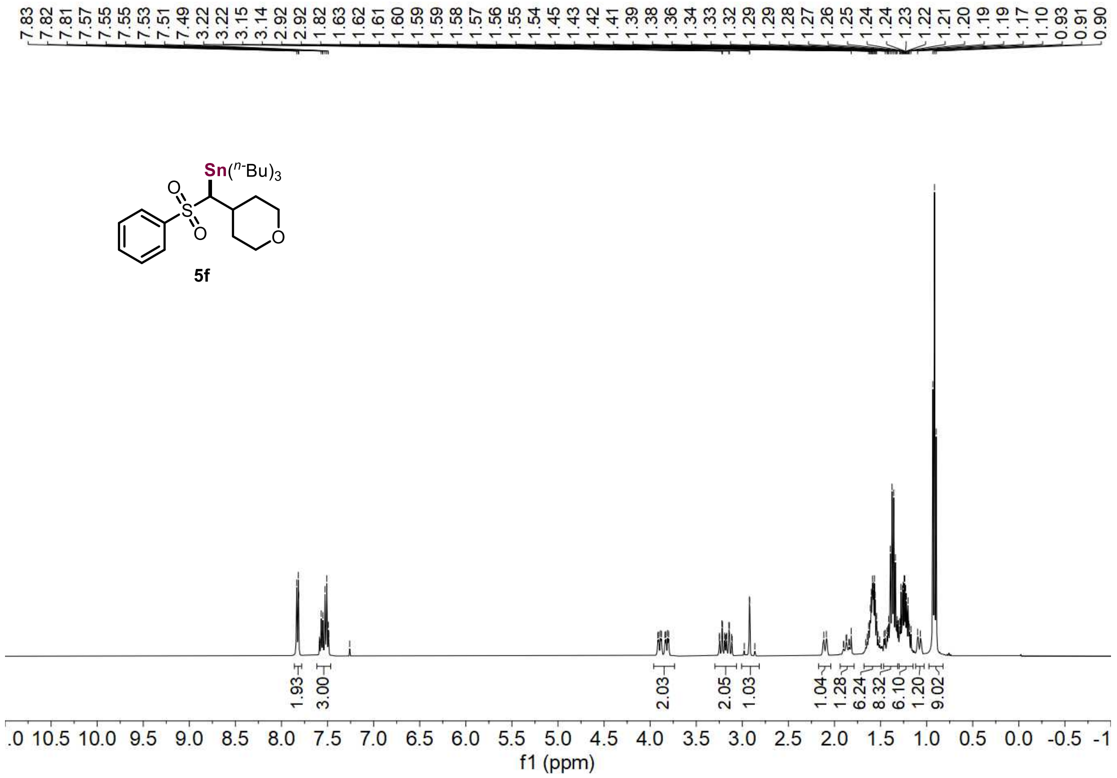


Figure S33. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5e**.



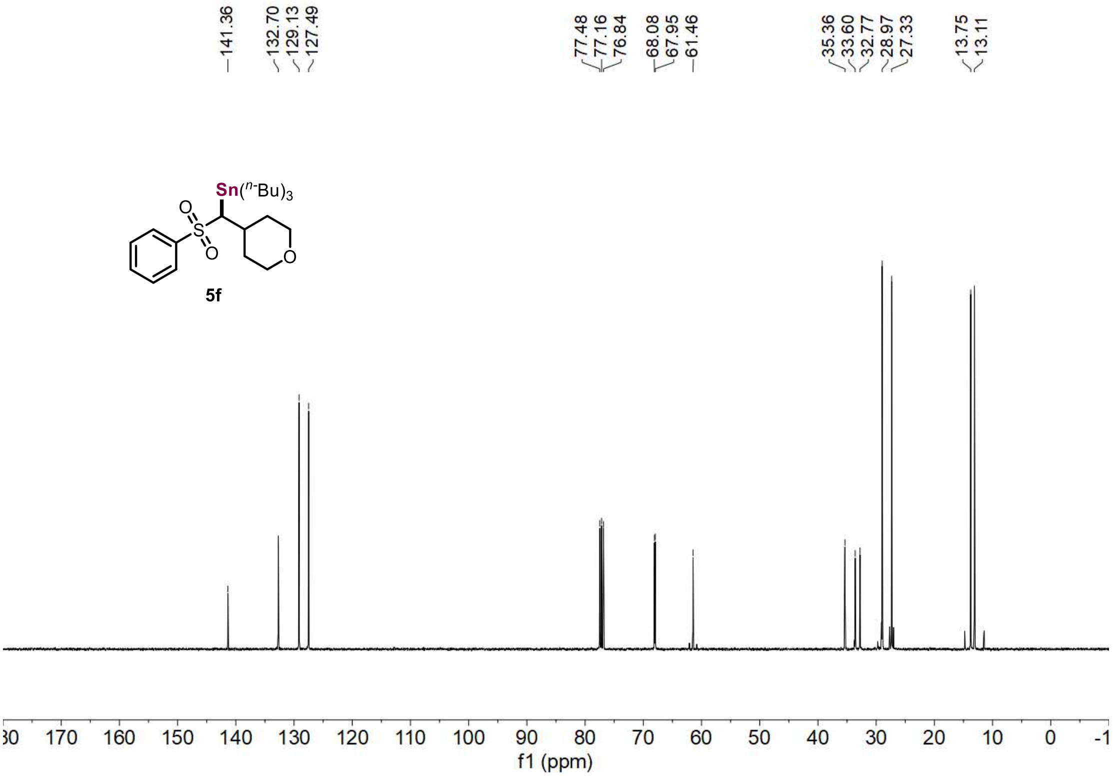
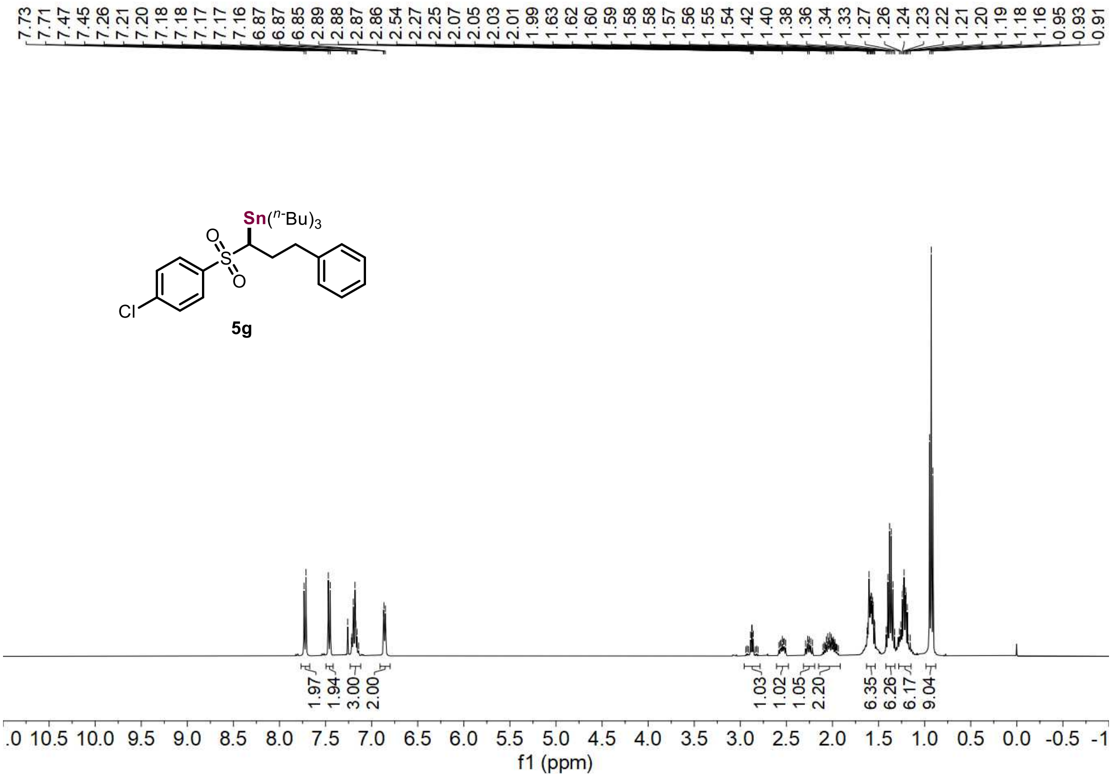


Figure S34. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5f**.



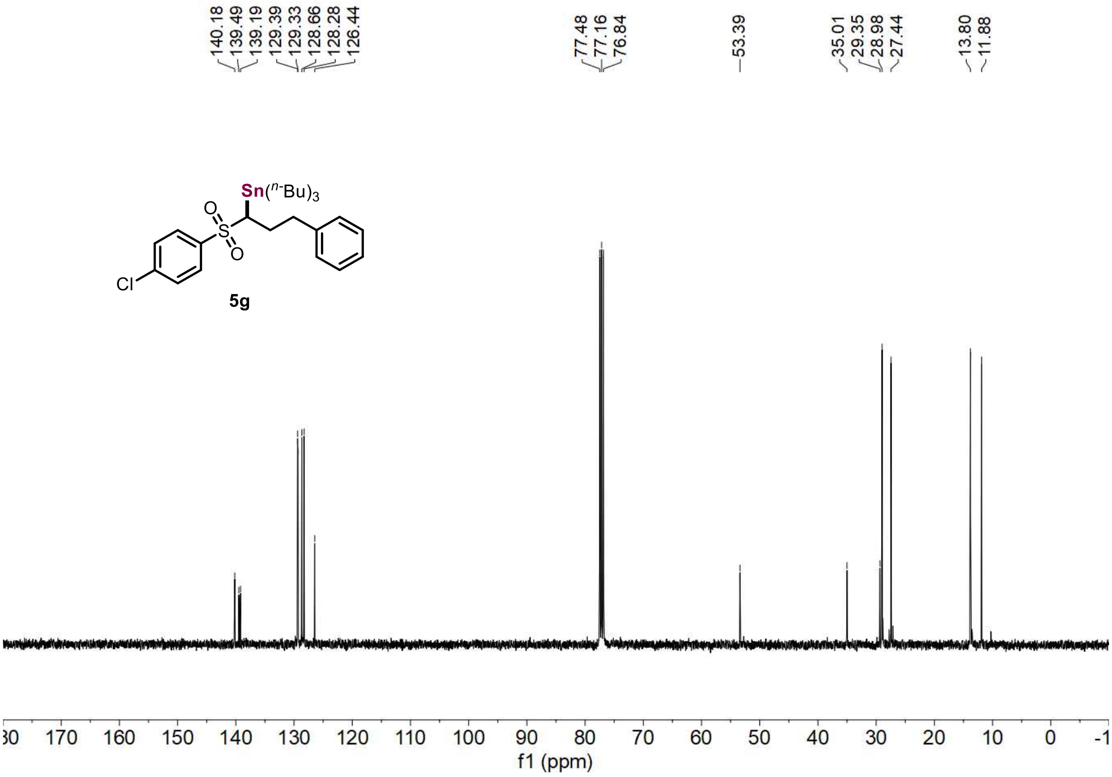
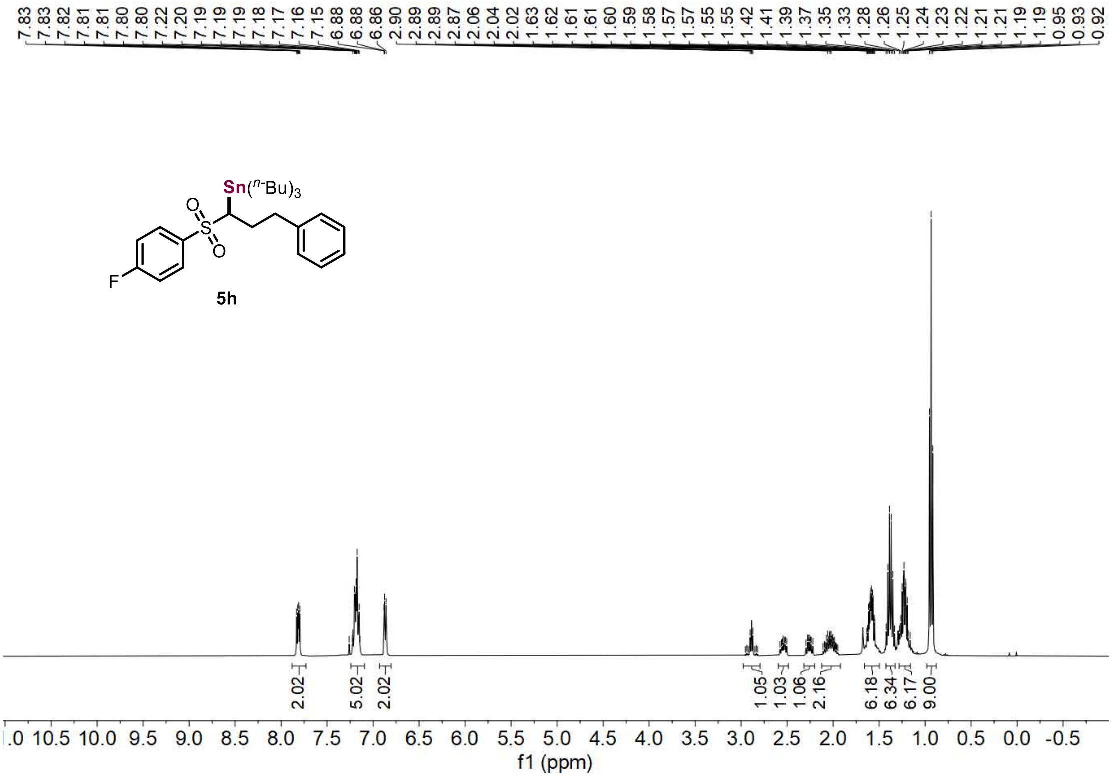


Figure S35. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5g**.



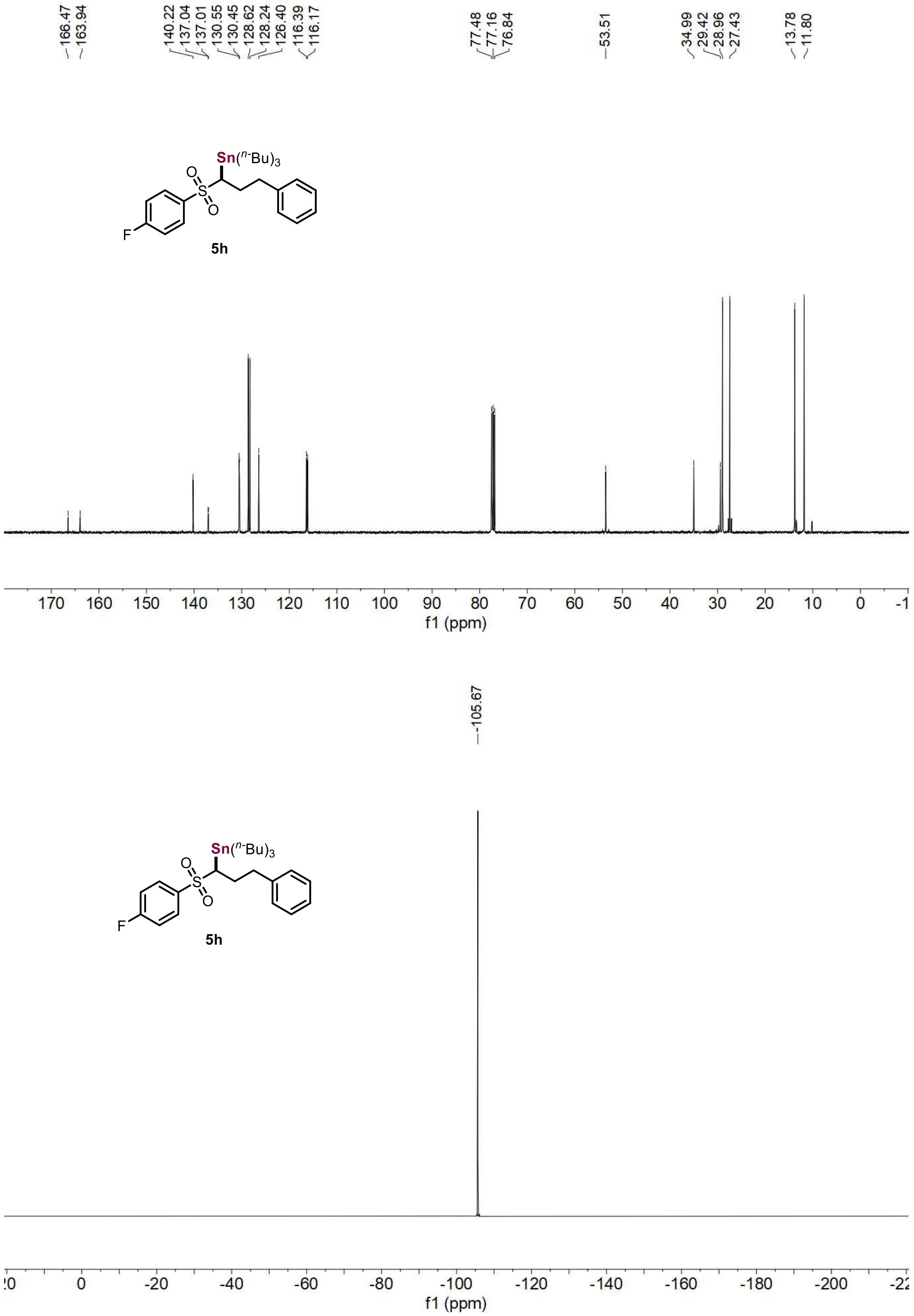


Figure S36. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{19}F (376 MHz, CDCl$_3$) NMR spectra for compound **5h**.

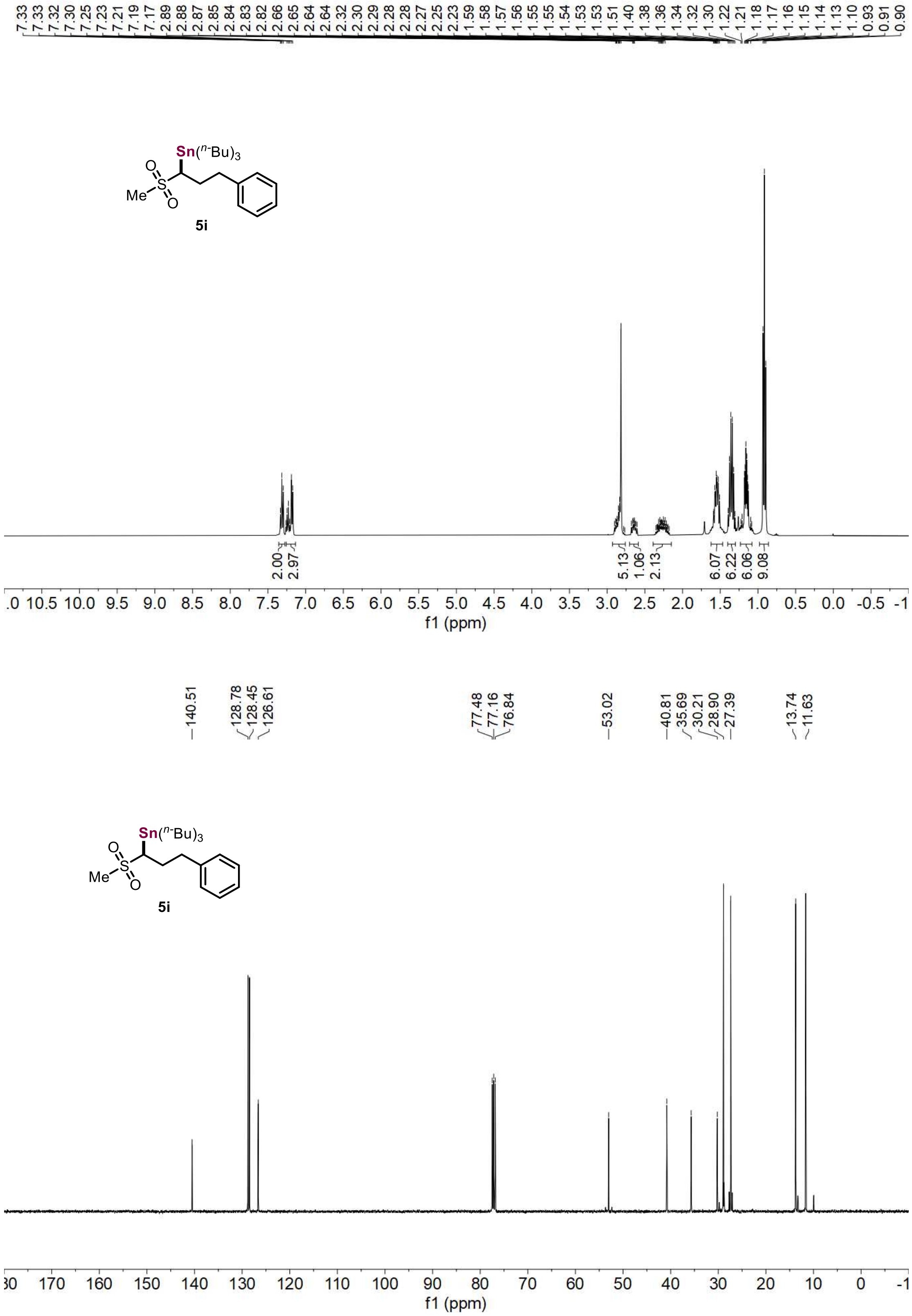


Figure S37. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5i**.

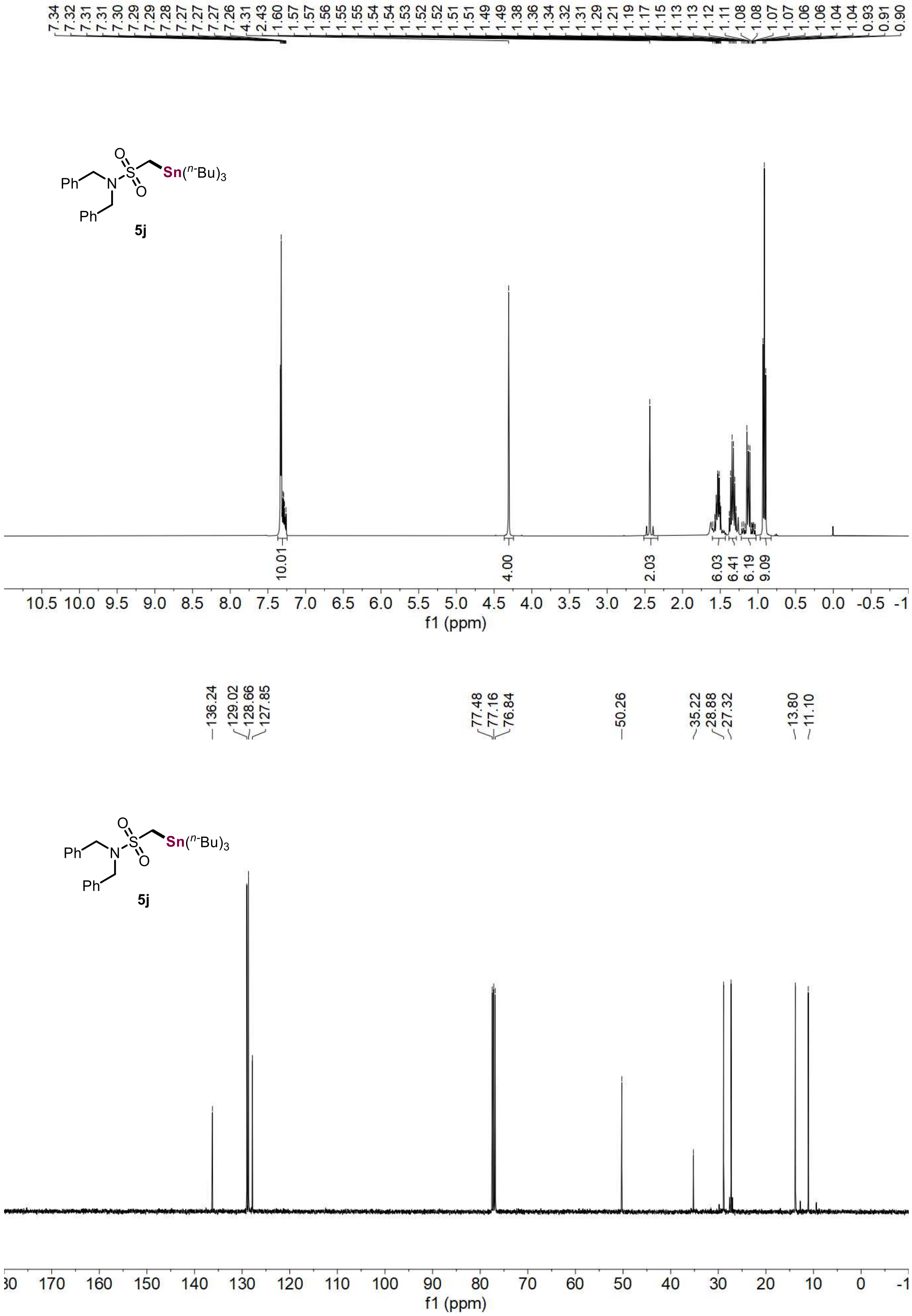


Figure S38. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **5j**.

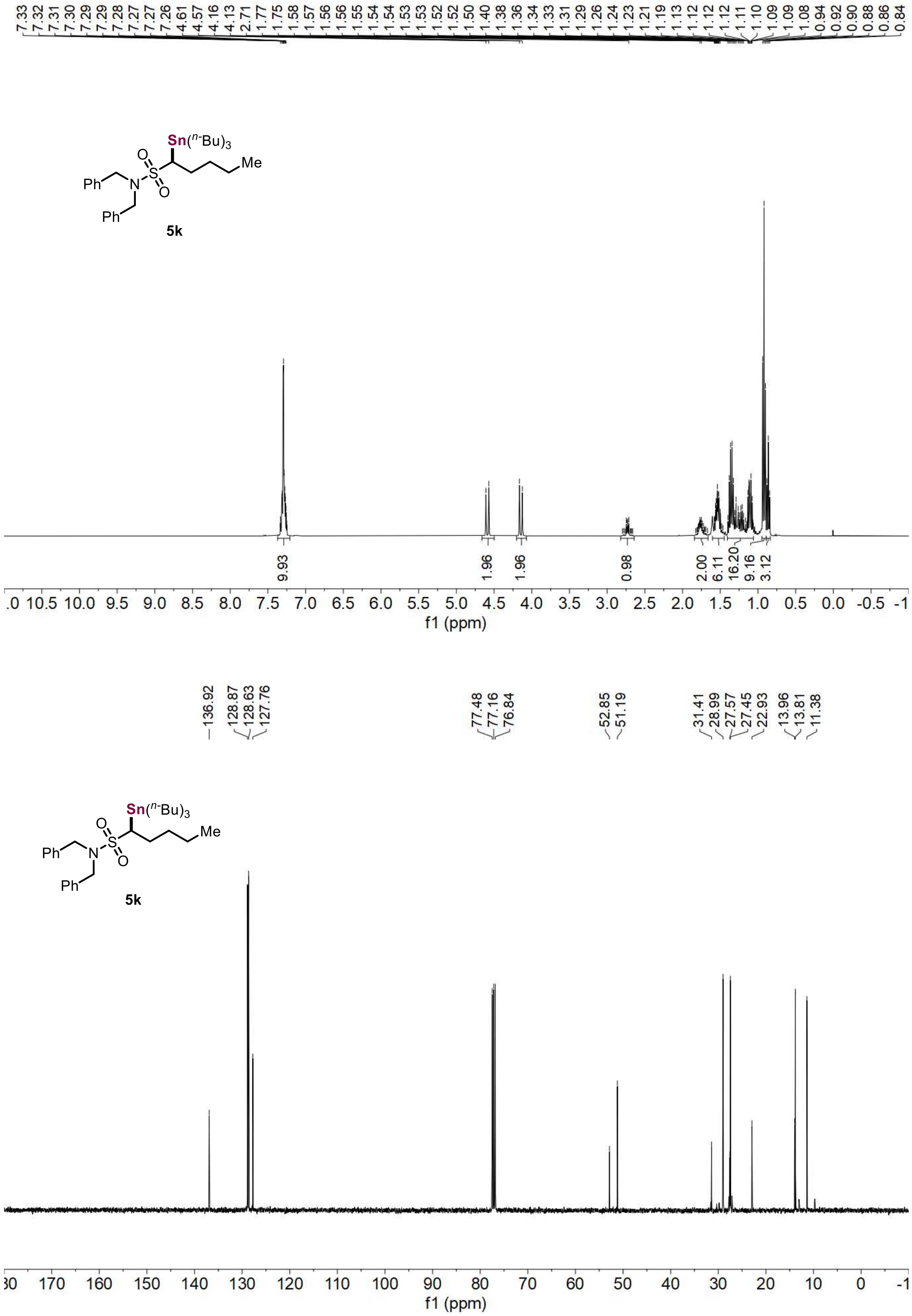


Figure S39. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **5k**.

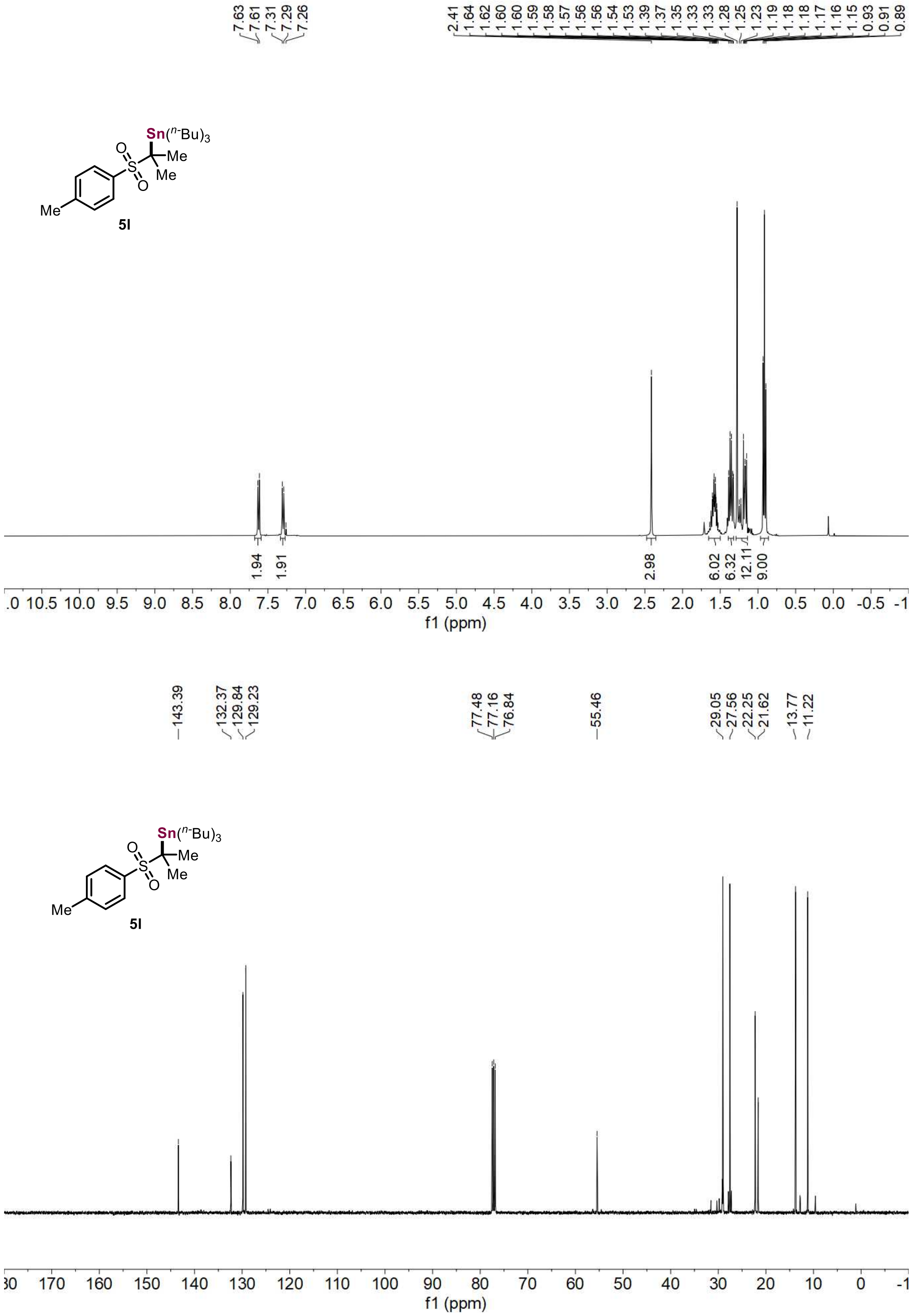
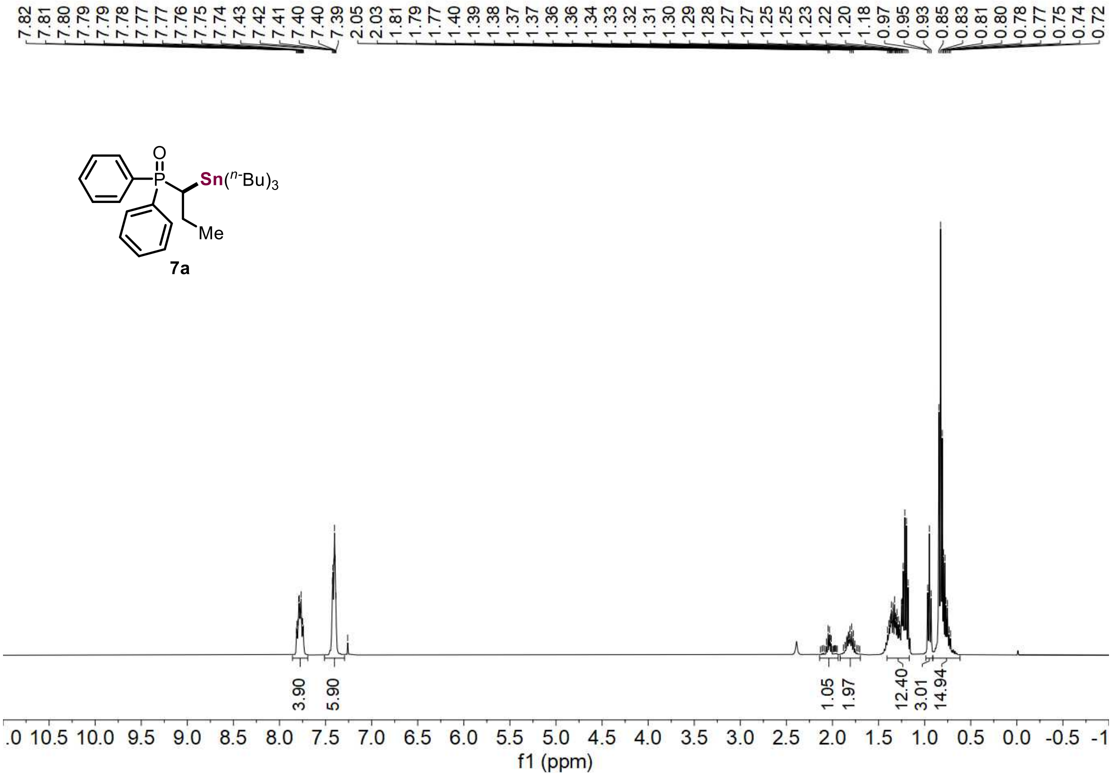


Figure S40. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **5l**.


