Catalytic Dehydrogenative Stannylation of C(sp)–H Bonds Involving Cooperative Sn–H Bond Activation of Hydrostannanes

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Supporting Information

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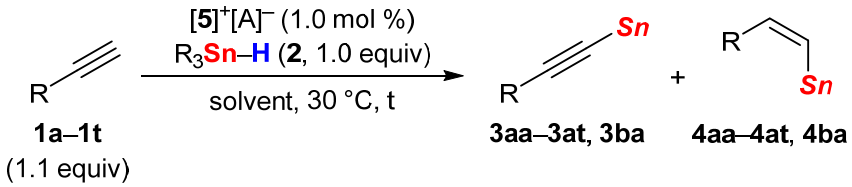
1 General Information

All reactions were performed in flame-dried glassware using a *MBraun* glove box (O_2 < 1.0 ppm, H_2O < 0.5 ppm) or conventional Schlenk techniques under a static pressure of argon (glove box) or nitrogen gas. Liquids and solutions were transferred with syringes or pipettes in the glove box. C_6H_6, CH_2Cl_2, and *n*-pentane were purified and dried using a *MBraun* solvent system. Technical grade solvents (*n*-pentane and Et_3N) were distilled prior to use. Tetracosane was purchased from commercially sources, dried via azeotropic distillation (benzene), degassed, and stored in a glove box. Alkynes **1a**–**1u**, *n*Bu_3SnH (**2a**), and Ph_3SnH (**2c**) were purchased from commercially sources. Liquid alkynes and *n*Bu_3SnH (**2a**) were freshly distilled and degassed prior to use. Ph_3SnH (**2c**) was degassed prior to use. Solid alkynes were dissolved in *n*-pentane and filtered over neutral Al_2O_3 (Brockmann Grade I, 58 Å, 60 mesh) by *Alfa Aesar* prior to use. We note that these purifications are absolutely crucial for the success of these dehydrogenative couplings as otherwise significant amounts of hydrostannylated products are formed. If not noted otherwise, the ratio of products was determined by GLC analysis. Et_3SnH (**2b**) was prepared according to a literature procedure.[S1] The ruthenium(II) chloride precatalysts as well as catalysts [**5a**]$^+$[$BAr^F{}_4$]$^-$, [**5b**]$^+$[$BAr^F{}_4$]$^-$, [**5b**]$^+$[$B(C_6F_5)_4$]$^-$, and [**5d**]$^+$[$BAr^F{}_4$]$^-$ were prepared according to literature procedures.[S2] C_6D_6 (purchased from *Eurisotop*) was stored over 4Å molecular sieves. CD_2Cl_2 was degassed and stored in a glove box over 4Å molecular sieves. ^1H, ^{11}B, ^{13}C, ^{19}F, ^{31}P, and ^{119}Sn NMR spectra were recorded in C_6D_6 or CD_2Cl_2 on *Bruker* AV 400, *Bruker* AV 500, and *Bruker* AV 700 instruments. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane and are referenced to the residual solvent resonance as the internal standard (C_6D_5H: δ = 7.16 ppm for ^1H NMR and C_6D_6: δ = 128.1 for ^{13}C NMR, and $CDHCl_2$: δ = 5.32 ppm for ^1H NMR and 53.8 ppm for ^{13}C NMR). ^{11}B, ^{19}F, ^{31}P, and ^{119}Sn NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of trimethylsilane as primary reference.[S3] Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetrical multiplet), coupling constant (Hz), and integration. For the hydrostannane adducts and the alkyne adducts integrals of protons overlayed by excess of R_3SnH, alkyne or the solvent are labeled with Δ. The assignment of atoms 2 and 6, 2'' and 6'' as well as 3'' and 5'' of the DmpS ligand [DmpS = 2,6-bis(2,4,6-trimethylphenyl)phenylthiolate] in the adducts was not possible. High-resolution mass spectrometry (HRMS) was performed by the Analytical Facility of the *Institut für Chemie, Technische Universität Berlin*. Gas liquid chromatography (GLC) was performed on an *Agilent*

Technologies 7890A gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 250 °C, detector temperature 300 °C, flow rate 1.7 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Infrared (IR) spectra were recorded on a *Jasco FT/IR-4100* spectrophotometer equipped with a FT-IR unit and are reported as wave numbers (cm^{-1}). Data are reported as follows: absorption, intensity (w = weak, m = medium, s = strong, vs = very strong).

2 General Procedures (GPs)

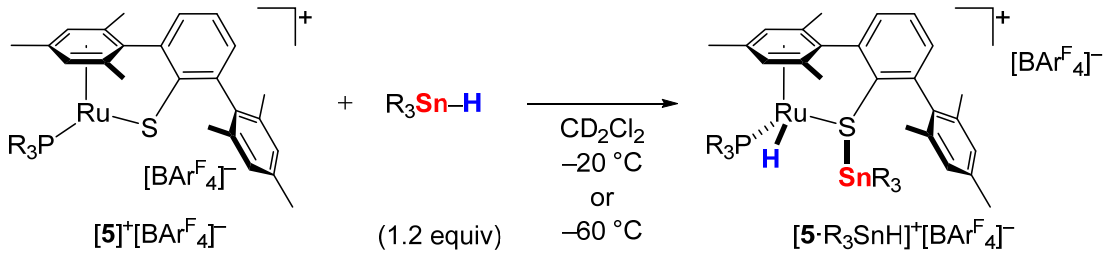
2.1 GP 1: Dehydrogenative Stannylation of Alkynes



Scheme S1 Dehydrogenative stannylation of alkynes.

In a glove box, a 2-mL screw-capped vial is charged with catalyst $[\mathbf{5}]^+[A]^-$ (2.0 µmol, 1.0 mol %), tetracosane as internal standard (1 mg), the solvent (1M), hydrostannane **2** (0.20 µmol, 1.0 equiv), and alkyne **1** (0.22 mmol, 1.1 equiv). The vial is sealed and stirred using a stir bar for 24 h to 48 h at 30 °C. The reaction is quenched using a solution of Et_3N in *n*-pentane (1%). Filtration over a plug of neutral Al_2O_3 and Celite yields after evaporation of the solvents the pure alkynyl stannanes **3aa**–**3at** and **3ba** with the corresponding alkenyl stannanes **4aa**–**4at** and **4ba**.

2.2 GP 2: NMR Investigations of Sulfur-Stabilized Stannylium Ions $[\mathbf{5}\cdot R_3SnH]^+[BAr^F{}_4]^-$

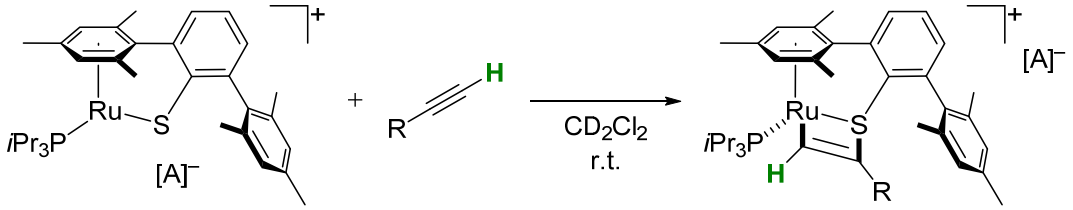


$[\mathbf{5}]^+[BAr^F{}_4]^-$ $[\mathbf{5}\cdot R_3SnH]^+[BAr^F{}_4]^-$

Scheme S2 NMR investigations of sulfur-stabilized stannylium ions.

In a glove box, a J. Young NMR tube is charged with ruthenium(II) thiolate complex $[\mathbf{1}]^+[A]^-$ (14 µmol, 1.0 equiv), CD_2Cl_2 (0.5 mL), and hydrostannane **2** (17 µmol, 1.2 equiv). The tube is sealed, cooled to –78 °C, shaken vigorously until the green solution turns yellow, and directly subjected to NMR analysis at –20 °C or –60 °C.

2.3 GP 3: NMR Investigations of Adducts [5b·RCCH]$^+$[A]$^-$



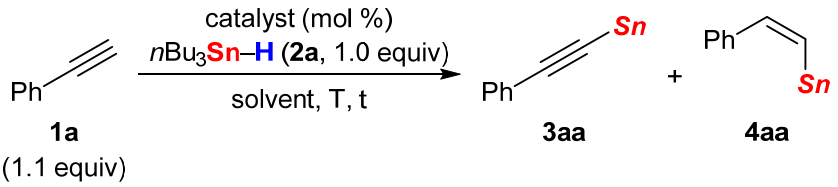
[**5b**]$^+$[A]$^-$ (1.2 equiv) [**5b**·RCCH]$^+$[A]$^-$

Scheme S3 NMR investigations of the alkyne adducts.

In a glove box, a J. Young NMR tube is charged with ruthenium(II) thiolate complex [**1**]$^+$[A]$^-$ (14 µmol, 1.0 equiv), CD_2Cl_2 (0.5 mL), and alkyne **1** (17 µmol, 1.2 equiv). The tube is sealed, shaken vigorously until the green solution turns yellow, and directly subjected to NMR analysis.

3 Detailed Optimization Studies

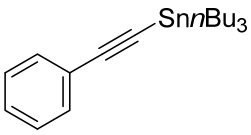
Table S1 Catalyst screening and optimizations[a]



entry	catalyst	mol %	R_3SnH	solvent	T (°C)	t (h)	**3aa**:**4aa**	conv. (%)
1[13]	NaOH	10	*n*Bu_3SnH	DME	80	72	dec.	>99
2[13]	KO*t*Bu	10	*n*Bu_3SnH	DME	80	72	dec.	>99
3[13]	NaO*t*Bu	10	*n*Bu_3SnH	DME	80	72	dec.	>99
4	[**5a**]$^+$[BAr^F_4]$^-$	1.0	*n*Bu_3SnH	CH_2Cl_2	30	18	>99:1	32
5	[**5b**]$^+$[BAr^F_4]$^-$	1.0	*n*Bu_3SnH	CH_2Cl_2	30	18	>99:1	>99
6	[**5c**]$^+$[BAr^F_4]$^-$	1.0	*n*Bu_3SnH	CH_2Cl_2	30	18	>99:1	80
7	[**5d**]$^+$[BAr^F_4]$^-$	1.0	*n*Bu_3SnH	CH_2Cl_2	30	18	96:4	32
8	[**5b**]$^+$[$B(C_6F_5)_4$]$^-$	1.0	*n*Bu_3SnH	CH_2Cl_2	30	18	>99:1	>99
9[c]	[**5b**]$^+$[$B(C_6F_5)_4$]$^-$	1.0	*n*Bu_3SnH	CH_2Cl_2	30	18	>99:1	>99
10	[**5b**]$^+$[$B(C_6F_5)_4$]$^-$	1.0	*n*Bu_3SnH	PhF	30	18	>99:1	98
11	[**5b**]$^+$[$B(C_6F_5)_4$]$^-$	1.0	*n*Bu_3SnH	PhCl	30	18	99:1	99
12	[**5b**]$^+$[$B(C_6F_5)_4$]$^-$	1.0	*n*Bu_3SnH	PhH	30	18	>99:1	53
13	[**5b**]$^+$[$B(C_6F_5)_4$]$^-$	1.0	*n*Bu_3SnH	*n*-C_7H_{16}	30	18	–	3
14	[**5b**]$^+$[BAr^F_4]$^-$	1.0	Et_3SnH	CH_2Cl_2	30	24	93:7	>99
15	[**5b**]$^+$[BAr^F_4]$^-$	1.0	Ph_3SnH	CH_2Cl_2	30	24	dec.	90

[a]All reactions were performed according to **GP 1**, if not otherwise noted. dec. = decomposition. [c]Catalyst was prepared *in situ*.

4 Experimental Details for the Preparation of Alkynyl Stannanes 3aa–3at, 3baTributyl(phenylethynyl)stannane (3aa)



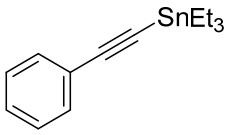
3aa
$C_{20}H_{32}Sn$
M = 391.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[BAr$^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu$_3$SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and phenyl acetylene (**1a**, 23 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3aa** (70 mg, 0.18 mmol, 90%) as a colorless oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 1.06 (t, ^3J = 7.9 Hz, $^2J_{H,^{119}Sn}$ = 53.4 Hz, 6H), 1.34–1.44 (m$_c$, 6H), 1.58–1.78 (m, $^3J_{H,^{119}Sn}$ = 59.2 Hz, 6H), 6.90–7.00 (m, 3H), 7.54–7.58 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 382.4 Hz, $^1J_{C,^{117}Sn}$ = 365.4 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 60.1 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.6 Hz), 93.3, 110.9, 124.9, 128.5, 132.3, 147.1. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –66.2. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2918 (m), 2135 (w), 1487 (m), 754 (s), 689 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 335.0816, found 335.0821.

The same reaction performed on a 1.0 mmol scale delivered the pure alkynyl stannane **3aa** as pale yellow oil in 91% yield.

The spectroscopic data are in accordance with those of the literature.[S4]

4.2 Triethyl(phenylethynyl)stannane (3ba)

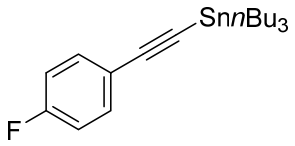


3ba
$C_{14}H_{20}Sn$
M = 307.0 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[B(C_6F_5)$_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using Et_3SnH (**2b**, 42 mg, 0.20 mmol, 1.0 equiv) and phenyl acetylene (**1a**, 23 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3ba** (41.0 mg, 0.13 mmol, 66%) as a colorless oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.94 (q, $^3J_{H,H}$ = 8.0 Hz, $^2J_{H,^{119}Sn}$ = 51.5 Hz, 6H), 1.28 (t, $^3J_{H,H}$ = 8.0 Hz, $^2J_{H,^{119}Sn}$ = 83.0 Hz, $^2J_{H,^{117}Sn}$ = 78.9 Hz, 9H), 6.85–7.02 (m, 3H), 7.45–7.65 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 2.6 ($^1J_{C,^{119}Sn}$ = 388.0 Hz, $^1J_{C,^{117}Sn}$ = 372.0 Hz), 11.1 ($^2J_{C,^{119}Sn}$ = 27.0 Hz), 92.6, 111.1, 124.8, 128.5, 132.3 148.6. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –51.5. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2944 (m), 2908 (m), 2867 (m), 2135 (w), 1487 (m), 1210 (w), 1010 (m), 755 (s), 665 (s), 510 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 279.0190, found 279.0204.

The spectroscopic data are in accordance with those of the literature.[S5]

4.3 Tributyl((4-fluorophenyl)ethynyl)stannane (3ab)

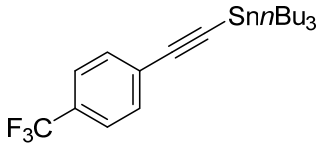


3ab
$C_{20}H_{31}FSn$
M = 409.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$B(C_6F_5)_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 1-ethynyl-4-fluorobenzene (**1b**, 27 mg, 0.22 mmol, 1.2 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3ab** (74 mg, 0.18 mmol, 90%) as a colorless oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.98–1.14 (m, $^2J_{H,^{119}Sn}$ = 53.5 Hz, 6H), 1.25–1.50 (m_c, 6H), 1.58–1.78 (m, $^3J_{H,^{119}Sn}$ = 59.6 Hz, 6H), 6.54–6.59 (m_c, 2H), 7.28–7.33 (m_c, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 381.9 Hz, $^1J_{C,^{117}Sn}$ = 365.5 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 59.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.5 Hz), 93.0 ($^1J_{C,^{119}Sn}$ = 340.0 Hz, $^1J_{C,^{117}Sn}$ = 326.0 Hz), 109.6 ($^2J_{C,^{119}Sn}$ = 65.3 Hz), 115.6 ($^3J_{C,^{19}F}$ = 22.0 Hz), 120.9 ($^4J_{C,^{19}F}$ = 3.6 Hz), 134.1 ($^3J_{C,^{19}F}$ = 8.2 Hz), 162.6 ($^1J_{C,^{19}F}$ = 248.8 Hz). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –65.9. **^{19}F{^{1}H} NMR** (471 MHz, C_6D_6) δ/ppm = –111.3. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2920 (m), 2138 (w), 1600 (m), 1504 (s), 1464 (m), 1229 (m), 1206 (m), 1154 (m), 834 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 353.0722, found 353.0714.

The spectroscopic data are in accordance with those of the literature.[S6]

4.4 Tributyl((4-(trifluoromethyl)phenyl)ethynyl)stannane (3ac)

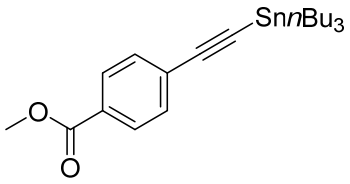


3ac
$C_{21}H_{31}F_3Sn$
M = 459.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[B(C_6F_5)$_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 4-ethynyl-*α,α,α*-trifluorotoluene (**1c**, 38 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 48 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3ac** in a ratio of 99:1 with **4ac** as a yellow oil (75 mg, 0.16 mmol, 82%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.97–1.20 (m, $^2J_{H,^{119}Sn}$ = 53.8 Hz, 6H), 1.20–1.48 (m_c, 6H), 1.50–1.80 (m, $^3J_{H,^{119}Sn}$ = 60.0 Hz, 6H), 7.11 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 7.31 (d, ^3J = 8.0 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 382.0 Hz, $^1J_{C,^{117}Sn}$ = 364.0 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 24.0 Hz), 97.1, 109.2 ($^2J_{C,^{119}Sn}$ = 60.0 Hz), 124.7 (q, $^1J_{C,^{19}F}$ = 272.2 Hz), 125.4 (q, $^3J_{C,^{19}F}$ = 4.0 Hz), 129.7 (q, $^2J_{C,^{19}F}$ = 33.0 Hz), 132.4 (2C). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –64.3. **^{19}F{^{1}H} NMR** (471 MHz, C_6D_6) δ/ppm = –62.6. $\mathbf{R_f}$ = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2957 (m), 2922 (m), 1738 (w), 1613 (m), 1320 (s), 1166 (w), 1127 (s), 1065 (s), 1017 (m), 841 (s), 608 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 403.0690, found 403.0697.