7.82
7.81
7.80
7.79
7.79
7.78
7.77
7.77
7.76
7.75
7.74
7.43
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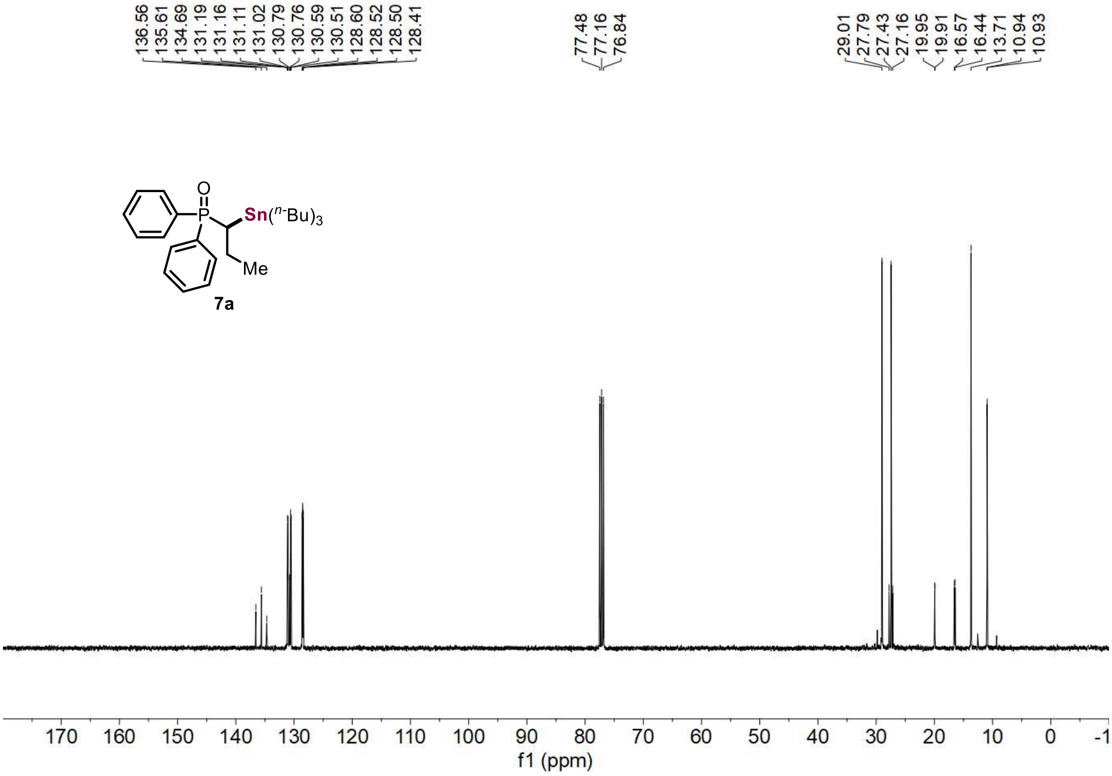
7.41
7.40
7.40
7.39
2.05
2.03
1.81
1.79
1.77
1.40
1.39
1.38
1.37
1.37
1.36
1.36
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.27
1.25
1.25
1.23
1.22
1.20
1.18
0.97
0.95
0.93
0.85
0.83
0.81
0.80
0.78
0.77
0.75
0.74
0.72
O
P
Sn(ⁿ-Bu)3
Me
7a
3.90
5.90
1.05
1.97
12.40
3.01
14.94
.0 10.5 10.0 9.5 9.0 8.5 8.0 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 -1
f1 (ppm)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131.11
131.02
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128.50
128.41
77.48
77.16
76.84
29.01
27.79
27.43
27.16
19.95
19.91
16.57
16.44
13.71
10.94
10.93
O
P
Sn(ⁿ-Bu)3
Me
7a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

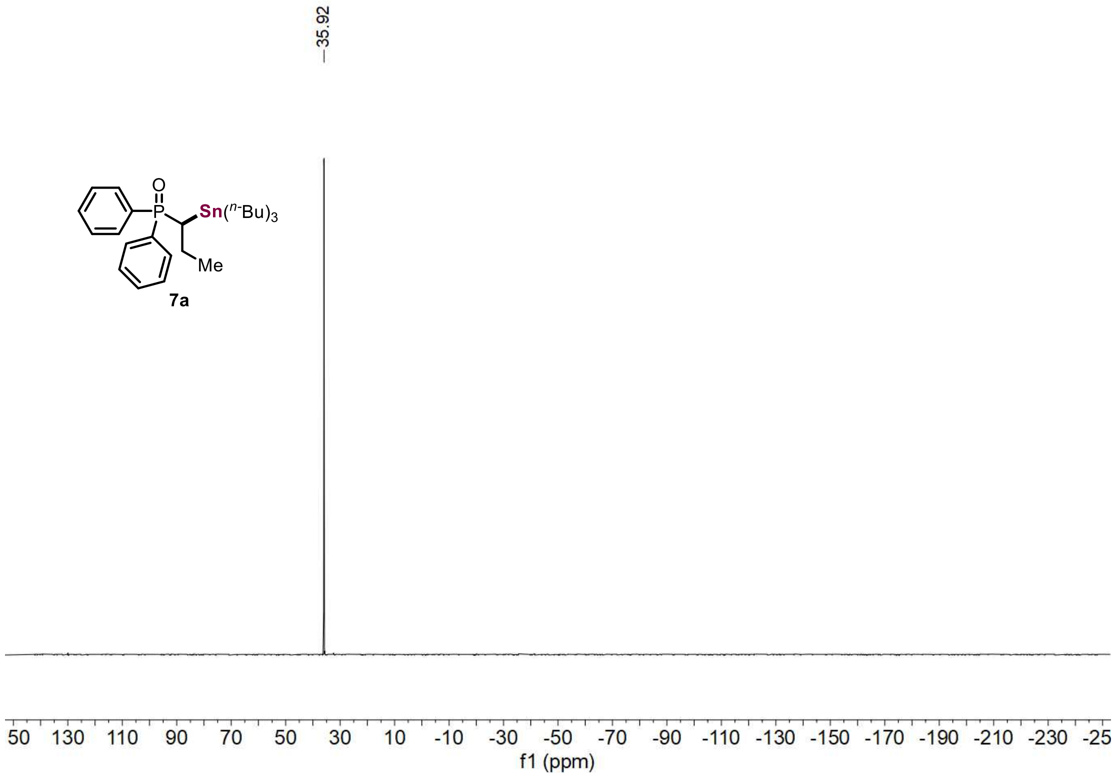
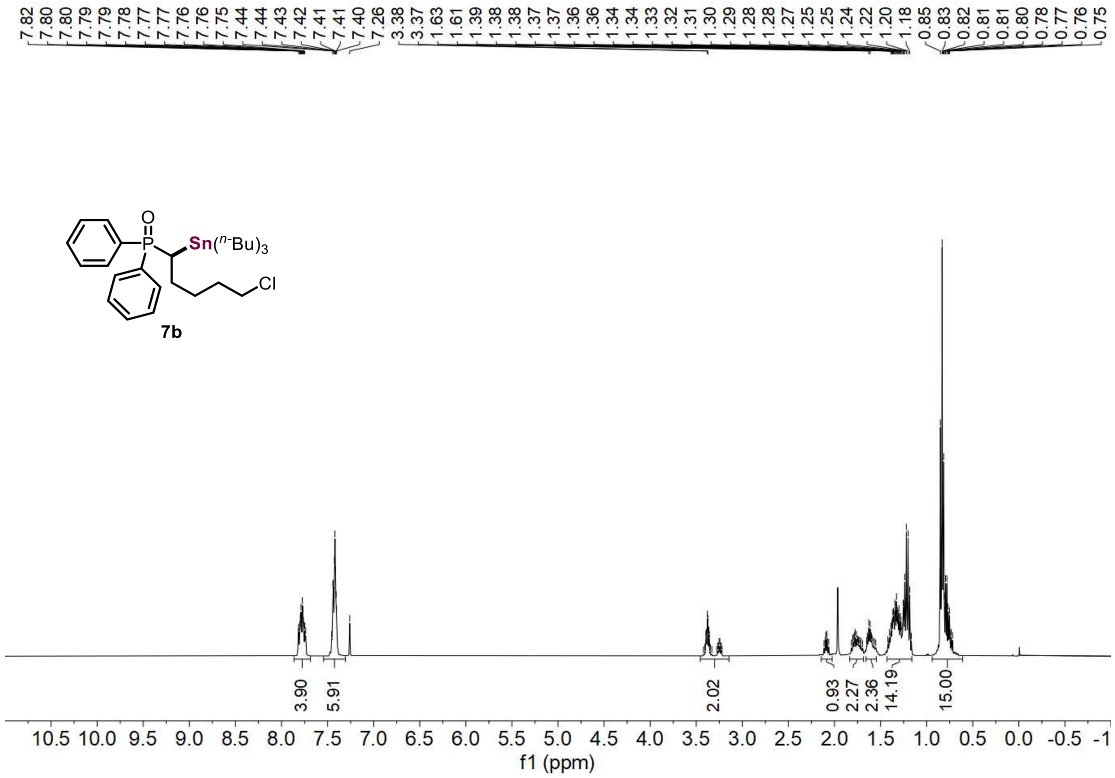


Figure S41. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7a**.



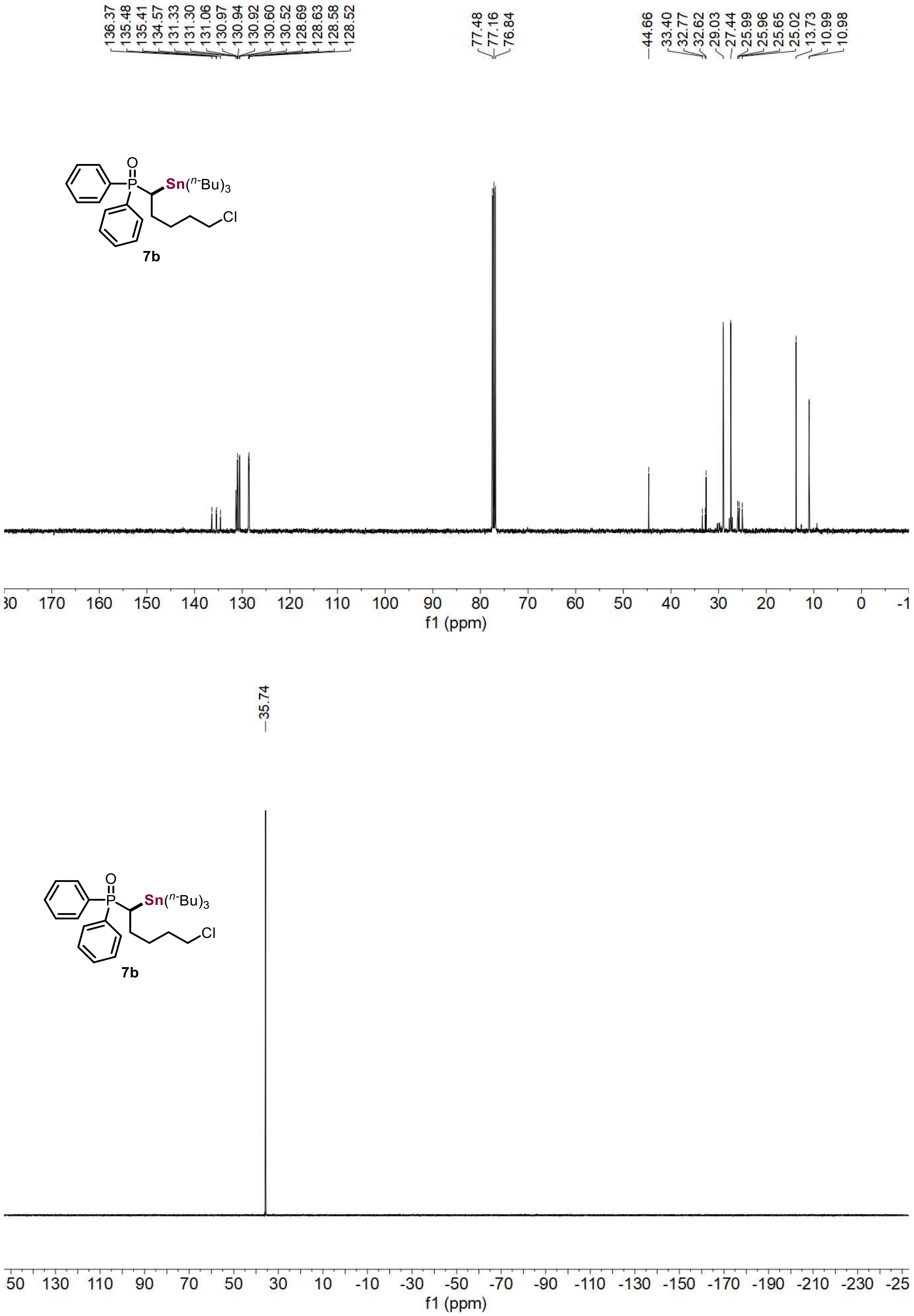
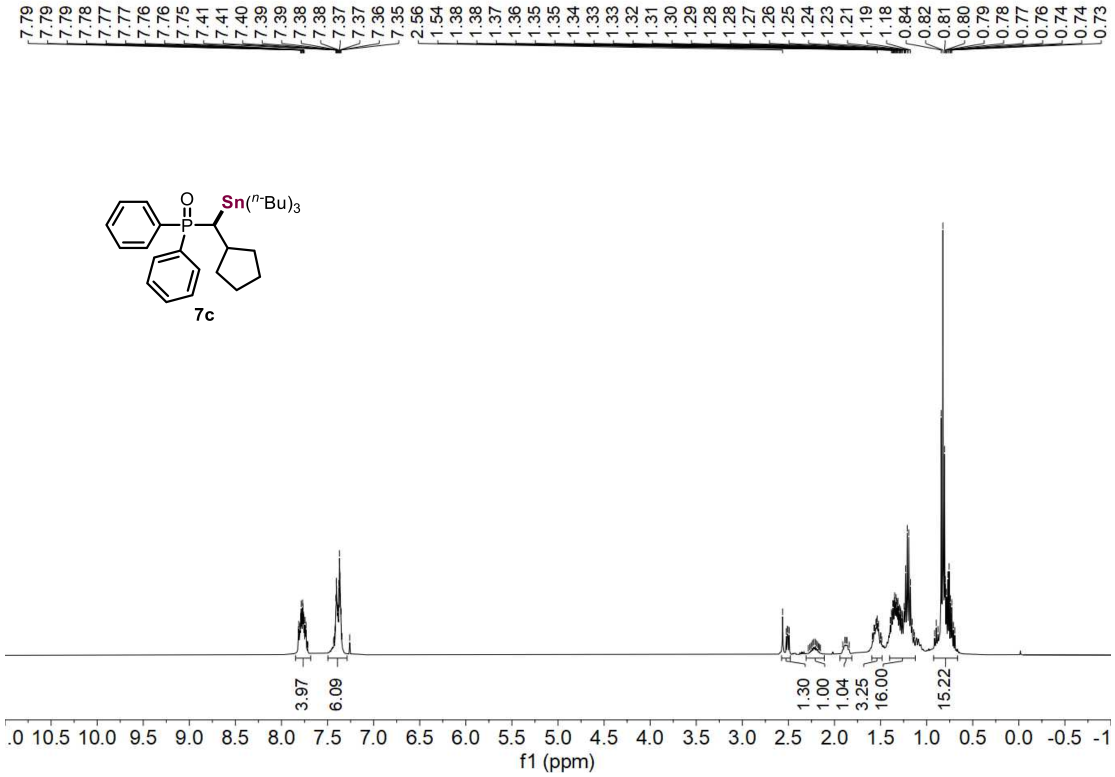


Figure S42. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7b**.


7.79
7.79
7.79
7.78
7.77
7.77
7.76
7.76
7.75
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7.38
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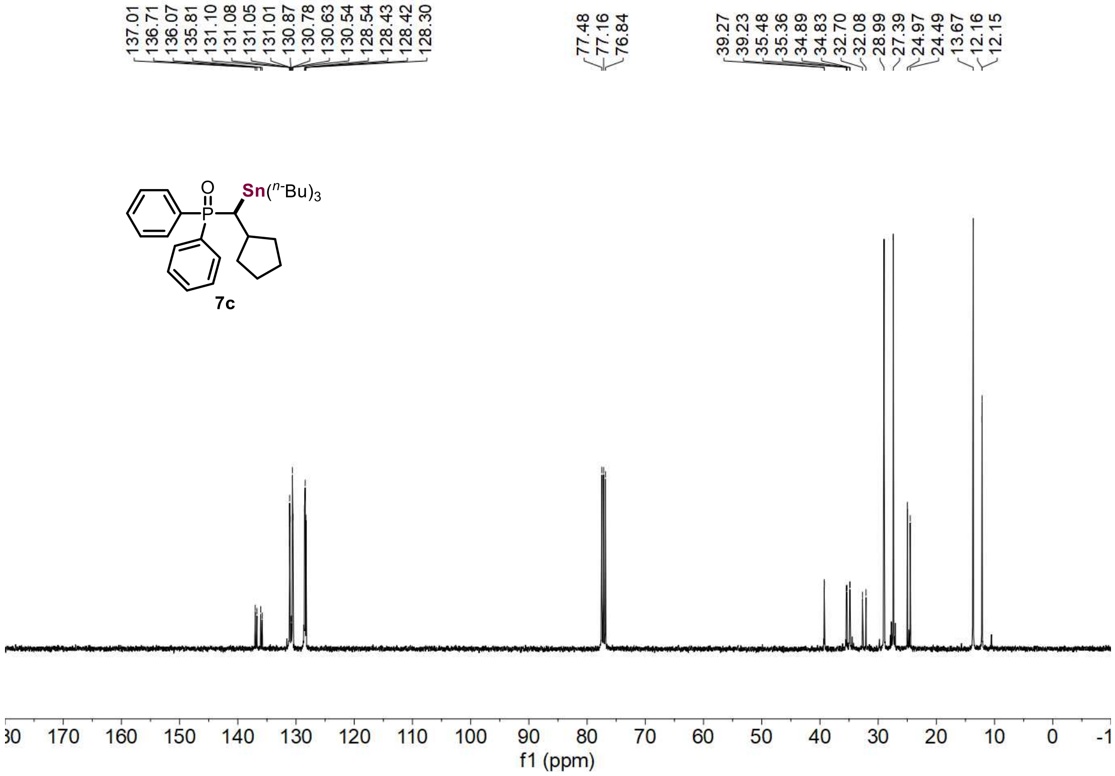
1.27
1.26
1.25
1.24
1.23
1.21
1.19
1.18
0.84
0.82
0.81
0.80
0.79
0.78
0.77
0.76
0.74
0.74
0.73
Sn(n-Bu)3
7c
3.97
6.09
1.30
1.00
1.04
3.25
16.00
15.22
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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131.10
131.08
131.05
131.01
130.87
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130.63
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128.43
128.42
128.30
77.48
77.16
76.84
39.27
39.23
35.48
35.36
34.89
34.83
32.70
32.08
28.99
27.39
24.97
24.49
13.67
12.16
12.15
Sn(n-Bu)3
7c
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

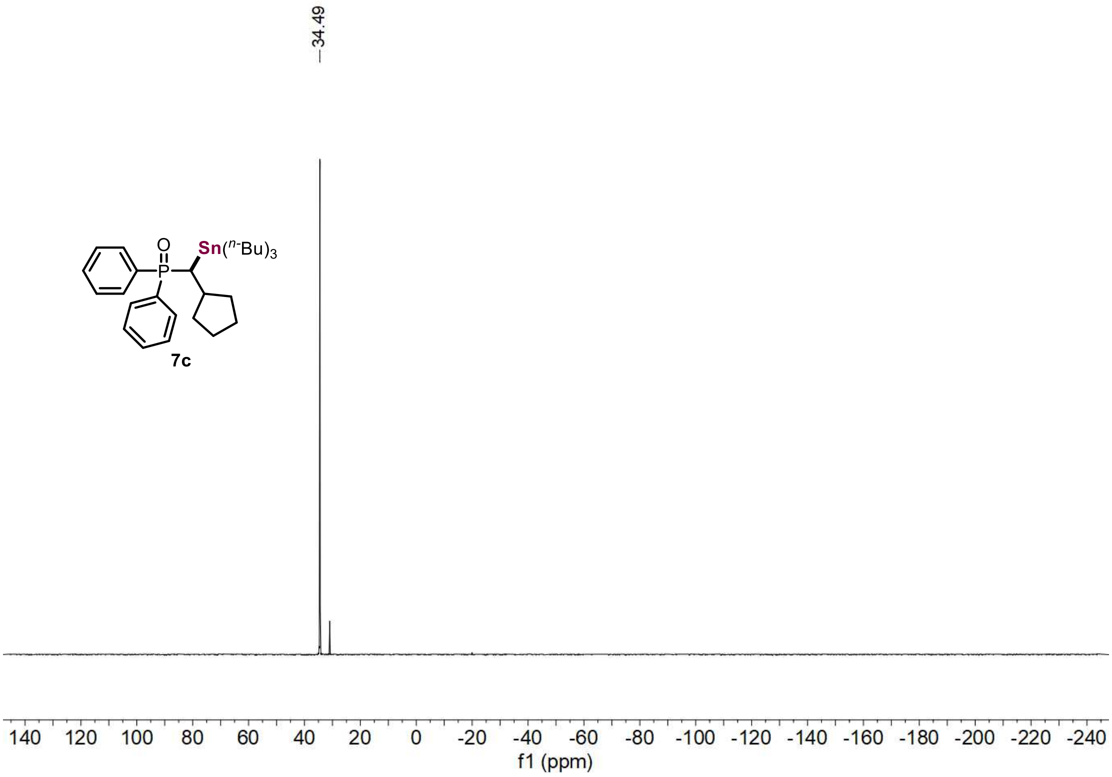
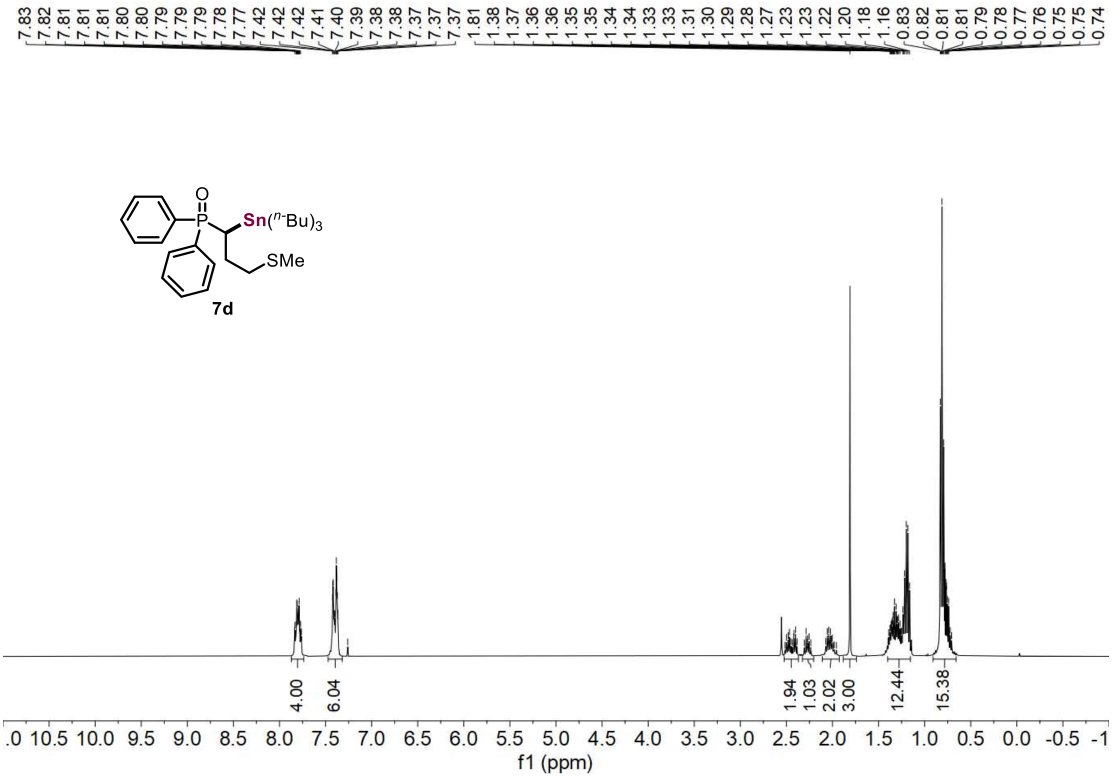


Figure S43. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7c**.



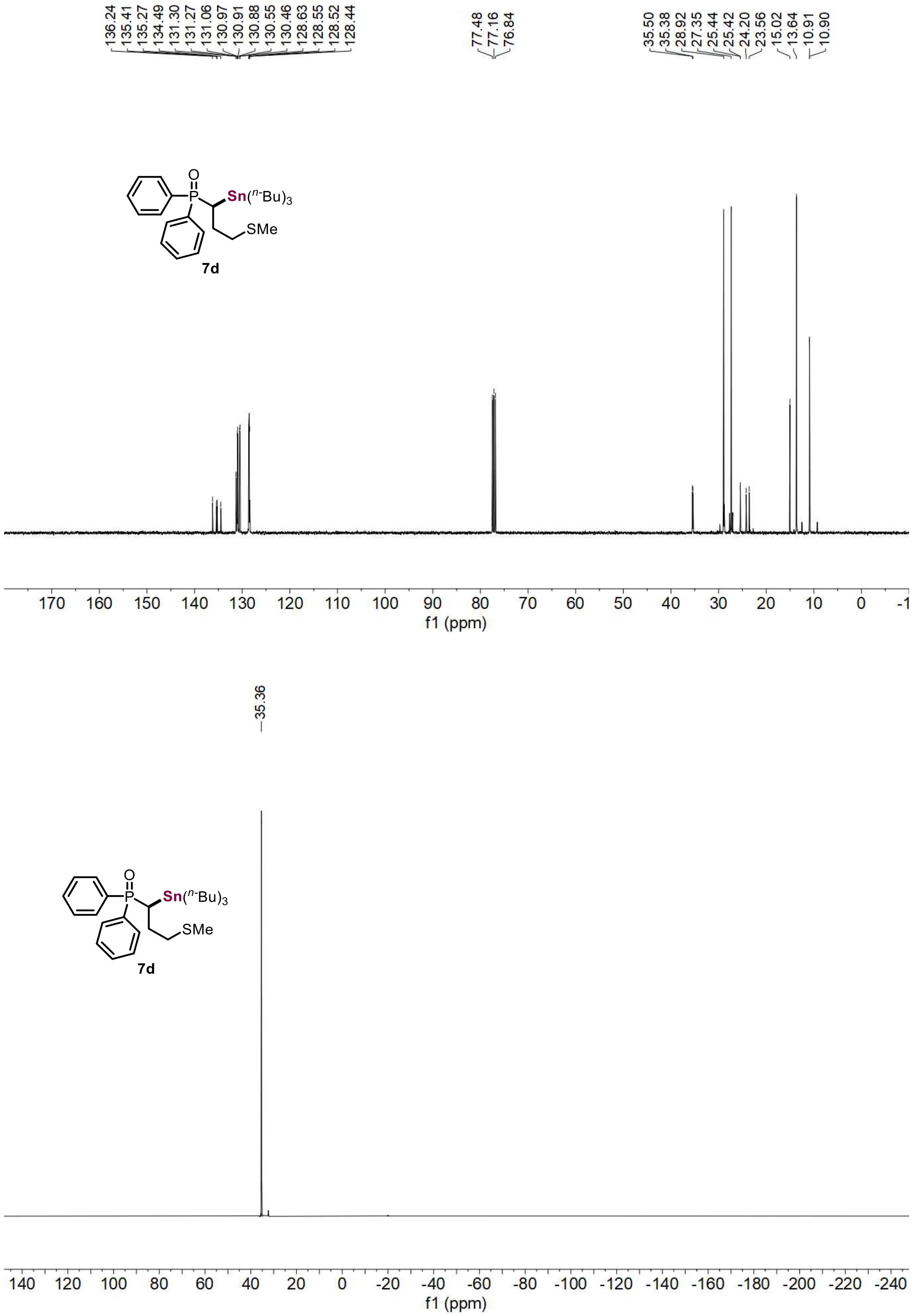
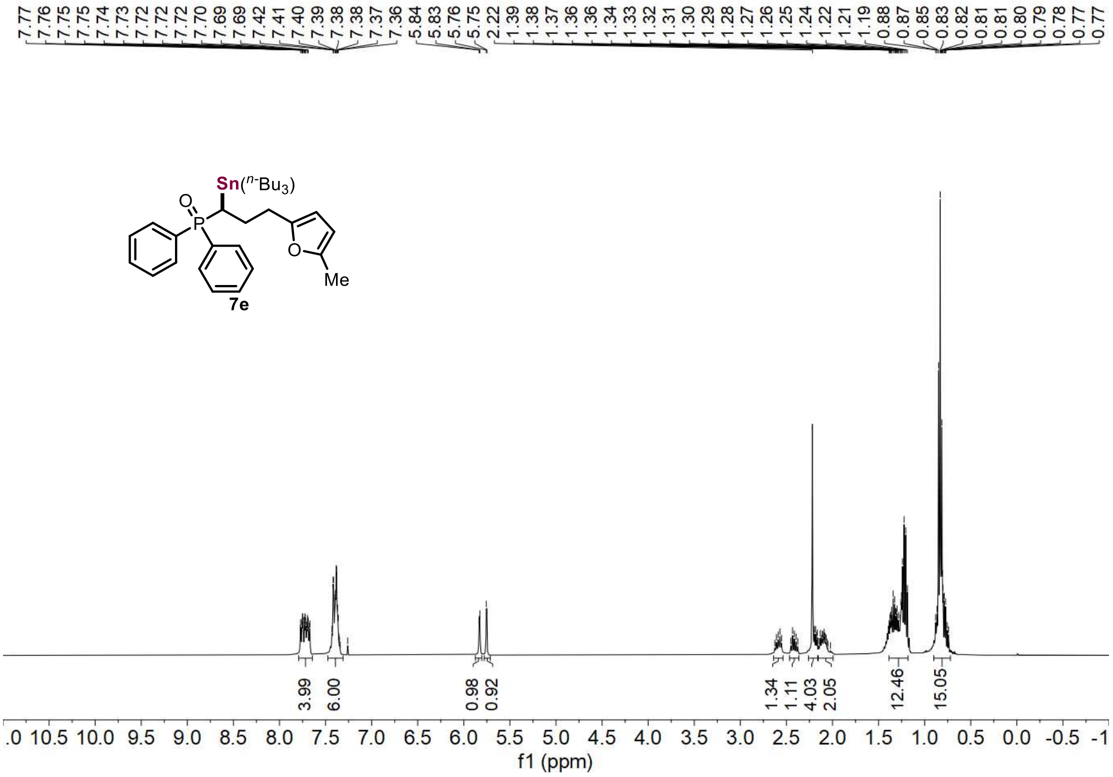
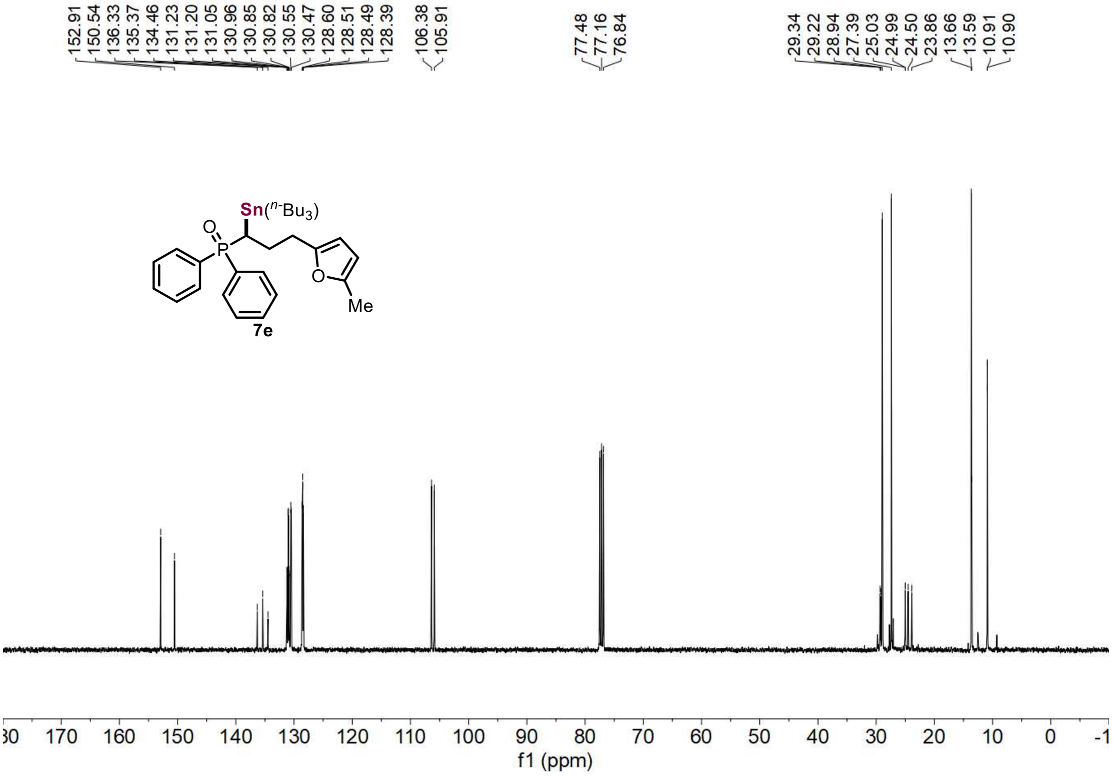


Figure S44. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7d**.


7.77 7.76 7.75 7.75 7.74 7.73 7.72 7.72 7.72 7.70 7.69 7.69 7.42 7.41 7.40 7.39 7.38 7.38 7.37 7.36 5.84 5.83 5.76 5.75 2.22 1.39 1.38 1.37 1.36 1.36 1.34 1.33 1.32 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.22 1.21 1.19 0.88 0.87 0.85 0.83 0.82 0.81 0.81 0.80 0.79 0.78 0.77 0.77
Sn(^n-Bu3)
O
P
O
Me
7e
3.99
6.00
0.98
0.92
1.34
1.11
4.03
2.05
12.46
15.05
.0 10.5 10.0 9.5 9.0 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 -1
f1 (ppm)


152.91 150.54 136.33 135.37 134.46 131.23 131.20 131.05 130.96 130.85 130.82 130.55 130.47 128.60 128.51 128.49 128.39 106.38 105.91 77.48 77.16 76.84 29.34 29.22 28.94 27.39 25.03 24.99 24.50 23.86 13.66 13.59 10.91 10.90
Sn(^n-Bu3)
O
P
O
Me
7e
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

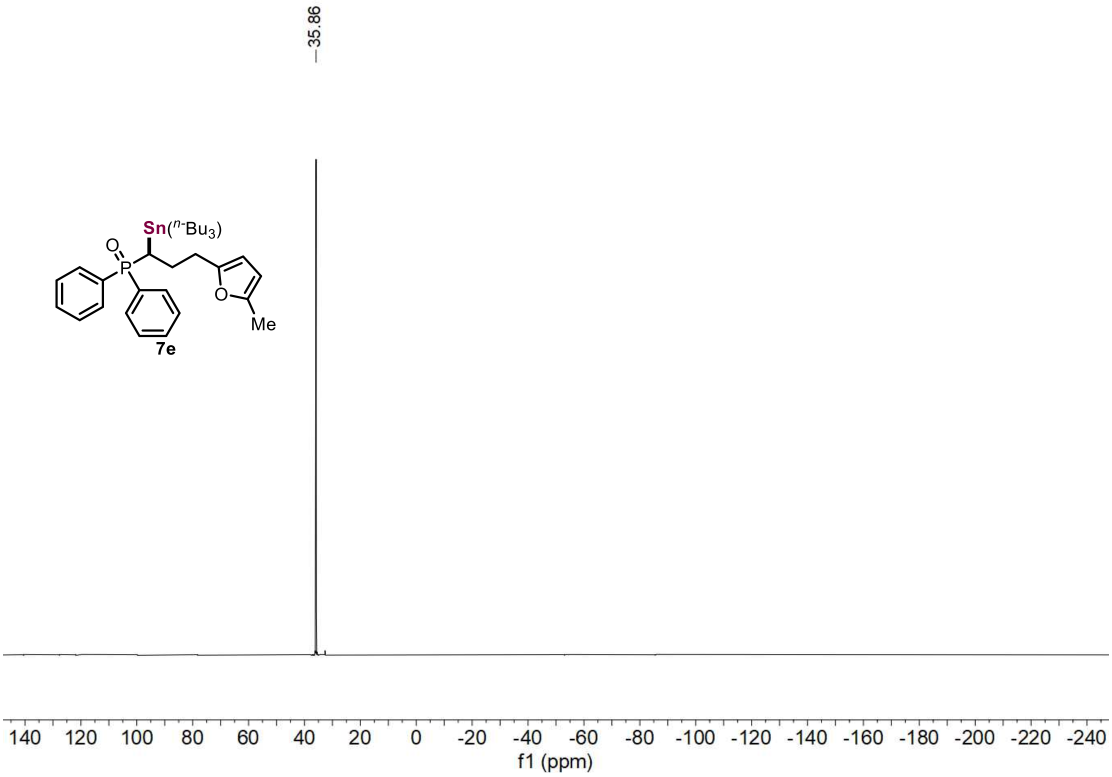
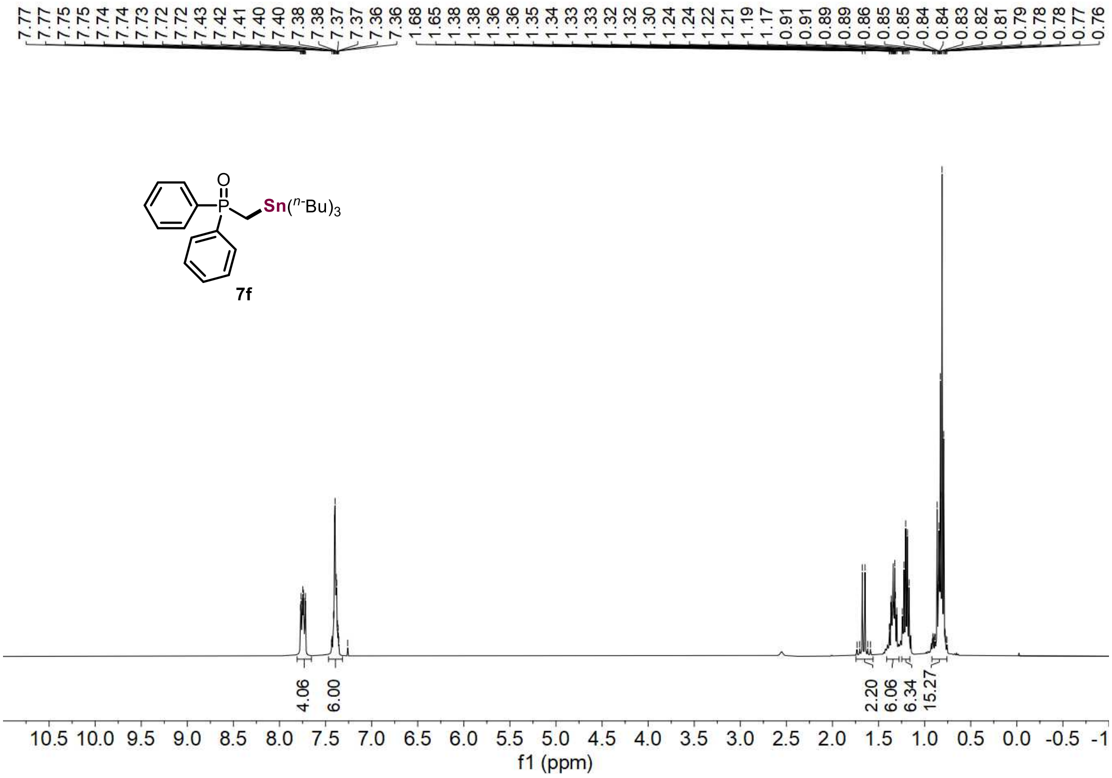


Figure S45. ^{1}H (400 MHz, $CDCl_3$), ^{13}C (100 MHz, $CDCl_3$) and ^{31}P (162 MHz, $CDCl_3$) NMR spectra for compound **7e**.