The spectroscopic data are in accordance with those of the literature.[S4]

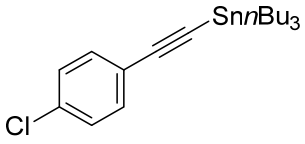
4.5 Methyl 4-((tributylstannyl)ethynyl)benzoate (3ad)



3ad
$C_{22}H_{34}OSn$
M = 449.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$BAr^F{}_4$]$^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 29 mg, 0.10 mmol, 1.0 equiv) and methyl 4-ethynylbenzoate (**1d**, 18 mg, 0.11 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 48 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3ad** in a ratio of >95:5 with **4ad** (determined by ^{1}H NMR spectroscopy) as a colorless oil (34 mg, 0.075 mmol, 75%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.99–1.15 (m, $^2J_{H,^{119}Sn}$ = 53.5 Hz, 6H), 1.24–1.50 (m_c, 6H), 1.58–1.77 (m_c, $^3J_{H,^{119}Sn}$ = 59.3 Hz, 6H), 3.42 (s, 3H), 7.43–7.49 (m, 2H), 7.90–7.94 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 381.6 Hz, $^1J_{C,^{117}Sn}$ = 364.6 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 60.4 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.6 Hz), 51.6, 97.5, 110.1, 129.1, 129.9, 129.9, 132.1, 166.1. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –64.7. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2918 (m), 2849 (m), 2131 (w), 1722 (s), 1603 (m), 1434 (m), 1272 (vs), 1173 (m), 1105 (m), 1017 (m), 768 (s), 694 (m). **HRMS** (APCI) for [M+H]$^+$: calcd *m/z* 451.1654, found 451.1655.

4.6 Tributyl((4-chlorophenyl)ethynyl)stannane (3ae)

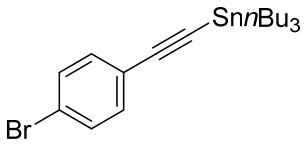


3ae
$C_{20}H_{31}ClSn$
M = 425.6 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex $[\mathbf{5b}]^+[B(C_6F_5)_4]^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 1-chloro-4-ethynylbenzene (**1e**, 30 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3ae** in a ratio of 96:4 with **4ae** as a yellow oil (74 mg, 0.17 mmol, 86%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.96–1.14 (m, $^2J_{H,^{119}Sn}$ = 53.7 Hz, 6H), 1.23–1.52 (m_c, 6H), 1.56–1.78 (m, $^3J_{H,^{119}Sn}$ = 60.3 Hz, 6H), 6.85–6.90 (m, 2H), 7.20–7.26 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 382.0 Hz, $^1J_{C,^{117}Sn}$ = 365.0 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 24.0 Hz), 94.8, 109.6 ($^2J_{C,^{119}Sn}$ = 63.0 Hz), 123.2, 128.9, 133.4, 134.1. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –65.5. $\mathbf{R_f}$ = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2919 (m), 2136 (w), 1486 (s), 1207 (w), 1094 (m), 1014 (m), 826 (s), 645 (s). **HRMS** (EI) for $[M–n\text{Bu}]^+$: calcd *m/z* 369.0427, found 369.0422.

The spectroscopic data are in accordance with those of the literature.[S7]

4.7 ((4-Bromophenyl)ethynyl)tributylstannane (3af)

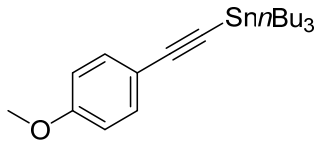


3af
$C_{20}H_{31}BrSn$
M = 470.1 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[B(C_6F_5)$_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 1-bromo-4-ethynylbenzene (**1f**, 40 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3af** in a ratio of >95:5 with **4af** (determined by ^{1}H NMR spectroscopy) as a yellow oil (78.0 mg, 0.17 mmol, 83%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.96–1.18 (m, $^2J_{H,^{119}Sn}$ = 54.1 Hz, 6H), 1.22–1.52 (m_c, 6H), 1.53–1.78 (m, $^3J_{H,^{119}Sn}$ = 60.6 Hz, 6H), 6.99–7.06 (m, 2H), 7.10–7.20 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 382.0 Hz, $^1J_{C,^{117}Sn}$ = 364.0 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 59.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.0 Hz), 95.0, 109.6, 122.3, 123.6, 131.8, 133.6. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –65.3. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2954 (m), 2919 (m), 2137 (w), 1483 (s), 1206 (w), 1070 (m), 1010 (m), 882 (s), 611 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 412.9921, found 412.9916.

The spectroscopic data are in accordance with those of the literature.[S4]

4.8 Tributyl((4-methoxyphenyl)ethynyl)stannane (3ag)

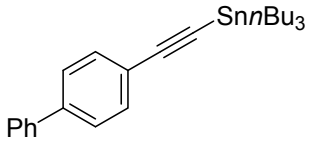


3ag
$C_{21}H_{34}OSn$
M = 421.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$B(C_6F_5)_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 4-ethynylanisole (**1g**, 29 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 48 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3ag** in a ratio of 96:4 with **4ag** as a yellow oil (72 mg, 0.17 mmol, 85%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.98–1.15 (m, $^2J_{H,^{119}Sn}$ = 53.3 Hz, 6H), 1.29–1.46 (m_c, 6H), 1.60–1.80 (m_c, $^3J_{H,^{119}Sn}$ = 59.3 Hz, 6H), 3.16 (s, 3H), 6.53–6.58 (m, 2H), 7.48–7.52 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 382.9 Hz, $^1J_{C,^{117}Sn}$ = 365.2 Hz), 13.9, 27.4 ($^2J_{C,^{119}Sn}$ = 58.4 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.5 Hz), 54.7, 91.1, 111.0, 114.2, 117.1, 133.7, 159.8. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –67.1. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2954 (m), 2919 (m), 2132 (w), 1604 (m), 1506 (s), 1245 (s), 1035 (s), 830 (s), 727 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 365.0922, found 365.0921.

The spectroscopic data are in accordance with those of the literature.[S4]

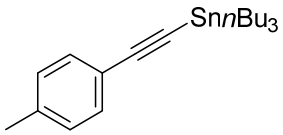
4.10 ([1,1'-biphenyl]-4-ylethynyl)tributylstannane (3ah)



3ah
$C_{26}H_{36}Sn$
M = 467.3 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[B(C_6F_5)$_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 4-ethynylbiphenyl (**1h**, 40 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3ah** in a ratio of 97:3 with **4ah** as a yellow oil (85 mg, 0.18 mmol, 90%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.99–1.24 (m, $^2J_{H,^{119}Sn}$ = 53.5 Hz, 6H), 1.25–1.60 (m_c, 6H), 1.61–1.84 (m, $^3J_{H,^{119}Sn}$ = 60.1 Hz, 6H), 7.06–7.12 (m, 1H), 7.13–7.20 (m, 2H), 7.23–7.28 (m_c, 2H), 7.28–7.34 (m, 2H), 7.56–7.66 (m_c, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.1 ($^1J_{C,^{119}Sn}$ = 382.0 Hz, $^1J_{C,^{117}Sn}$ = 364.0 Hz), 13.6, 27.0 ($^2J_{C,^{119}Sn}$ = 59.0 Hz), 29.0 ($^3J_{C,^{119}Sn}$ = 23.0 Hz), 93.8, 110.5, 123.4, 126.9, 127.0, 127.3, 128.6, 132.4, 140.4, 140.6. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –66.1. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2954 (m), 2919 (m), 2131 (w), 1483 (m), 1073 (w), 1007 (w), 838 (s), 762 (s), 695 (s), 577 (s). **HRMS** (EI) for [($C_{26}H_{36}{}^{116}$Sn)-*n*Bu]$^+$: calcd *m/z* 407.1125, found 407.1141.

4.11 Tributyl(4-tolylethynyl)stannane (3ai)

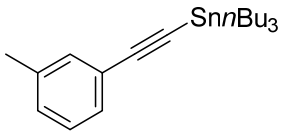


3ai
$C_{21}H_{34}Sn$
M = 405.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$BAr^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and *p*-ethynyltoluene (**1i**, 25 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded alkynyl stannane **3ai** in a ratio of 97:3 with **4ai** as a yellow oil (70 mg, 0.17 mmol, 86%). **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.98–1.15 (m, $^2J_{H,^{119}Sn}$ = 53.6 Hz, 6H), 1.34–1.44 (m_c, 6H), 1.59–1.79 (m, $^3J_{H,^{119}Sn}$ = 59.7 Hz, 6H), 1.96 (s, 3H), 6.79 (d, ^3J = 7.7 Hz, 2H), 7.52 (d, ^3J = 8.0 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 381.7 Hz, $^1J_{C,^{117}Sn}$ = 365.7 Hz), 13.9, 21.3, 27.4 ($^2J_{C,^{119}Sn}$ = 59.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.3 Hz), 92.3, 111.2, 122.0, 129.3, 132.3, 138.0. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –66.7. $\mathbf{R_f}$ = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2919 (m), 2134 (w), 1507 (m), 815 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 349.0973, found 349.0975.

The spectroscopic data are in accordance with those of the literature.[S8]

4.12 Tributyl(3-tolylethynyl)stannane (3aj)

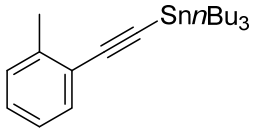


3aj
$C_{21}H_{34}Sn$
M = 405.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[BAr$^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu$_3$SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and *m*-ethynyltoluene (**1j**, 25 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3aj** (70 mg, 0.17 mmol, 86%) as a yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.98–1.16 (m, $^2J_{H,^{119}Sn}$ = 53.8 Hz, 6H), 1.34–1.44 (m$_c$, 6H), 1.58–1.78 (m, $^3J_{H,^{119}Sn}$ = 59 Hz, 6H), 1.95 (s, 3H), 6.80 (d, ^3J = 7.8 Hz, 1H), 6.93 (t, ^3J = 7.7 Hz, 1H), 7.37–7.46 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 381.8 Hz, $^1J_{C,^{117}Sn}$ = 365.6 Hz), 13.9, 21.1, 27.4 ($^2J_{C,^{119}Sn}$ = 59.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.8 Hz), 92.7, 111.2, 124.9, 128.5, 129.0, 129.5, 133.0, 138.0. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –66.4. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2919 (m), 2129 (w), 1463 (m), 781 (s), 690 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 349.0973, found 349.0969.

The spectroscopic data are in accordance with those of the literature.[S4]

4.13 Tributyl(2-tolylethynyl)stannane (3ak)

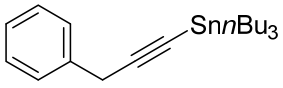


3ak
$C_{21}H_{34}Sn$
M = 405.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and *o*-ethynyltoluene (**1k**, 25 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3ak** (77 mg, 0.19 mmol, 94%) as a yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.93 (t, $^{3}J_{H,H}$ = 7.4 Hz, 9H), 0.98–1.13 (m, $^{2}J_{H,^{119}Sn}$ = 53.4 Hz, 6H), 1.35–1.44 (m_c, 6H), 1.59–1.79 (m, $^{3}J_{H,^{119}Sn}$ = 59.6 Hz, 6H), 2.49 (s, 3H), 6.86–6.92 (m, 1H), 6.92–6.99 (m, 2H), 7.58 (d, ^{3}J = 7.8 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.5 ($^{1}J_{C,^{119}Sn}$ = 381.9 Hz, $^{1}J_{C,^{117}Sn}$ = 365.0 Hz), 13.9, 21.1, 27.4 ($^{2}J_{C,^{119}Sn}$ = 59.0 Hz), 29.4 ($^{3}J_{C,Sn}$ = 23.5 Hz), 97.2, 109.8, 124.7, 125.9, 128.2, 129.7, 132.6, 140.4. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –65.2. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2920 (m), 2130 (w), 1456 (m), 754 (s). **HRMS** (EI) for [M–*n*Bu]$^{+}$: calcd *m/z* 349.0973, found 349.0977.

The spectroscopic data are in accordance with those of the literature.[S4]

4.14 Tributyl(3-phenylprop-1-yn-1-yl)stannane (3al)

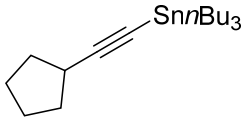


3al
$C_{21}H_{34}Sn$
M = 405.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using nBu_3SnH (**2a**, 57 mg, 0.20 mmol, 1.0 equiv) and prop-2-yn-1-ylbenzene (**1l**, 25 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3al** (71 mg, 0.18 mmol, 88%) as a pale yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^{3}J_{H,H}$ = 7.4 Hz, 9H), 0.94–1.09 (t, $^{3}J_{H,H}$ = 8.1 Hz, $^{2}J_{H,^{119}Sn}$ = 53.5 Hz, 6H), 1.33–1.43 (m, 6H), 1.57–1.77 (m, $^{3}J_{H,^{119}Sn}$ = 59.0 Hz, 6H), 3.53 (s, $^{4}J_{H,^{119}Sn}$ = 10.5 Hz, 2H), 7.00–7.06 (m, 1H), 7.14 (d, $^{3}J_{H,H}$ = 7.7 Hz, 2H), 7.33 (d, $^{3}J_{H,H}$ = 7.7 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.3 ($^{1}J_{C,^{119}Sn}$ = 382.8 Hz, $^{1}J_{C,^{117}Sn}$ = 366.6 Hz), 13.9, 26.9, 27.4 ($^{2}J_{C,^{119}Sn}$ = 58.1 Hz), 29.4 ($^{3}J_{C,Sn}$ = 21.6 Hz), 84.5, 109.0, 126.7, 128.3, 128.6, 137.6. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –68.7. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2954 (m), 2919 (m), 2870 (m), 2850 (m), 2153 (w), 1453 (m), 727 (s), 694 (vs). **HRMS** (EI) for [M–*n*Bu]$^{+}$: calcd *m/z* 349.0973, found 349.0988.

The spectroscopic data are in accordance with those of the literature.[S4]

4.15 Tributyl(cyclopentylethynyl)stannane (3am)

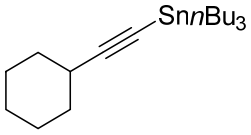


3am
$C_{19}H_{36}Sn$
M = 383.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and cyclopentyl acetylene (**1m**, 21 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3am** (69 mg, 0.18 mmol, 90%) as a yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^{3}J_{H,H}$ = 7.4 Hz, 9H), 0.95–1.08 (m, 6H), 1.22–1.34 (m, 2H), 1.34–1.44 (m_c, 6H), 1.55–1.63 (m, 2H), 1.63–1.70 (m, 6H), 1.70–1.76 (m, 2H), 1.76–1.84 (m, 2H), 2.56–2.70 (q, $^{3}J_{H,H}$ = 7.5 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.3 ($^{1}J_{C,^{119}Sn}$ = 383.4 Hz, $^{1}J_{C,^{117}Sn}$ = 366.5 Hz), 13.9, 25.2, 27.4 ($^{2}J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^{3}J_{C,^{119}Sn}$ = 23.3 Hz), 32.1, 34.8, 80.6, 116.7. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –70.1. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2920 (m), 2146 (w), 1738 (w), 1455 (m), 1376 (m), 1071 (m), 866 (m), 667 (m), 504 (m). **HRMS** (EI) for [M–*n*Bu]$^{+}$: calcd *m/z* 327.1129, found 327.1114.

The spectroscopic data are in accordance with those of the literature.[S4]

4.16 Tributyl(cyclohexylethynyl)stannane (3an)



3an
$C_{20}H_{38}Sn$
M = 397.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[BAr$^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu$_3$SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and cyclohexyl acetylene (**1n**, 24 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3an** (71 mg, 0.18 mmol, 89%) as a yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.95–1.08 (m, 6H), 1.09–1.34 (m, 4H), 1.34–1.44 (m$_c$, 6H), 1.50–1.62 (m, 2H), 1.62–1.72 (m, 8H), 1.72–1.85 (m, 2H), 2.40–2.48 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.3 ($^1J_{C,^{119}Sn}$ = 383.8 Hz, $^1J_{C,^{117}Sn}$ = 366.8 Hz), 13.9, 24.9, 26.3, 27.4 ($^2J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.9 Hz), 30.8, 33.5, 80.9, 116.5. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –69.5. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (m), 2926 (s), 2852 (m), 2147 (w), 1448 (m), 1064 (w), 956 (w), 664 (m), 582 (m). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 341.1286, found 341.1288.

The spectroscopic data are in accordance with those of the literature.[S9]

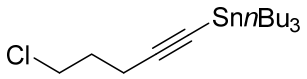
4.17 Tributyl(hex-1-yn-1-yl)stannane (3ao)

3ao
$C_{18}H_{36}Sn$
M = 371.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 1-hexyne (**1o**, 18 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3ao** (68 mg, 0.18 mmol, 92%) as a colorless oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.80 (t, $^{3}J_{H,H}$ = 7.2 Hz, 3H), 0.92 (t, $^{3}J_{H,H}$ = 7.4 Hz, 9H), 0.95–1.10 (m, 6H), 1.20–1.55 (m, 10H), 1.55–1.80 (m, $^{3}J_{H,^{119}Sn}$ = 59 Hz, 6H), 2.14–2.22 (m_c, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.3 ($^{1}J_{C,^{119}Sn}$ = 384.3 Hz, $^{1}J_{C,^{117}Sn}$ = 366.3 Hz), 13.8, 13.9, 20.3, 22.2, 27.4 ($^{2}J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^{3}J_{C,^{119}Sn}$ = 23.6 Hz), 31.6, 81.4 ($^{1}J_{C,^{119}Sn}$ = 397.9 Hz, $^{1}J_{C,^{117}Sn}$ = 379.7 Hz), 112.0 ($^{2}J_{C,^{119}Sn}$ = 75.0 Hz). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –70.2. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (s), 2927 (s), 2149 (m), 1464 (m), 1376 (w), 1073 (w), 875 (w), 669 (m). **HRMS** (EI) for [M–*n*Bu]$^{+}$: calcd *m/z* 315.1129, found 315.1131.

The spectroscopic data are in accordance with those of the literature.[S8]

4.18 Tributyl(5-chloropent-1-yn-1-yl)stannane (3ap)

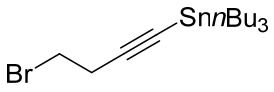


3ap
$C_{17}H_{33}ClSn$
M = 391.6 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$BAr^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 5-chloro-1-pentyne (**1p**, 23 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3ap** (69 mg, 0.17 mmol, 88%) as a pale yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.95–1.10 (m, 6H), 1.25–1.48 (m_c, 6H), 1.50–1.76 (m, 8H), 2.10–2.26 (m, 2H), 3.20–3.40 (t, $^3J_{H,H}$ = 6.5 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.3 ($^1J_{C,^{119}Sn}$ = 383.5 Hz, $^1J_{C,^{117}Sn}$ = 366.7 Hz), 13.9, 17.9, 27.4 ($^2J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 24.0 Hz), 32.1, 43.5, 82.9 ($^1J_{C,^{119}Sn}$ = 377.0 Hz, $^1J_{C,^{117}Sn}$ = 360.0 Hz), 109.7 ($^2J_{C,^{119}Sn}$ = 70.0 Hz). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –69.1. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (s), 2919 (s), 2150 (w), 2022 (w), 1463 (m), 1289 (m), 1073 (w), 864 (w), 658 (m). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 335.0583, found 335.0573.

The spectroscopic data are in accordance with those of the literature.[S4]

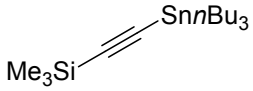
4.19 (4-bromobut-1-yn-1-yl)tributylstannane (3aq)



3aq
$C_{16}H_{31}BrSn$
M = 422.0 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 4-bromo-1-butyne (**1q**, 30 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 48 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3aq** (55 mg, 0.13 mmol, 66%) as a pale yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.93 (t, $^{3}J_{H,H}$ = 7.4 Hz, 9H), 0.95–1.10 (m, 6H), 1.20–1.50 (m_c, 6H), 1.55–1.80 (m, $^{3}J_{H,^{119}Sn}$ = 60.2 Hz, 6H), 2.30–2.50 (m, 2H), 2.90–3.06 (t, $^{3}J_{H,H}$ = 7.0 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.3 ($^{1}J_{C,^{119}Sn}$ = 383.8 Hz, $^{1}J_{C,^{117}Sn}$ = 365.2 Hz), 13.9, 24.8, 27.4 ($^{2}J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^{3}J_{C,^{119}Sn}$ = 24.0 Hz), 30.3, 84.6, 107.9 ($^{2}J_{C,^{119}Sn}$ = 70.0 Hz). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –67.8. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2955 (s), 2920 (s), 2151 (w), 1463 (m), 1209 (m), 982 (w), 875 (w), 665 (s). **HRMS** (EI) for [M–*n*Bu]$^{+}$: calcd *m/z* 364.9921, found 364.9924.

4.20 Trimethyl((tributylstannyl)ethynyl)silane (3ar)

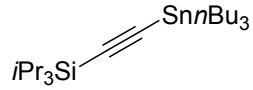


3ar
$C_{17}H_{36}SiSn$
M = 387.3 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[B(C_6F_5)$_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and trimethylsilyl acetylene (**1r**, 22 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 48 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3ar** (68 mg, 0.17 mmol, 87%) as a pale yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.21 (s, 9H), 0.90 (t, $^3J_{H,H}$ = 7.3 Hz, 9H), 0.97 (t, $^3J_{H,H}$ = 7.9 Hz, 6H), 1.22–1.48 (m_c, 6H), 1.48–1.76 (m, $^3J_{H,^{119}Sn}$ = 60.4 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 0.43 ($^1J_{C,^{29}Si}$ = 56.0 Hz), 11.3 ($^1J_{C,^{119}Sn}$ = 380.5 Hz, $^1J_{C,^{117}Sn}$ = 363.4 Hz), 13.9, 27.3 ($^2J_{C,^{119}Sn}$ = 58.0 Hz), 29.3 ($^3J_{C,^{119}Sn}$ = 24.0 Hz), 113.4, 118.9 ($^1J_{C,^{29}Si}$ = 42.0 Hz). **^{29}Si{^{1}H} NMR** (99 MHz, C_6D_6) δ/ppm = –21.0. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –73.6. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2956 (m), 2922 (m), 2150 (w), 1560 (w), 1464 (w), 1376 (w), 1248 (m), 839 (s), 759 (m), 693 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 331.0898, found 331.0908.

The spectroscopic data are in accordance with those of the literature.[S4, S8]

4.21 Triisopropyl((tributylstannyl)ethynyl)silane (3as)

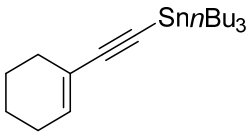


3as
$C_{23}H_{48}SiSn$
M = 471.4 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$BAr^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and (triisopropylsilyl)acetylene (**1s**, 40 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3as** (42 mg, 0.090 mmol, 45%) as a pale yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.88–1.00 (m, 15H), 1.05–1.15 (m, 3H), 1.16–1.26 (m, 18H), 1.30–1.45 (m_c, 6H), 1.56–1.80 (m, $^3J_{H,^{119}Sn}$ = 60.1 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 380.6 Hz, $^1J_{C,^{117}Sn}$ = 362.2 Hz), 11.7, 14.0, 19.0, 27.3 ($^2J_{C,^{119}Sn}$ = 56.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 24.6 Hz), 114.9, 115.1. **^{29}Si{^{1}H} NMR** (99 MHz, C_6D_6) δ/ppm = –3.6. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –71.1. **R_f** = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2956 (m), 2922 (m), 2864 (m), 2150 (w), 1463 (m), 1377 (w), 1073 (w), 995 (w), 882 (m), 712 (s), 671 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 415.1837, found 415.1845.

The spectroscopic data are in accordance with those of the literature.[S10]

4.22 Tributyl(cyclohex-1-en-1-ylethynyl)stannane (3at)

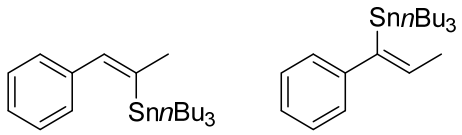


3at
$C_{20}H_{36}Sn$
M = 395.2 g/mol

Prepared according to **GP 1** with ruthenium thiolate complex [**5b**]$^+$[$BAr^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.0 mol %) in CH_2Cl_2 (0.1 mL) using *n*Bu_3SnH (**2a**, 58 mg, 0.20 mmol, 1.0 equiv) and 1-ethynylcyclohexene (**1t**, 24 mg, 0.22 mmol, 1.1 equiv) at 30 °C. The reaction was quenched after 24 h. Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded the pure alkynyl stannane **3at** (67 mg, 0.17 mmol, 84%) as a yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ/ppm = 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 9H), 0.94–1.09 (m, $^2J_{H,^{119}Sn}$ = 53.3 Hz, 6H), 1.25–1.32 (m, 2H), 1.32–1.42 (m_c, 8H), 1.54–1.77 (m, $^3J_{H,^{119}Sn}$ = 59.6 Hz, 6H), 1.77–1.84 (m, 2H), 2.17–2.25 (m, 2H), 6.18–6.26 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.4 ($^1J_{C,^{119}Sn}$ = 383.0 Hz, $^1J_{C,^{117}Sn}$ = 365.9 Hz), 13.9, 21.9, 22.7, 25.8, 27.4 ($^2J_{C,^{119}Sn}$ = 58.0 Hz), 29.4 ($^3J_{C,^{119}Sn}$ = 23.4 Hz), 30.1, 89.3, 113.2, 122.3, 134.4. **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –67.6. $\mathbf{R_f}$ = 0.80 (*n*-pentane). **IR** (ATR): $\tilde{\nu}$/cm^{-1} = 2954 (m), 2923 (s), 2126 (w), 1463 (m), 1376 (m), 1073 (m), 664 (m), 443 (s). **HRMS** (EI) for [M–*n*Bu]$^+$: calcd *m/z* 339.1129, found 339.1133.

The spectroscopic data are in accordance with those of the literature.[S4, S8]

4.23 Tributyl(1-phenylprop-1-en-1-yl)stannane (*β*-(*Z*)-4au) and Tributyl(1-phenylprop-1-en-2-yl)stannane (*α*-(*Z*)-4au)



β-(*Z*)-**4au** : α-(*Z*)-**4au**
75 : 25

$C_{21}H_{36}Sn$
M = 407.2 g/mol

Prepared according to a slightly modified **GP 1** with ruthenium thiolate complex [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ (1.4 mg, 1.0 µmol, 1.2 mol %) in PhCl (0.05 mL) using *n*Bu_3SnH (**2a**, 25 mg, 0.086 mmol, 1.0 equiv) and prop-1-yn-1-ylbenzene (**1u**, 16 mg, 0.14 mmol, 1.6 equiv) at 80 °C. After evaporation of the solvent, NMR analysis of the crude reaction mixture showed a 75:25 ratio of the regioisomers *β*-(*Z*)-**4au** and *α*-(*Z*)-**4au**.

*Spectroscopic data for β-(Z)-**4au**:*

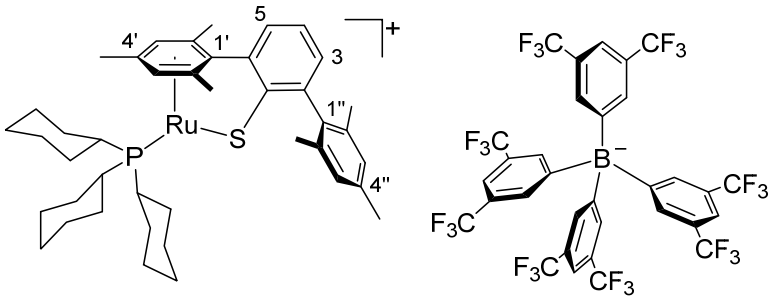
^{1}H NMR (500 MHz, C_6D_6) δ/ppm = 0.85–1.00 (m, 15H$^{\Delta}$, SnCH_2, SnCH_3), 1.27–1.42 (m, 6H$^{\Delta}$, SnCH_2), 1.45–1.67 (m, 6H$^{\Delta}$, SnCH_2), 2.14 (d, $^{4}J_{H,H}$ = 1.7 Hz, $^{3}J_{H,^{119}Sn}$ = 41.5 Hz, 3H, CH_3), 7-02–7.10 (m, 2H, H_{Ar}), 7.12–7.21 (m, 1H$^{\Delta}$, H_{Ar}), 7.24–7.29 (m, 2H, H_{Ar}), 7.37 (bs, $^{3}J_{H,^{119}Sn}$ = 128.0 Hz, 1H, H_{vinyl}). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 11.0 (SnCH_2), 14.0 (SnCH_3), 27.8 (SnCH_2), 28.3 (CH_3), 29.8 (SnCH_2), 127.1 (CH_{Ar}), 128.3 (CH_{Ar}), 128.4 (CH_{Ar}), 141.9 (CH_{vinyl}), 142.0 (C_q) 144.3 (*C*Sn). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –48.6.

*Spectroscopic data for α-(Z)-**4au**:*

^{1}H NMR (500 MHz, C_6D_6) δ/ppm = 1.81 (d, $^{3}J_{H,H}$ =6.7 Hz, 3H, CH_3), 6.35 (q, $^{3}J_{H,H}$ =6.7 Hz, $^{3}J_{H,^{119}Sn}$ = 126.5 Hz, 1H, H_{vinyl}). The butyl groups as well as the aromatic signals are overlapping with the major compound. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ/ppm = 9.1 (SnCH_2), 13.9 (SnCH_2), 20.5 (CH_3), 27.9 (SnCH_2), 29.6 (SnCH_2), 125.7 (CH_{Ar}), 127.3 (CH_{Ar}), 128.6 (CH_{Ar}), 138.5 (CH_{vinyl}), 146.9 (*C*Sn), 148.3 (C_q). **^{119}Sn{^{1}H} NMR** (186 MHz, C_6D_6) δ/ppm = –51.3.

The signals found were different to the reported data of *α-(E)-**4au*** and *β-(E)-**4au***.[S11]

5 2,6-η^6:η^1-Bis(2',4',6'-trimethylphenyl)phenylthiolato](tricyclohexylphosphino)-ruthenium(II)-tetrakis[3,5-bis(trifluormethyl)phenyl]borate ([5c]$^+$[BAr$^F_4$]$^-$)

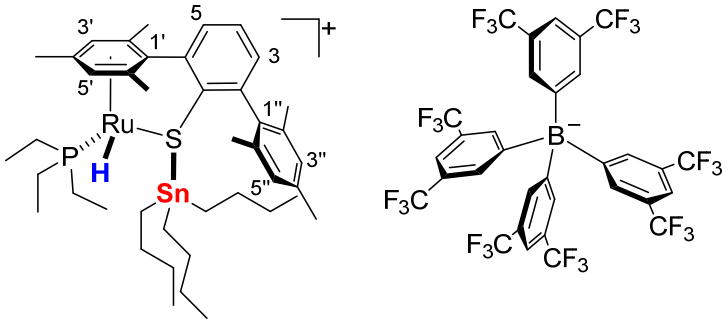


[5c]$^+$[BAr$^F_4$]$^-$
$C_{74}H_{70}PRuSBF_{24}$
M = 1590.3 g/mol

Prepared in a glove box from the neutral chloride[S2g] (50 mg, 66 µmol, 1.0 equiv) and Na$^+$[BAr$^F_4$]$^-$ (55 mg, 79 µmol, 1.2 equiv) in CH_2Cl_2 (8 mL). The reaction mixture was stirred for 3 h at r.t. and filtrated over a PTFE syringe filter. Subsequent evaporation of the solvent afforded complex [**5c**]$^+$[BAr$^F_4$]$^-$ as a green solid (65 mg, 46 µmol, 71%). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ/ppm = 1.01–1.32 (m, 15H, PCH_2), 1.65–1.83 (m, 15H, PCH_2), 1.87 (s, 6H, 2'-CH_3), 1.94 (s, 6H, 2''-CH_3), 2.05–2.17 (m, 3H, PCHCH$_2$), 2.29 (s, 3H, 4''-CH$_3$), 2.35 (s, 3H, 4'-CH$_3$), 4.82 (s, 2H, H-3'), 6.91 (s, 2H, H-3''), 7.39–7.44 (s, 1H, H-3), 7.56 (s, 4H, *o*-BAr$^F_4$), 7.65–7.79 (m, 10H, H-4, H-5, *p*-BAr$^F_4$). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2) δ/ppm = 18.7 (2'-*C*H$_3$), 20.4 (4'-*C*H$_3$, 2''-*C*H$_3$), 21.2 (4''-*C*H$_3$), 26.7 (P*C*H$_2$), 27.7 (d, $^2J_{C,P}$ = 10.9 Hz, P*C*H$_2$), 31.1 (P*C*H$_2$), 34.8 (d, $^1J_{C,P}$ = 20.5 Hz, P*C*H), 72.0 (C-3'), 102.9 (d, $^1J_{C,P}$ = 2.8 Hz, C-2'), 106.9 (C-4'), 109.6 (d, $J_{C,P}$ = 8.9 Hz, C-1'), 117.9 (*p*-*C*H-BAr$^F_4$), 125.1 (q, $^1J_{C,F}$ = 271.8 Hz, *C*F$_3$-BAr$^F_4$), 128.4 (C-3''), 128.4 (C-5), 129.3 (q, $^2J_{C,F}$= 31.9 Hz, *m*-*C*-BAr$^F_4$), 130.3 (C-4), 132.5 (C-3, C-6), 135.2 (*p*-*C*H-BAr$^F_4$), 135.8 (C-2''), 136.0 (C-1''), 138.1 (C-4''), 142.7 (C-2), 162.2 (q, $^1J_{C,B}$= 49.9 Hz, *i*-*C*H-BAr$^F_4$), 163.3 (d, $^3J_{C,P}$ = 8.3 Hz, C-1). **^{11}B NMR** (161 MHz, CD_2Cl_2) δ/ppm = –6.6. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2) δ/ppm = –62.9. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ/ppm = 41.5. **HRMS** (ESI) for [**5c**]$^+$: calcd *m/z* 727.3035, found 727.3055, for [BAr$^F_4$]$^-$: calcd *m/z* 863.0654, found 863.0662.