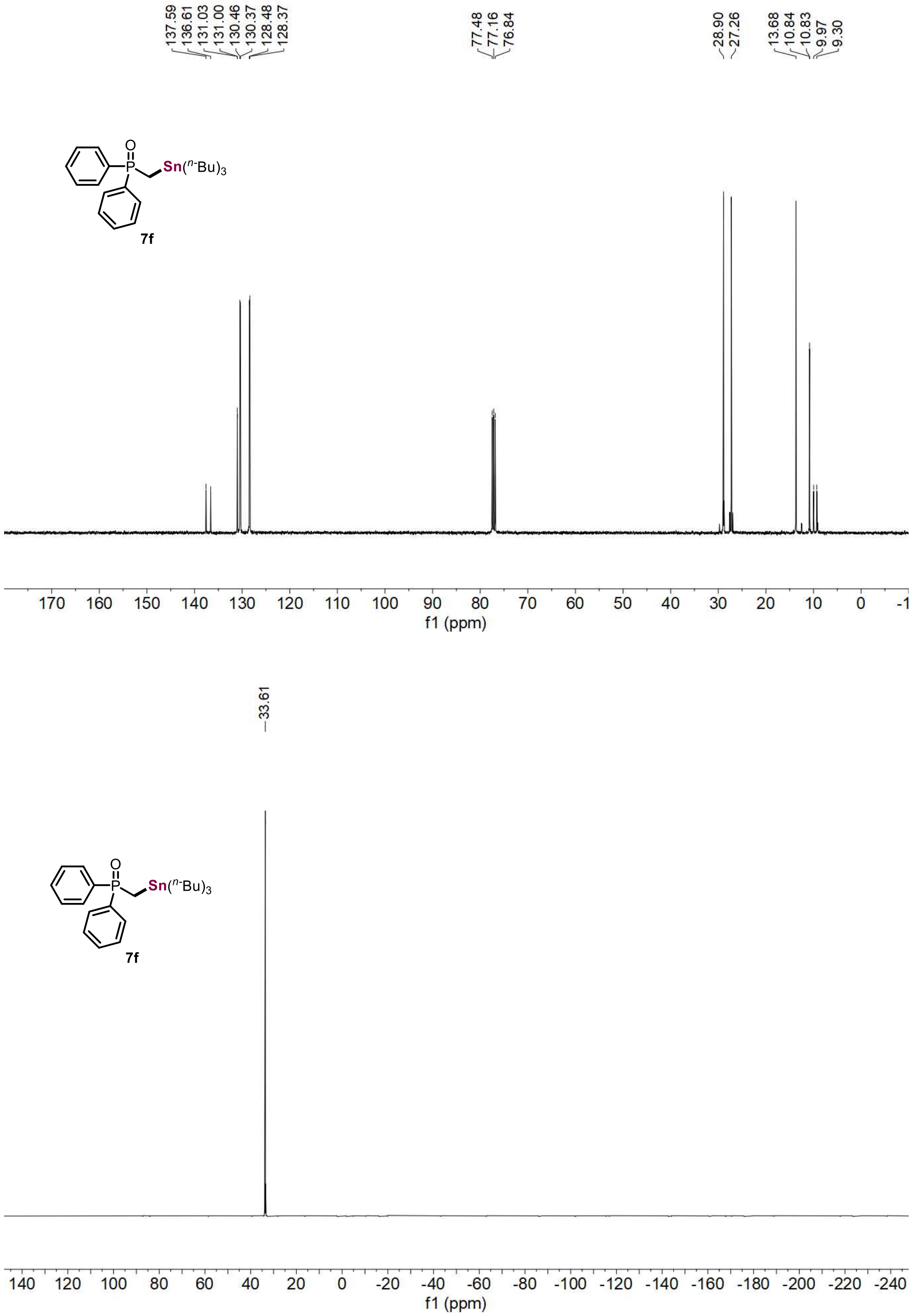
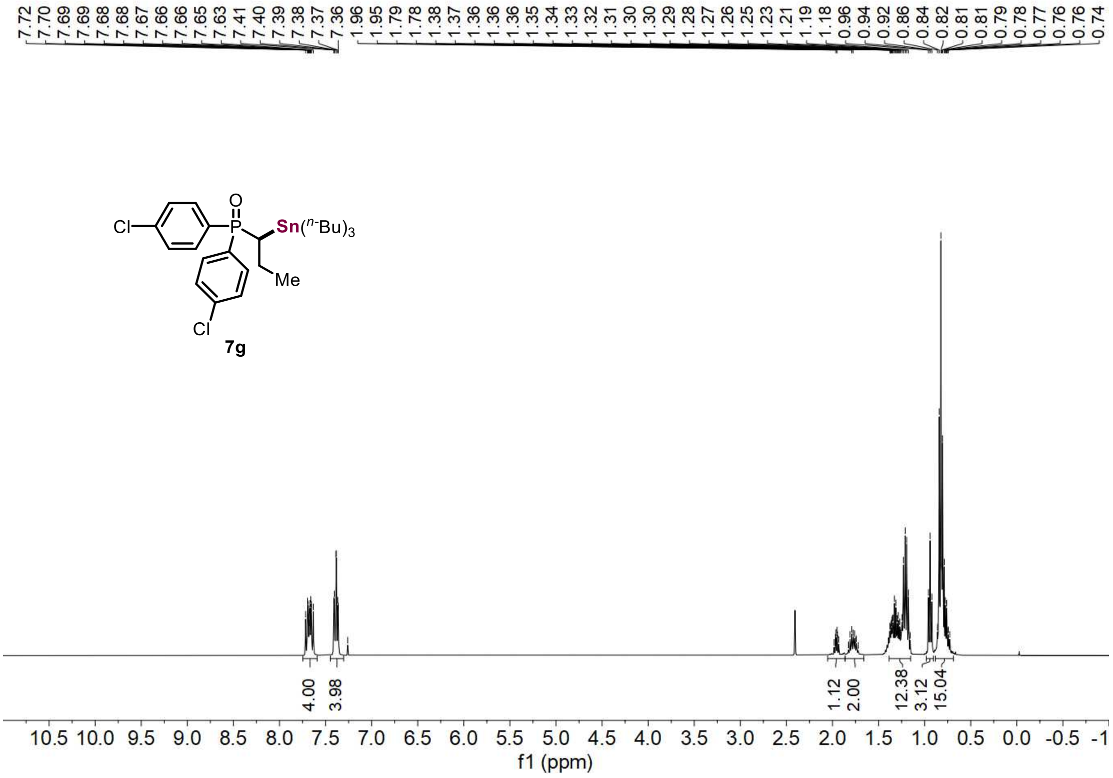
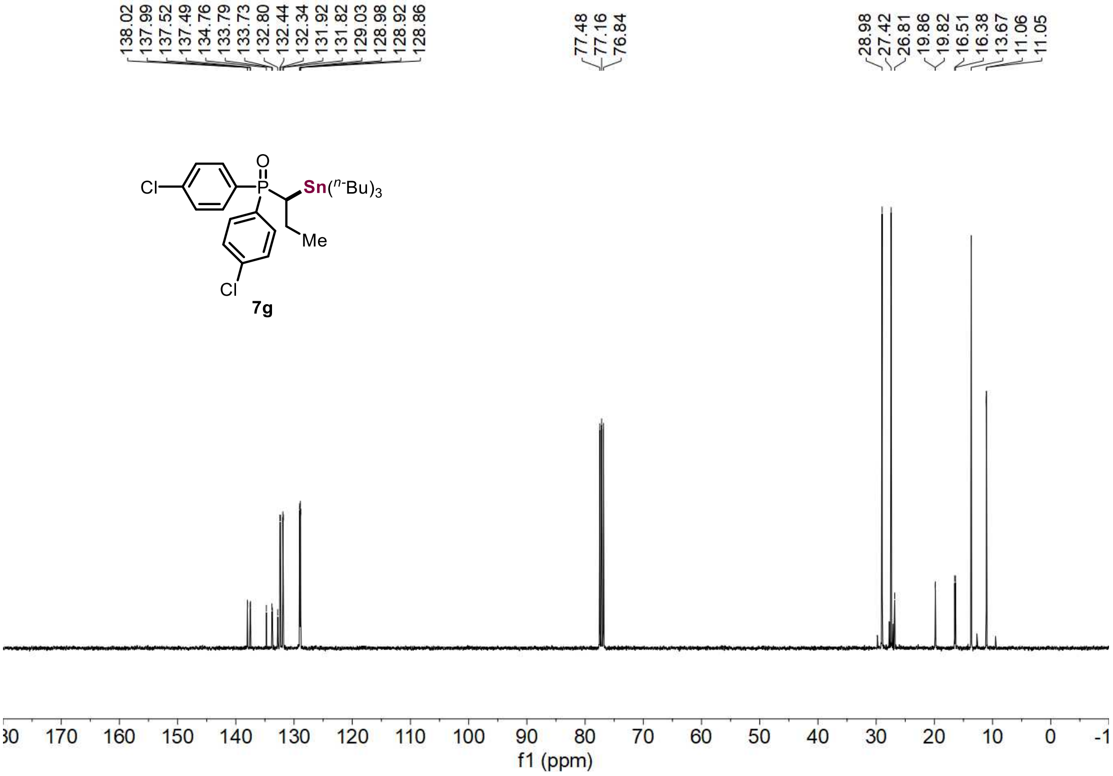


Figure S46. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7f**.


7.72
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.65
7.63
7.41
7.40
7.39
7.38
7.37
7.36
1.96
1.95
1.79
1.78
1.38
1.37
1.36
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.25
1.23
1.21
1.19
1.18
0.96
0.94
0.92
0.86
0.84
0.82
0.81
0.81
0.79
0.78
0.77
0.76
0.76
0.74
Cl
O
P
Sn($^{n-}$Bu)$_3$
Me
Cl
7g
4.00
3.98
1.12
2.00
12.38
3.12
15.04
10.5 10.0 9.5 9.0 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 -1
f1 (ppm)


138.02
137.99
137.52
137.49
134.76
133.79
133.73
132.80
132.44
132.34
131.92
131.82
129.03
128.98
128.92
128.86
77.48
77.16
76.84
28.98
27.42
26.81
19.86
19.82
16.51
16.38
13.67
11.06
11.05
Cl
O
P
Sn($^{n-}$Bu)$_3$
Me
Cl
7g
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

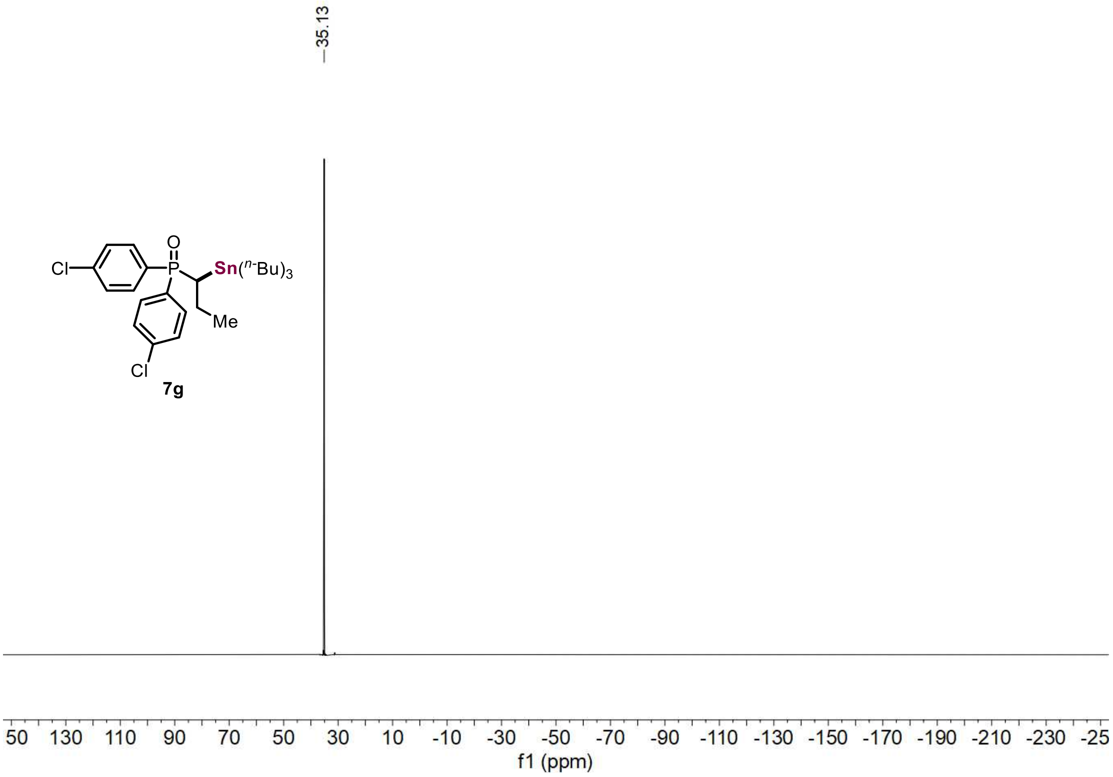
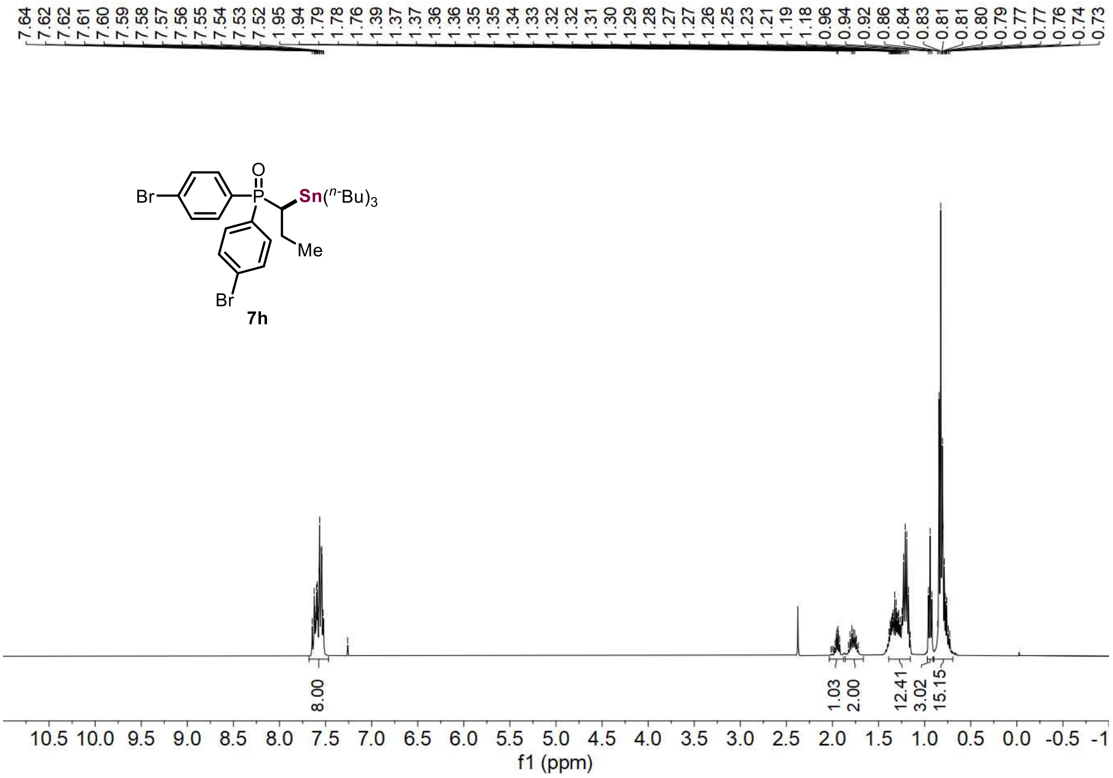


Figure S47. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7g**.



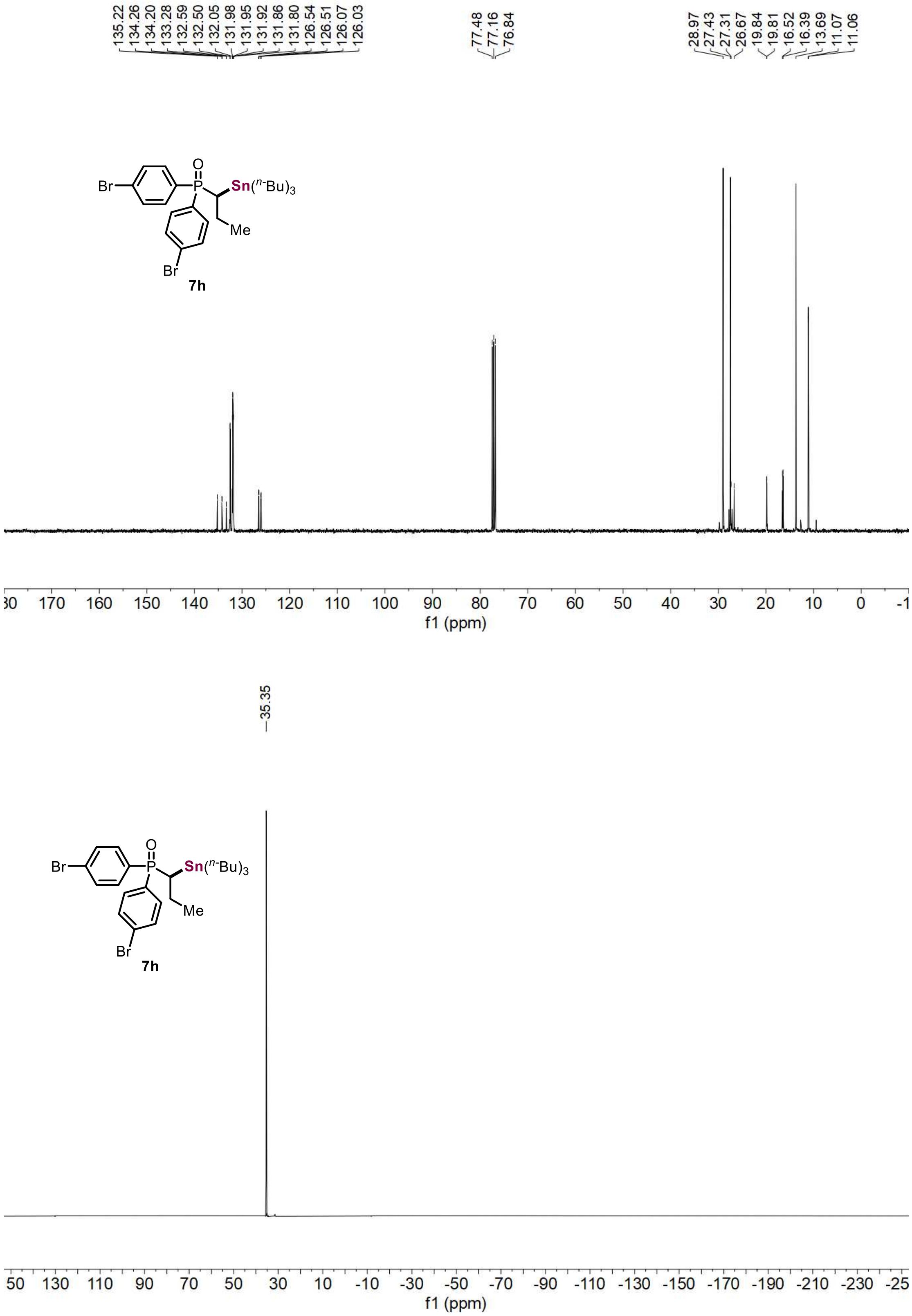
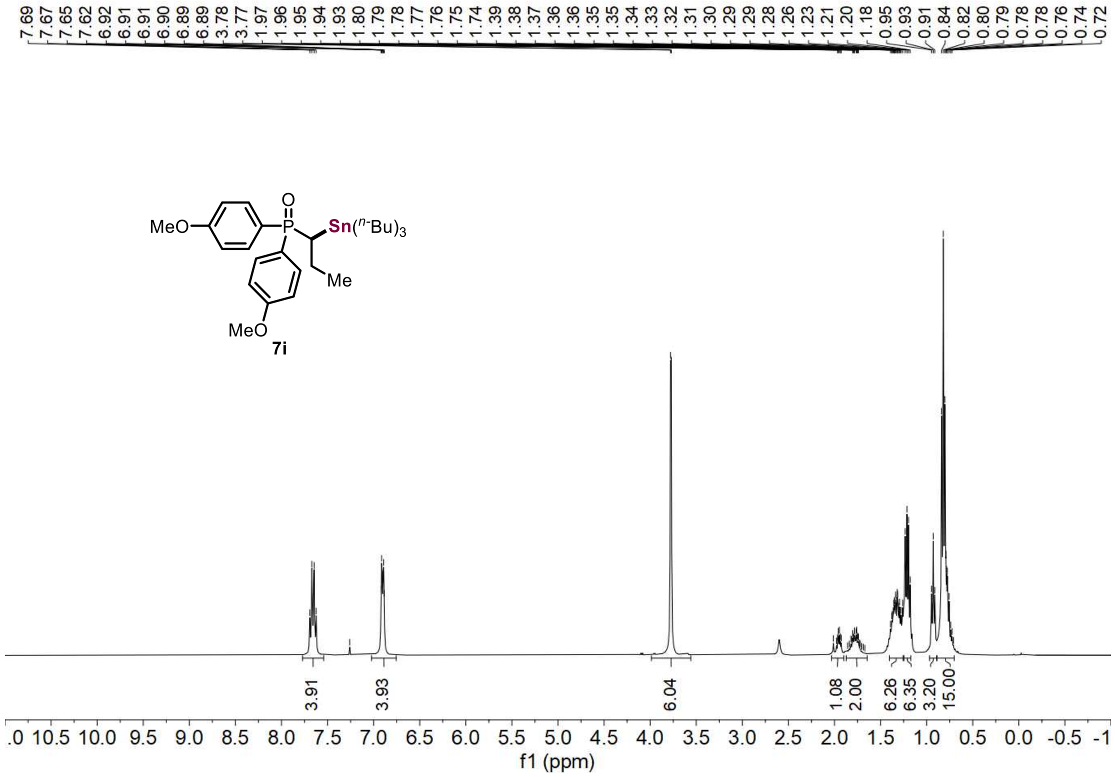
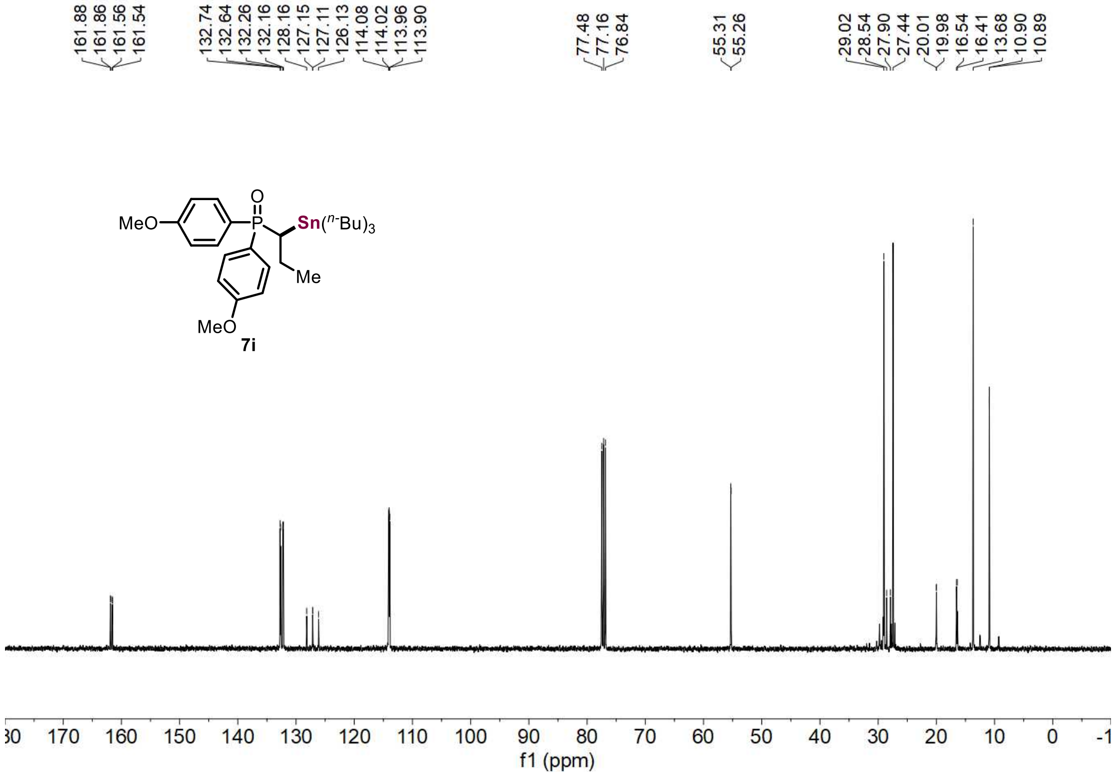


Figure S48. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7h**.


7.69 7.67 7.65 7.62 6.92 6.91 6.91 6.90 6.89 6.89 3.78 3.77 1.97 1.96 1.95 1.94 1.93 1.80 1.79 1.78 1.77 1.76 1.75 1.74 1.39 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.33 1.32 1.31 1.30 1.29 1.29 1.28 1.26 1.23 1.21 1.20 1.18 0.95 0.93 0.91 0.84 0.82 0.80 0.79 0.78 0.78 0.76 0.74 0.72
MeO
O
P
Sn(n-Bu)3
Me
MeO
7i
3.91
3.93
6.04
1.08
2.00
6.26
6.35
3.20
15.00
.0 10.5 10.0 9.5 9.0 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 -1
f1 (ppm)


161.88 161.86 161.56 161.54
132.74 132.64 132.26 132.16 128.16 127.15 127.11 126.13 114.08 114.02 113.96 113.90
77.48 77.16 76.84
55.31 55.26
29.02 28.54 27.90 27.44 20.01 19.98 16.54 16.41 13.68 10.90 10.89
MeO
O
P
Sn(n-Bu)3
Me
MeO
7i
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

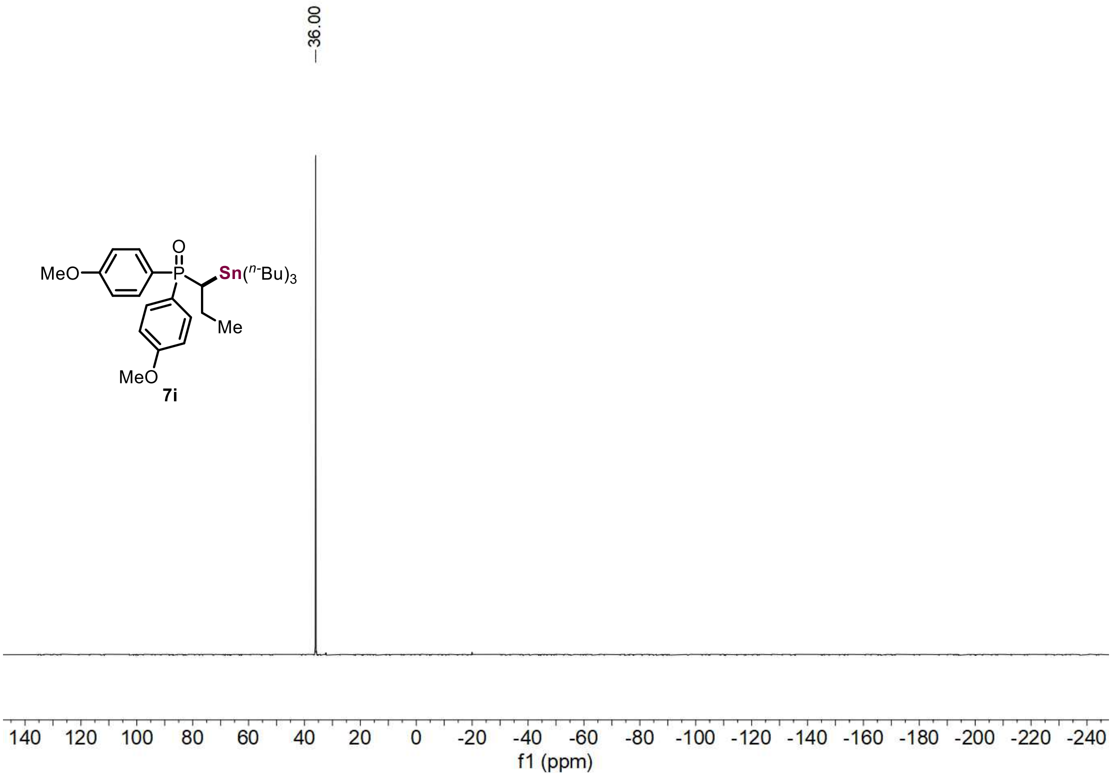
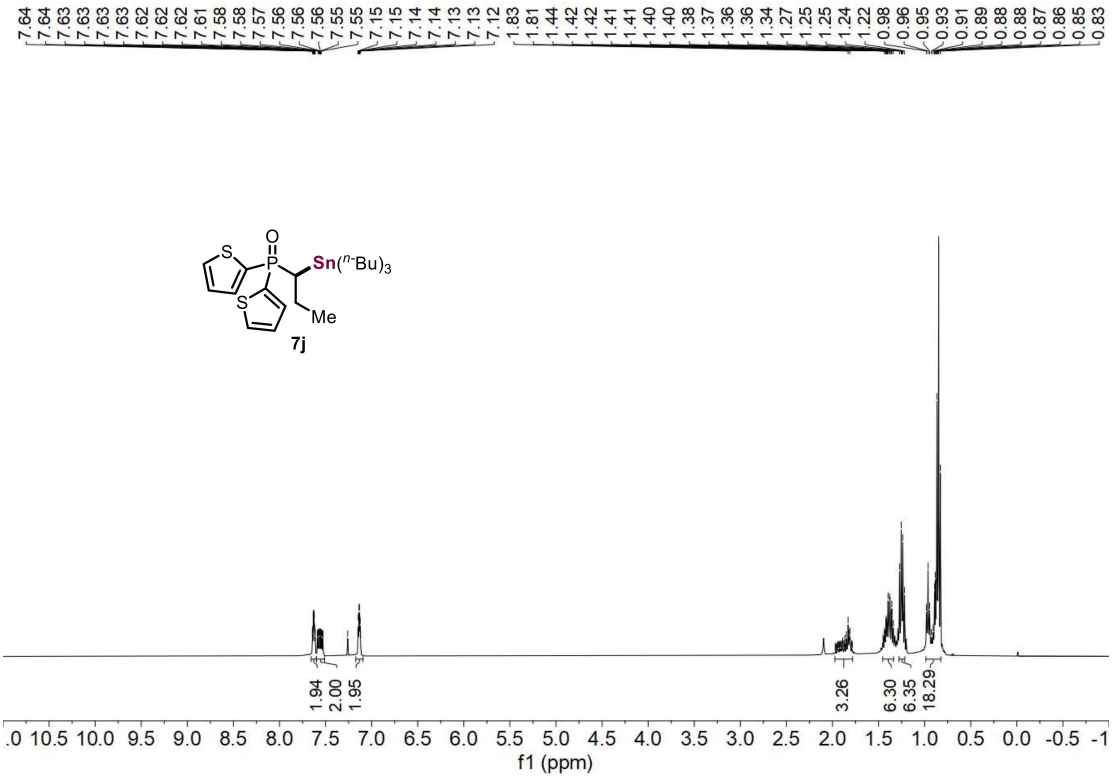


Figure S49. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7i**.



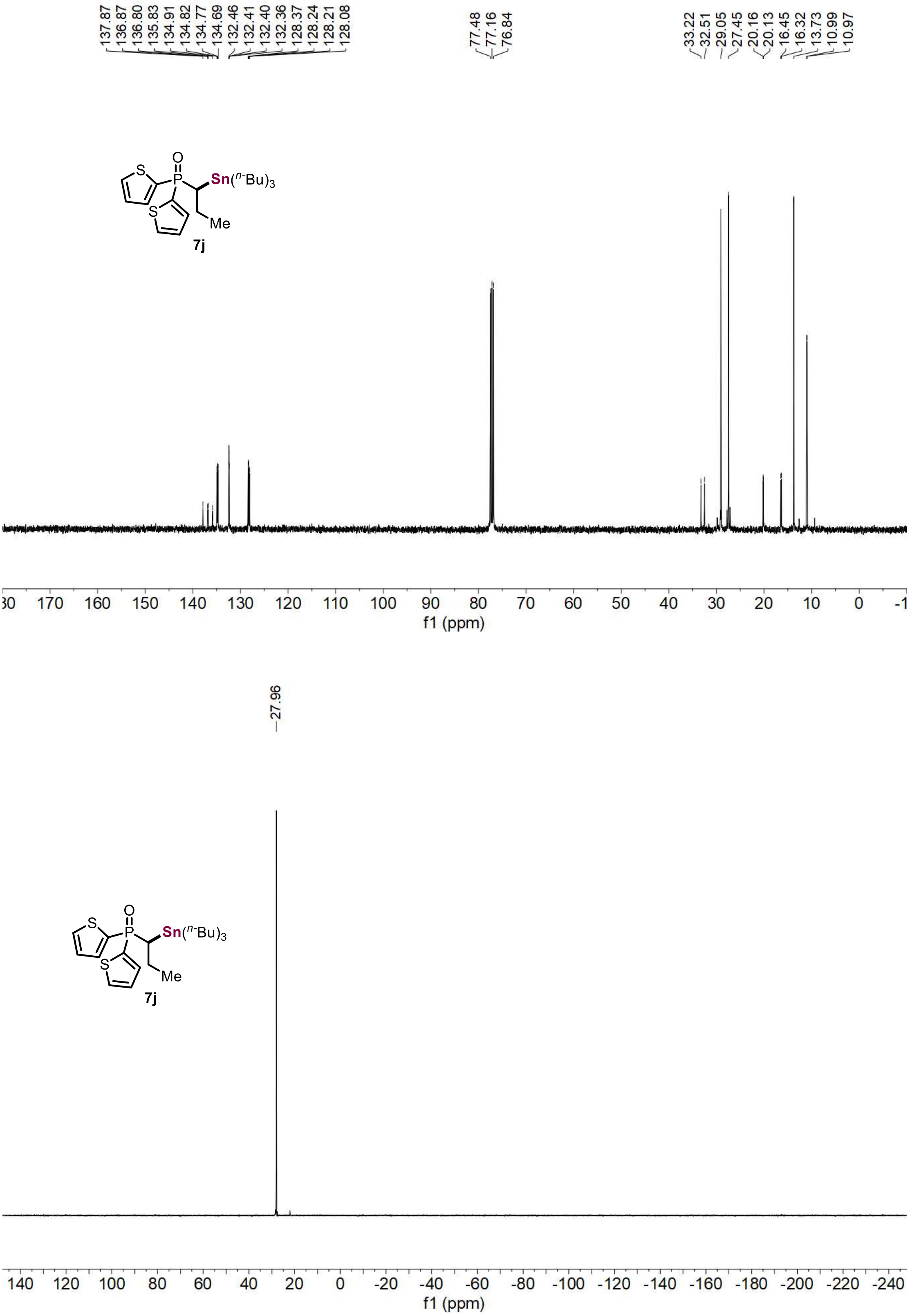
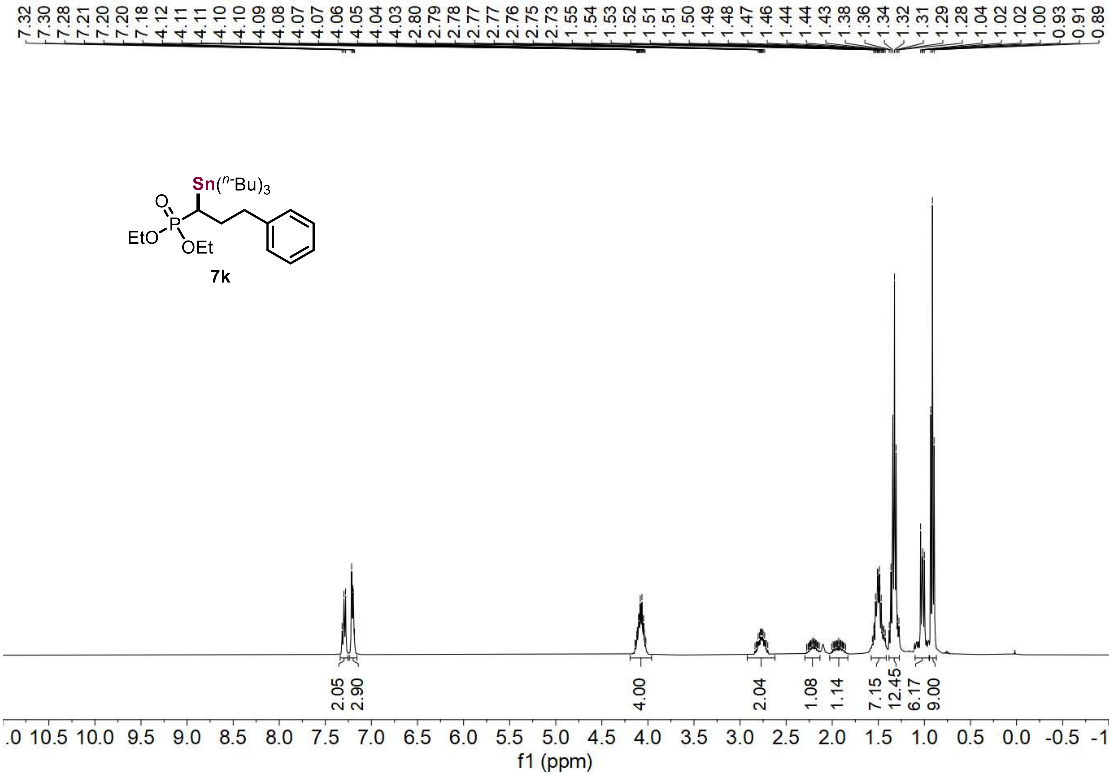
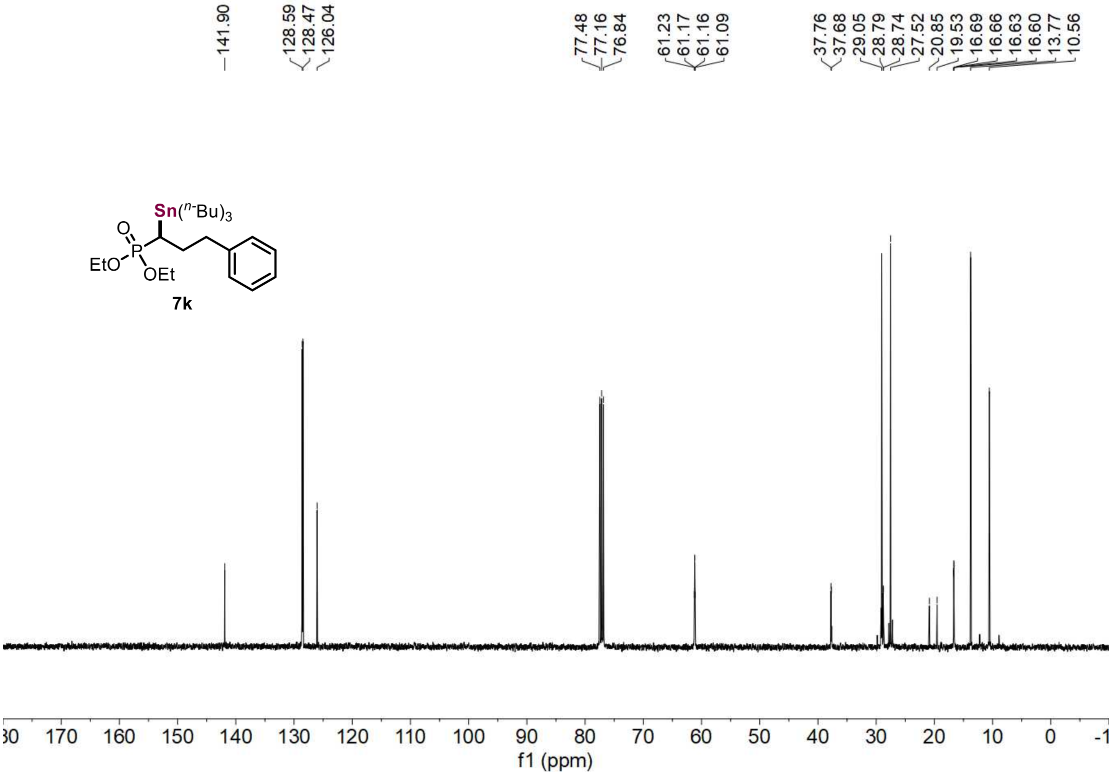


Figure S50. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7j**.


7.32
7.30
7.28
7.21
7.20
7.20
7.18
4.12
4.11
4.11
4.10
4.09
4.08
4.07
4.07
4.06
4.05
4.04
4.03
2.80
2.79
2.78
2.77
2.76
2.75
2.73
1.55
1.54
1.53
1.52
1.51
1.51
1.50
1.49
1.48
1.47
1.46
1.44
1.44
1.43
1.38
1.36
1.34
1.32
1.31
1.29
1.28
1.04
1.02
1.02
1.00
0.93
0.91
0.89
Sn($^{n-}$Bu)$_3$
O
P
EtO
OEt
7k
2.05
2.90
4.00
2.04
1.08
1.14
7.15
12.45
6.17
9.00
.0 10.5 10.0 9.5 9.0 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 -1
f1 (ppm)


141.90
128.59
128.47
126.04
77.48
77.16
76.84
61.23
61.17
61.16
61.09
37.76
37.68
29.05
28.79
28.74
27.52
20.85
19.53
16.69
16.66
16.63
16.60
13.77
10.56
Sn($^{n-}$Bu)$_3$
O
P
EtO
OEt
7k
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

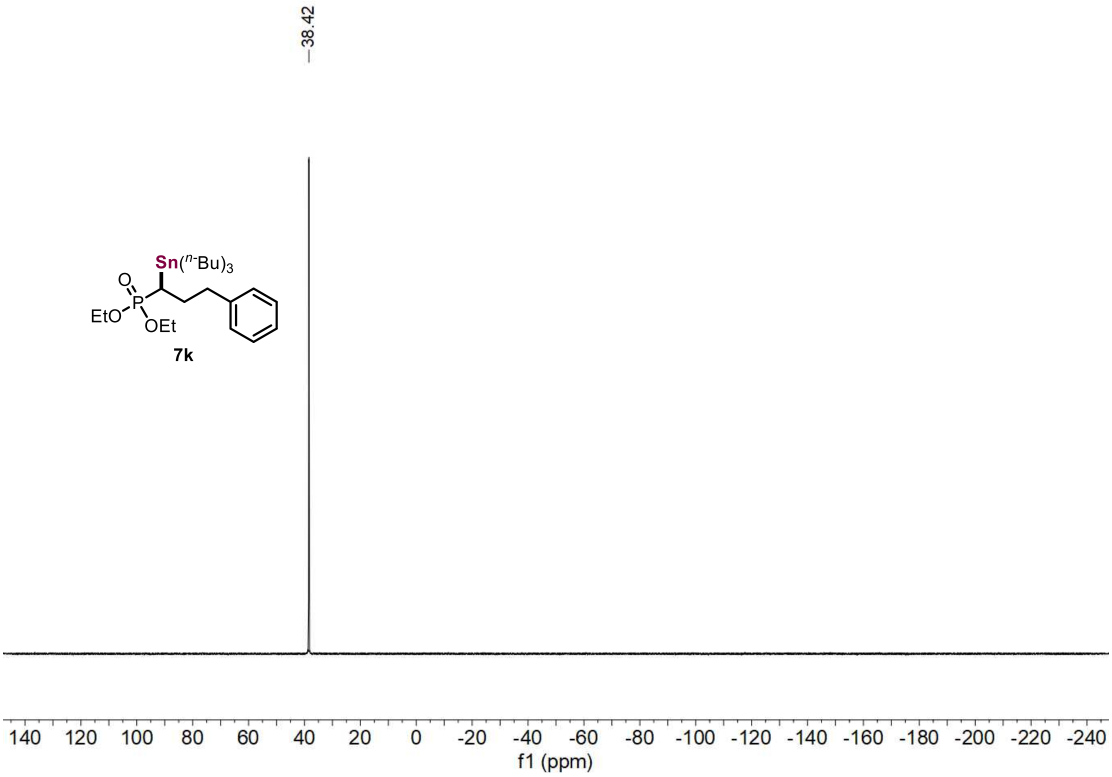
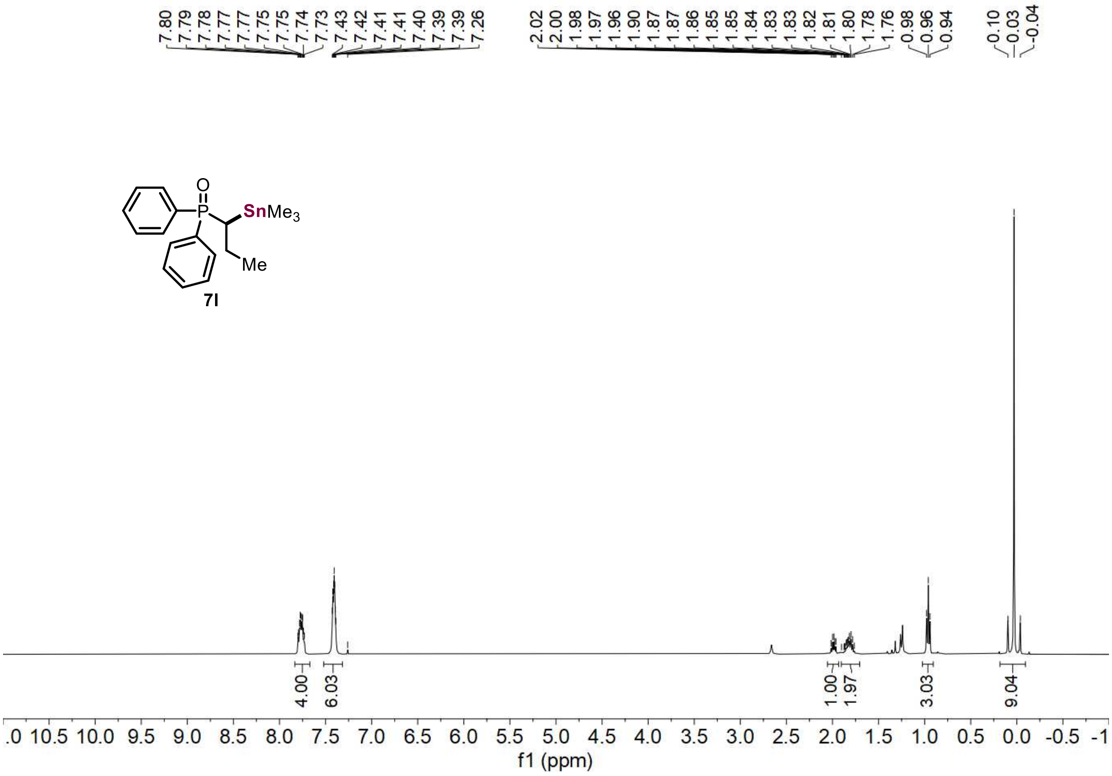


Figure S51. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7k**.



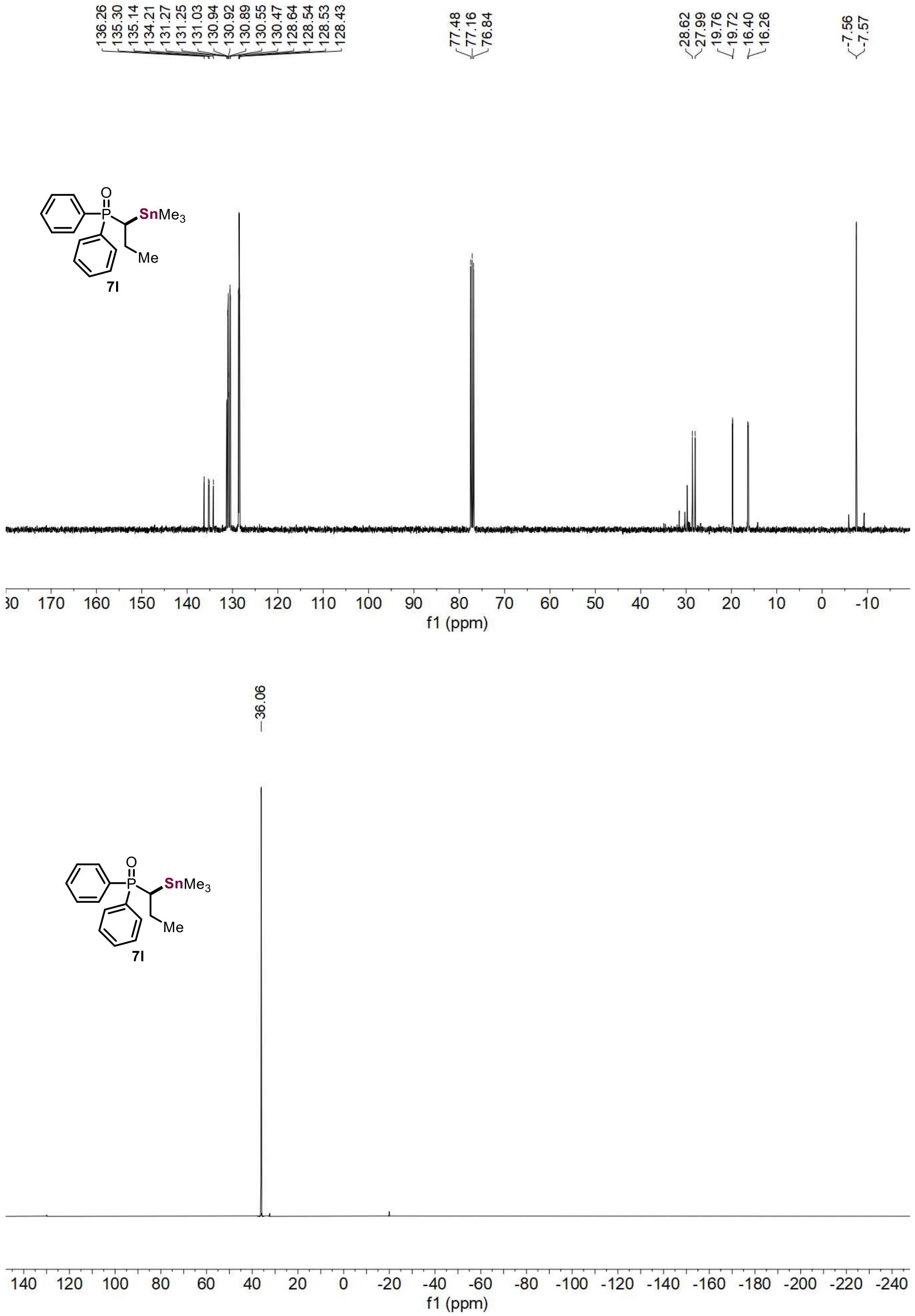


Figure S52. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **7l**.

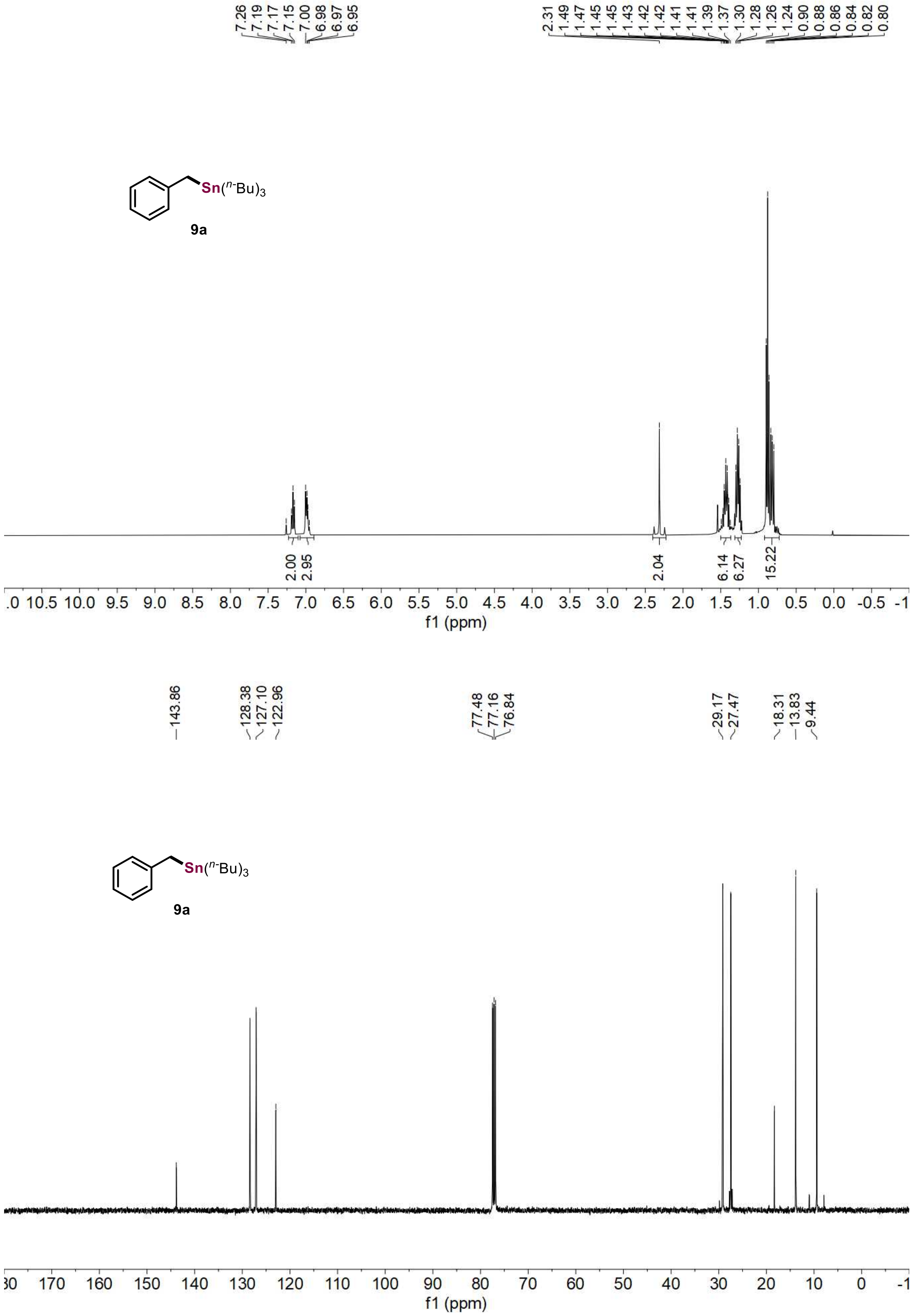


Figure S53. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **9a**.

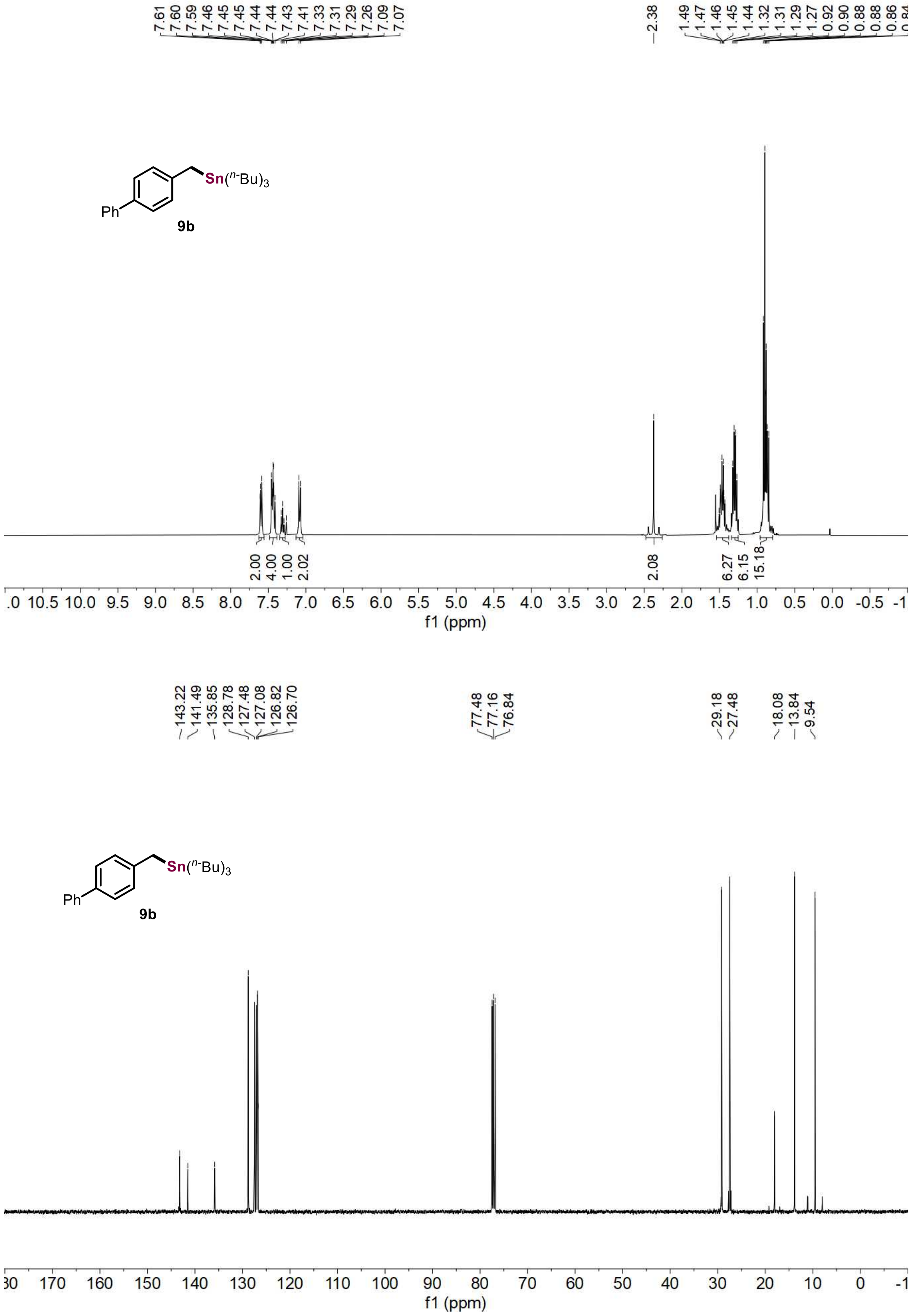


Figure S54. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **9b**.

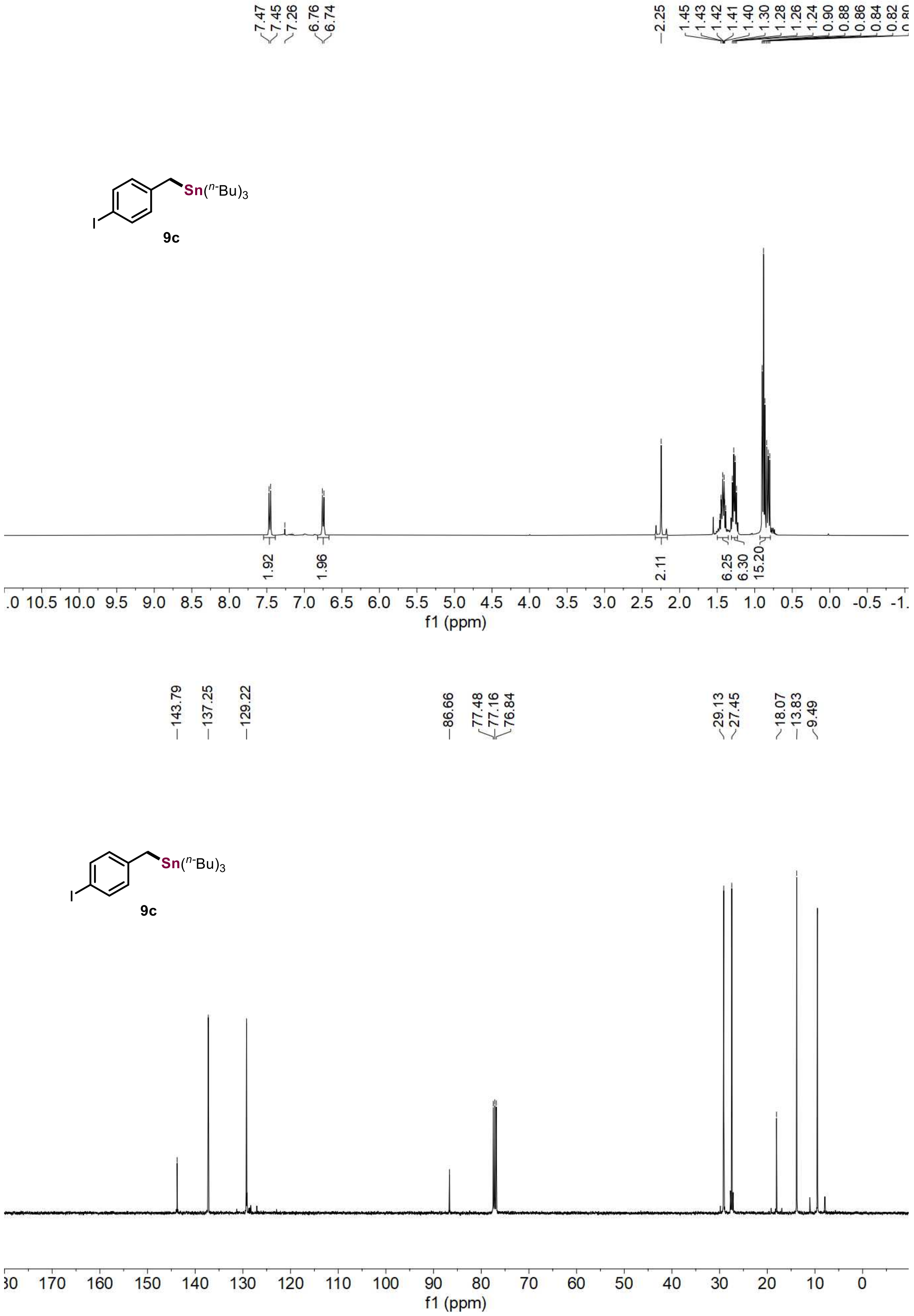


Figure S55. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **9c**.

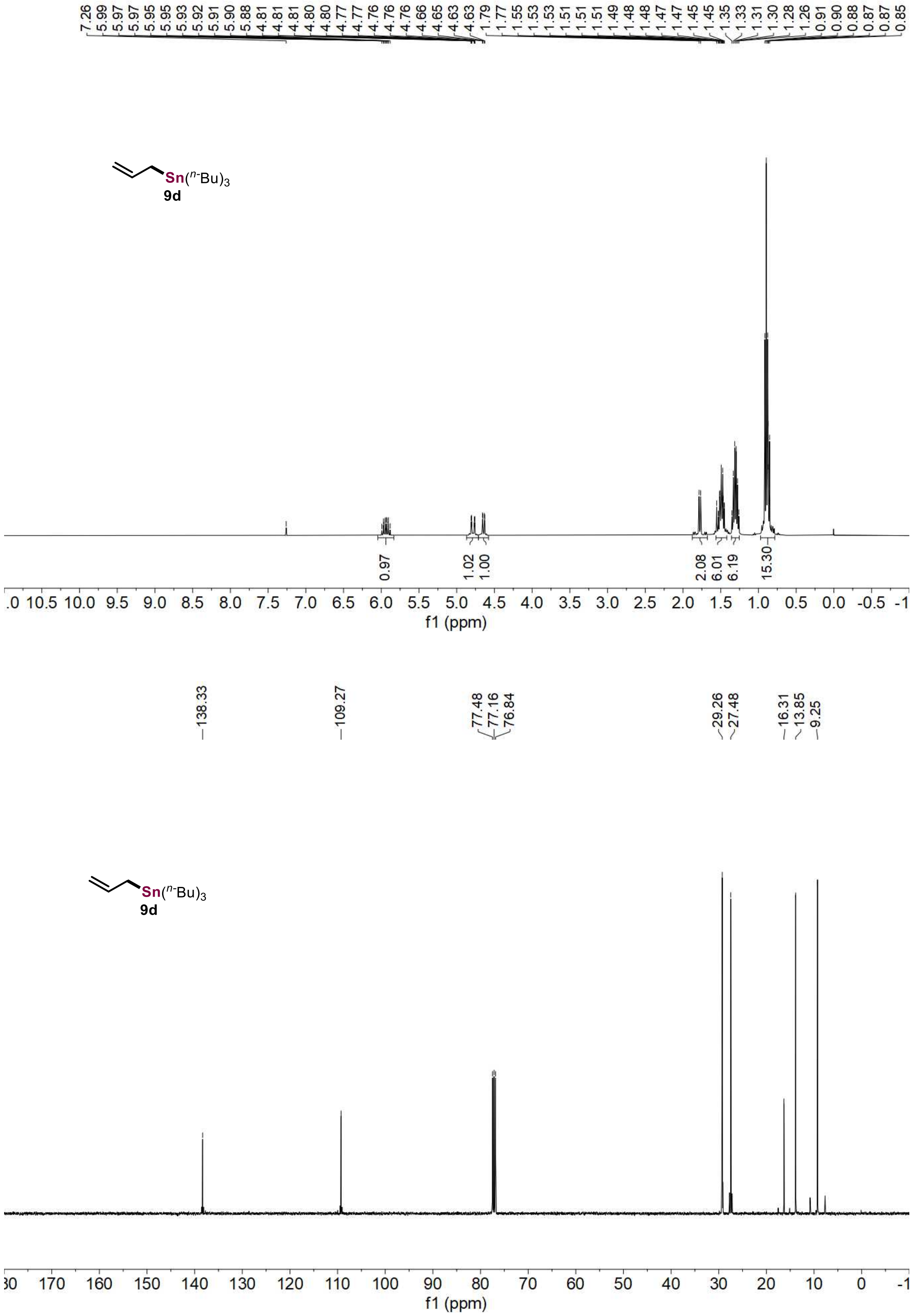


Figure S56. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **9d**.

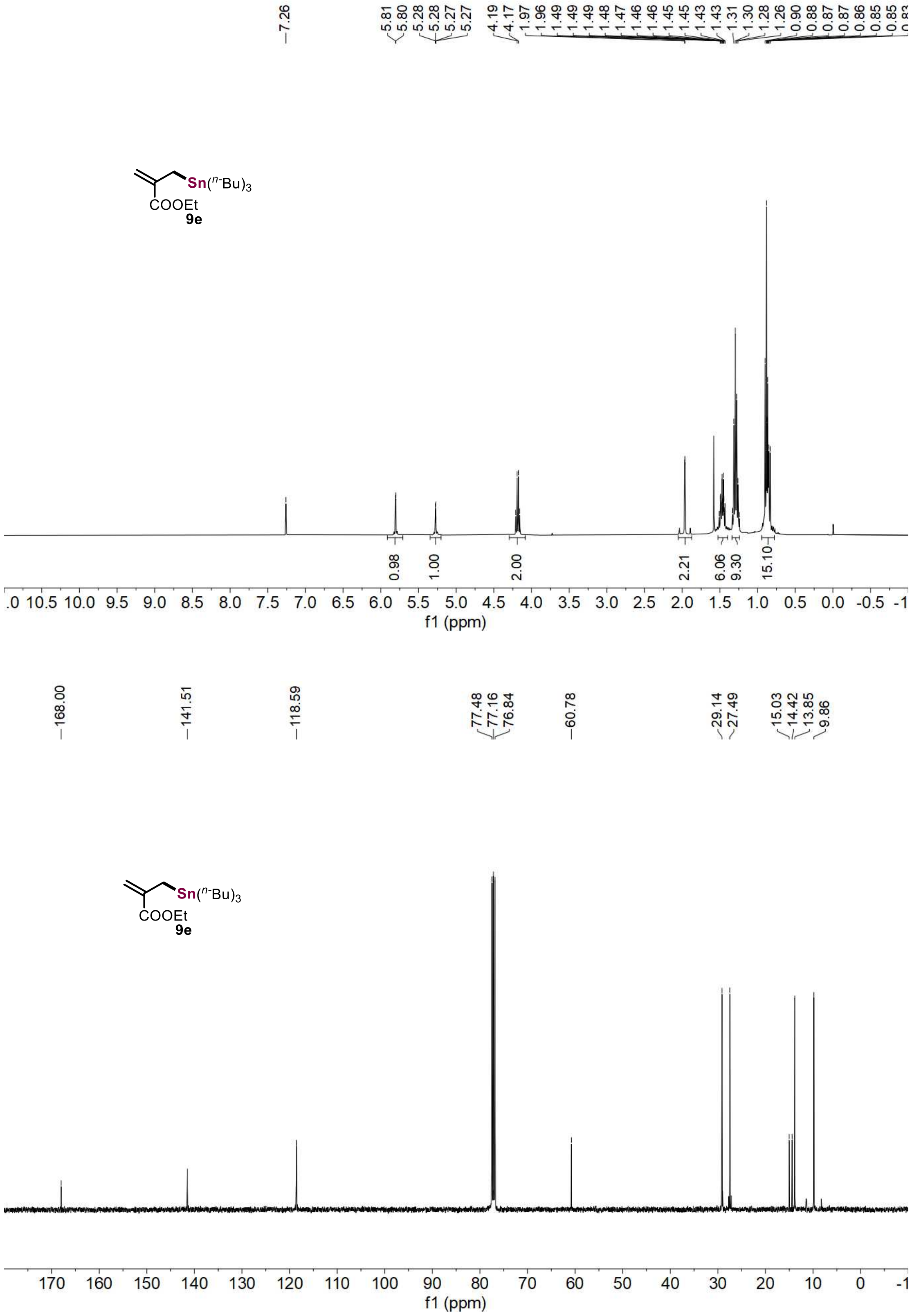


Figure S57. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **9e**.