6 Experimental Details for the NMR Investigations of Sulfur-Stabilized Stannylium Ions $[5{\cdot}R_3SnH]^+[BAr^F{}_4]^-$

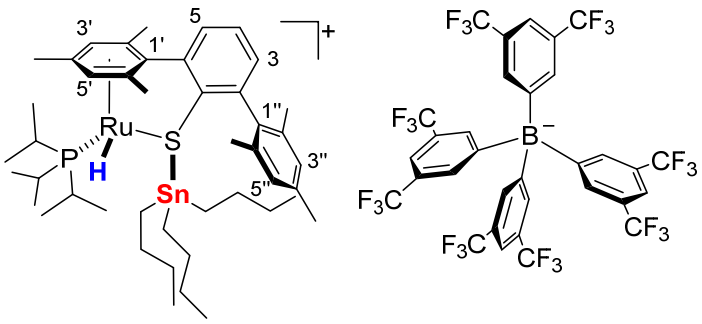
6.1 $[5a{\cdot}n Bu_3SnH]^+[BAr^F{}_4]^-$



$[\mathbf{5a}{\cdot}n Bu_3Sn{-}H]^+[BAr^F{}_4]^-$
$C_{74}H_{80}PRuSBF_{24}Sn$
M = 1719.0 g/mol

Prepared according to **GP 2** from $[\mathbf{5a}]^+[BAr^F{}_4]^-$ (20 mg, 14 µmol, 1.0 equiv) and $n Bu_3SnH$ (**2b**, 5.0 mg, 17 µmol, 1.2 equiv) in CD_2Cl_2 (0.5 mL). **^{1}H NMR** (500 MHz, CD_2Cl_2, 213 K): δ/ppm = –8.59 (d, $^2J_{H,P}$ = 49.7 Hz, 1H, Ru*H*), 0.57–0.86 (m, 15H$^\Delta$, SnCH_2, SnCH_3), 0.85–0.96 (m, 9H, PCH$_2$CH_3), 1.06–1.29 (m, 12H$^\Delta$, SnCH_2), 1.38–1.49 (m, 3H$^\Delta$, PCH_2CH$_{3,A}$), 1.49–1.63 (m, 3H, PCH_2CH$_{3,B}$), 1.84 (s, 6H, 4'-CH_3, 6''-CH_3), 1.91 (s, 3H, 2'-CH_3), 2.02 (s, 3H, 2''-CH_3), 2.12 (s, 3H, 6''-CH_3), 2.27 (s, 3H, 4''-CH_3), 5.32 (s, 1H$^\Delta$, H-3'), 6.05 (s, 1H, H-5'), 6.90 (s, 1H, H-3''), 6.99 (s, 1H, H-5''), 7.12–7.19 (m, 1H, H-3), 7.39–7.49 (m, 2H, H-4, H-5), 7.55 (s, 4H, *p*-C*H*-BAr$^F{}_4$), 7.73 (s, 8H, *o*-C*H*-BAr$^F{}_4$). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 213 K): δ/ppm = 7.2 (d, $^2J_{C,P}$ = 2.5 Hz, PCH$_2$*C*H$_3$), 13.6 (Sn*C*H$_3$), 17.5 (Sn*C*H$_2$), 18.3 (4'-CH$_3$)*, 18.8 (2'-CH$_3$), 19.1 (P*C*H$_2$CH$_3$), 19.4 (6'-CH$_3$)*, 20.7 (4''-CH$_3$), 20.9 (2''-CH$_3$), 21.2 (6''-CH$_3$), 27.0 ($^2J_{C,Sn}$ = 80.2 Hz, Sn*C*H$_2$), 28.2 ($^3J_{C,Sn}$ = 17.2 Hz, Sn*C*H$_2$), 85.2 (C-4'), 91.3 (d, $J_{C,P}$ = 10.0 Hz, C-6'), 91.9 (C-5'), 92.7 (C-3'), 98.6 (C-2'), 114.4 (d, $J_{C,P}$ = 2.7 Hz, C-1'), 117.3 (*p*-*C*H-BAr$^F{}_4$), 124.3 (q, $^1J_{C,F}$ = 272.0 Hz, *C*F$_3$-BAr$^F{}_4$), 127.8 (C-4), 127.9 (C-5), 128.4 (q, $^2J_{C,F}$= 31.9 Hz, *m*-*C*-BAr$^F{}_4$), 128.9 (C-3''), 129.0 (C-5''), 132.2 (C-3), 134.5 (C-1'', *o*-*C*H-BAr$^F{}_4$), 135.4 (C-6''), 136.5 (C-2''), 138.0 (C-4''), 139.6 (C-6), 143.4 (C-2), 143.9 (C-1), 161.5 (q, $^1J_{C,B}$= 49.7 Hz, *i*-*C*-BAr$^F{}_4$). *The peaks are interconvertible. **^{11}B NMR** (161 MHz, CD_2Cl_2, 213 K): δ/ppm = –6.8. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2, 213 K): δ/ppm = –62.5. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2, 213 K): δ/ppm = 42.4. **^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2, 213 K): δ/ppm = 158.6.

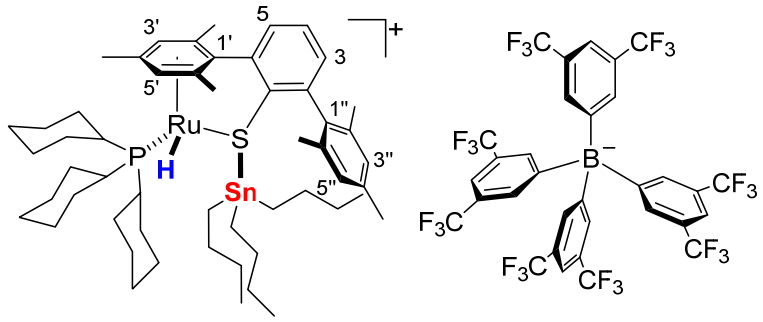
6.2 [5b·*n*Bu$_3$SnH]$^+$[BAr$^F_4$]$^-$



[5a·*n*Bu$_3$Sn–H]$^+$[BAr$^F_4$]$^-$
$C_{77}H_{86}PRuSBF_{24}Sn$
M = 1761.1 g/mol

Prepared according to **GP 2** from [**5b**]$^+$[BAr$^F_4$]$^-$ (20 mg, 15 µmol, 1.0 equiv) and *n*Bu$_3$SnH (**2b**, 5.0 mg, 17 µmol, 1.2 equiv) in CD_2Cl_2 (0.50 mL). **^{1}H NMR** (500 MHz, CD_2Cl_2, 253 K): δ/ppm = –8.35 (d, $^2J_{H,P}$ = 47.6 Hz, 1H, Ru*H*), 0.82 (d, $^2J_{H,H}$ = 7.0 Hz, 9H, SnC*H*$_3$), 1.08–1.33 (m, 36H$^\Delta$, PCHC*H*$_3$, SnC*H*$_2$), 1.82–1.89 (m, 6H, 4'-C*H*$_3$, 6'-C*H*$_3$), 1.94–2.07 (m, 9H, PC*H*CH$_3$, 2'-C*H*$_3$, 2''-C*H*$_3$), 2.17 (s, 3H, 6''-C*H*$_3$), 2.28 (s, 3H, 4''-C*H*$_3$), 5.77–5.84 (bs, 1H, H-3'), 6.14 (s, 1H, H-5'), 6.91 (s, 1H, H-3''), 6.99 (s, 1H, H-5''), 7.17–7.23 (m, 1H, H-4), 7.42–7.49 (m, 2H, H-3, H-5), 7.55 (s, 4H, *p*-C*H*-BAr$^F_4$), 7.71 (s, 8H, *o*-C*H*-BAr$^F_4$). **^{1}H/^{13}C-HSQC/HMBC-NMR** (500/126 MHz, CD_2Cl_2, 253 K): δ(^{13}C)/ppm = 13.6 (Sn*C*H$_3$), 18.4 (4'-*C*H$_3$)*, 19.0 (PCH*C*H$_{3,A}$), 19.3 (6'-*C*H$_3$)*, 19.4 (2'-*C*H$_3$), 19.6 (Sn*C*H$_2$, PCH*C*H$_3$), 20.9 (4''-*C*H$_3$), 21.7 (2''-*C*H$_3$), 21.9 (6''-*C*H$_3$), 27.1 (Sn*C*H$_2$), 28.3 (Sn*C*H$_2$), 85.9 (C-4'), 90.4 (C-6'), 92.0 (C-5'), 92.7 (C-3'), 100.1 (C-2'), 115.0 (C-1'), 117.6 (*p*-*C*H-BAr$^F_4$), 124.5 (*C*F$_3$-BAr$^F_4$), 128.2 (C-3, C-5, C-6, *m*-*C*-BAr$^F_4$), 129.1 (C-3''), 129.4 (C-5''), 132.7 (C-4), 134.3 (C-1''), 134.8 (*o*-*C*H-BAr$^F_4$), 135.6 (C-6''), 136.5 (C-2''), 138.0 (C-4''), 144.1 (C-1), 144.6 (C-2), 161.8 (*i*-*C*-BAr$^F_4$).*The peaks are interconvertible. **^{11}B NMR** (161 MHz, CD_2Cl_2, 253 K): δ/ppm = –6.7. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2, 253 K): δ/ppm = –62.7. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2, 253 K): δ/ppm = 69.0. **^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2, 253 K): δ/ppm = 155.9.

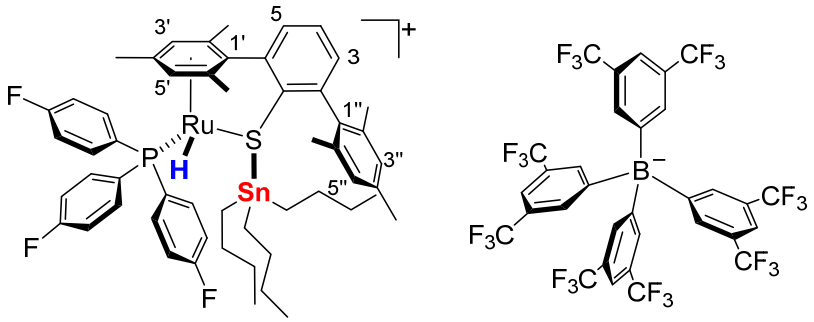
6.3 [5c·*n*Bu$_3$SnH]$^+$[BAr$^F{}_4$]$^-$



[**5c**·*n*Bu$_3$Sn–H]$^+$[BAr$^F{}_4$]$^-$
$C_{86}H_{98}PRuSBF_{24}Sn$
M = 1881.3 g/mol

Prepared according to **GP 2** from [**5c**]$^+$[BAr$^F{}_4$]$^-$ (20 mg, 14 µmol, 1.0 equiv) and *n*Bu$_3$SnH (**2b**, 5.0 mg, 14 µmol, 1.2 equiv) in CD_2Cl_2 (0.5 mL). **^{1}H NMR** (700 MHz, CD_2Cl_2, 253 K): δ/ppm = –8.54 (d, $^2J_{H,P}$ = 48.7 Hz, 1H, Ru*H*), 0.82 (d, $^2J_{H,H}$ = 7.0 Hz, 9H, SnCH_3), 1.06–1.43 (m, 33H$^\Delta$, PCHCH_2, SnCH_2), 1.57–1.83 (m, 18H$^\Delta$, PCHCH_2, PC*H*CH$_2$), 1.84 (m, 3H, 4'-CH_3), 1.94 (d, $J_{H,P}$ = 2.1 Hz, 3H, 6'-CH_3), 2.00 (s, 3H, 2'-CH_3), 2.01 (s, 3H, 2''-CH_3), 2.20 (s, 3H, 6''-CH_3), 2.27 (s, 3H, 4''-CH_3), 5.86 (br s, 1H, H-3'), 6.09 (s, 1H, H-5'), 6.91 (s, 1H, H-3''), 7.00 (s, 1H, H-5'') 7.17–7.24 (m, 1H, H-4), 7.43–7.49 (m, 2H, H-3, H-5), 7.55 (s, 4H, *p*-C*H*-BAr$^F{}_4$), 7.71 (s, 8H, *o*-C*H*-BAr$^F{}_4$). **^{13}C{^{1}H} NMR** (175 MHz, CD_2Cl_2, 253 K): δ/ppm = 13.4 (Sn*C*H$_3$), 18.6 (6'-*C*H$_3$), 19.6 (4'-*C*H$_3$), 19.9 (2'-*C*H$_3$), 20.9 (4''-*C*H$_3$), 21.6 (2''-*C*H$_3$), 21.6 (6''-*C*H$_3$), 26.3 (Sn*C*H$_2$, PCH*C*H$_2$), 27.3 (Sn*C*H$_2$), 27.6 (m, PCH*C*H$_2$), 27.7 (m, PCH*C*H$_2$), 28.4 (Sn*C*H$_2$), 29.3 (m, PCH*C*H$_2$), 30.7 (m, PCH*C*H$_2$), 37.3 (m, P*C*HCH$_2$), 86.5 (C-4'), 90.0 (d, $J_{C,P}$ = 9.7 Hz, C-6'), 90.6 (C-5'), 94.8 (C-3'), 100.7 (C-2'), 114.9 (C-1'), 117.6 (*p*-*C*H-BAr$^F{}_4$), 124.7 (q, $^1J_{C,F}$ = 271.8 Hz, *C*F$_3$-BAr$^F{}_4$), 128.2 (C-3), 128.4 (C-5), 128.6 (q, $^2J_{C,F}$= 31.9 Hz, *m*-*C*-BAr$^F{}_4$), 129.1 (C-3''), 129.5 (C-5''), 132.6 (C-4), 134.5 (C-1''), 134.9 (*o*-*C*H-BAr$^F{}_4$), 135.4 (C-6''), 137.0 (C-2''), 138.3 (C-4''), 140.2 (C-1), 143.3 (C-6), 144.3 (C-2), 161.8 (q, $^1J_{C,B}$= 50.1 Hz, *i*-*C*H-BAr$^F{}_4$). **^{11}B NMR** (224 MHz, CD_2Cl_2, 253 K): δ/ppm = –6.7. **^{19}F{^{1}H} NMR** (659 MHz, CD_2Cl_2, 253 K): δ/ppm = –62.7. **^{31}P{^{1}H} NMR** (283 MHz, CD_2Cl_2, 253 K): δ/ppm = 56.3. **^{119}Sn{^{1}H} NMR** (261 MHz, CD_2Cl_2, 253 K): δ/ppm = 151.1.

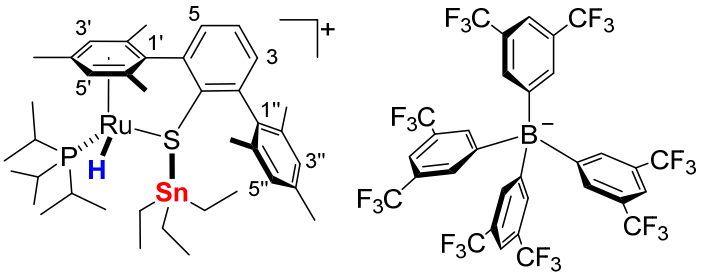
6.4 [5d·*n*Bu$_3$SnH]$^+$[BAr$^F_4$]$^-$



[**5d**·*n*Bu$_3$Sn–H]$^+$[BAr$^F_4$]$^-$
$C_{85}H_{77}PRuSBF_{27}Sn$
M = 1917.1 g/mol

Prepared according to **GP 2** from [**5d**]$^+$[BAr$^F_4$]$^-$ (20 mg, 15 µmol, 1.0 equiv) and *n*Bu$_3$SnH (**2a**, 5.0 mg, 17 µmol, 1.2 equiv) in CD_2Cl_2 (0.5 mL). **^{1}H NMR** (500 MHz, CD_2Cl_2, 213 K): δ/ppm = –8.33 (d, $^2J_{H,P}$ = 49.3 Hz, 1H, Ru*H*), 0.73–0.80 (m, 9H, SnCH_3), 1.01–1.30 (m, 18H$^\Delta$, SnCH_2), 1.42 (s, 3H$^\Delta$, 4'-CH_3), 1.69 (s, 3H, 2'-CH_3), 1.83 (s, 3H, 6''-CH_3), 2.00 (s, 3H, 6'-CH_3), 2.11 (s, 3H, 2''-CH_3), 2.24 (s, 3H, 4''-CH_3), 4.56 (bs, 1H, H-3') 6.22 (s, 1H, H-5'), 6.75 (s, 1H, H-5''), 6.92 (s, 1H, H-3''), 7.06–7.15 (m, 6H, *m*-C*H*-PAr), 7.18–7.23 (m, 1H, H-5), 7.29–7.38 (m, 6H, *o*-C*H*-PAr), 7.38–7.48 (m, 2H, H-3, H-4), 7.53 (s, 4H, *p*-C*H*-BAr$^F_4$), 7.72 (s, 8H, *o*-C*H*-BAr$^F_4$). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 213 K): δ/ppm = 13.4 (Sn*C*H$_3$), 18.3 (2'-*C*H$_3$), 18.5 (4'-*C*H$_3$), 18.7 (6'-*C*H$_3$), 20.6 (4''-*C*H$_3$), 21.0 (2''-*C*H$_3$), 21.0 (6''-*C*H$_3$), 27.1 (Sn*C*H$_2$), 28.0 (Sn*C*H$_2$), 29.7 (Sn*C*H$_2$), 86.1 (C-4'), 90.8 (C-5'), 90.0 (d, $J_{C,P}$ = 10.3 Hz, C-6'), 100.3 (C-3'), 101.6 (C-2'), 114.8 ($J_{C,P}$ = 3.9 Hz, C-1'), 115.7 (dd, $^3J_{C,P}$ = 10.8 Hz, $^2J_{C,F}$ = 21.4 Hz, *m*-*C*H-PAr), 117.3 (*p*-*C*H-BAr$^F_4$), 124.2 (q, $^1J_{C,F}$ = 272.7 Hz, *C*F$_3$-BAr$^F_4$), 127.9 (C-5), 128.4 (C-4), 128.4 (q, $^2J_{C,F}$= 31.8 Hz, *m*-*C*-BAr$^F_4$), 128.6 (C-5''), 129.2 (C-3''), 129.7 (d, $^1J_{C,P}$ = 49.9 Hz, *i*-*C*-PAr), 132.1 (C-3), 133.7 (C-1''), 134.4 (*o*-*C*H-BAr$^F_4$), 134.8 (C-2''), 135.1 (dd, $^2J_{C,P}$ = 12.5 Hz, $^3J_{C,F}$ = 8.7 Hz, *o*-*C*H-PAr), 136.2 (C-6''), 138.0 (C-4''), 139.2 (C-6), 143.1 (C-2), 143.3 (C-1), 161.5 (q, $^1J_{C,B}$= 49.9 Hz, *i*-*C*H-BAr$^F_4$), 163.5 (d, $^1J_{C,F}$ = 252.8 Hz, *p*-*C*-PAr). **^{11}B NMR** (161 MHz, CD_2Cl_2, 213 K): δ/ppm = –6.7. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2, 253 K): δ/ppm = –109.0 (*p*-C*F*-PAr), –62.7 (C*F*$_3$-BAr$^F_4$). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2, 213 K): δ/ppm = 49.6. **^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2, 213 K): δ/ppm = 154.5.