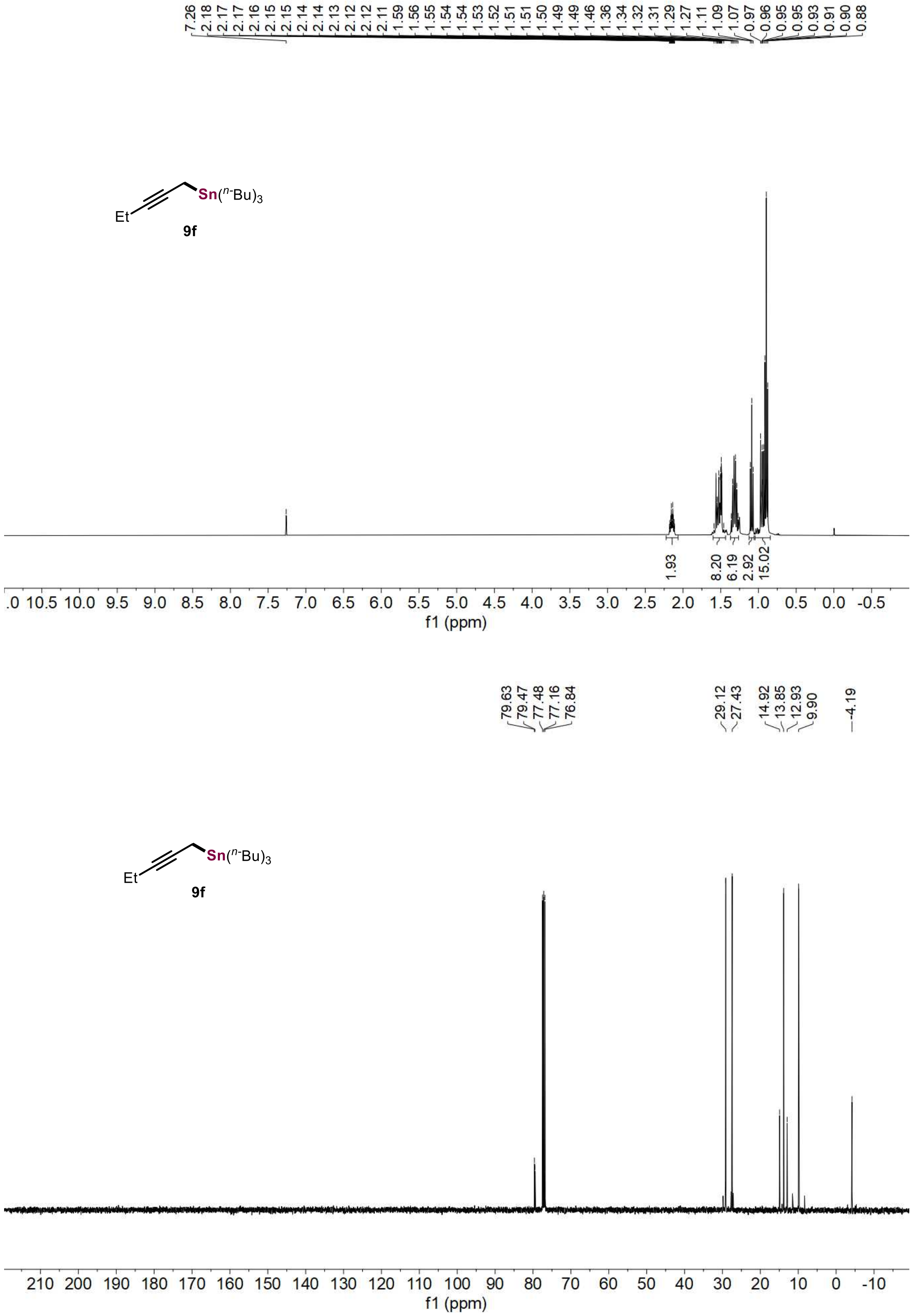
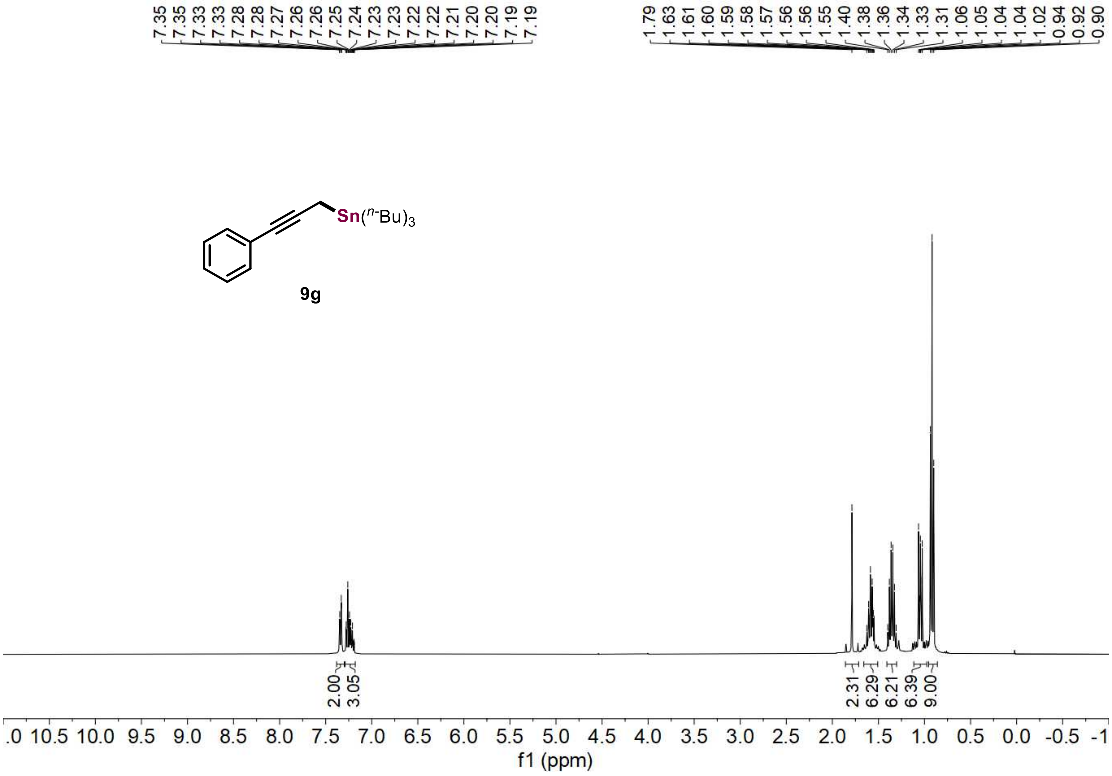


Figure S58. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **9f**.



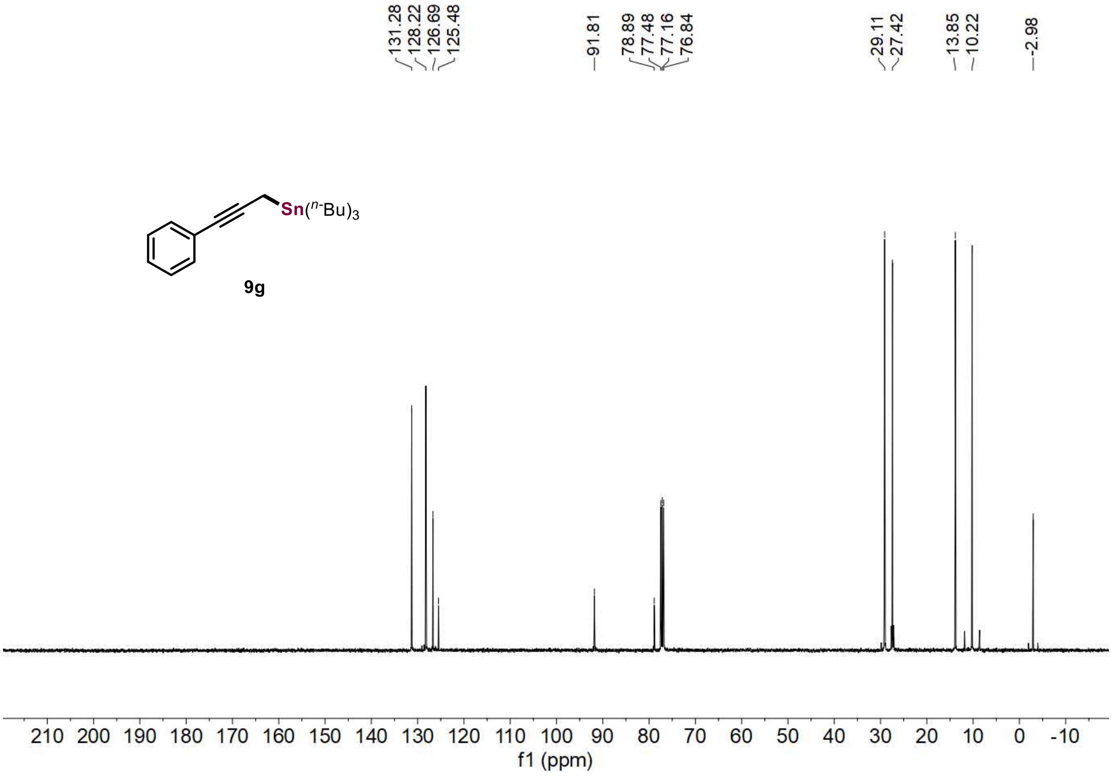
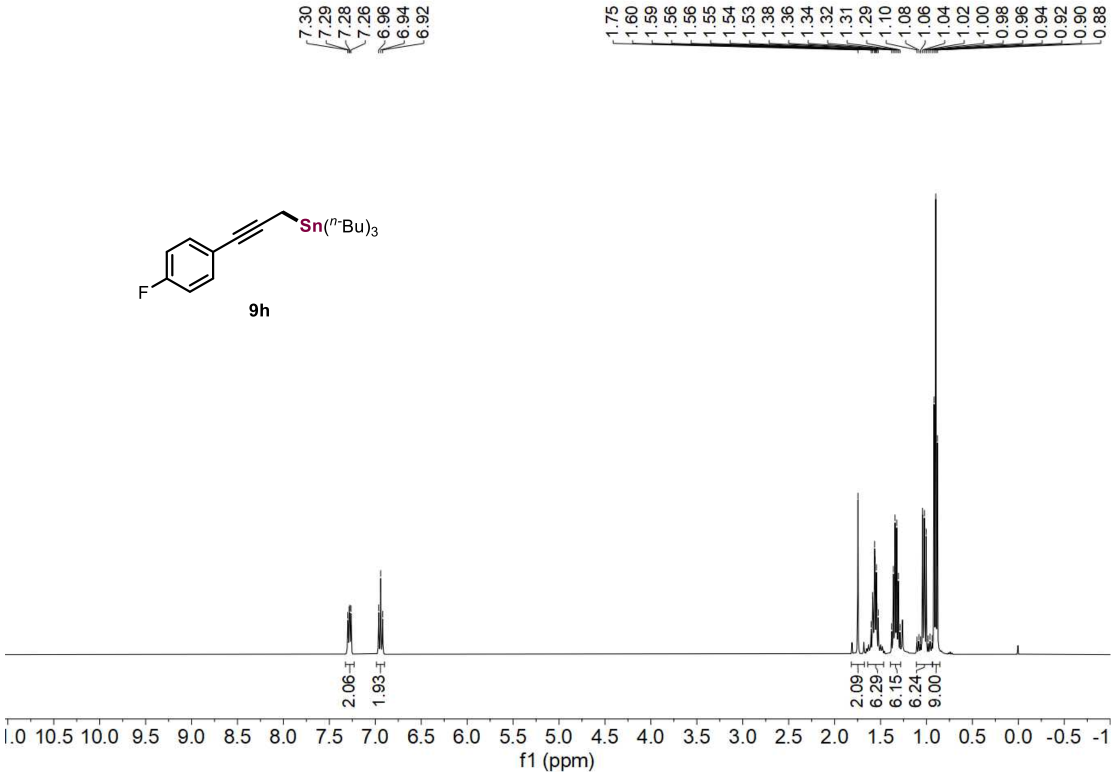
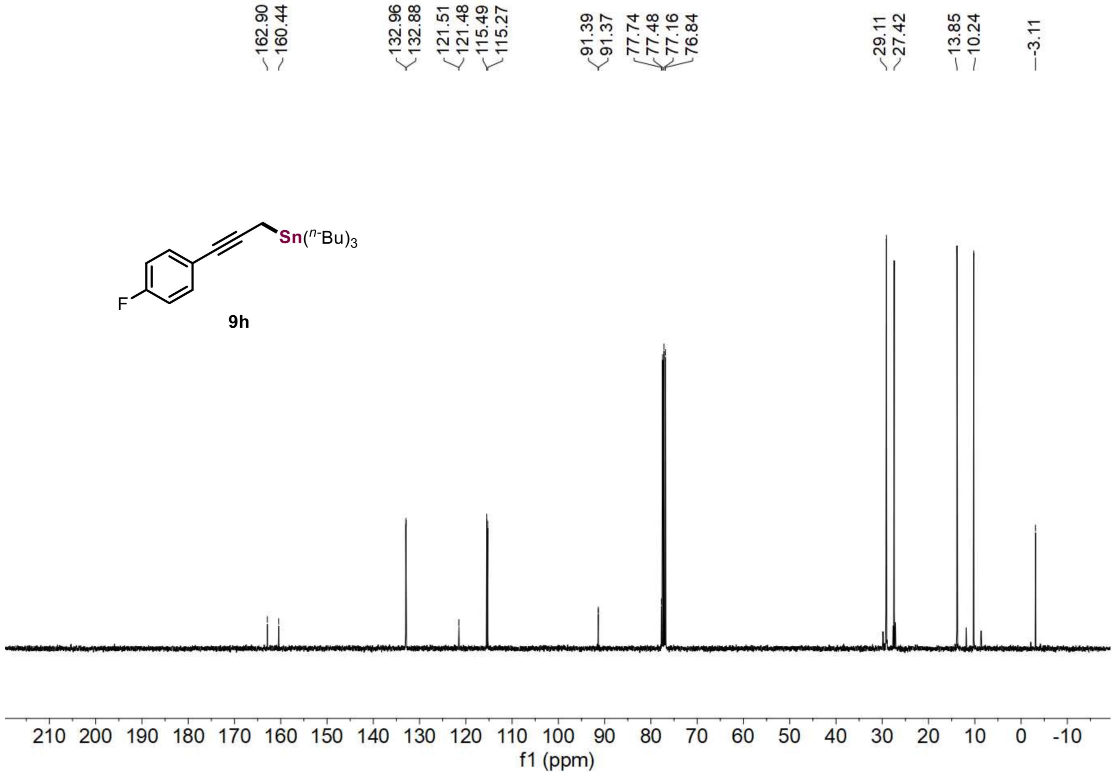


Figure S59. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **9g**.


7.30
7.29
7.28
7.26
6.96
6.94
6.92
1.75
1.60
1.59
1.56
1.56
1.55
1.54
1.53
1.38
1.36
1.34
1.32
1.31
1.29
1.10
1.08
1.06
1.04
1.02
1.00
0.98
0.96
0.94
0.92
0.90
0.88
Sn(^{n}-Bu)$_3$
F
9h
2.06
1.93
2.09
6.29
6.15
6.24
9.00
1.0 10.5 10.0 9.5 9.0 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 -1
f1 (ppm)


162.90
160.44
132.96
132.88
121.51
121.48
115.49
115.27
91.39
91.37
77.74
77.48
77.16
76.84
29.11
27.42
13.85
10.24
-3.11
Sn(^{n}-Bu)$_3$
F
9h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

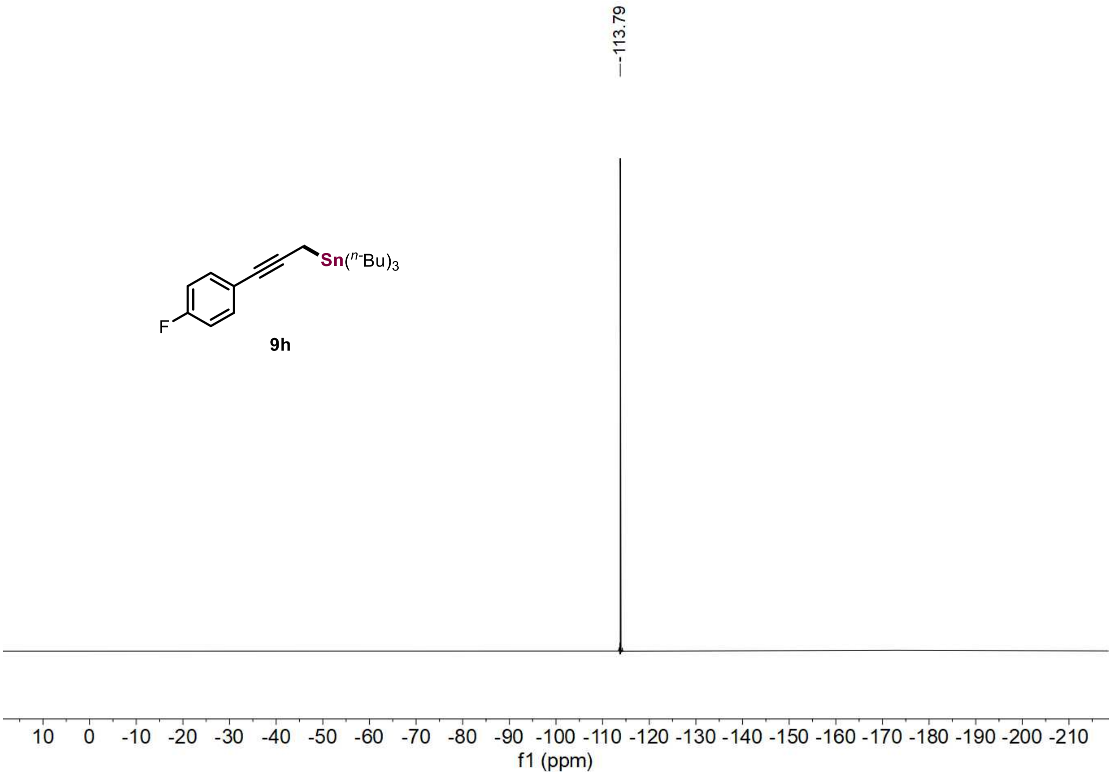
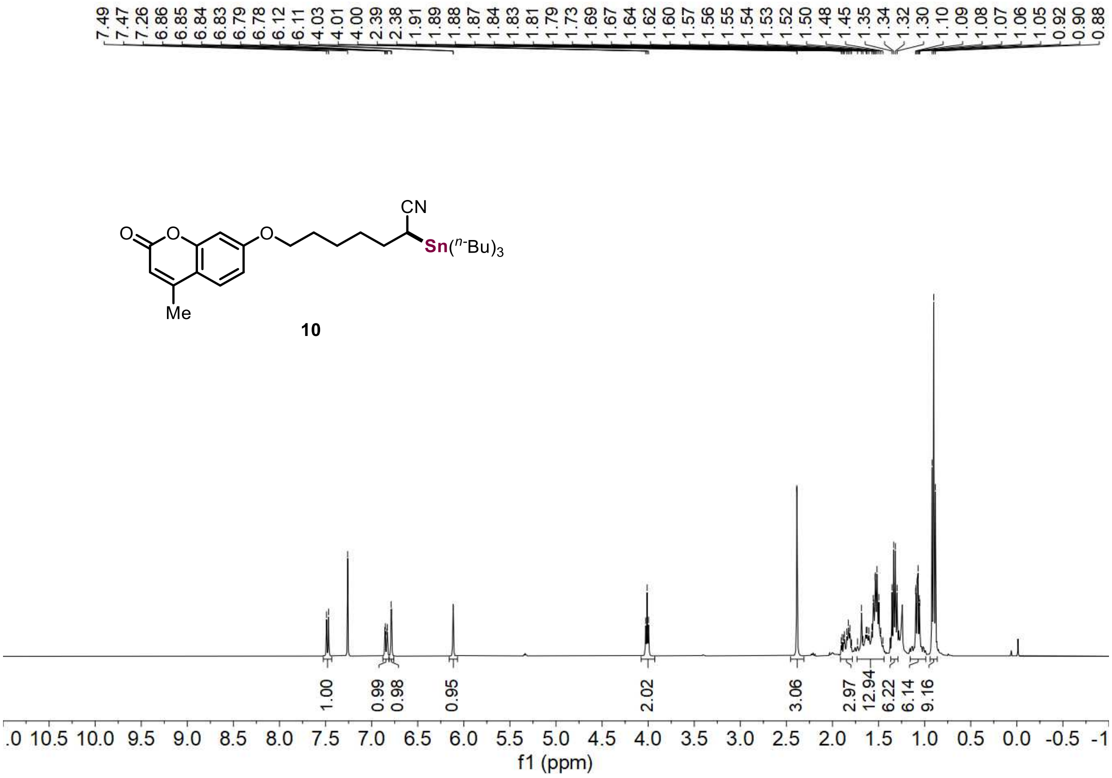


Figure S60. ^{1}H (400 MHz, $CDCl_3$), ^{13}C (100 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectra for compound **9h**.



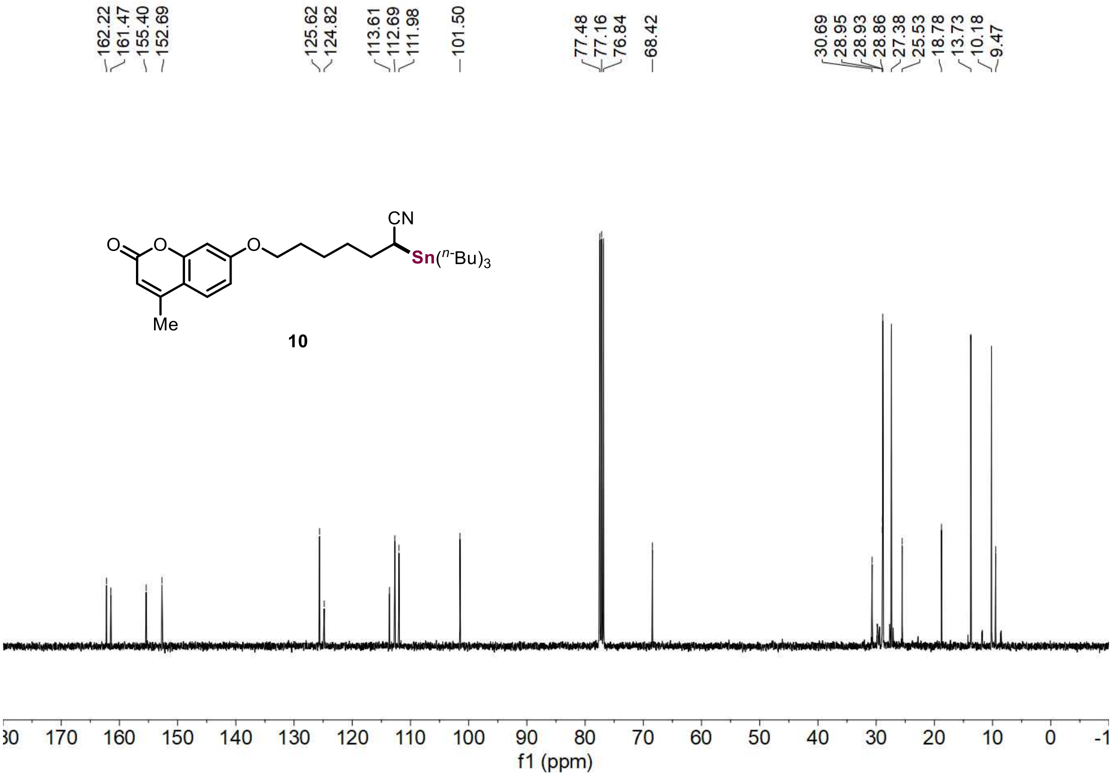
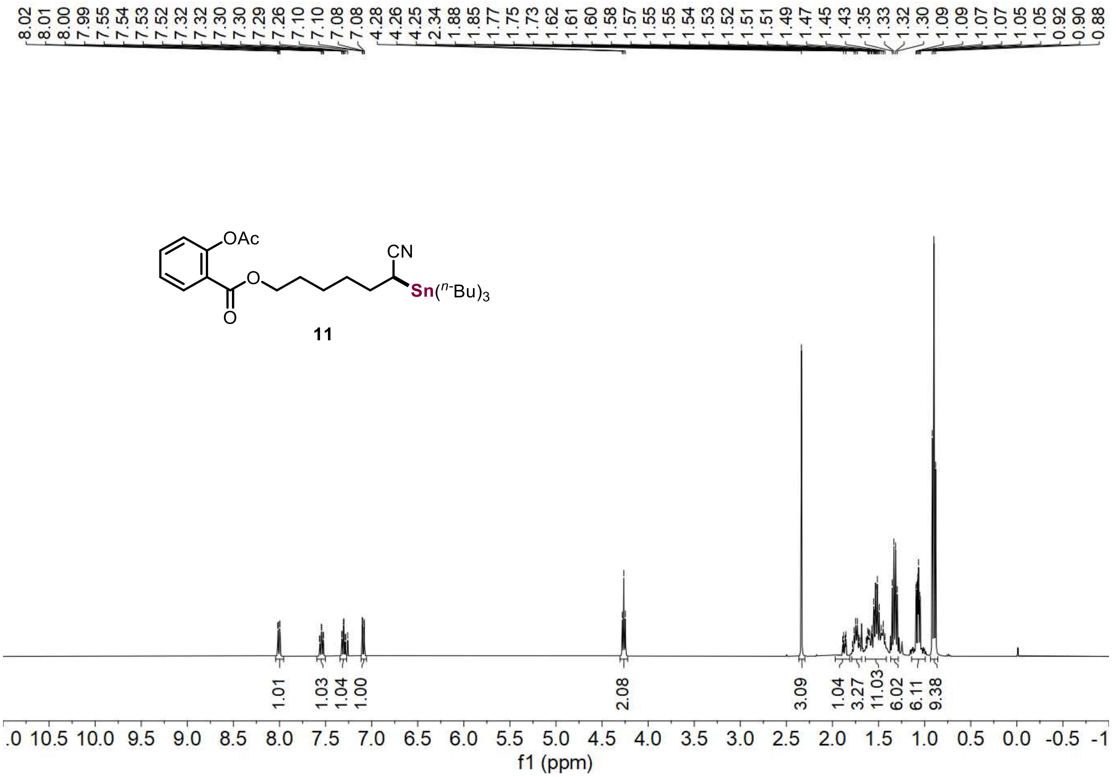


Figure S61. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **10**.



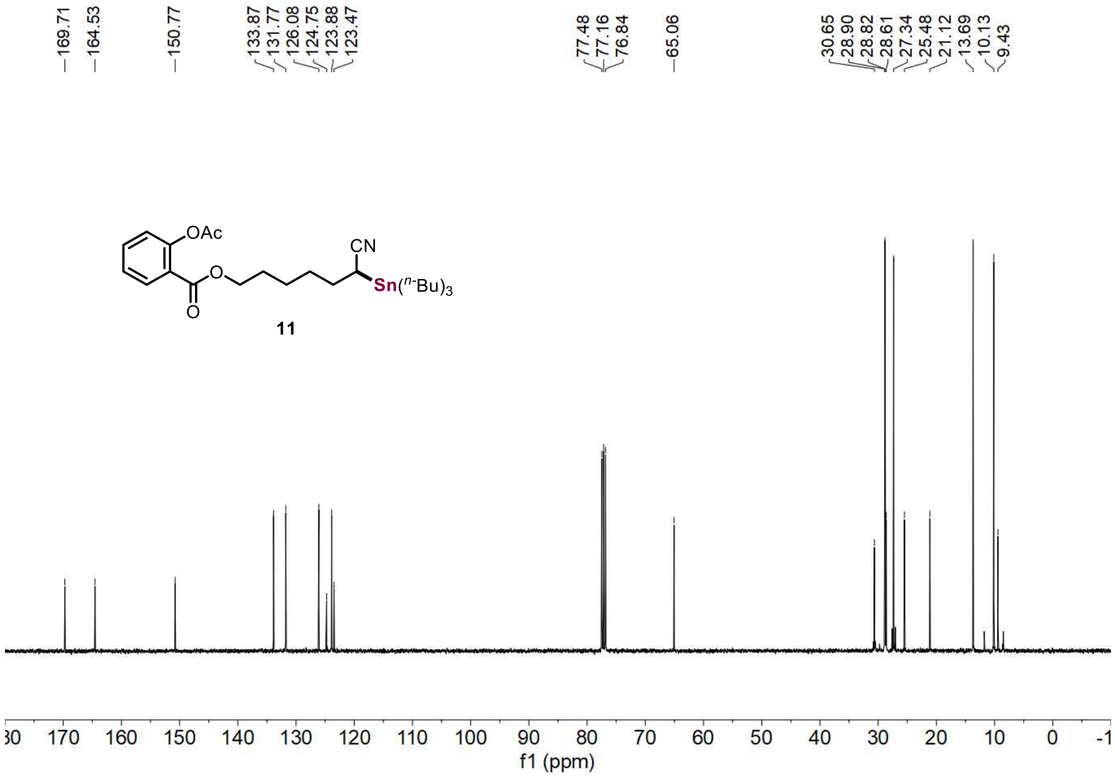
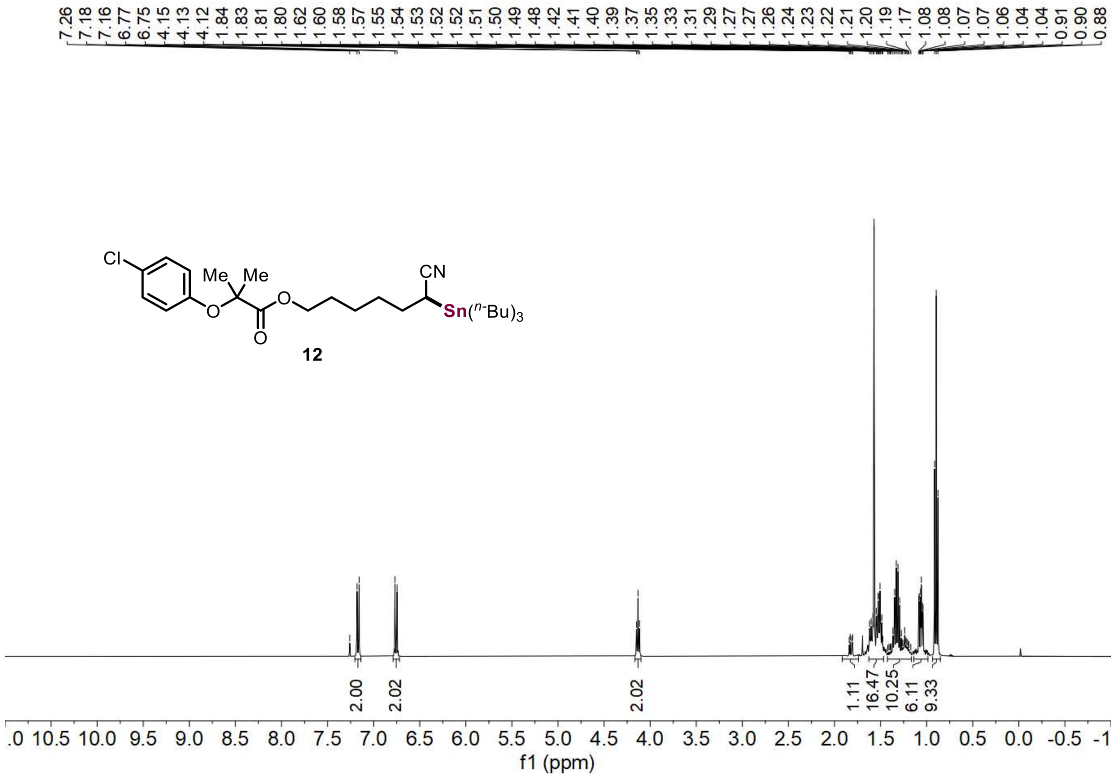


Figure S62. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **11**.



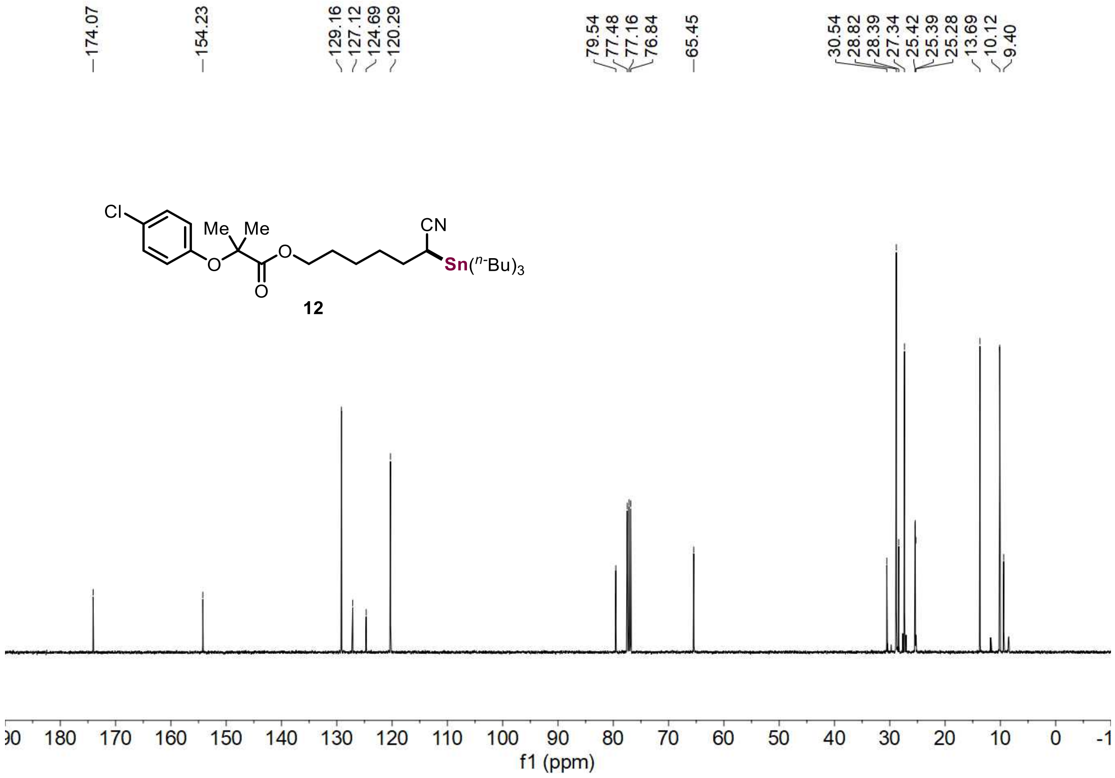
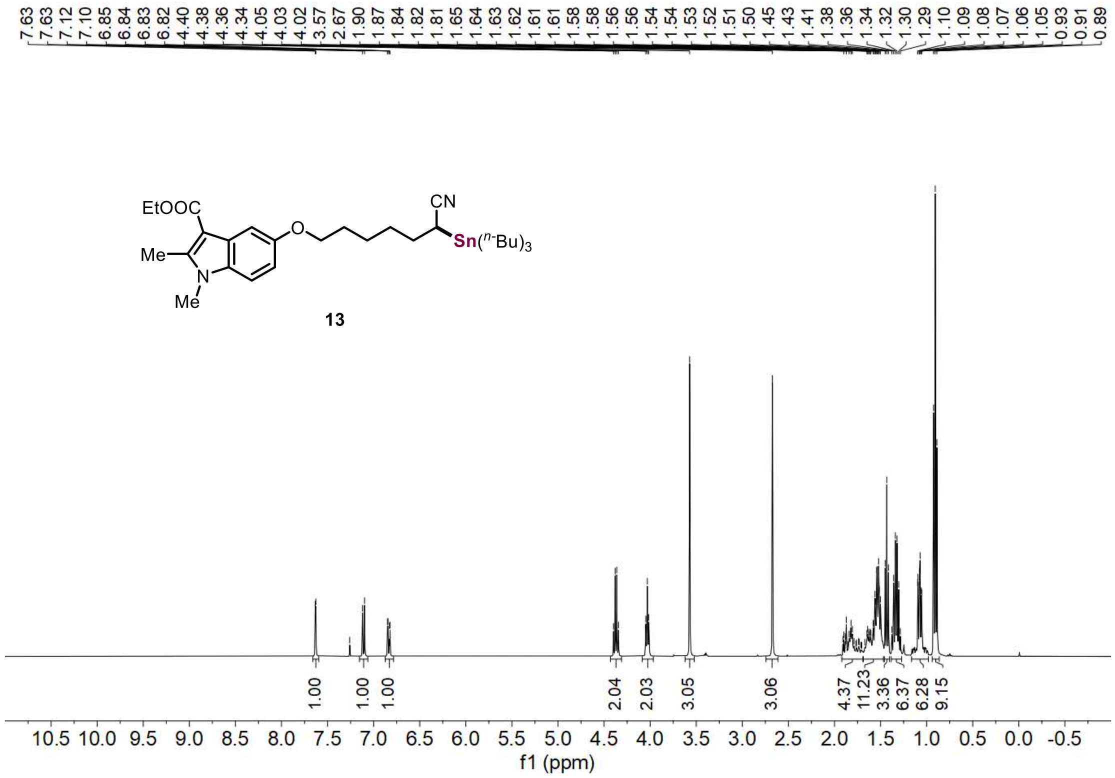


Figure S63. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **12**.