6.5 [5b·Et_3SnH]$^+$[BAr^F_4]$^-$

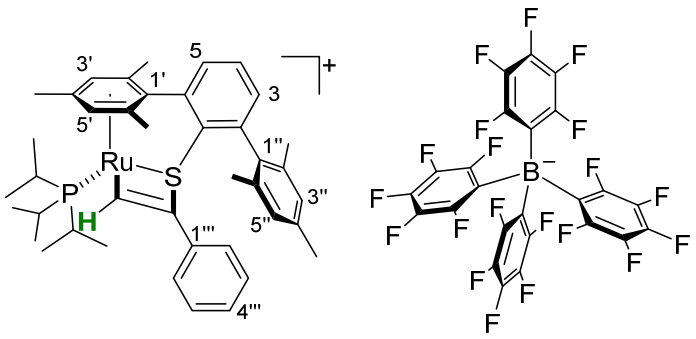


[**5b**·Et_3Sn–H]$^+$[BAr^F_4]$^-$
$C_{71}H_{74}PRuSBF_{24}Sn$
M = 1877.0 g/mol

Prepared according to **GP 2** from [**5b**]$^+$[BAr^F_4]$^-$ (20 mg, 15 µmol, 1.0 equiv) and Et_3SnH (**2b**, 5.0 mg, 17 µmol, 1.2 equiv) in CD_2Cl_2 (0.5 mL). **^{1}H NMR** (500 MHz, CD_2Cl_2, 253 K): δ/ppm = –8.38 (d, $^2J_{H,P}$ = 47.1 Hz, 1H, Ru*H*), 0.92–1.08 (m, 15H$^\Delta$, SnCH_3, SnCH_2), 1.10–1.17 (m, 18H$^\Delta$, PCHCH_3), 1.83 (s, 3H, 6'-CH_3), 1.86 (s, 3H, 4'-CH_3), 1.97–2.01 (m, 6H, PC*H*CH_3, 2''-CH_3), 2.05 (s, 3H, 2'-CH_3), 2.17 (s, 3H, 6''-CH_3), 2.28 (s, 3H, 4''-CH_3), 5.79 (s, 1H, H-3'), 6.17 (s, 1H, H-5'), 6.93 (s, 1H, H-3''), 7.00 (s, 1H, H-5''), 7.19–7.26 (m, 1H, H-4), 7.42–7.50 (m, 2H, H-3, H-5), 7.56 (s, 4H, *p*-C*H*-BAr^F_4), 7.72 (s, 8H, *o*-C*H*-BAr^F_4). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 253 K): δ/ppm = 10.4 (Sn*C*H_3), 11.1 (Sn*C*H_2), 18.2 (6'-*C*H_3), 19.1 (PCH*C*$H_{3,A}$), 19.2 (4'-*C*H_3), 19.4 (2'-*C*H_3), 20.1 (PCH*C*$H_{3,B}$), 20.8 (4''-*C*H_3), 21.7 (2''-*C*H_3), 21.8 (6''-*C*H_3), 27.2 (d, $^1J_{C,P}$ = 23.6 Hz, P*C*HCH$_3$), 86.0 (C-4'), 90.4 (d, $J_{C,P}$ = 10.3 Hz, C-6'), 92.4 (d, $J_{C,P}$ = 3.5 Hz, C-5'), 92.5 (C-3'), 100.0 (C-2'), 115.0 (C-1'), 117.6 (*p*-*C*H-BAr^F_4), 124.6 (q, $^1J_{C,F}$ = 272.7 Hz, *C*F_3-BAr^F_4), 128.1 (C-3), 128.3 (C-5), 128.8 (q, $^2J_{C,F}$= 31.5 Hz, *m*-*C*-BAr^F_4), 129.1 (C-3''), 129.2 (C-5''), 132.7 (C-4), 134.3 (C-1''), 134.8 (*o*-*C*H-BAr^F_4), 135.6 (C-2''), 136.8 (C-6''), 138.4 (C-4''), 140.0 (C-6), 143.4 (C-1), 144.3 (C-2), 161.8 (q, $^1J_{C,B}$= 49.8 Hz, *i*-*C*-BAr^F_4).**^{11}B NMR** (161 MHz, CD_2Cl_2, 253 K): δ/ppm = –6.7. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2, 253 K): δ/ppm = –62.7. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2, 253 K): δ/ppm = 69.3. **^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2, 253 K): δ/ppm = 150.2.

7. Experimental Details for the NMR Investigations of Adducts $[5b{\cdot}RCCH]^+[A]^-$

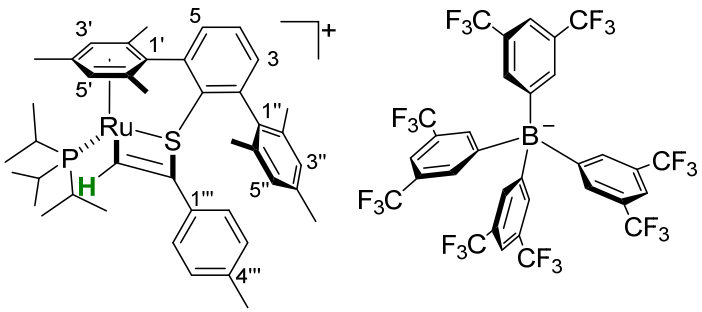
7.1 $[5b{\cdot}PhCCH]^+[B(C_6F_5)_4]^-$



$[\mathbf{5b}{\cdot}PhCCH]^+[B(C_6F_5)_4]^-$
$C_{65}H_{52}PRuSBF_{20}$
M = 1388.0 g/mol

Prepared according to **GP 3** from $[\mathbf{5b}]^+[B(C_6F_5)_4]^-$ (20 mg, 15 µmol, 1.0 equiv) and phenyl acetylene (**1a**, 5.0 mg, 17 µmol, 1.2 equiv) in CD_2Cl_2 (0.5 mL). **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ/ppm = 1.07 (s, 3H, 2''-CH_3), 1.10 (dd, $^3J_{H,H}$= 7.3 Hz, $^3J_{H,P}$= 13.1 Hz, 9H, PCHC$H_{3,A}$), 1.18 (dd, $^3J_{H,H}$= 7.3 Hz, $^3J_{H,P}$= 14.6 Hz, 9H, PCHC$H_{3,B}$), 1.87 (s, 3H, 6'-CH_3), 2.02 (s, 3H, 6''-CH_3), 2.06–2.20 (m, 9H, PCHCH_3, 2'-CH_3, 4'-CH_3), 2.40 (s, 3H, 4''-CH_3), 5.59 (s, 1H, H-3'), 6.11 (s, 1H, H-5'), 6.49 (d, $^3J_{H,H}$= 7.7 Hz, 2H, H-2'''), 6.68 (s, 1H, H-3''), 6.93–7.05 (m, 2H, H-5'', H-3'''), 7.12–7.14 (m, 3H, H-3, H-4'''), 7.51–7.54 (m, 1H$^\Delta$, H-5), 7.60–7.70 (m, 1H, H-4), 8.99 (d, $^3J_{H,P}$= 4.7 Hz, PhCCH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 298 K): δ/ppm = 17.9 (2'-CH$_3$), 18.6 (d, $^2J_{C,P}$= 2.5 Hz, PCHCH$_{3,A}$), 18.7 (6'-CH$_3$), 19.6 (4'-CH$_3$), 20.0 (2''-CH$_3$), 20.9 (PCHCH$_{3,B}$), 21.1 (6''-CH$_3$), 21.3 (4''-CH$_3$), 26.1 (d, $^1J_{C,P}$ = 21.8 Hz, PCHCH$_3$), 86.3 (C-3'), 97.2 (C-5'), 100.2 (C-4'), 103.0 (d, $J_{C,P}$ = 7.6 Hz, C-2'), 107.1 (d, $J_{C,P}$ = 6.5 Hz, C-1'), 107.3 (C-6'), 124.5 (C-2''', *i*-*C*-B(C_6F_5)$_4$), 127.9 (C-4'''), 128.6 (C-5''), 128.9 (C-3'''), 130.1 (C-5), 130.5 (C-3''), 132.4 (C-4), 133.5 (C-3), 135.1 (C-1''), 135.4 (C-6''), 136.7 (d, $^1J_{C,F}$ = 244 Hz, *m*-*C*-B(C_6F_5)$_4$), 134.5 (C-1'''), 138.0 (C-2''), 138.4 (C-4''), 138.6 (d, $^1J_{C,F}$ = 244.5 Hz, *p*-*C*-B(C_6F_5)$_4$), 139.7 (d, $^3J_{C,P}$= 3.7 Hz, PhCCH), 141.0 (C-1), 141.9 (C-6), 147.9 (C-2), 148.6 (d, $^1J_{C,F}$ = 244.5 Hz, *o*-*C*-B(C_6F_5)$_4$), 156.0 (d, $^2J_{C,P}$= 18.2 Hz, PhCCH).**^{11}B NMR** (161 MHz, CD_2Cl_2, 298 K): δ/ppm = –16.6. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2, 298 K): δ/ppm = –167.5 (m, 8F, *m*-*F*-B(C_6F_5)$_4$), –163.6 (t, $^3J_{F,F}$ = 20.4 Hz, 4F, *p*-*F*-B(C_6F_5)$_4$), –133.2 (m, 8F, *o*-*F*-B(C_6F_5)$_4$). **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, 298 K): δ/ppm = 53.8.

7.2 [5b·4-TolCCH]$^+$[BAr$^F_4$]$^-$

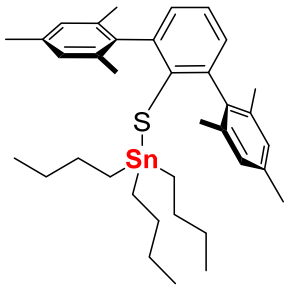


[**5b**·4-TolCCH]$^+$[BAr$^F_4$]$^-$
$C_{74}H_{66}PRuSBF_{24}$
M = 1586.2 g/mol

Prepared according to **GP 3** from [**5b**]$^+$[BAr$^F_4$]$^-$ (20 mg, 15 µmol, 1.0 equiv) and 1-ethynyl-4-methylbenzene (**1h**, 5.0 mg, 17 µmol, 1.2 equiv) in CD_2Cl_2 (0.5 mL). **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ/ppm = 1.07 (s, 3H, 2''-CH_3), 1.10 (dd, $^3J_{H,H}$= 7.2 Hz, $^3J_{H,P}$= 13.3 Hz 9H, PCHC$H_{3,A}$), 1.18 (dd, $^3J_{H,H}$= 7.2 Hz, $^3J_{H,P}$= 14.6 Hz 9H, PCHC$H_{3,B}$), 1.86 (s, 3H, 6'-CH_3), 2.00 (s, 3H, 6''-CH_3), 2.06–2.16 (m, 9H, PCHCH$_3$, 2'-CH_3, 4'-CH_3), 2.30 (s, 3H, 4'''-CH_3), 2.39 (s, 3H, 4''-CH_3), 5.56 (s, 1H, H-3'), 6.10 (s, 1H, H-5'), 6.38 (d, $^3J_{H,H}$= 8.0 Hz, 2H, H-2'''), 6.67 (s, 1H, H-3''), 6.81 (d, $^3J_{H,H}$= 8.0 Hz, 2H, H-3'''), 6.99 (s, 1H, H-5''), 7.18 (m, 1H, H-3), 7.49 (m, 1H, H-5), 7.57 (s, 4H, *p*-CH-BAr$^F_4$), 7.62 (m, 1H, H-4), 7.74 (s, 8H, *o*-CH-BAr$^F_4$), 8.86 (d, $^3J_{H,P}$= 4.8 Hz, 1H, 4-TolCCH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 298 K): δ/ppm = 17.9 (2'-CH$_3$), 18.7 (d, $^2J_{C,P}$= 2.9 Hz, PCHCH$_{3,A}$), 18.8 (6'-CH$_3$), 19.7 (4'-CH$_3$), 20.1 (2''-CH$_3$), 20.9 (PCHCH$_{3,B}$), 21.1 (6''-CH$_3$), 21.3 (4'''-CH$_3$), 21.3 (4''-CH$_3$), 26.1 (d, $^1J_{C,P}$ = 22.0 Hz, PCHCH$_3$), 86.3 (C-3'), 97.1 (C-5'), 100.1 (C-4'), 102.9 (d, $J_{C,P}$ = 7.9 Hz, C-2'), 107.1 (d, $J_{C,P}$ = 6.3 Hz, C-1'), 107.2 (C-6'), 117.9 (*p*-CH-BAr$^F_4$), 125.6 (C-2'''), 125.0 (q, $^1J_{C,F}$ = 272.7 Hz, CF$_3$-BAr$^F_4$), 128.5 (C-5''), 128.8 (q, $^2J_{C,F}$= 31.5 Hz, *m*-C-BAr$^F_4$), 129.5 (C-3'''), 130.5 (C-5), 130.4 (C-3''), 132.3 (C-4), 133.5 (C-3), 134.5 (d, $^4J_{C,P}$= 2.6 Hz, C-1'''), 135.1 (C-1''), 135.2 (*o*-CH-BAr$^F_4$, C-6'), 138.0 (C-2''), 138.1 (C-4'''), 138.5 (C-4''), 139.8 (d, $^3J_{C,P}$= 4.3 Hz, 4-Tol$C$CH), 141.1 (C-1), 141.9 (C-6), 147.9 (C-2), 154.0 (d, $^2J_{C,P}$= 18.7 Hz, 4-TolCCH), 162.1 (q, $^1J_{C,B}$= 49.8 Hz, *i*-C-BAr$^F_4$).**^{11}B NMR** (161 MHz, CD_2Cl_2, 298 K): δ/ppm = –6.6. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2, 298 K): δ/ppm = –62.8. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, 298 K): δ/ppm = 53.6.

8. Experimental Details of Mechanistic Studies

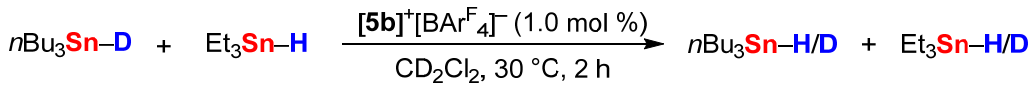
8.1 Preparation of Stannyl Thioether DmpSSn*n*Bu$_3$



DmpSSn*n*Bu$_3$
$C_{36}H_{52}SSn$
M = 635.6 g/mol

In a glove box, a 2-mL screw-capped vial was charged with DmpSH (33 mg, 0.10 mmol, 1.0 equiv), *n*Bu$_3$SnH (**2a**, 37 mg, 0.13 mmol, 1.3 equiv), and B(C_6F_5)$_3$ (5.1 mg, 10 µmol, 1.0 mol %) in CD_2Cl_2 (0.50 mL). The reaction was quenched after 24 h using a solution of Et_3N in *n*-pentane (1%). After filtration over a plug of neutral Al_2O_3 and Celite and subsequent evaporation of the solvents, the sample was directly submitted to NMR spectroscopy. DmpSSn*n*Bu$_3$ was observed in a mixture with DmpSH. The product decomposed on silica gel. **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ/ppm = 0.68 (t, $^3J_{H,H}$= 8.0 Hz, 6H), 0.81 (t, $^3J_{H,H}$= 7.0 Hz, 9H), 1.09–1.23 (m, 12H), 2.08 (s, 12H), 2.32 (s, 6H), 6.92 (s, 4H), 7.03 (d, $^3J_{H,H}$= 7.6 Hz, 2H), 7.26 (t, $^3J_{H,H}$= 7.6 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 298 K): δ/ppm = 13.8, 14.6 ($^1J_{C,^{119}Sn}$ = 321.6 Hz, $^1J_{C,^{117}Sn}$ = 307.0 Hz), 27.4 ($^2J_{C,^{119}Sn}$ = 66.8 Hz), 28.6 ($^3J_{C,^{119}Sn}$ = 19.3 Hz), 126.3, 128.4, 129.7, 134.9, 136.1, 136.4, 140.1, 147.4. **^{119}Sn{^{1}H} NMR** (186 MHz, CD_2Cl_2, 298 K): δ/ppm = 79.6.

8.2 Promoted $^{1}H/^{2}H$ Scrambling Between *n*Bu_3SnD (2a-d_1) and Et_3SnH (2b)



2a-d_1 (1.0 equiv)	**2b** (1.3 equiv)	H/D:	55:45	45:55

Scheme S4 Scrambling experiment between *n*Bu_3SnD (**2a**-d_1) and Et_3SnH (**2b**).

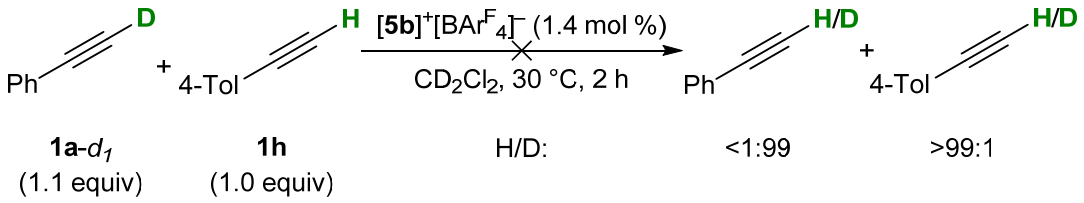
In a glove box, a 2-mL screw-capped vial was charged with catalyst [**5b**]$^+$[$BAr^F{}_4$]$^-$ (1.4 mg, 1.0 µmol, 1.0 mol %), CD_2Cl_2 (0.05 mL), *n*Bu_3SnD (**2a**-d_1, 26 mg, 0.11 mmol, 1.0 equiv) and Et_3SnH (**2b**, 23 mg, 0.089 mmol, 1.3 equiv). The mixture was stirred for 2 h, transferred to a J. Young NMR tube using CD_2Cl_2 (0.45 mL) and subjected to NMR spectroscopy. Promoted $^{1}H/^{2}H$ scrambling between *n*Bu_3SnD (**2a**-d_1) and Et_3SnH (**2b**) was observed by ^{1}H, ^{2}H, and ^{119}Sn NMR spectroscopy.

Selected spectroscopic data of the resulting mixture:

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ/ppm = 4.65 (s, 1H, *n*Bu_3Sn***H***), 4.73 (s, 1H, Et_3Sn***H***). **^{2}H NMR** (77 MHz, CD_2Cl_2, 298 K): δ/ppm = 4.74 (s, 1H, *n*Bu_3Sn***D***), 4.82 (s, 1H, Et_3Sn***D***). **$^{119}Sn\{^{1}H\}$ NMR** (186 MHz, CD_2Cl_2, 298 K): δ/ppm = –88.4 (t, $^{1}J_{Sn,D}$ = 241.7 Hz, *n*Bu_3***Sn***D), –86.7 (s, *n*Bu_3***Sn***H), –67.1 (t, $^{1}J_{Sn,D}$ = 239.1 Hz, Et_3***Sn***D), –65.4 (s, Et_3***Sn***H).

The same reaction performed without catalyst [**5b**]$^+$[$BAr^F{}_4$]$^-$ did not lead to $^{1}H/^{2}H$ scrambling between *n*Bu_3SnD (**2a**-d_1) and Et_3SnH (**2b**).

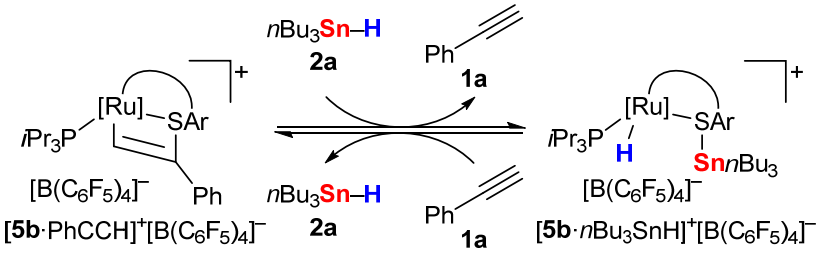
8.3 Attempted Scrambling Between Phenyl Acetylene-d_1 (1a-d_1) and 1-Ethynyl-4-methylbenzene (1h)



Scheme S5 Scrambling experiment between phenyl acetylene-d_1 (**1a**-d_1) and 1-ethynyl-4-methylbenzene (**1b**).