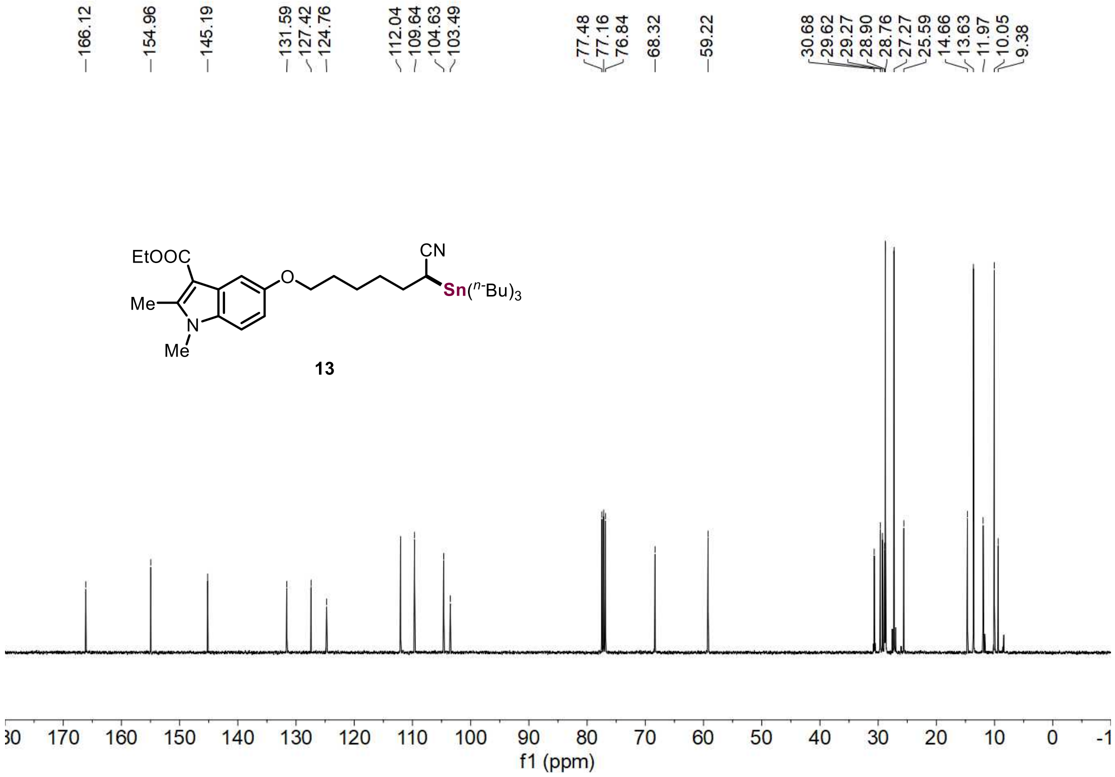
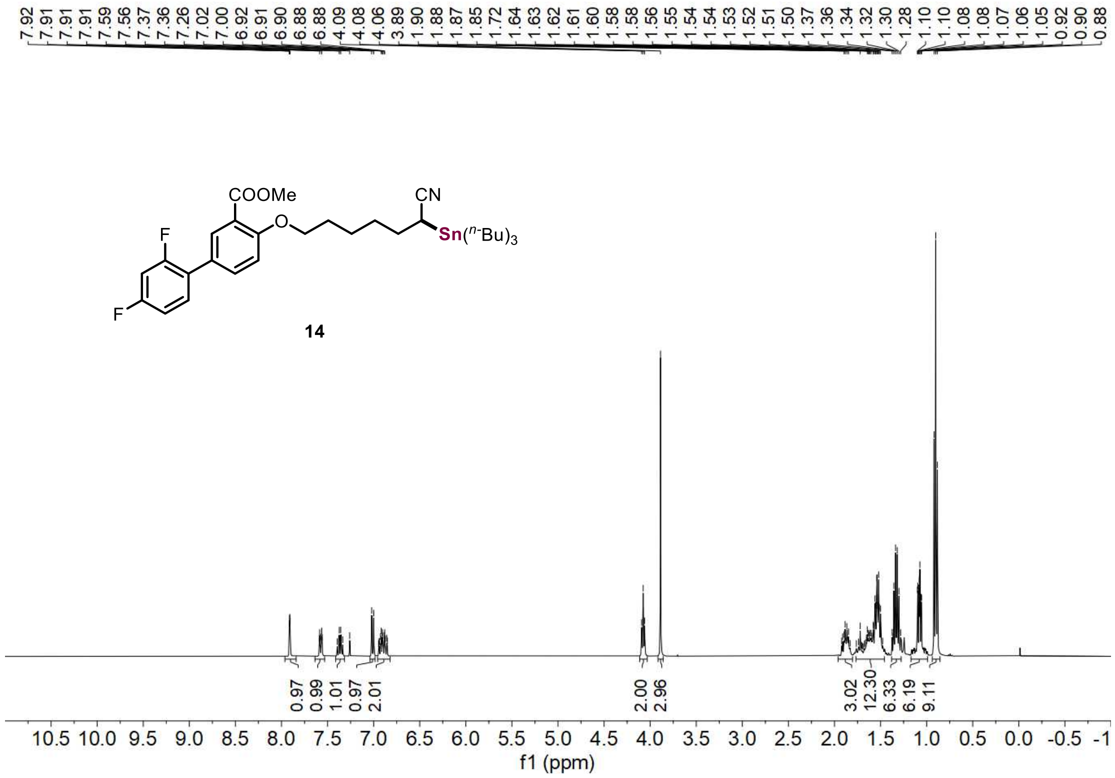


Figure S64. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **13**.



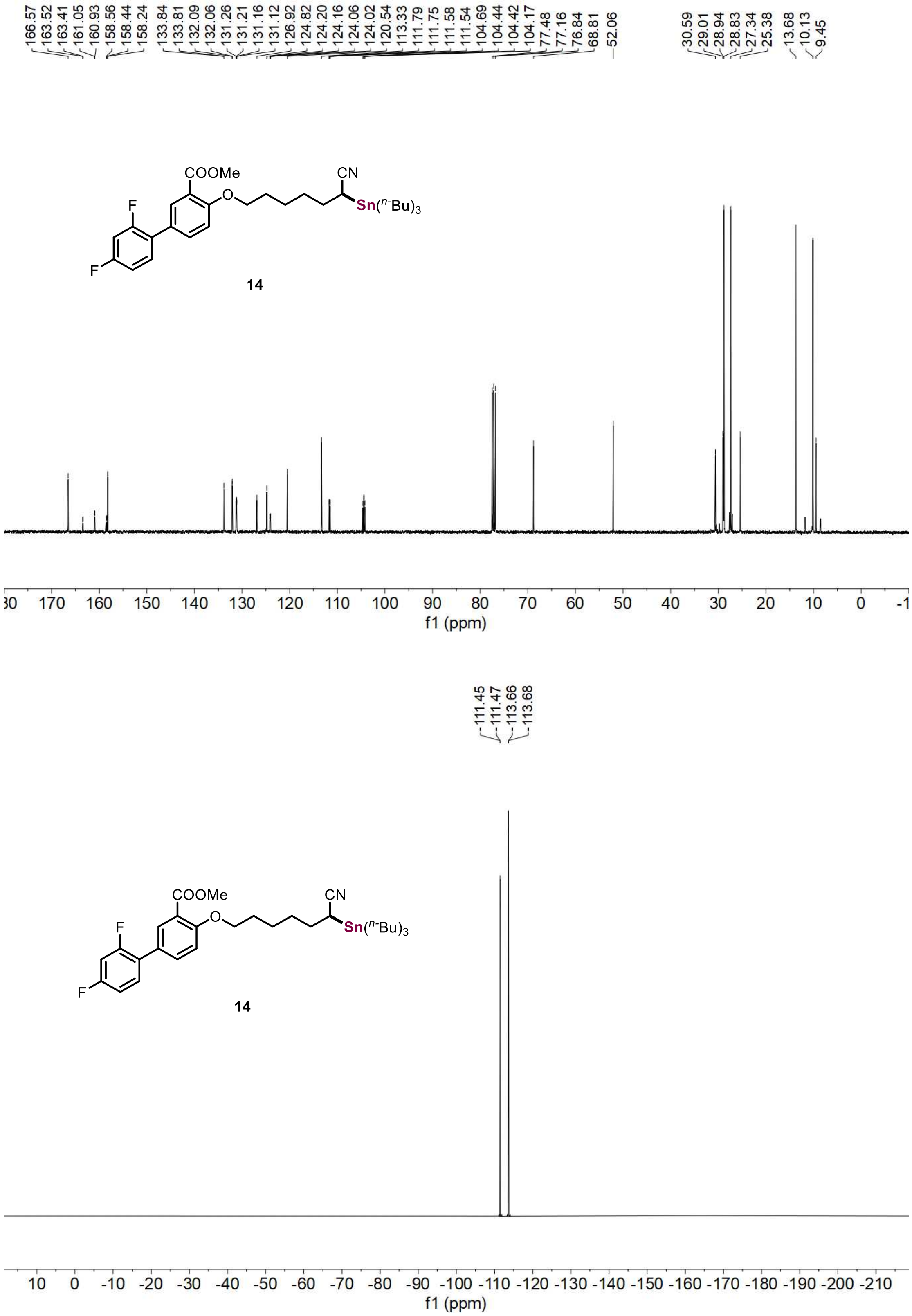


Figure S65. ^{1}H (400 MHz, $CDCl_3$), ^{13}C (100 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectra for compound **14**.

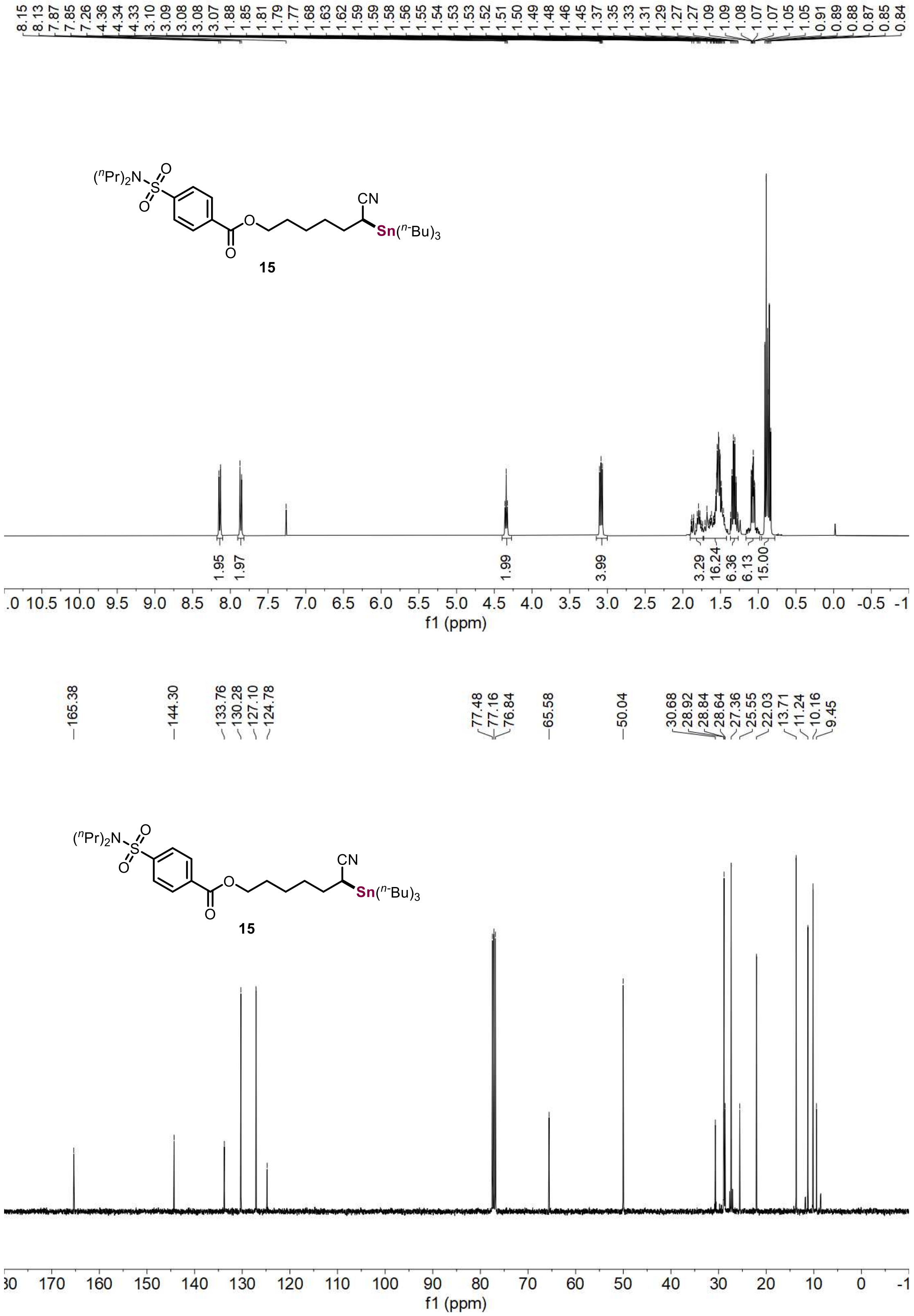


Figure S66. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **15**.

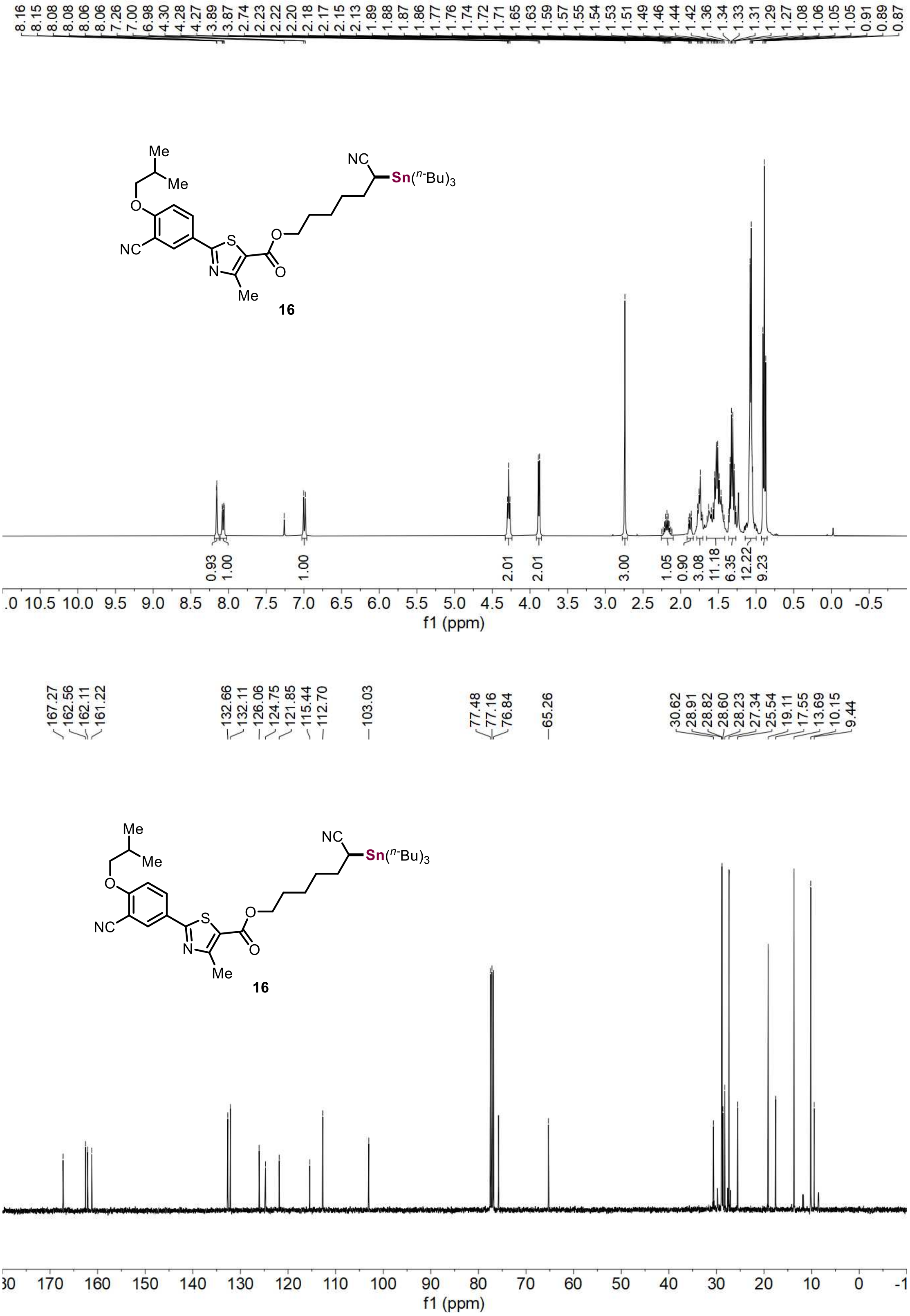


Figure S67. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **16**.

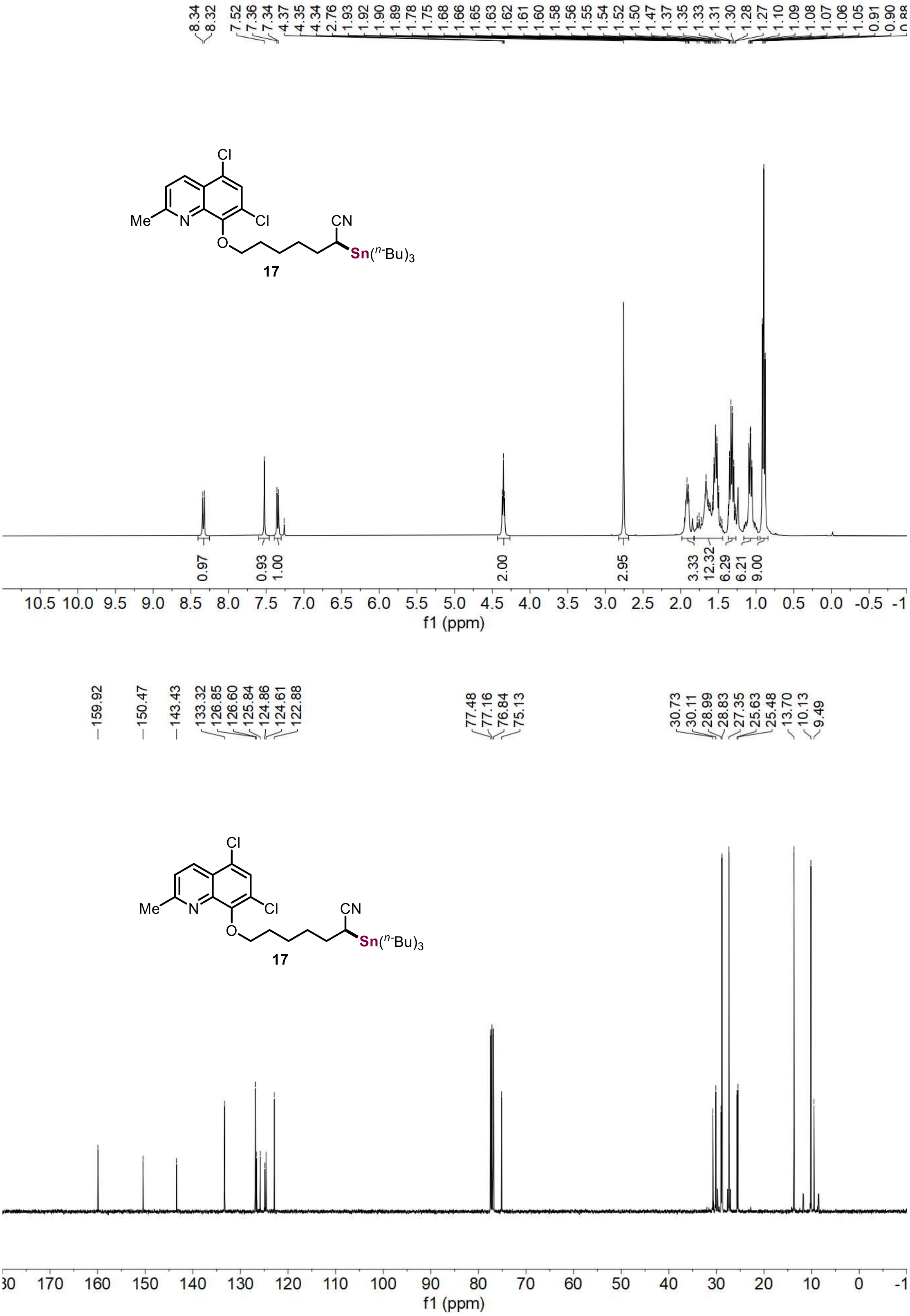
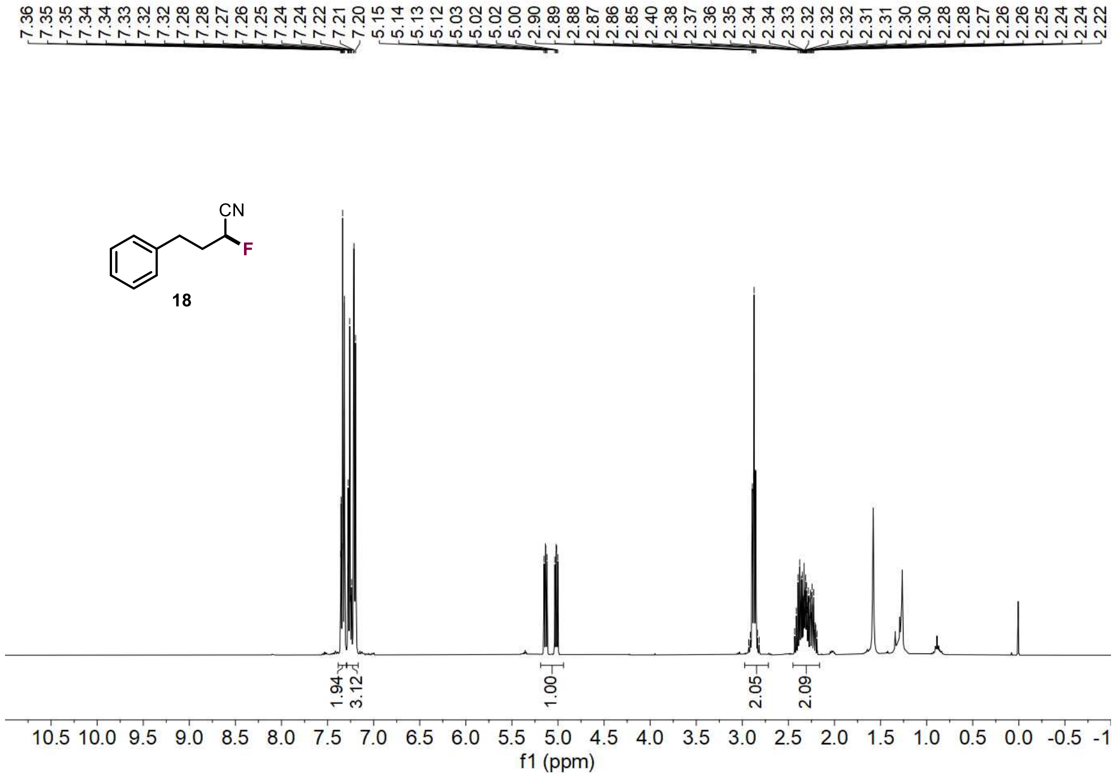
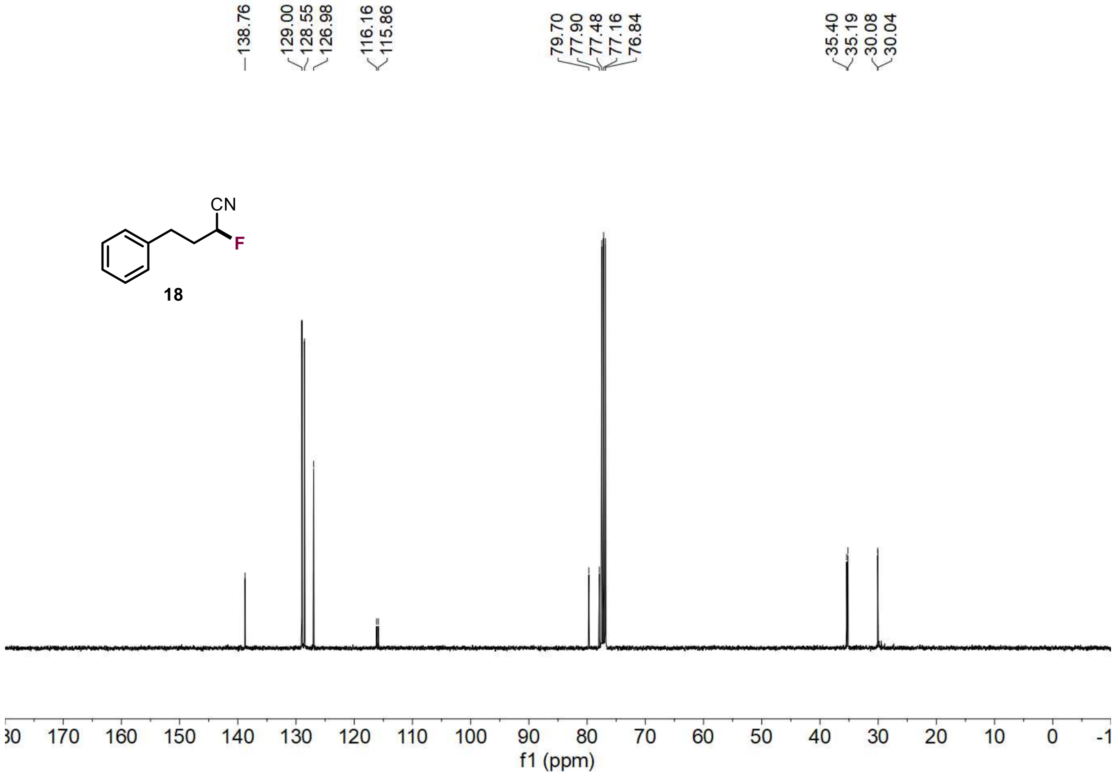


Figure S68. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **17**.


7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.22
7.21
7.20
5.15
5.14
5.13
5.12
5.03
5.02
5.02
5.00
2.90
2.89
2.88
2.87
2.86
2.85
2.40
2.38
2.37
2.36
2.35
2.34
2.34
2.33
2.32
2.32
2.32
2.31
2.31
2.30
2.30
2.28
2.28
2.27
2.26
2.26
2.25
2.24
2.24
2.22
CN
F
18
1.94
3.12
1.00
2.05
2.09
10.5 10.0 9.5 9.0 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 -1
f1 (ppm)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129.00
128.55
126.98
116.16
115.86
79.70
77.90
77.48
77.16
76.84
35.40
35.19
30.08
30.04
CN
F
18
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

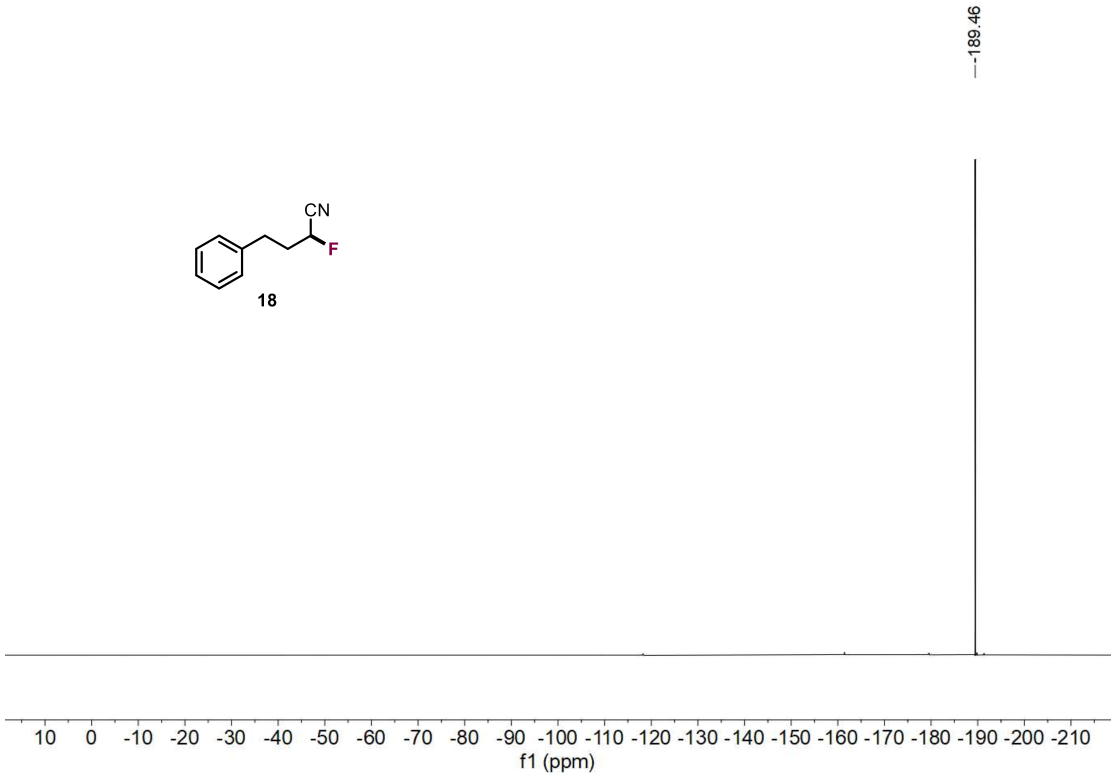
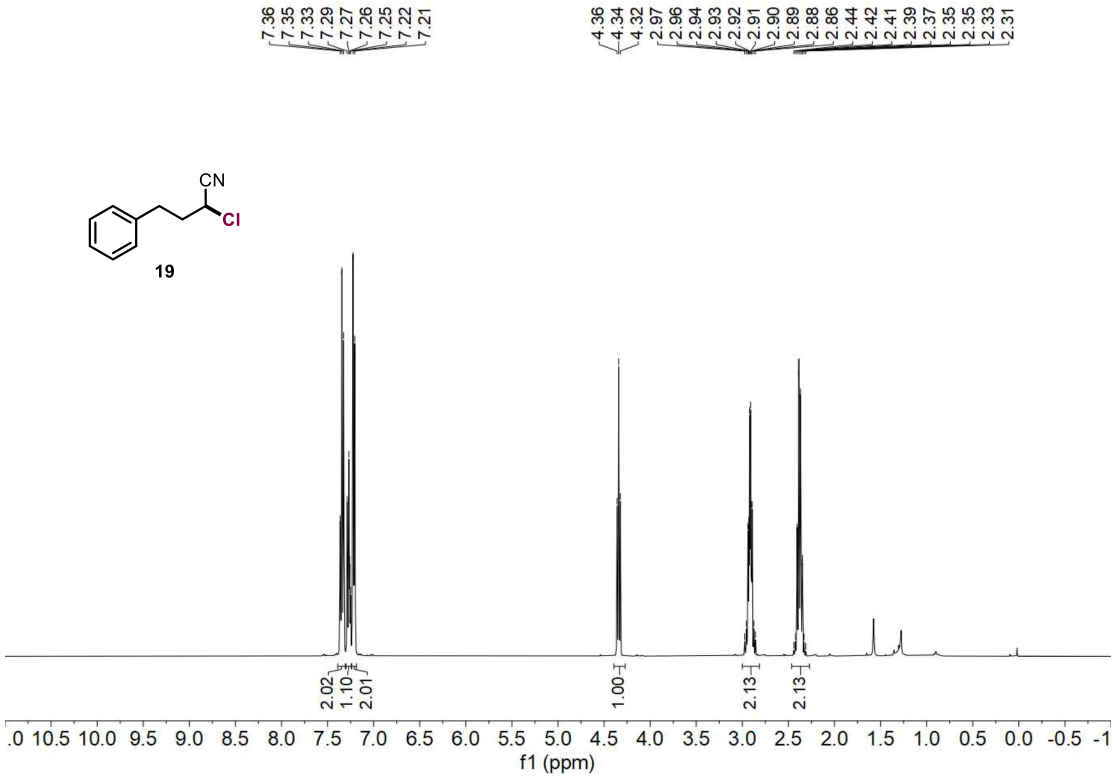


Figure S69. ^{1}H (400 MHz, $CDCl_3$), ^{13}C (100 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectra for compound **18**.



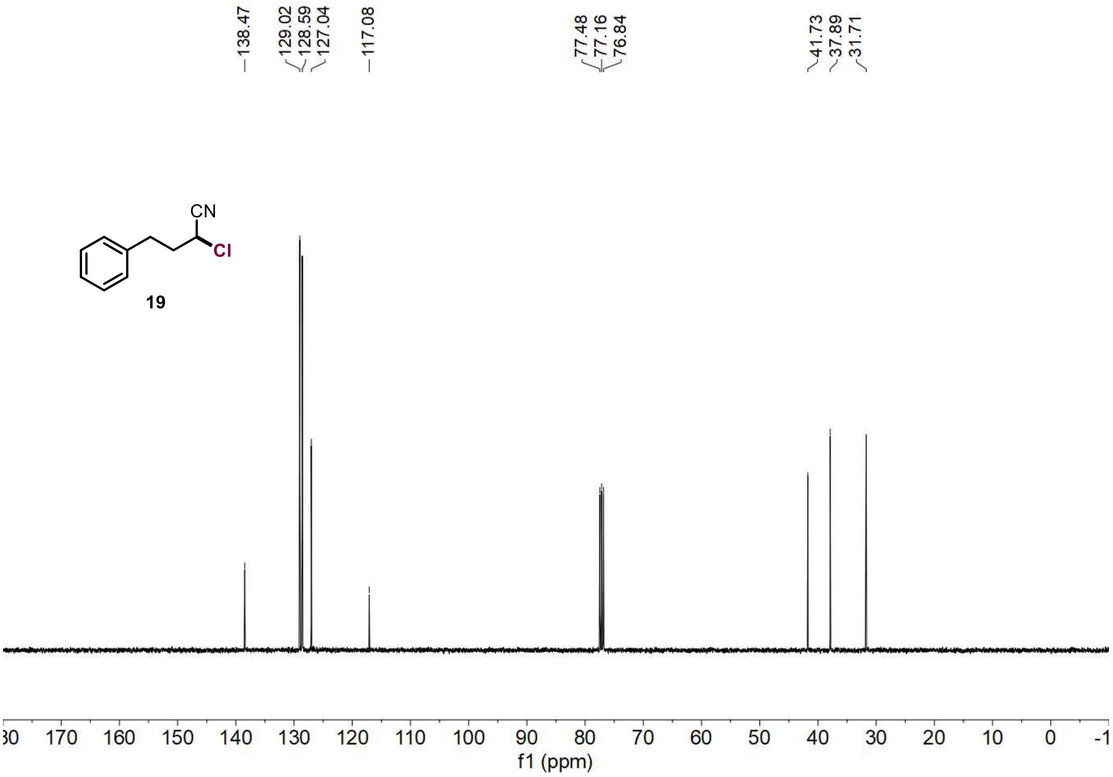
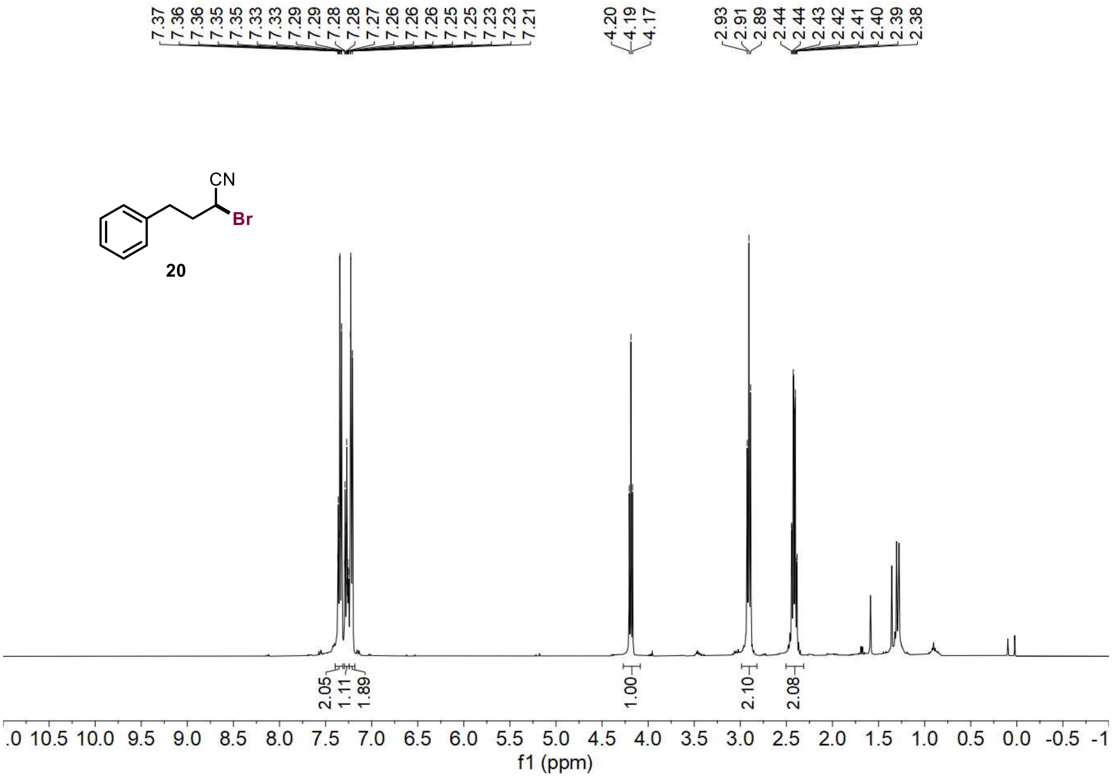


Figure S70. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **19**.