In a glove box, a 2-mL screw-capped vial was charged with catalyst [**5b**]$^+$[$BAr^F{}_4$]$^-$ (2.8 mg, 2.0 µmol, 1.4 mol %), CH_2Cl_2 (0.05 mL), phenyl acetylene-d_1 (**1a**-d_1, 16 mg, 0.16 mmol, 1.0 equiv) and 1-ethynyl-4-methylbenzene (**1h**, 16 mg, 0.14 mmol, 1.1 equiv). The mixture was stirred for 2 h, transferred to a J. Young NMR tube using CD_2Cl_2 (0.45 mL) and subjected to NMR spectroscopy. No $^1H/^2H$ scrambling between phenyl acetylene-d_1 (**1a**-d_1) and 1-ethynyl-4-methylbenzene (**1h**) was observed by ^1H and ^2H NMR spectroscopy.

8.4 Competition Experiment



Scheme S6 Competition experiment between [**5b**·nBu$_3$SnH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and [**5b**·PhCCH]$^+$[B(C$_6$F$_5$)$_4$]$^-$.

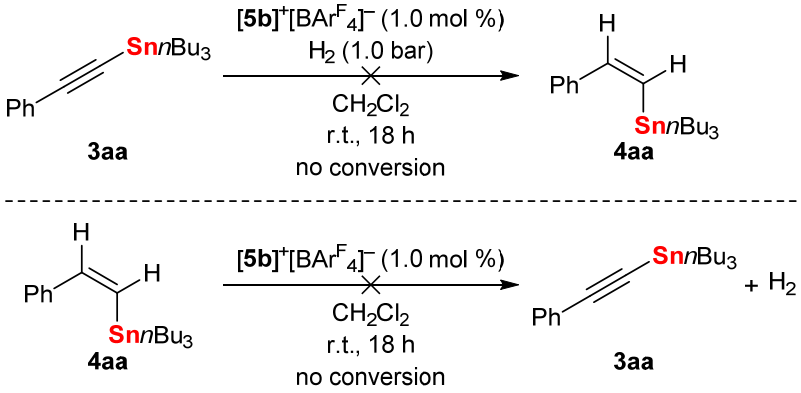
*a) Premixing [**5b**]$^+$[B(C$_6$F$_5$)$_4$]$^-$ with phenyl acetylene (**1a**):*

In a glove box a J. Young NMR tube was charged with [**5b**]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (21 mg, 15 µmol, 1.0 equiv) and CD_2Cl_2 (0.5 mL). After addition of phenyl acetylene (**1a**, 4.0 mg, 39 µmol, 2.9 equiv) the sample was directly subjected to ^{1}H NMR spectroscopy and the formation of [**5b**·PhCCH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ was confirmed. After subsequent addition of nBu$_3$SnH (**2a**, 4.0 mg, 15 µmol, 1.0 equiv) in the glove box the sample was again subjected to NMR spectroscopy and the formation of [**5b**·nBu$_3$SnH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ was confirmed.

*b) Premixing [**5b**]$^+$[B(C$_6$F$_5$)$_4$]$^-$ with nBu$_3$SnH (**2a**):*

In a glove box a J. Young NMR tube was charged with [**5b**]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (21 mg, 15 µmol, 1.0 equiv) and CD_2Cl_2 (0.5 mL). After addition of nBu$_3$SnH (**2a**, 4.0 mg, 15 µmol, 1.0 equiv) the sample was directly subjected to ^{1}H NMR spectroscopy and the formation of [**5b**·nBu$_3$SnH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ was confirmed. After subsequent addition of phenyl acetylene (**1a**, 4.0 mg, 39 µmol, 2.9 equiv) in the glove box the sample was again subjected to NMR spectroscopy and the formation of [**5b**·PhCCH]$^+$[B(C$_6$F$_5$)$_4$]$^-$ was confirmed.

8.5 Attempted Hydrogenation of Alkynyl Stannane 3aa and Dehydrogenation of Vinyl Stannane 4aa



Scheme S7 Attempted hydrogenation of **3aa** and dehydrogenation of **4aa**.

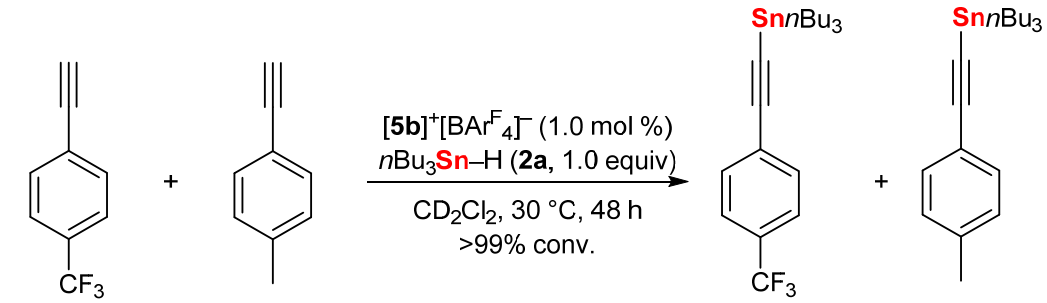
*a) Attempted hydrogenation of **3aa**:*

In a glove box, a Schlenk tube was charged with catalyst [**5b**]$^+$[BAr$^F_4$]$^-$ (1.4 mg, 1.0 µmol, 1.3 mol %), tetracosane as internal standard (1 mg), CH_2Cl_2 (0.05 mL), and **3aa** (30 mg, 77 µmol, 1.0 equiv). Outside the glove box, the Schlenk tube was connected to a hydrogen balloon and the atmosphere was flushed with dihydrogen. The mixture was stirred for 24 h at r.t.. GLC analysis showed no conversion.

*b) Attempted dehydrogenation of **4aa**:*

In a glove box, a 2-mL screw-capped vial was charged with catalyst [**5b**]$^+$[BAr$^F_4$]$^-$ (1.4 mg, 1.0 µmol, 1.3 mol %), tetracosane as internal standard (1 mg), CH_2Cl_2 (0.05 mL), and **4aa** (30 mg, 77 µmol, 1.0 equiv). The mixture was stirred for 24 h at r.t.. GLC analysis showed no conversion.

8.6 Intermolecular Competition Experiment between 1c and 1i

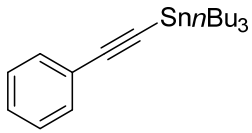


1c		**1i**		**3ac**		**3ai**
(1.1 equiv)		(1.1 equiv)		13	:	87

Scheme S8 Intermolecular Competition Experiment between **1c** and **1i**.

In a glove box, a 2-mL screw-capped vial was charged with catalyst [**5b**]$^{+}$[BAr$^{F}_{4}$]$^{-}$ (1.4 mg, 1.0 µmol, 1.0 mol %), CH_2Cl_2 (0.05 mL), nBu$_3$SnH (29 mg, 0.10 mmol, 1.0 equiv), 4-ethynyl-*α,α,α*-trifluorotoluene (**1c**, 19 mg, 0.11 mmol, 1.1 equiv) and 1-ethynyl-4-methylbenzene (**1i**, 13 mg, 0.11 mmol, 1.1 equiv). The mixture was stirred at 30 °C. The reaction was quenched after 48 h using a solution of Et_3N in *n*-pentane (1%). Filtration over a plug of Al_2O_3 and subsequent evaporation of the solvents afforded a mixture of the alkynyl stannanes **3ac** and **3ai** as colorless oil. A ratio of **3ac**:**3ai** = 13:87 was determined by GLC analysis and was confirmed by ^{1}H NMR spectroscopy.

9 Spectra



3aa

Figure S1 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(phenylethynyl)stannane (**3aa**)

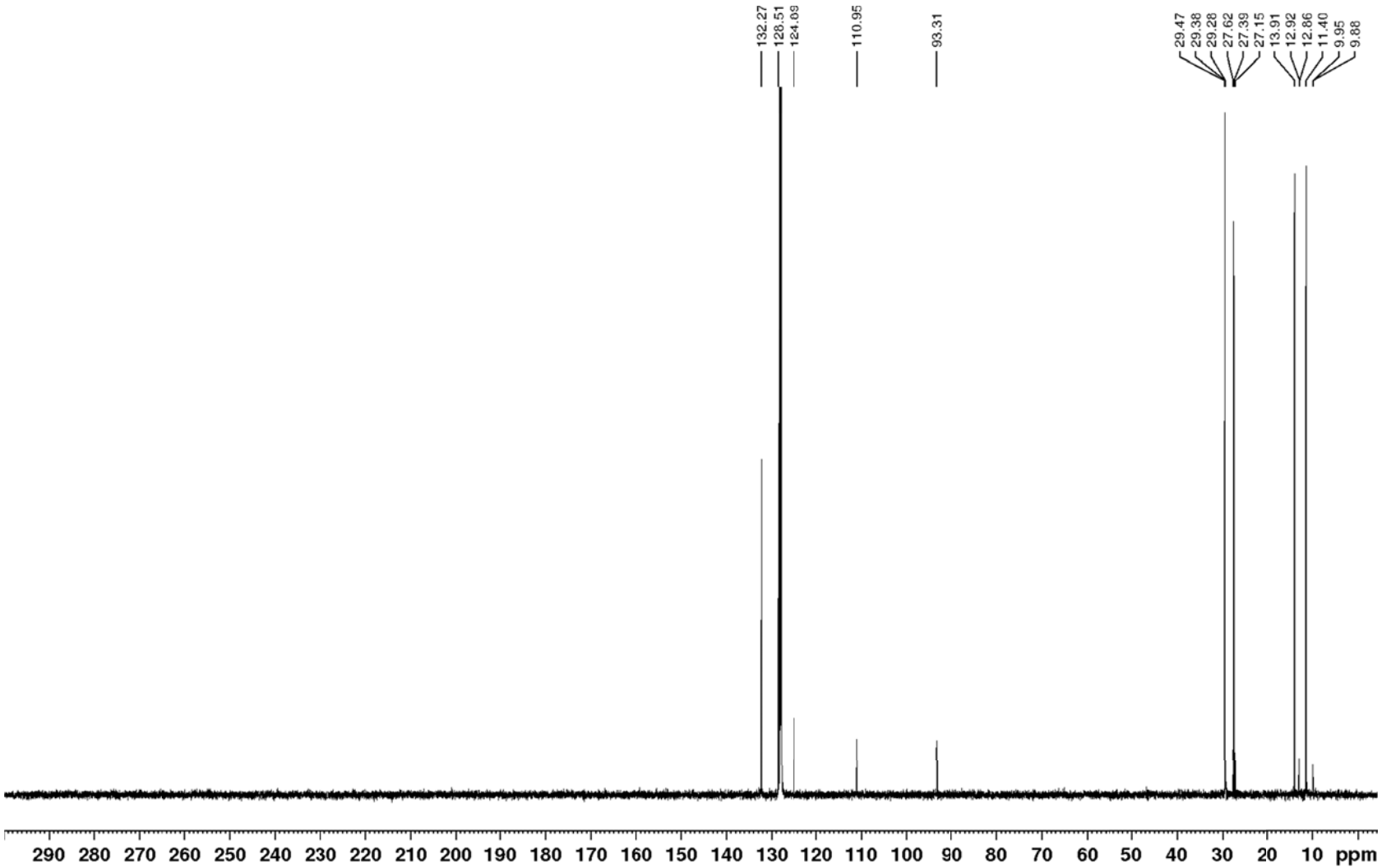


Figure S2 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(phenylethynyl)stannane (**3aa**)

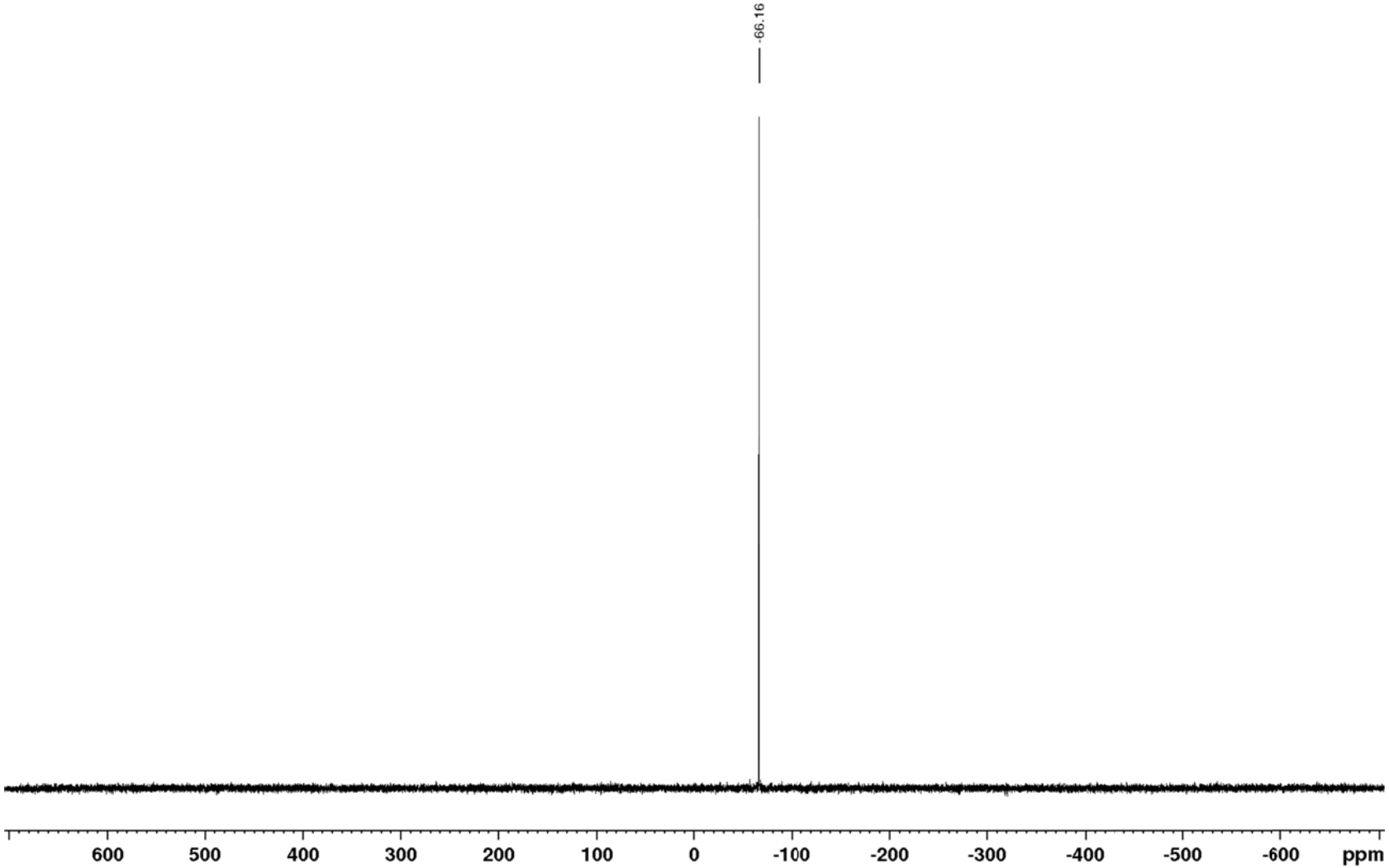


Figure S3 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(phenylethynyl)stannane (**3aa**)

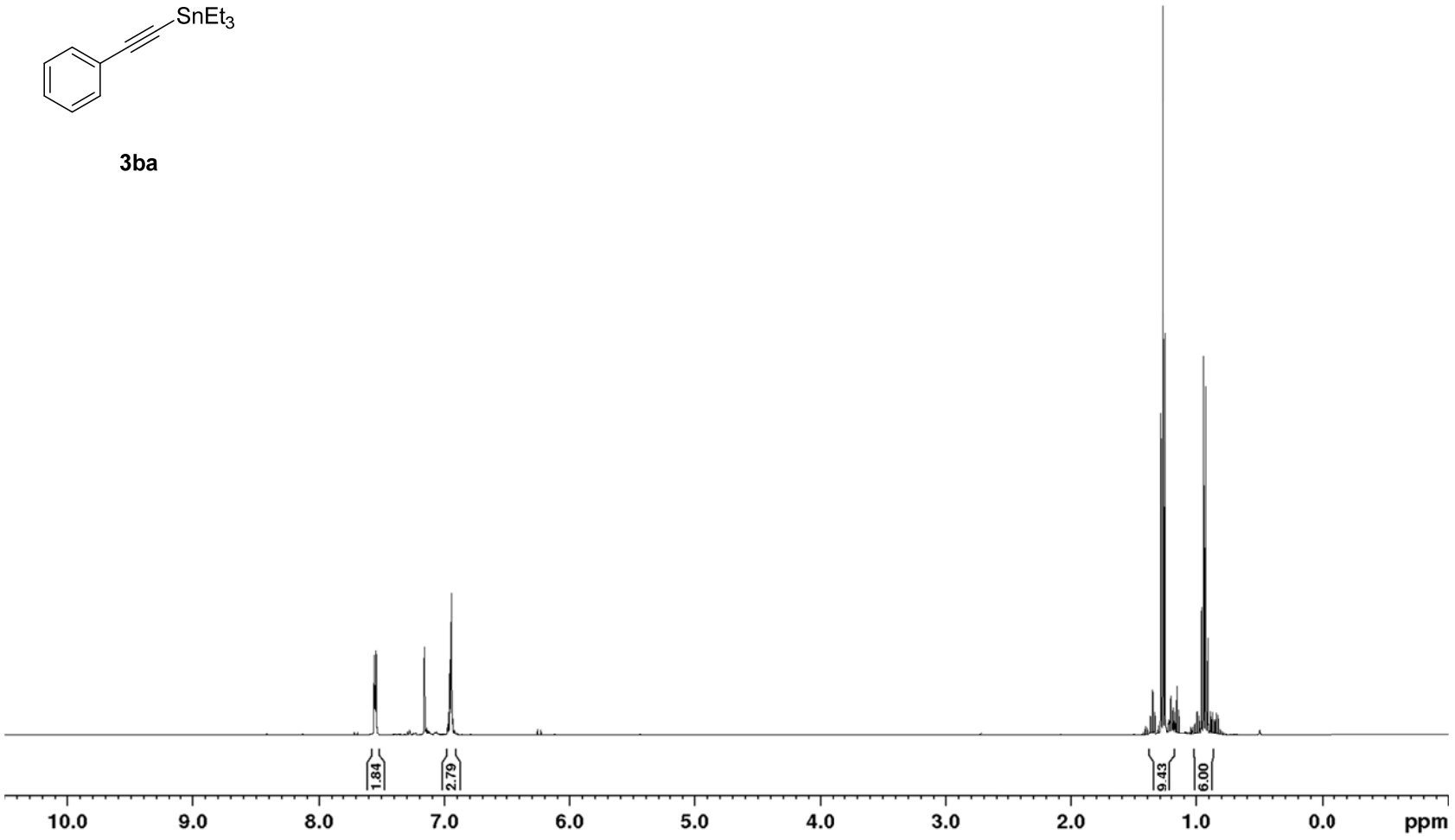


Figure S4 ^{1}H NMR (500 MHz, C_6D_6): Triethyl(phenylethynyl)stannane (**3ba**)

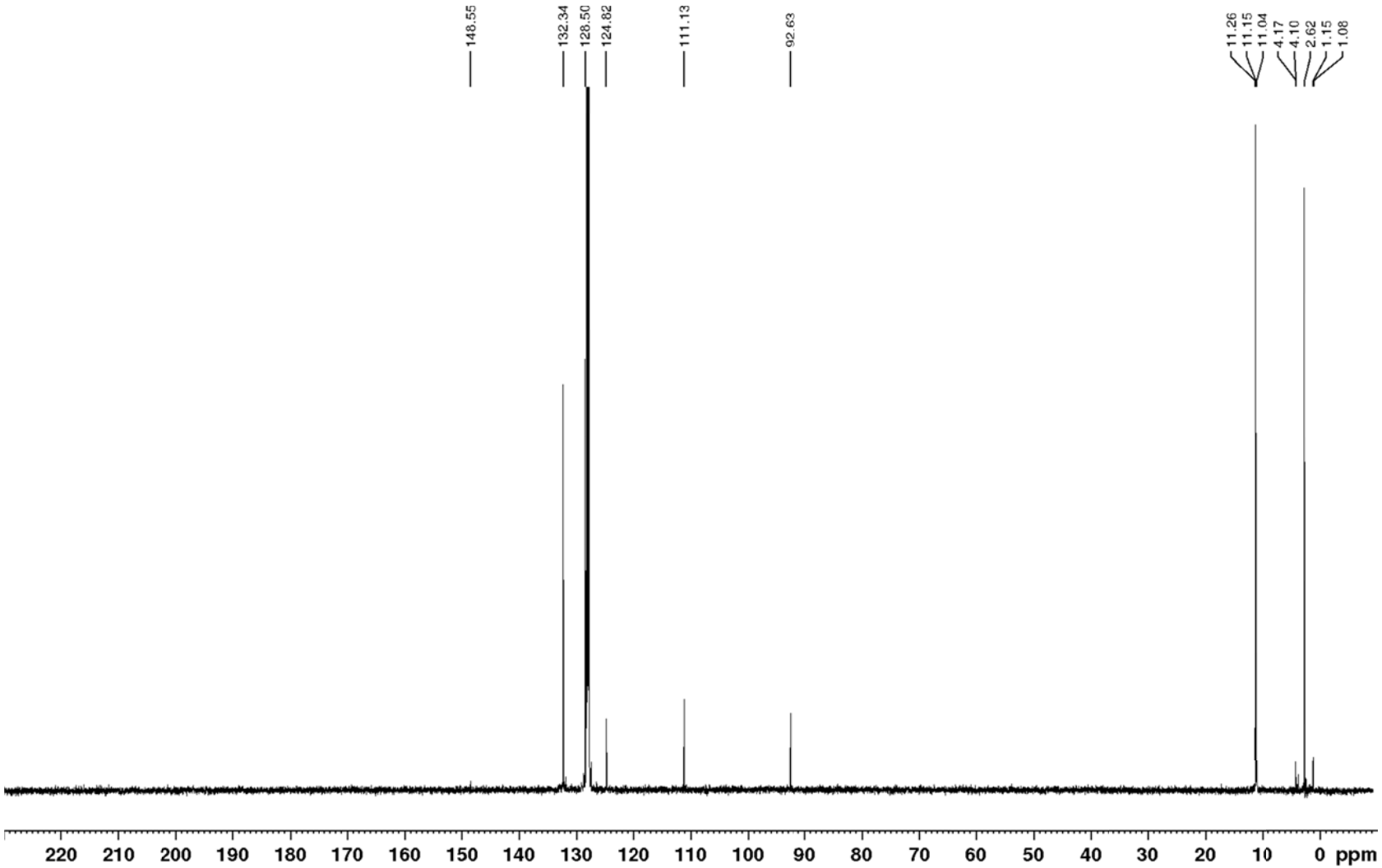


Figure S5 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Triethyl(phenylethynyl)stannane (**3ba**)

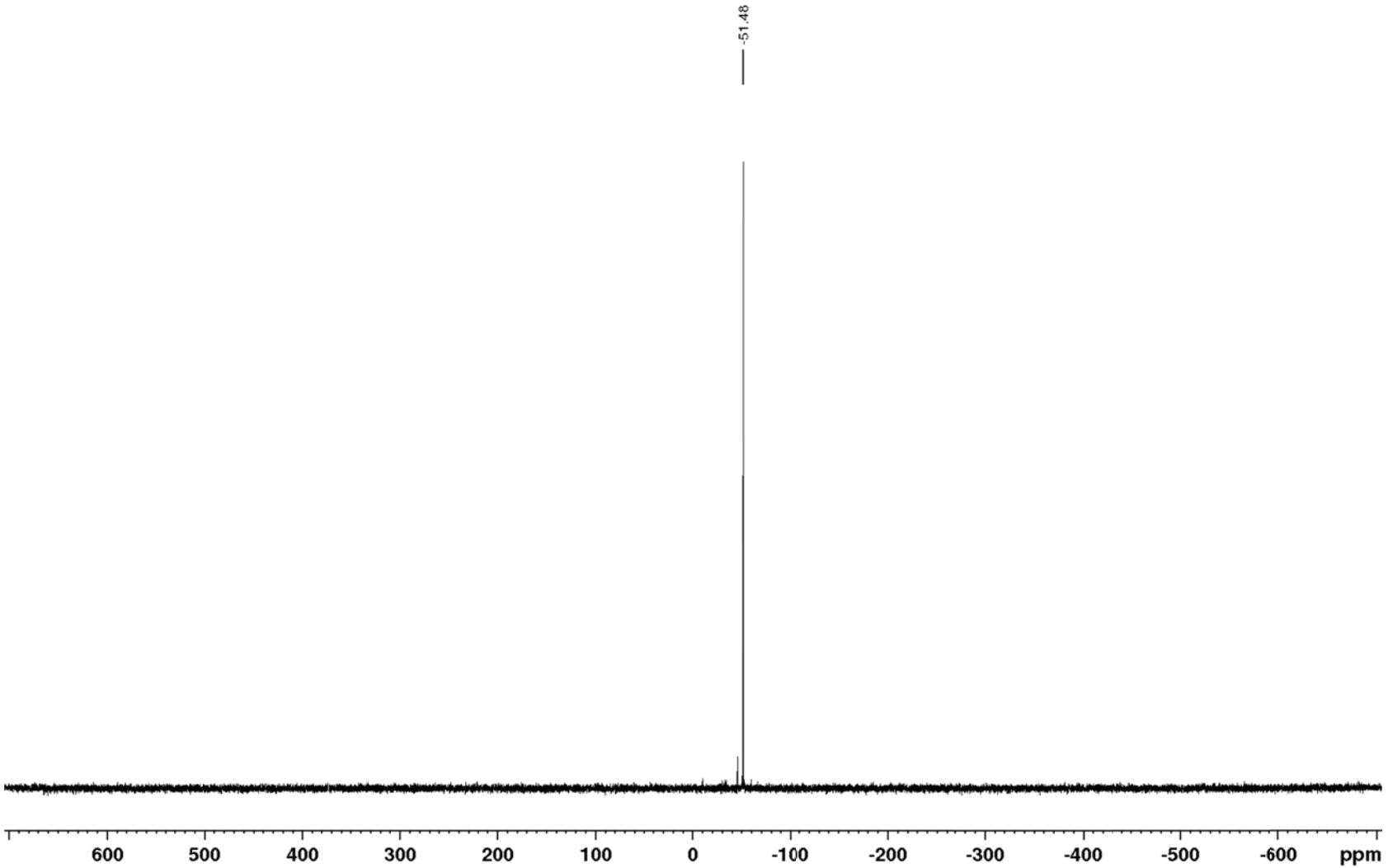


Figure S6 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Triethyl(phenylethynyl)stannane (**3ba**)

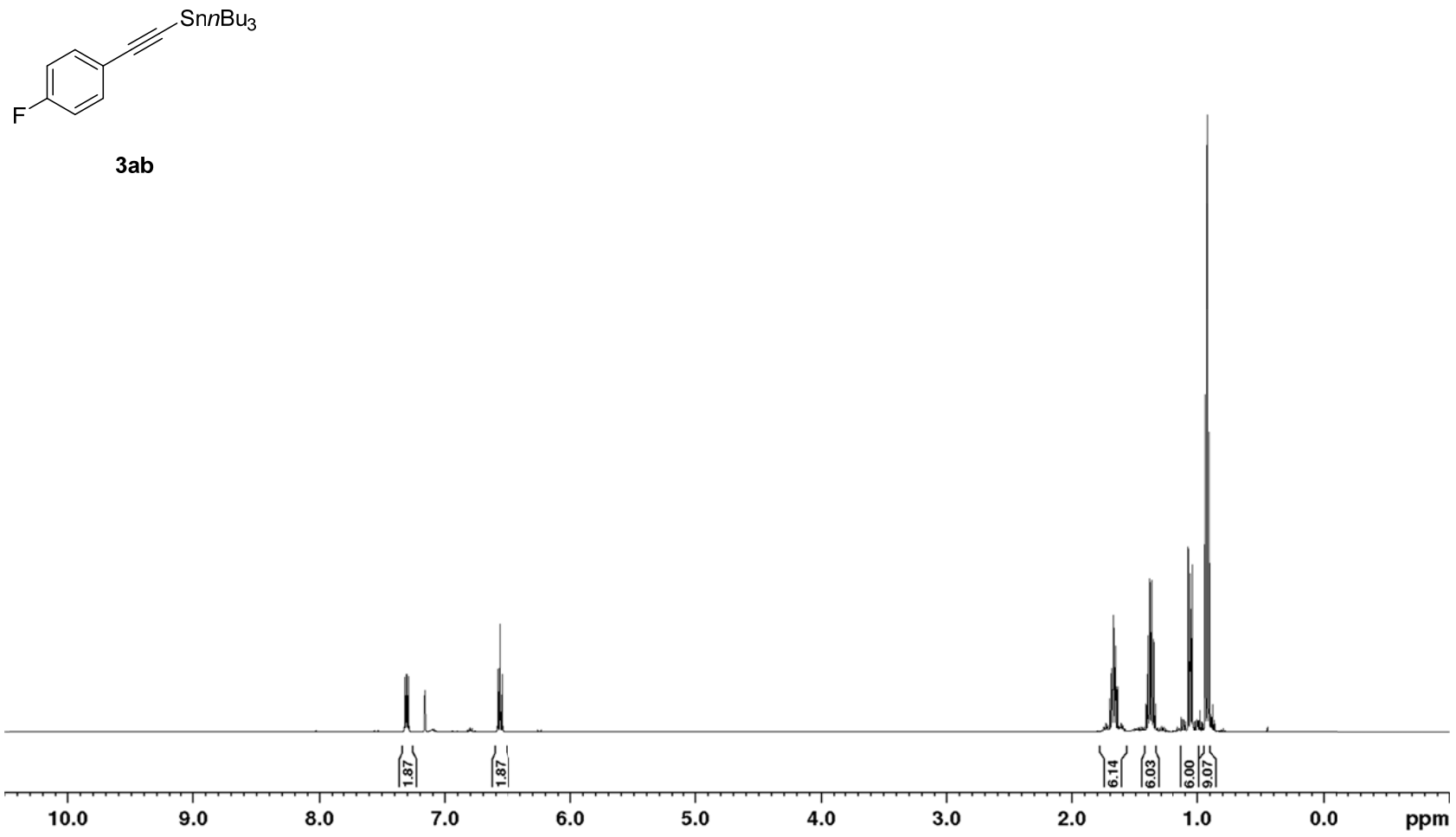


Figure S7 ^{1}H NMR (500 MHz, C_6D_6): Tributyl((4-fluorophenyl)ethynyl)stannane (**3ab**)

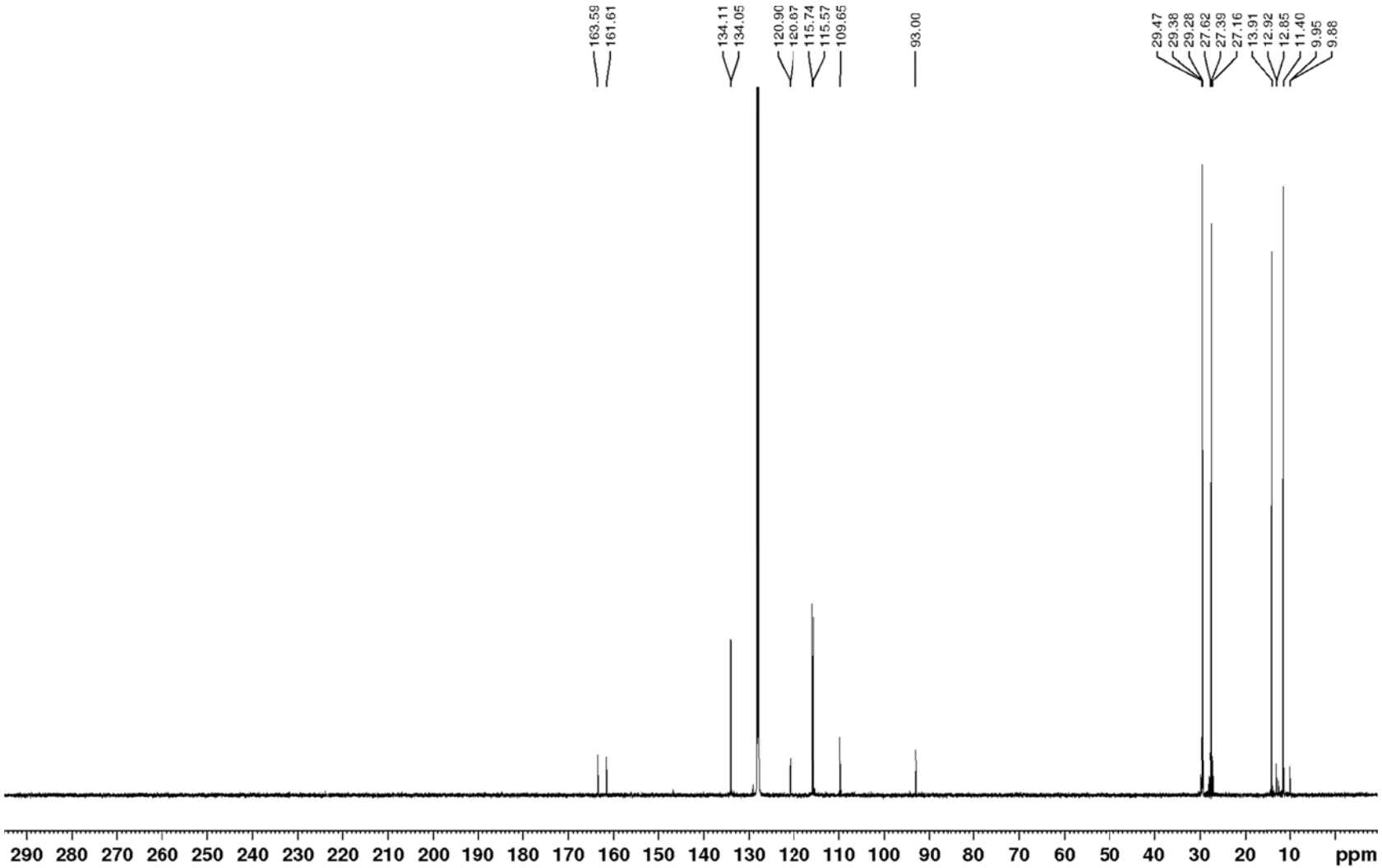


Figure S8 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl((4-fluorophenyl)ethynyl)stannane (**3ab**)