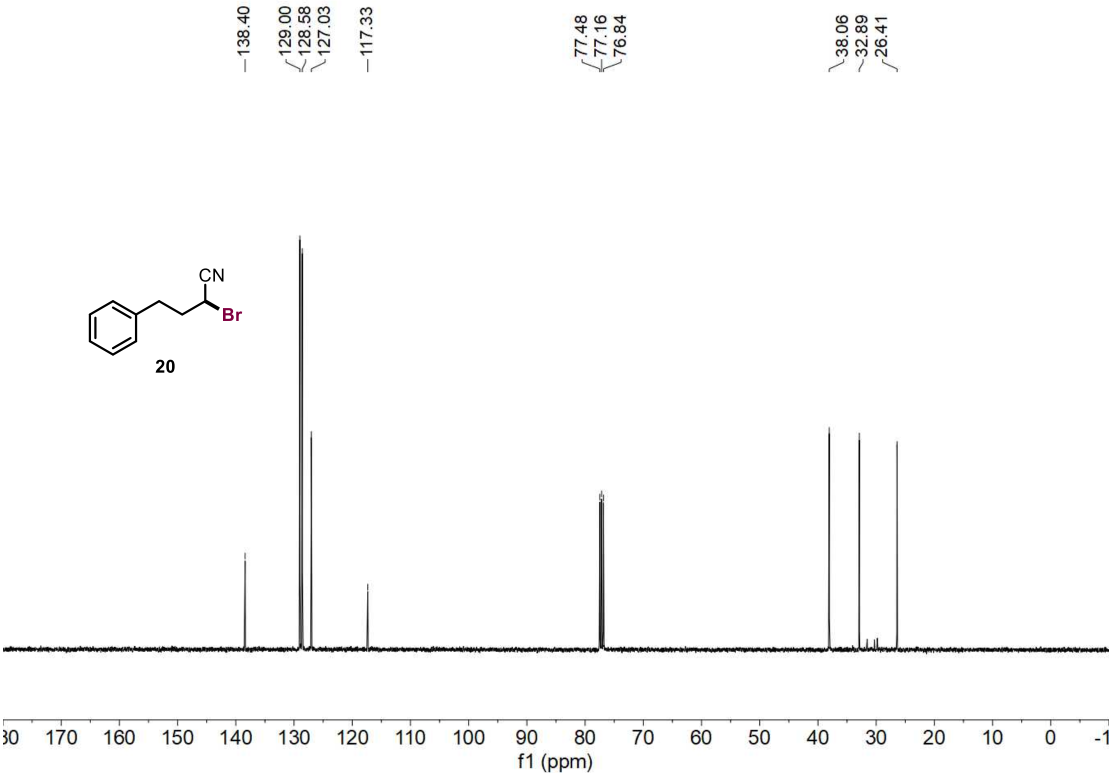
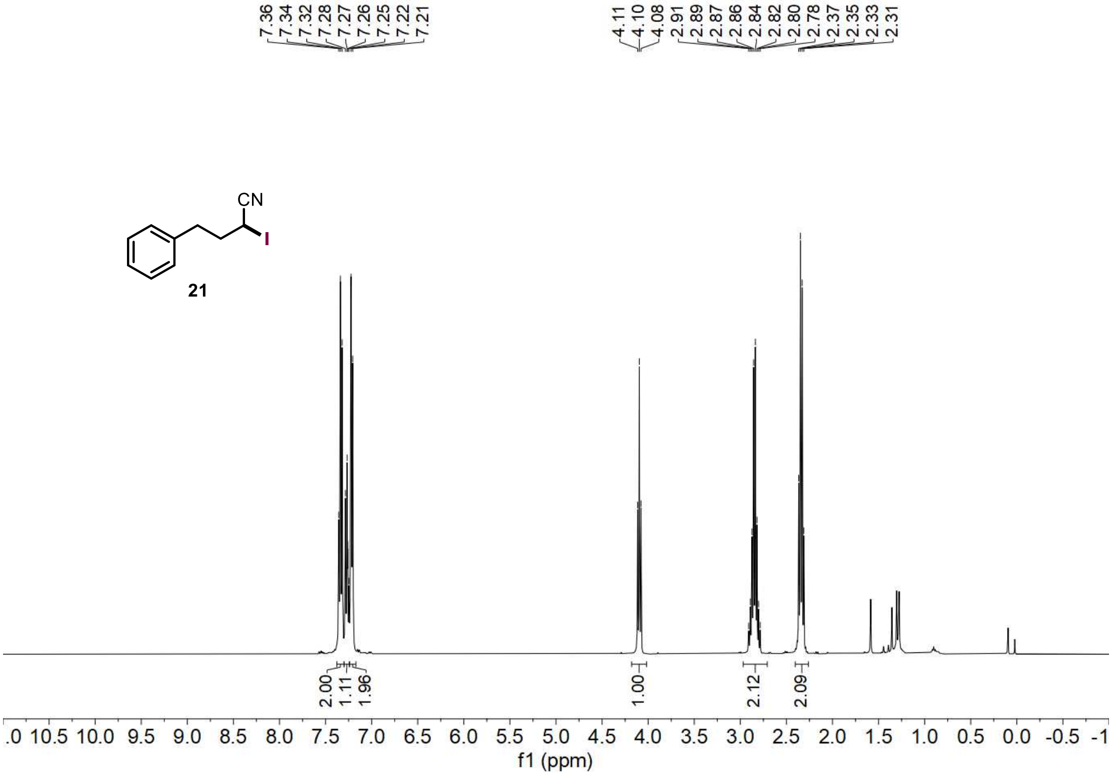


Figure S71. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **20**.



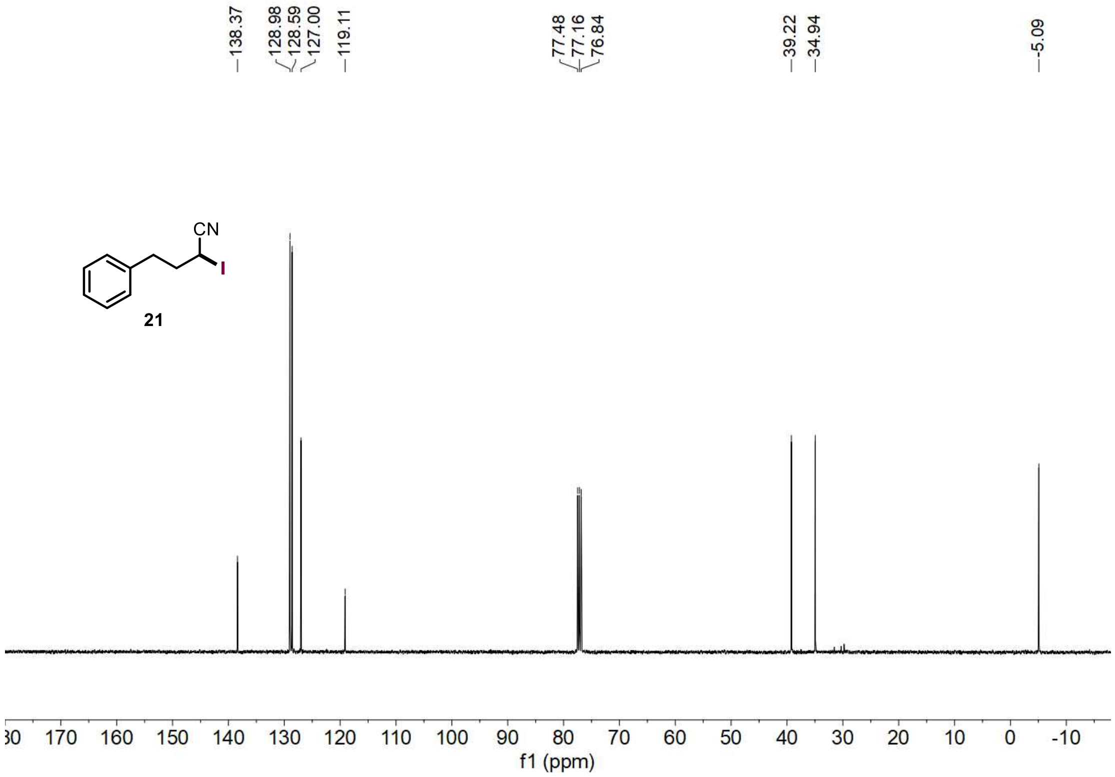
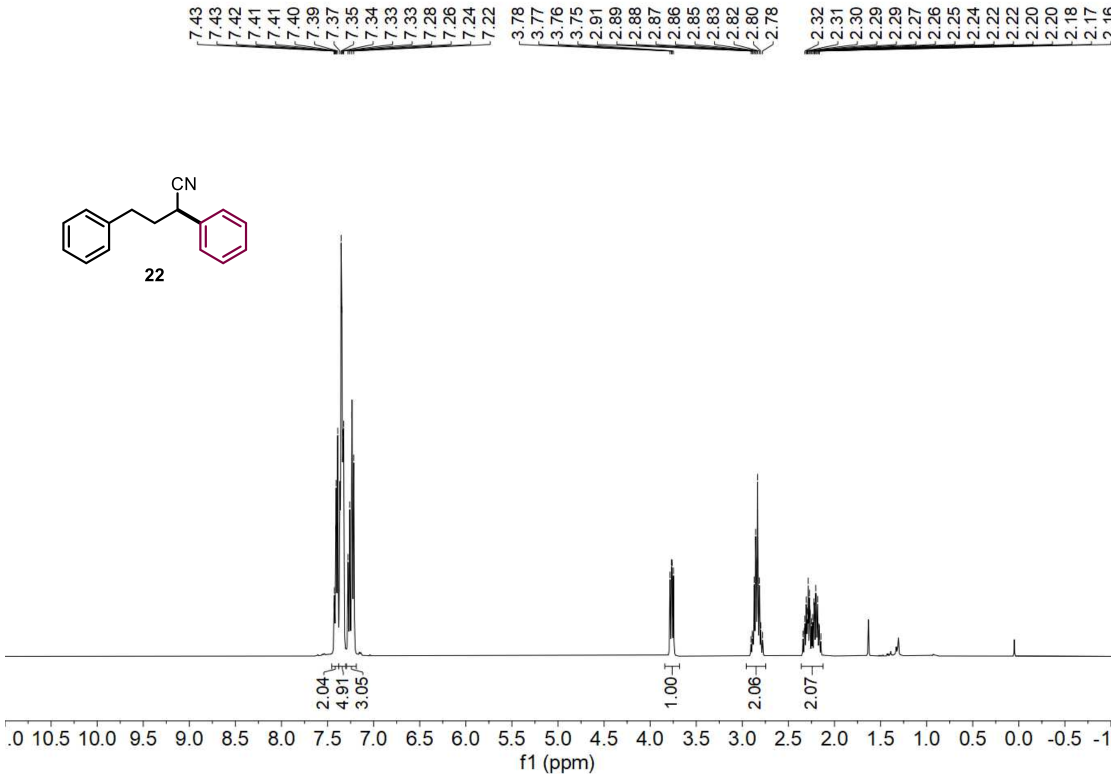


Figure S72. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **21**.



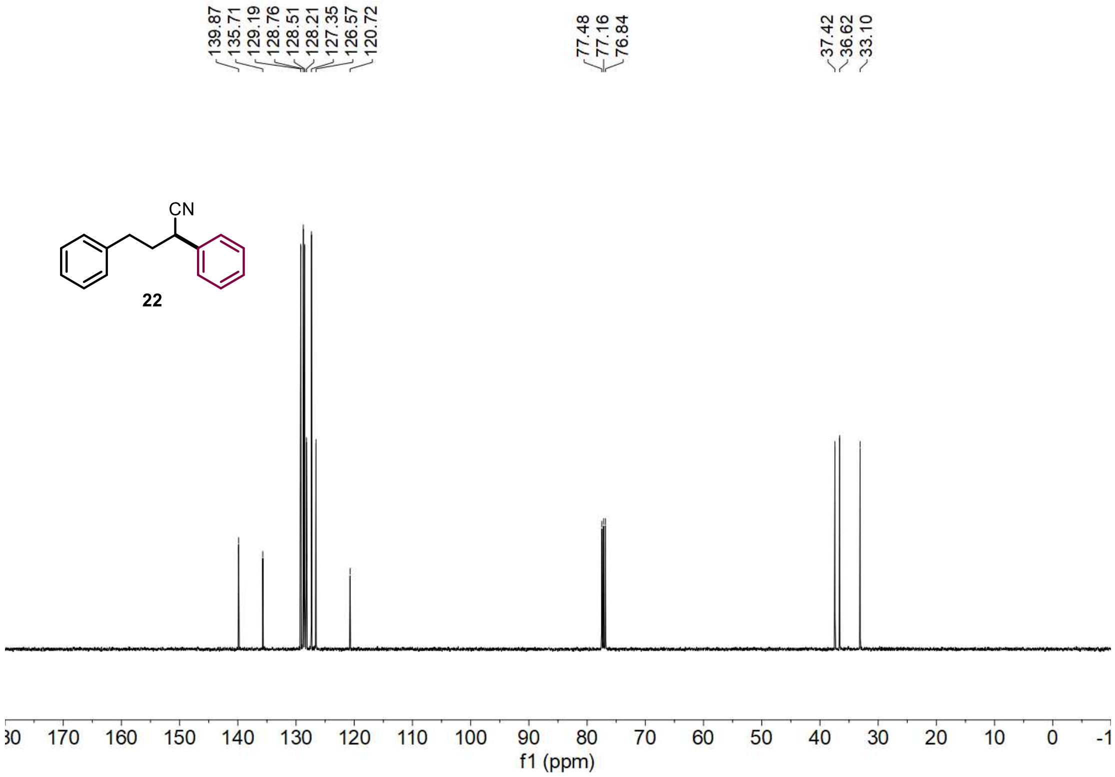
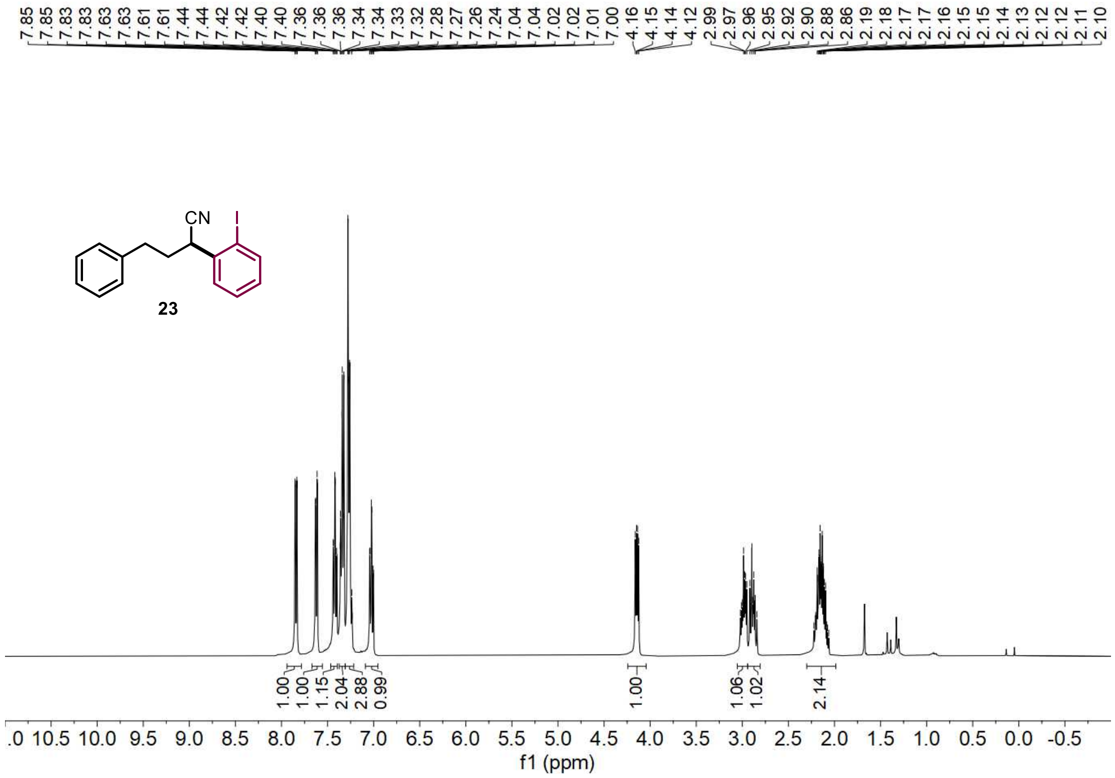


Figure S73. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **22**.



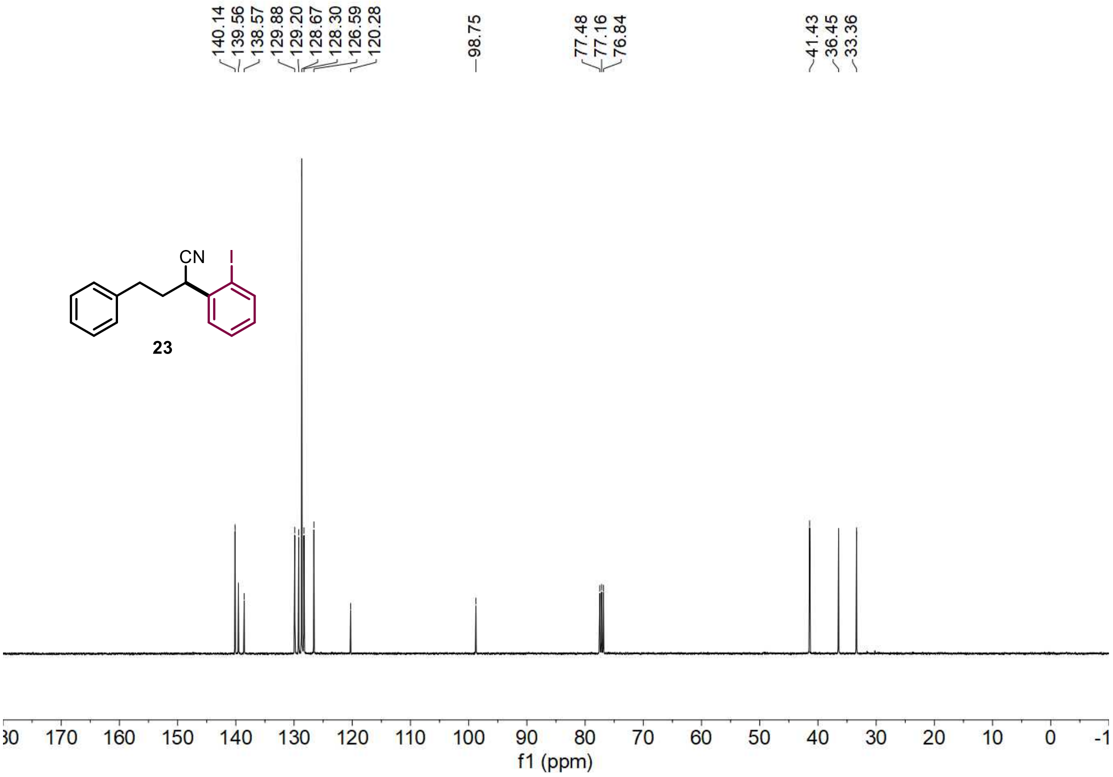
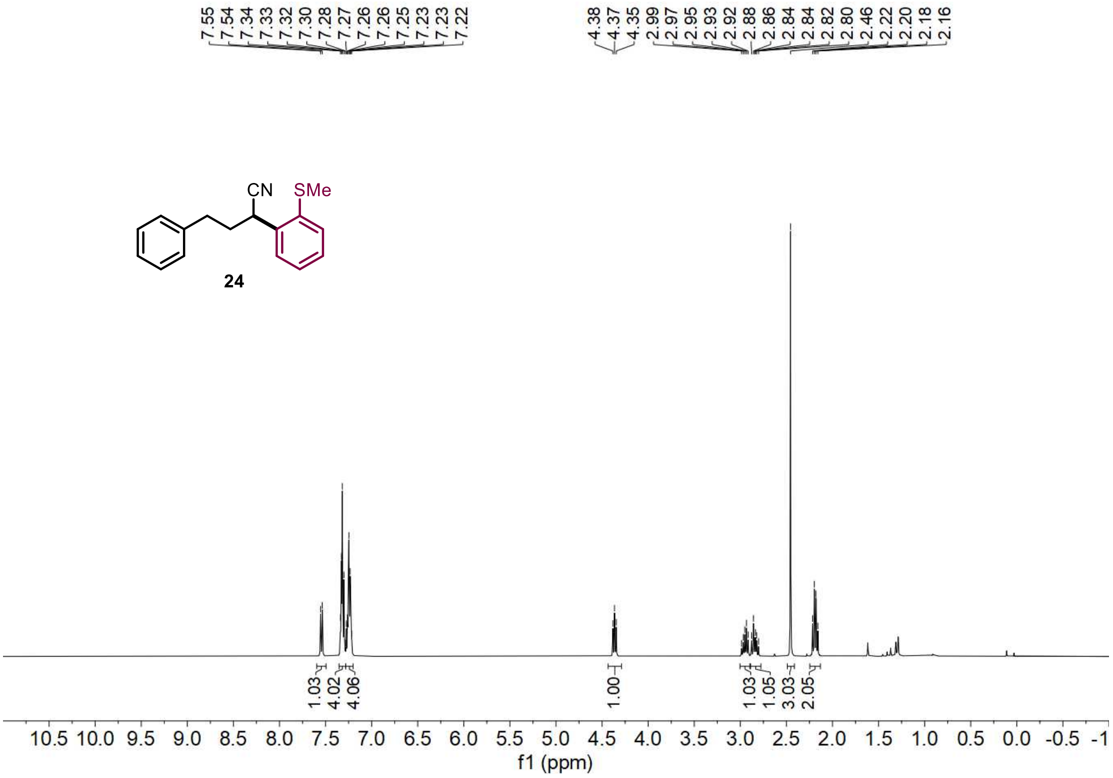


Figure S74. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **23**.



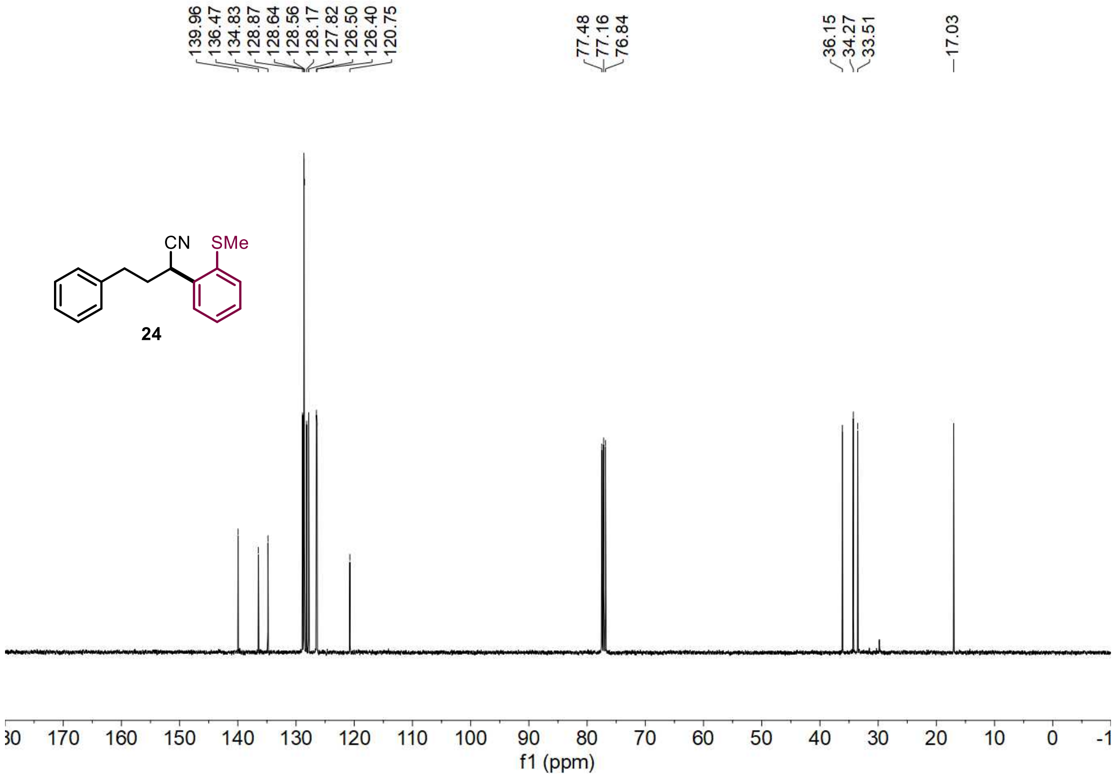


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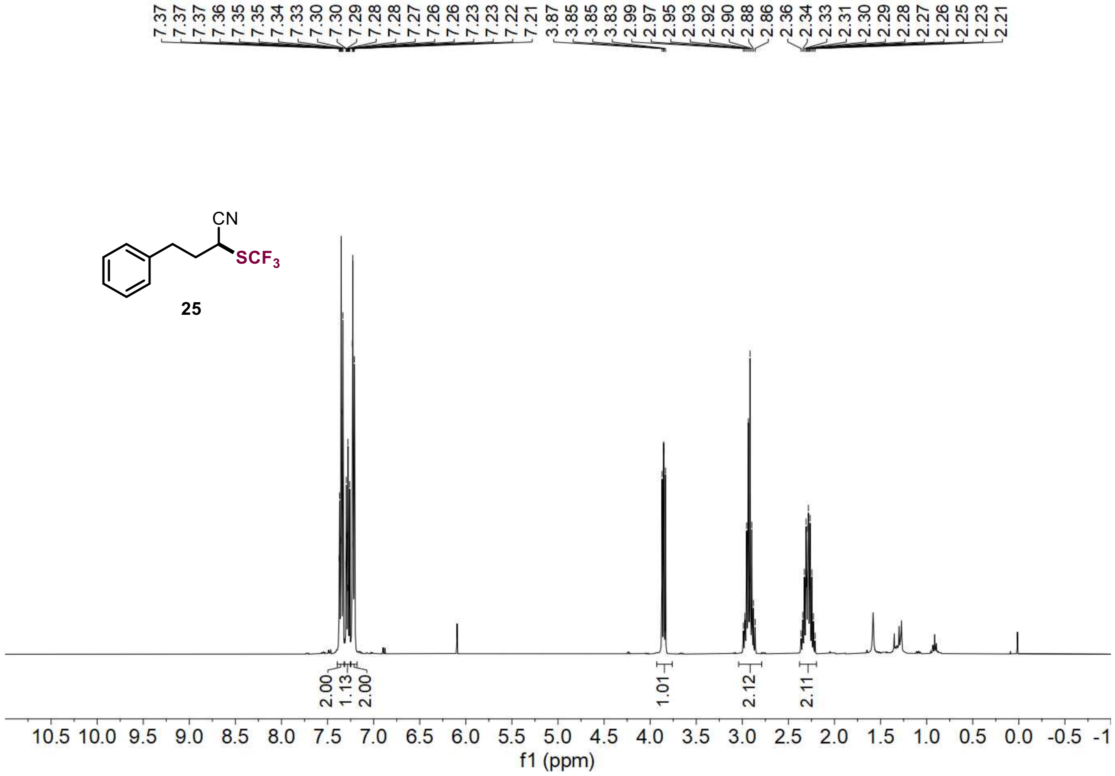
Figure S75. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **24**.



25

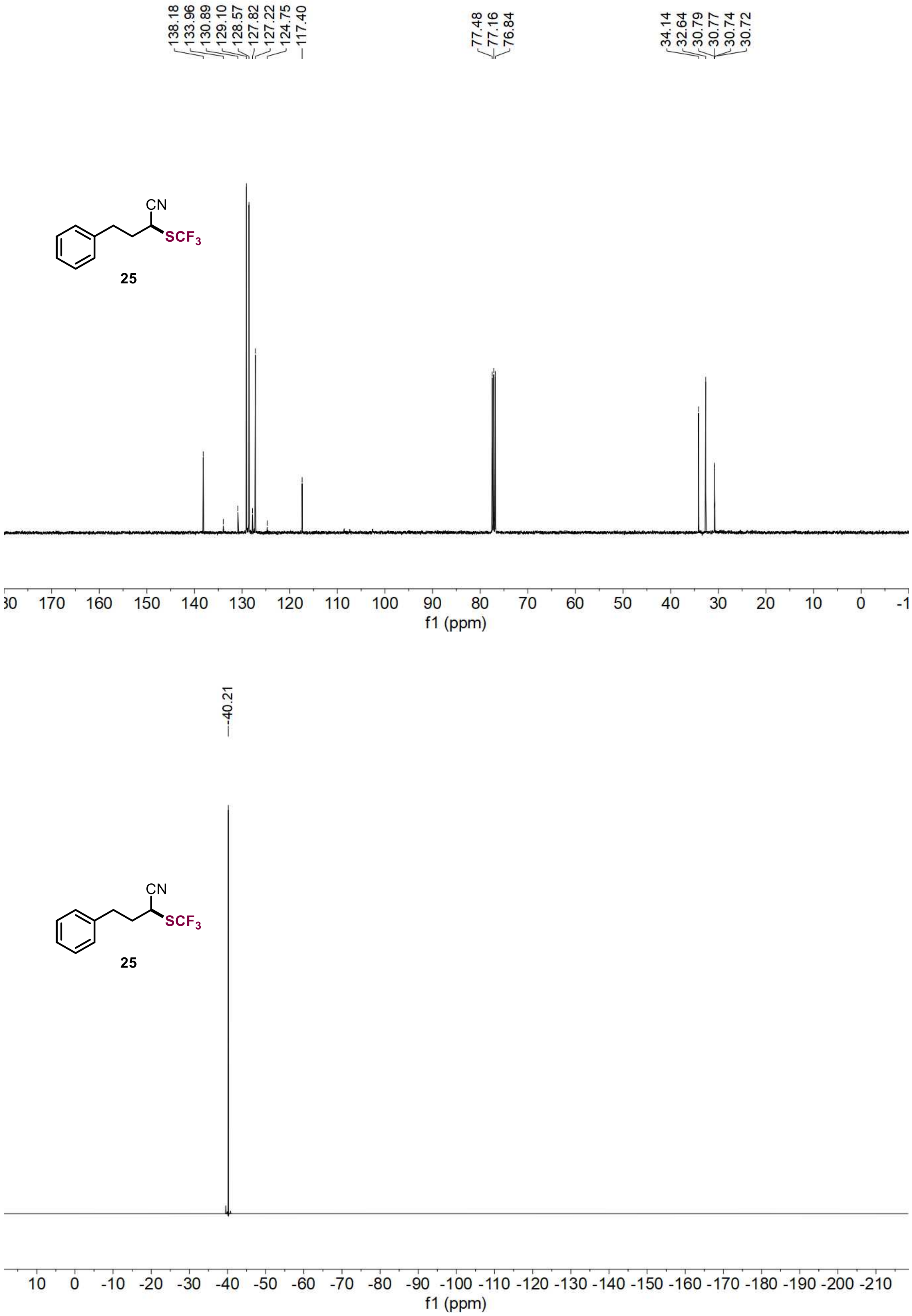


Figure S76. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{19}F (376 MHz, CDCl$_3$) NMR spectra for compound **25**.

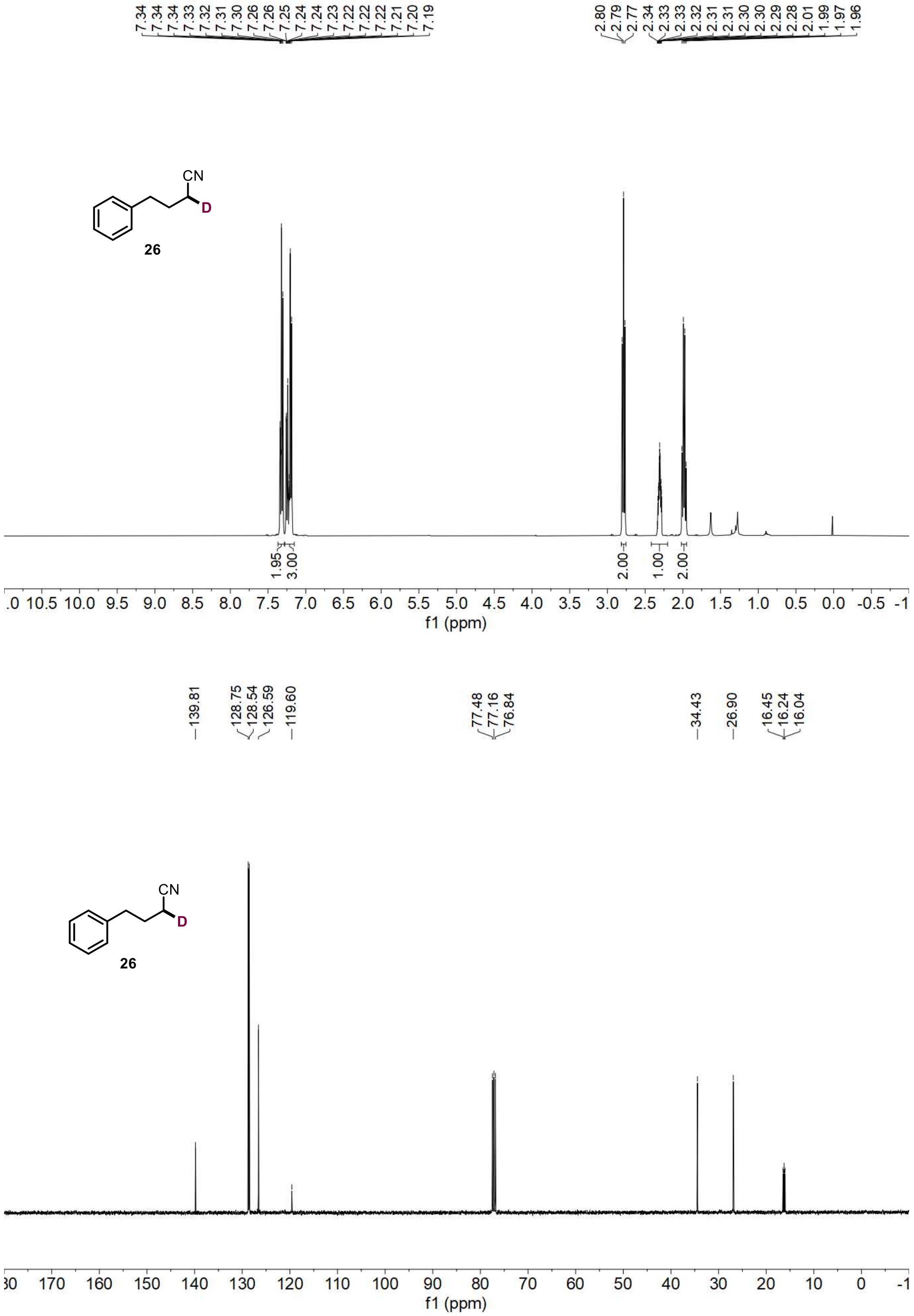
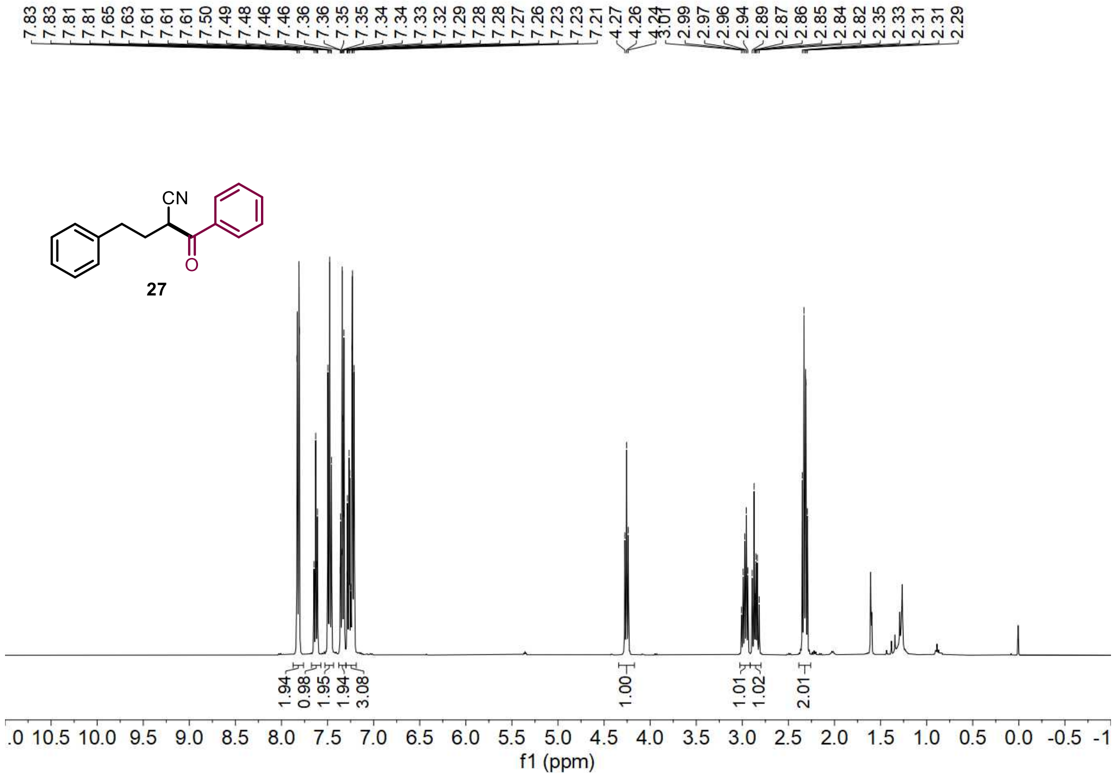


Figure S77. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **26**.



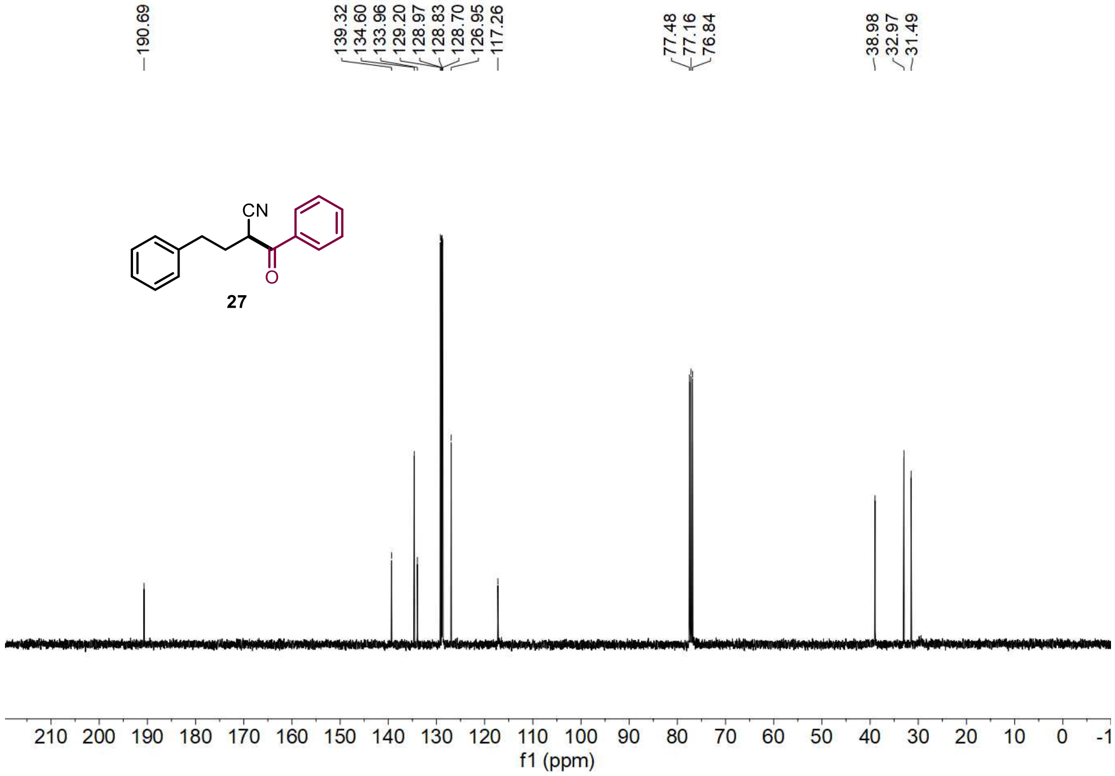


Figure S78. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **27**.

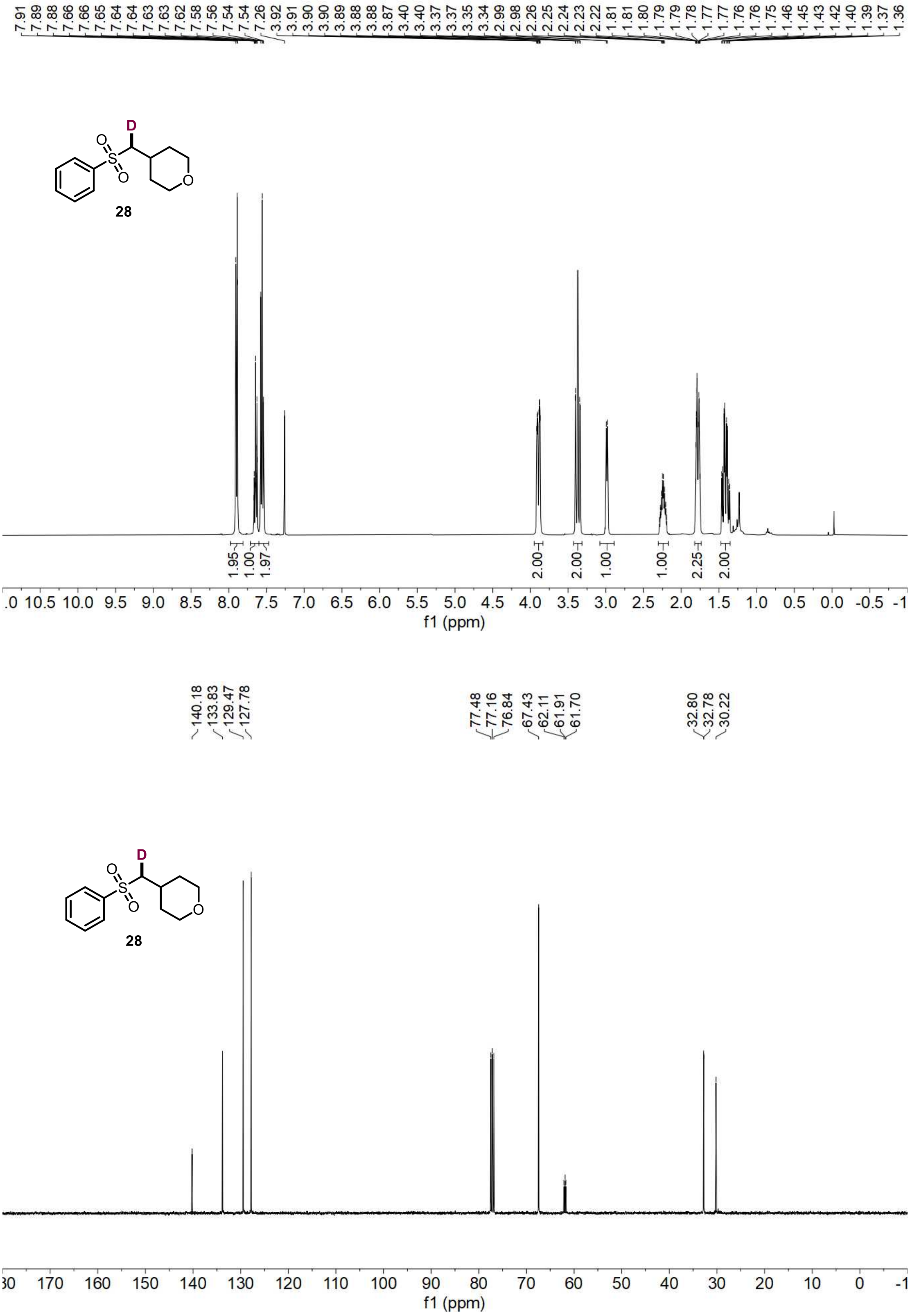


Figure S79. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **28**.

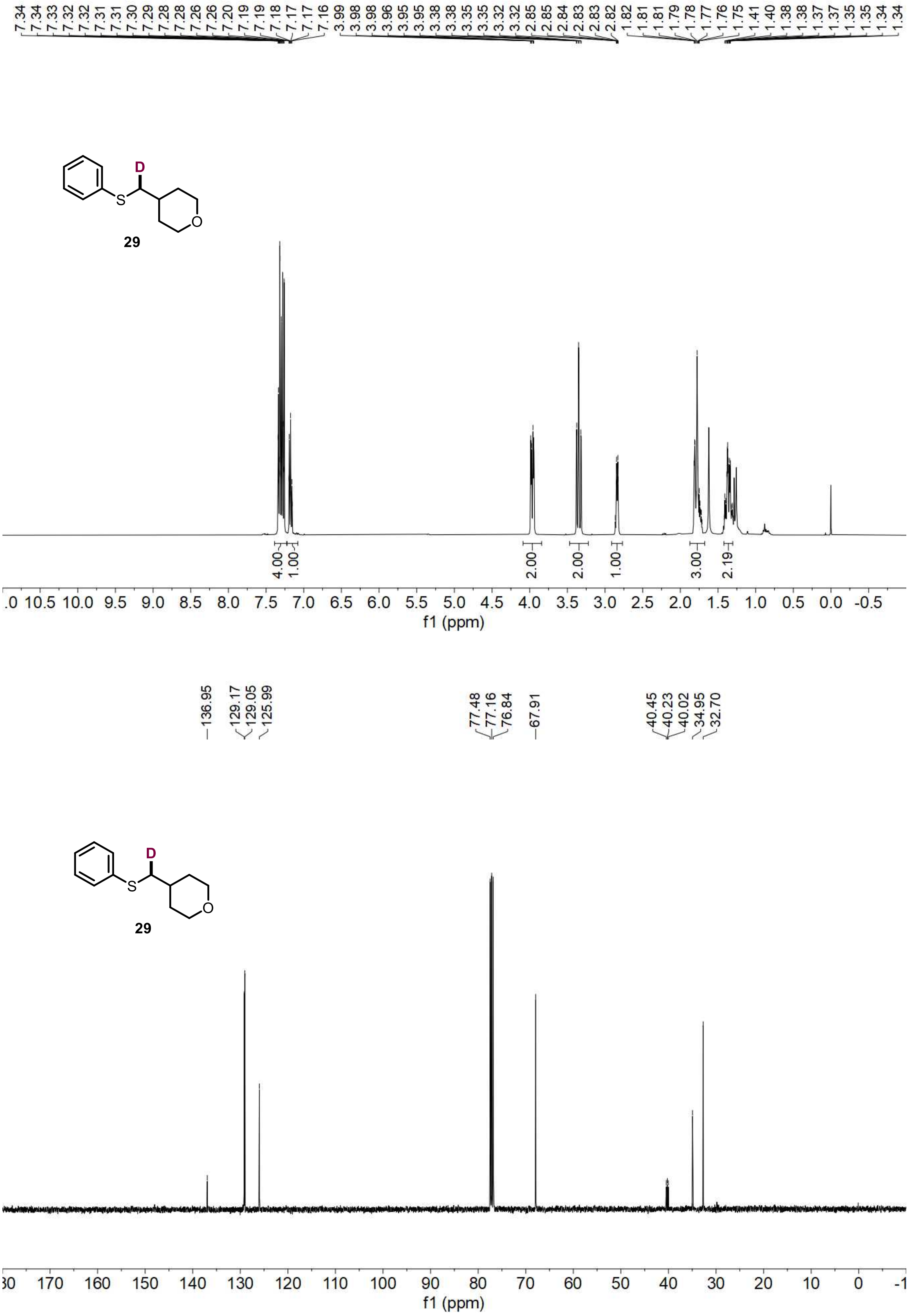
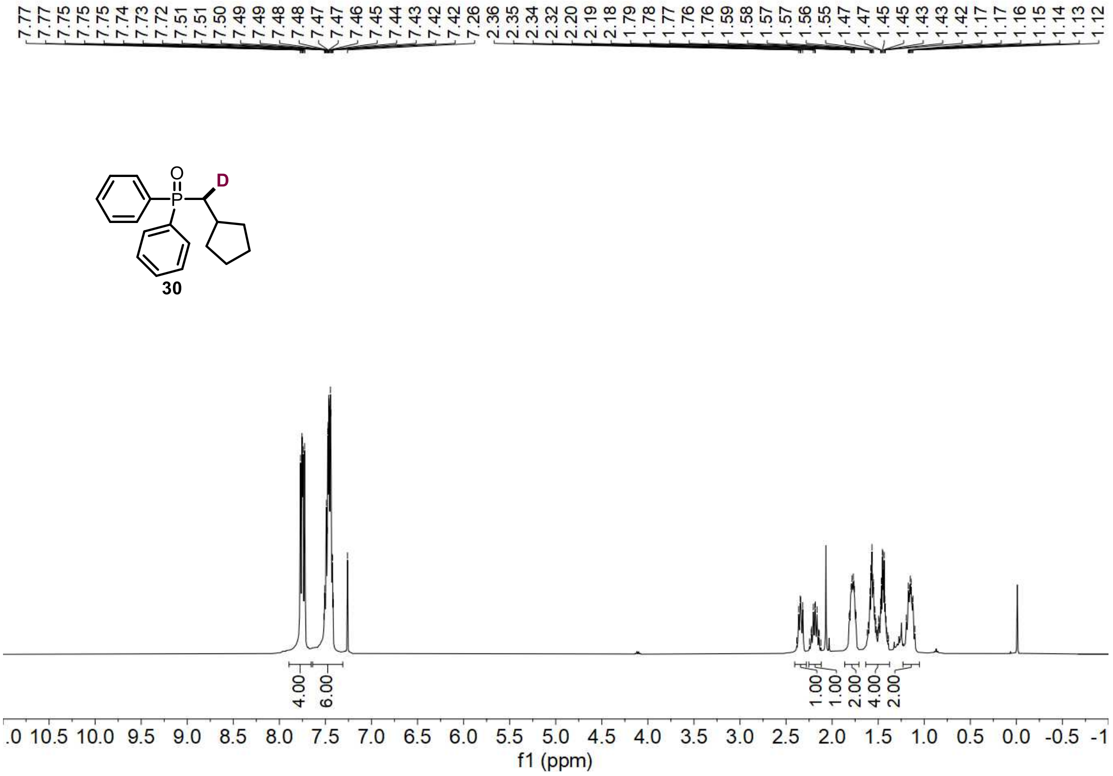


Figure S80. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **29**.


7.77
7.77
7.75
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7.51
7.51
7.50
7.49
7.49
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7.48
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1.17
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1.14
1.13
1.12
O
P
D
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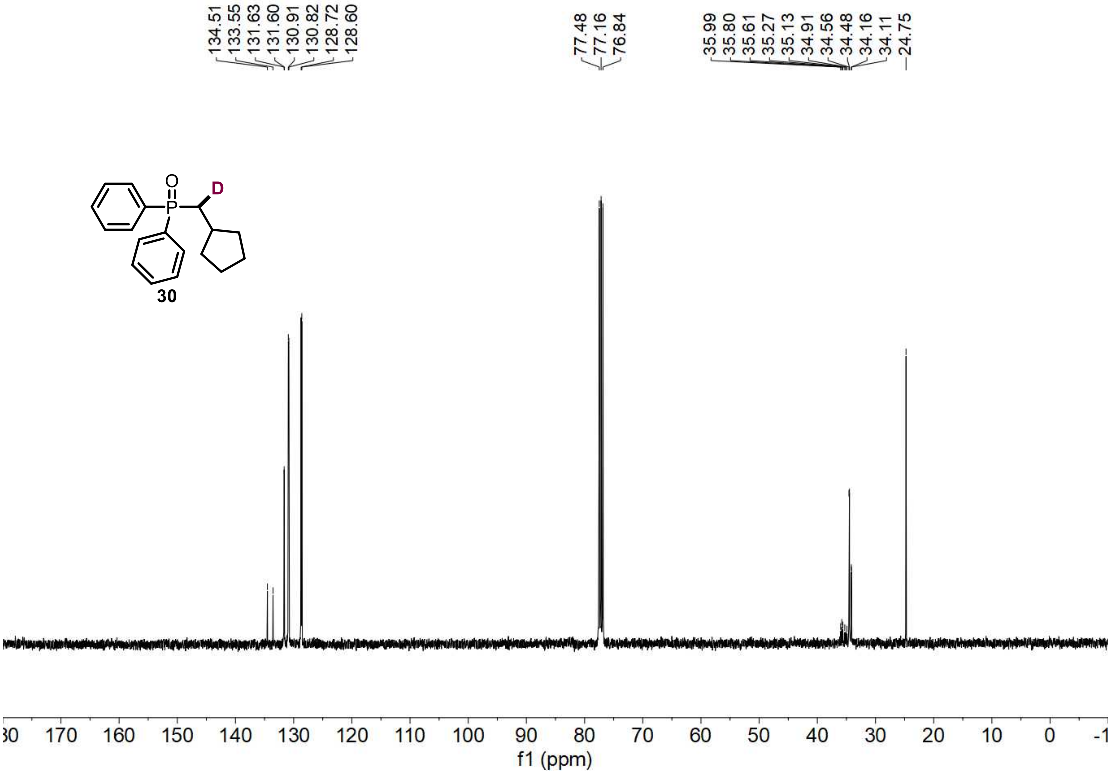
6.00
1.00
1.00
2.00
4.00
2.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


134.51
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128.60
77.48
77.16
76.84
35.99
35.80
35.61
35.27
35.13
34.91
34.56
34.48
34.16
34.11
24.75
O
P
D
30
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

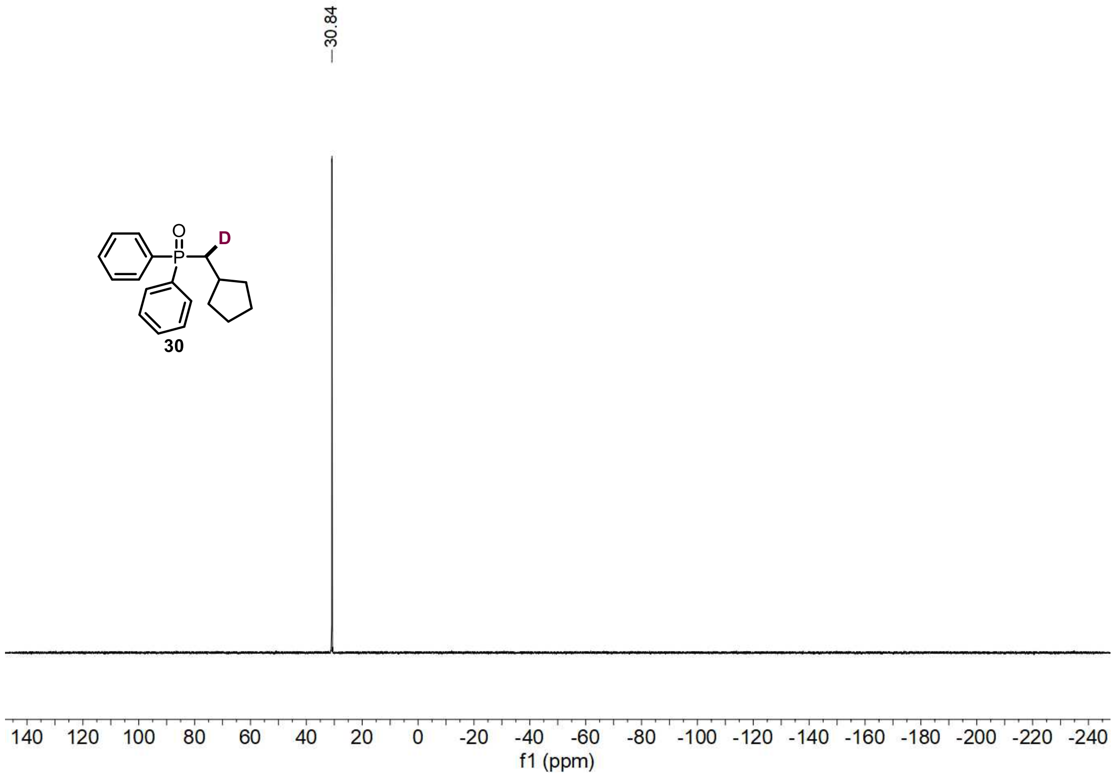
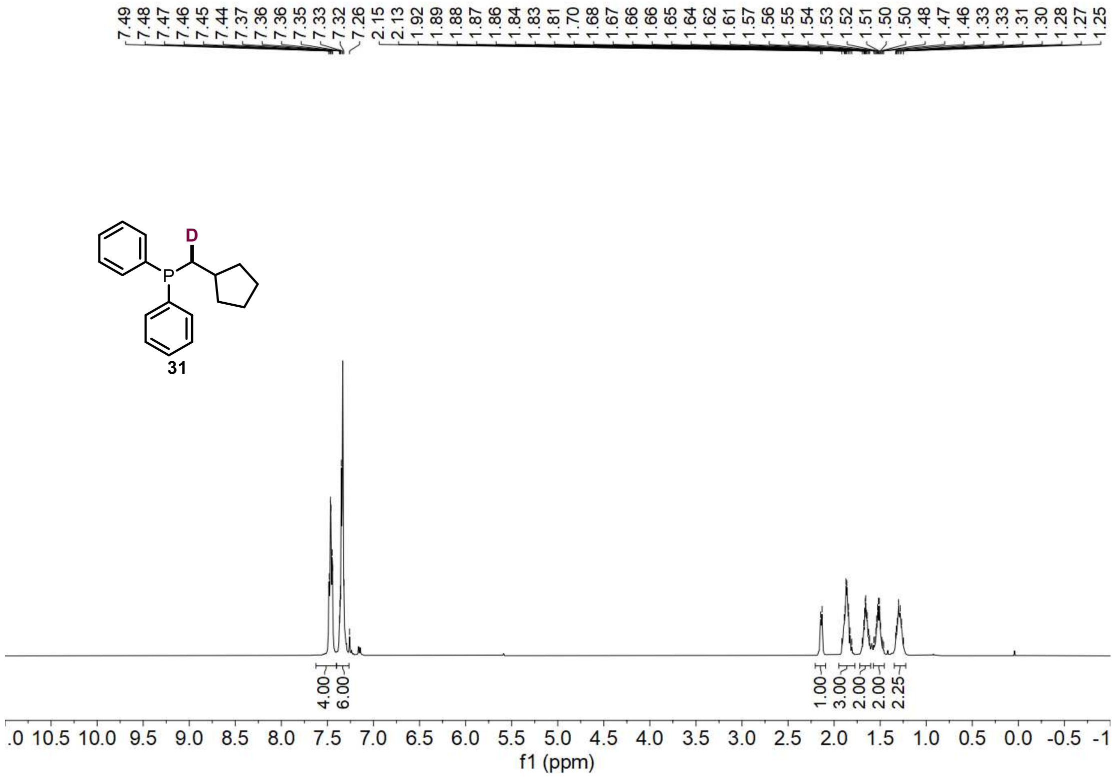


Figure S81. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **30**.



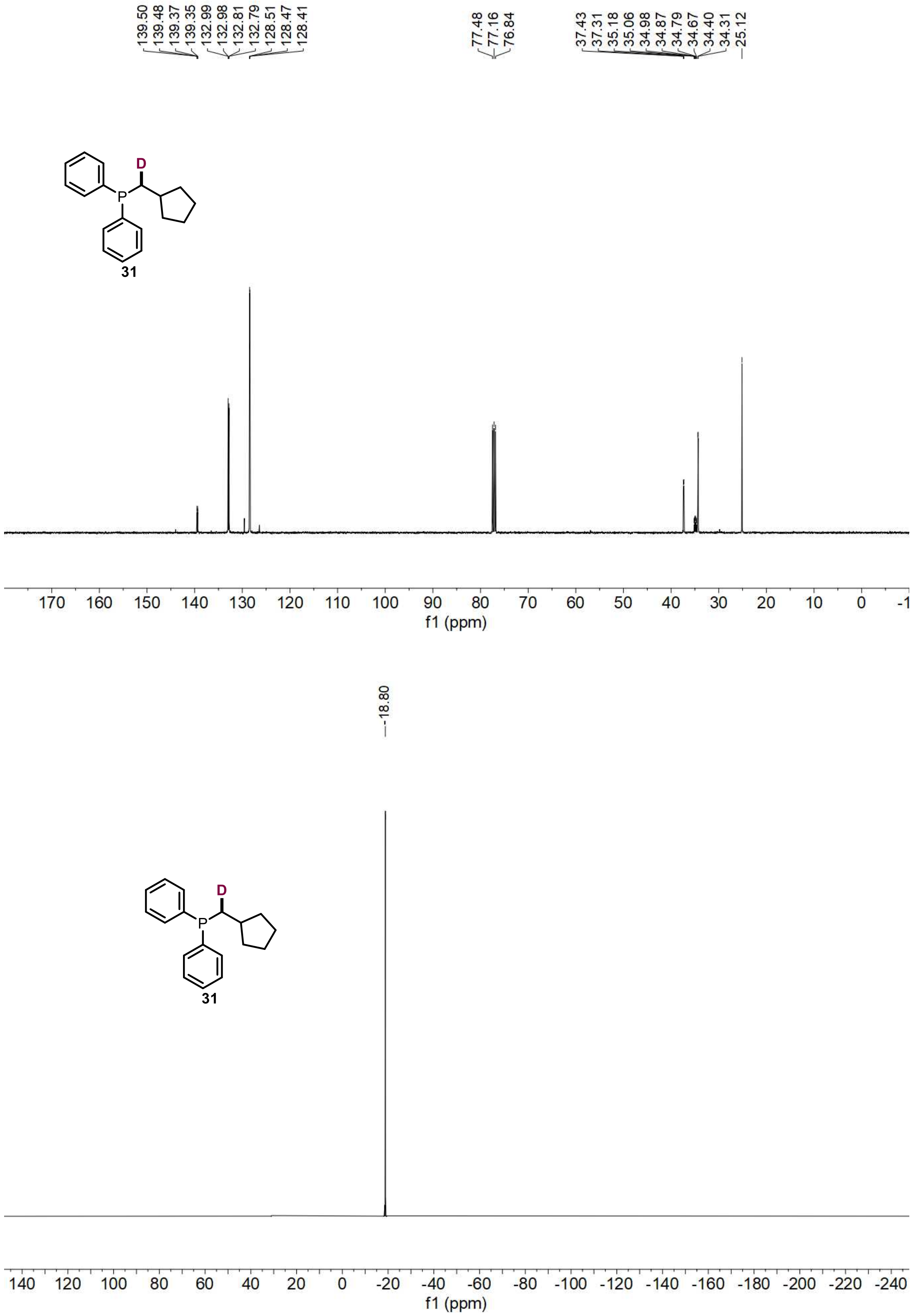
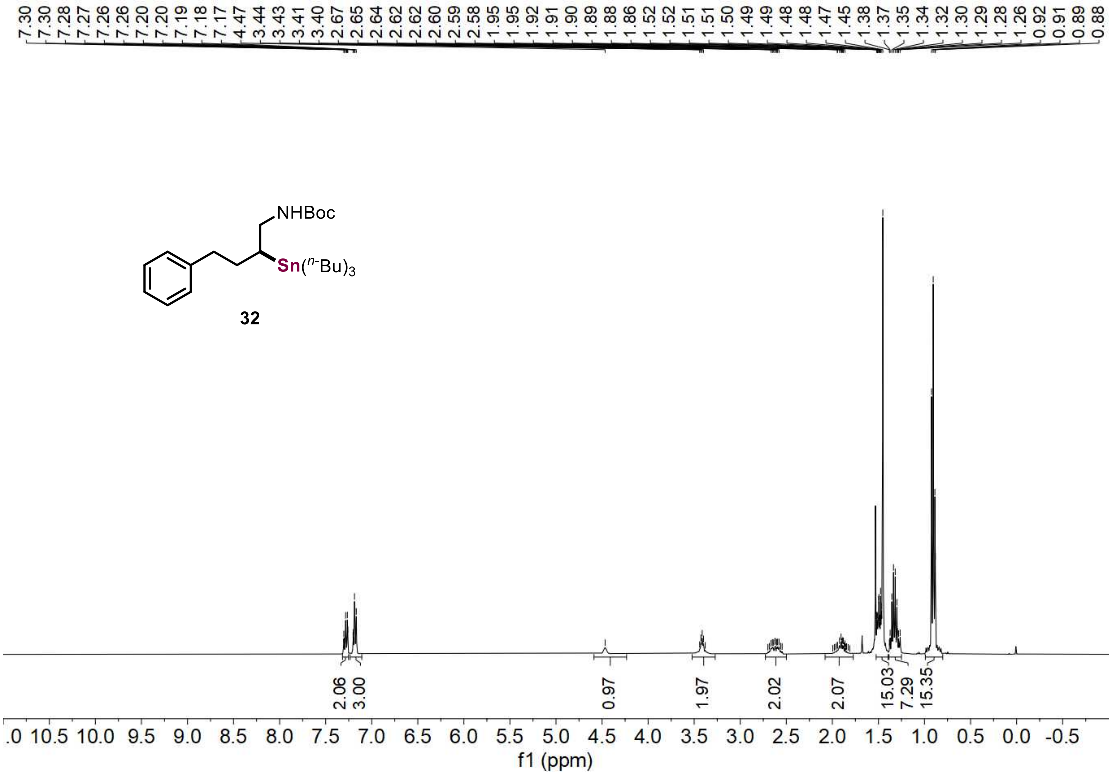


Figure S82. ^{1}H (400 MHz, CDCl$_3$), ^{13}C (100 MHz, CDCl$_3$) and ^{31}P (162 MHz, CDCl$_3$) NMR spectra for compound **31**.



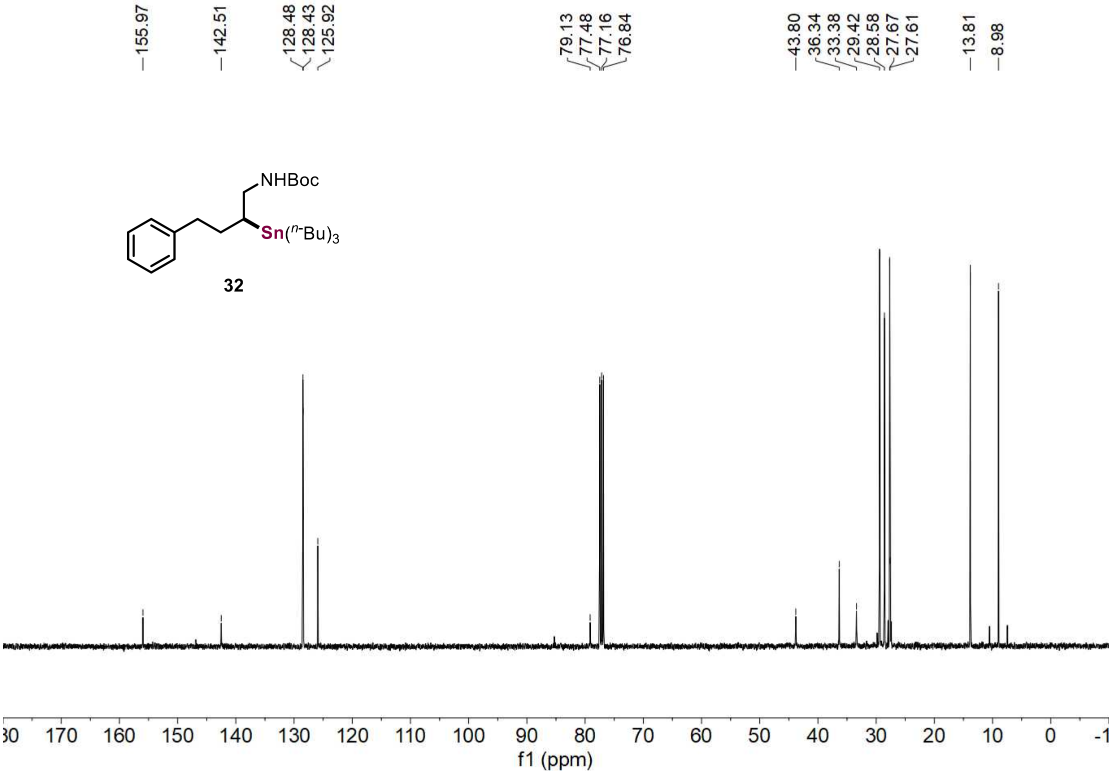


Figure S83. ^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR spectra for compound **32**.

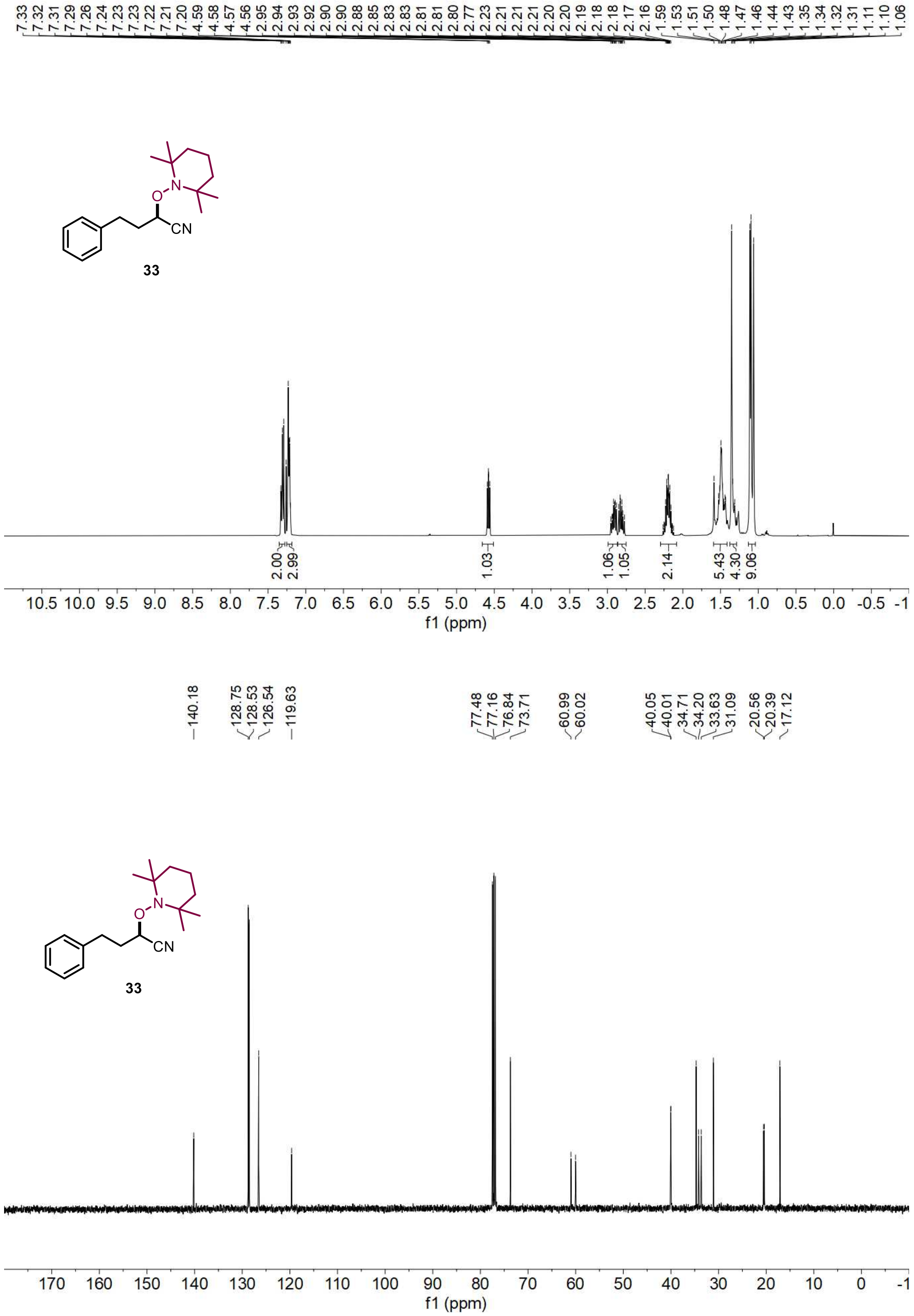


Figure S84. ^{1}H (400 MHz, CDCl$_3$) and ^{13}C (100 MHz, CDCl$_3$) NMR spectra for compound **33**.