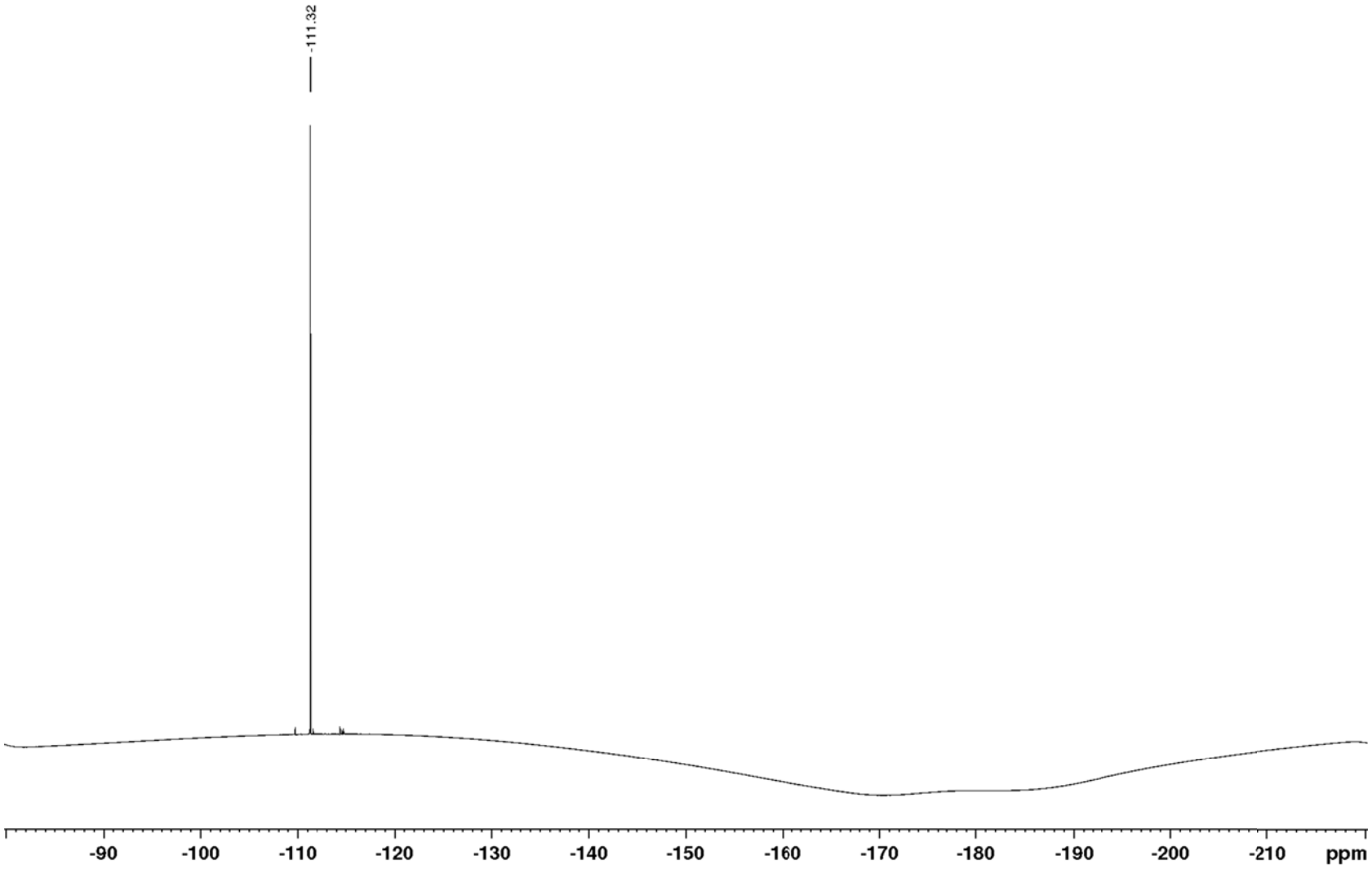


Figure S9 $^{19}F\{^{1}H\}$ NMR (659 MHz, C_6D_6): Tributyl((4-fluorophenyl)ethynyl)stannane (**3ab**)

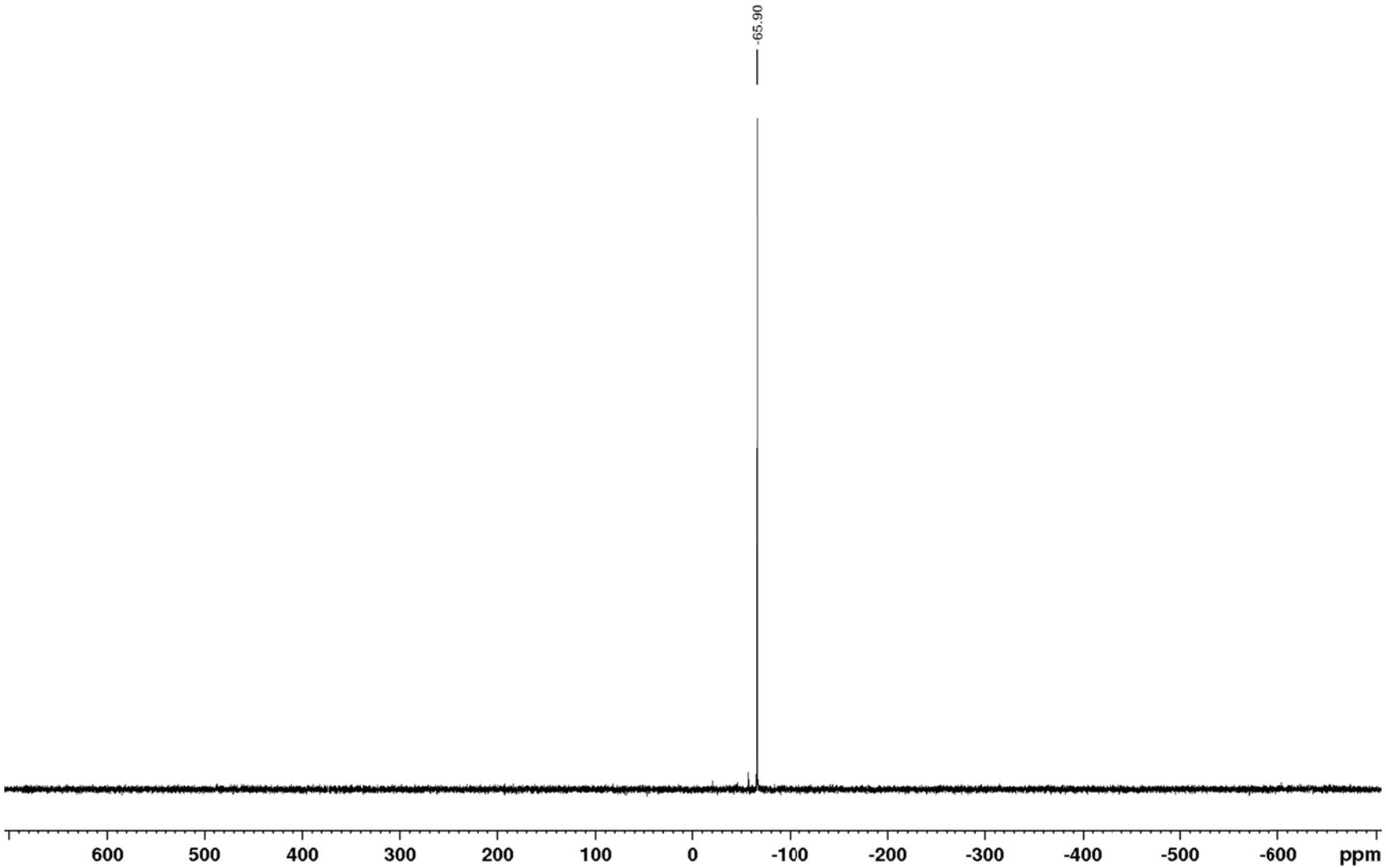


Figure S10 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl((4-fluorophenyl)ethynyl)stannane (**3ab**)

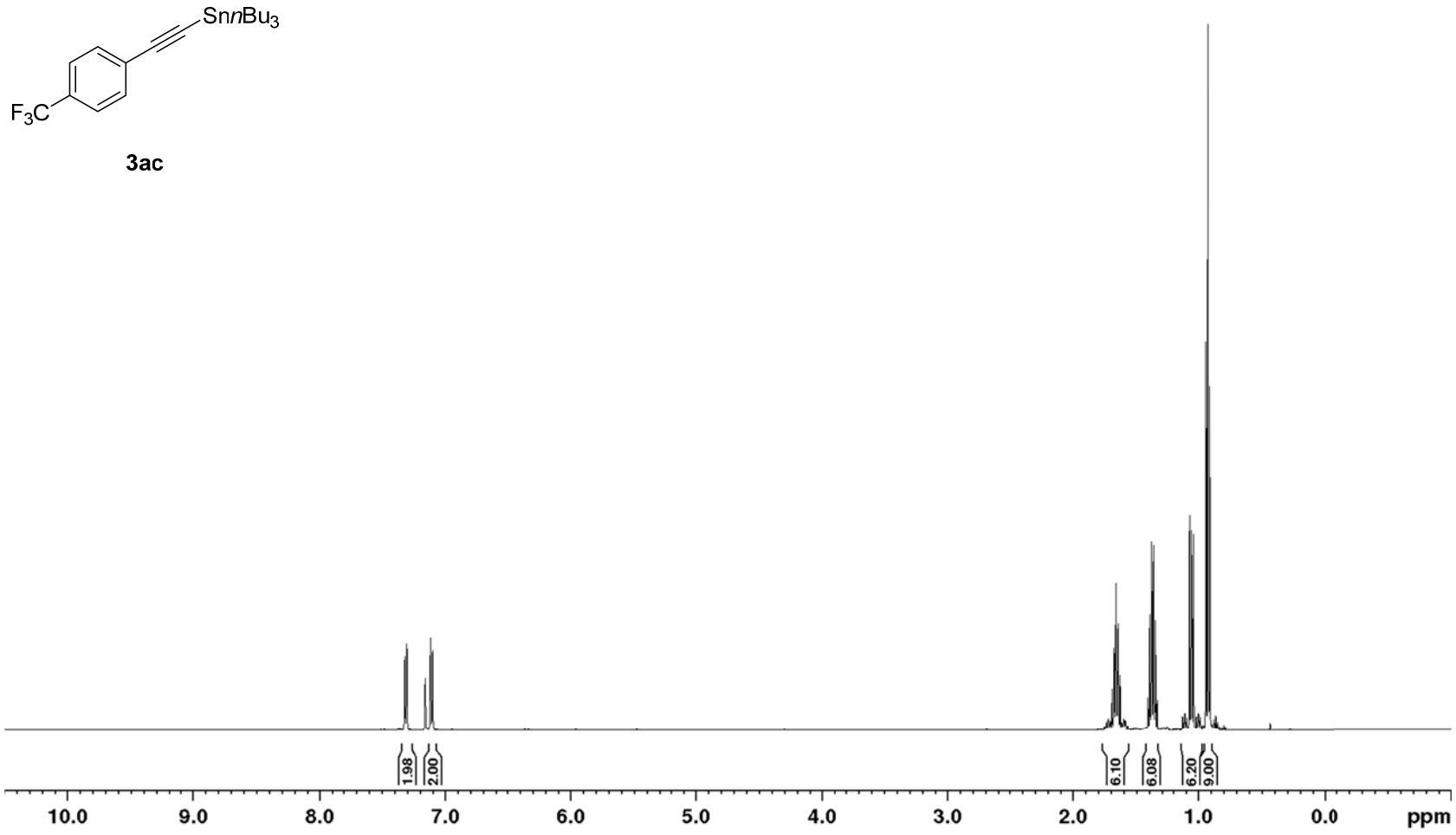


Figure S11 ^{1}H NMR (500 MHz, C_6D_6): Tributyl((4-(trifluoromethyl)phenyl)ethynyl)stannane (**3ac**)

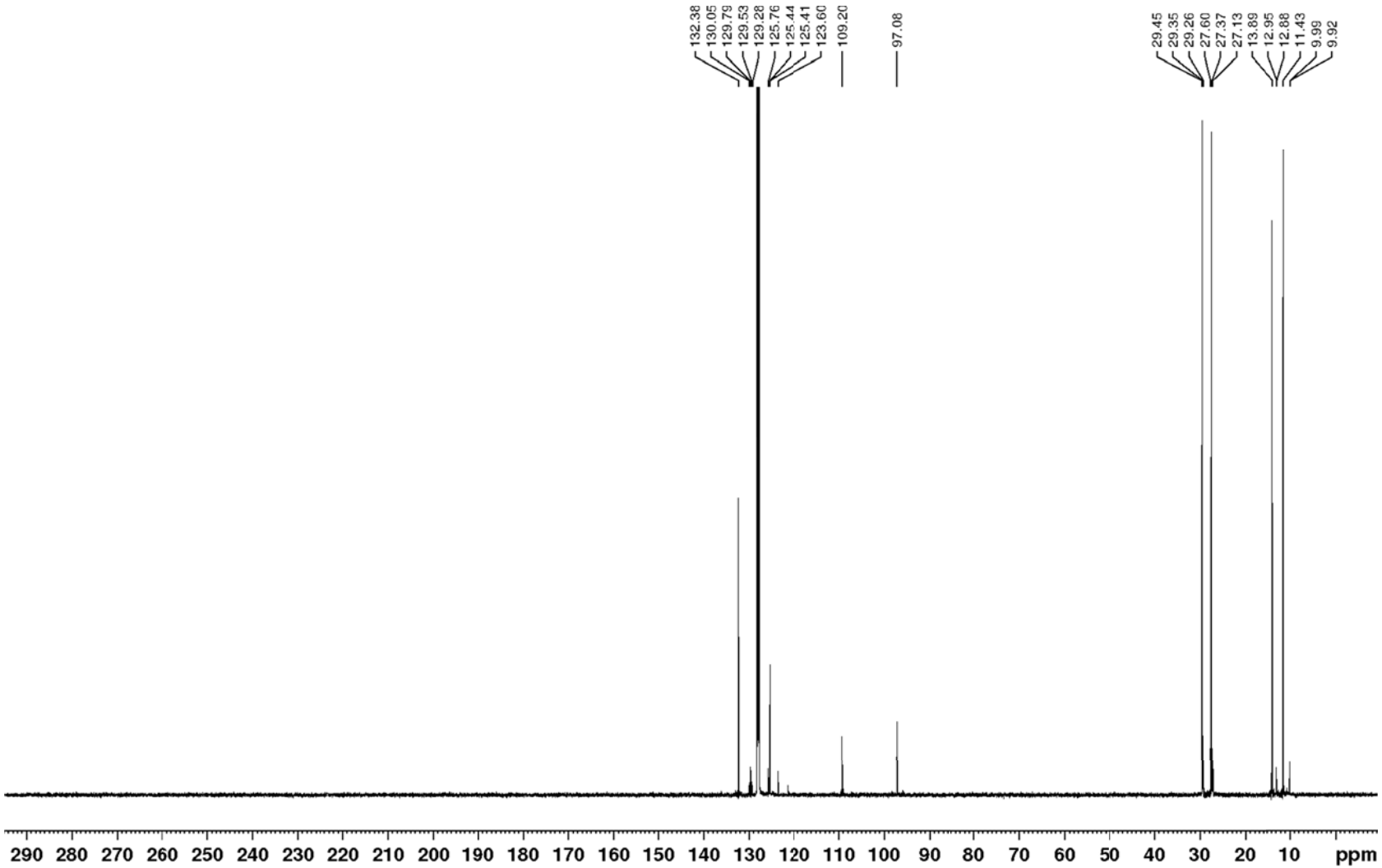


Figure S12 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl((4-(trifluoromethyl)phenyl)ethynyl)stannane (**3ac**)

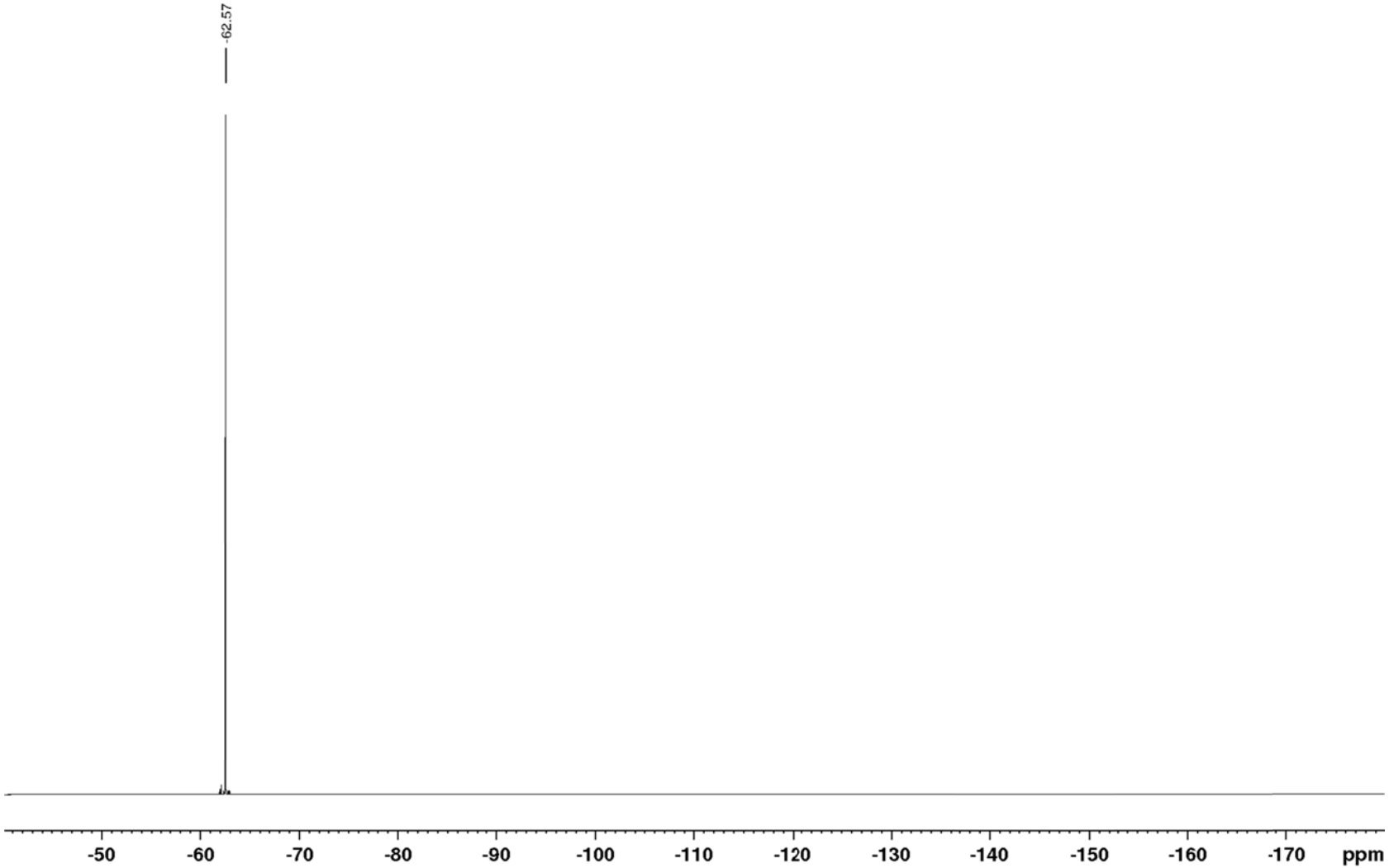


Figure S13 $^{19}F\{^{1}H\}$ NMR (471 MHz, C_6D_6): Tributyl((4-(trifluoromethyl)phenyl)ethynyl)stannane (**3ac**)

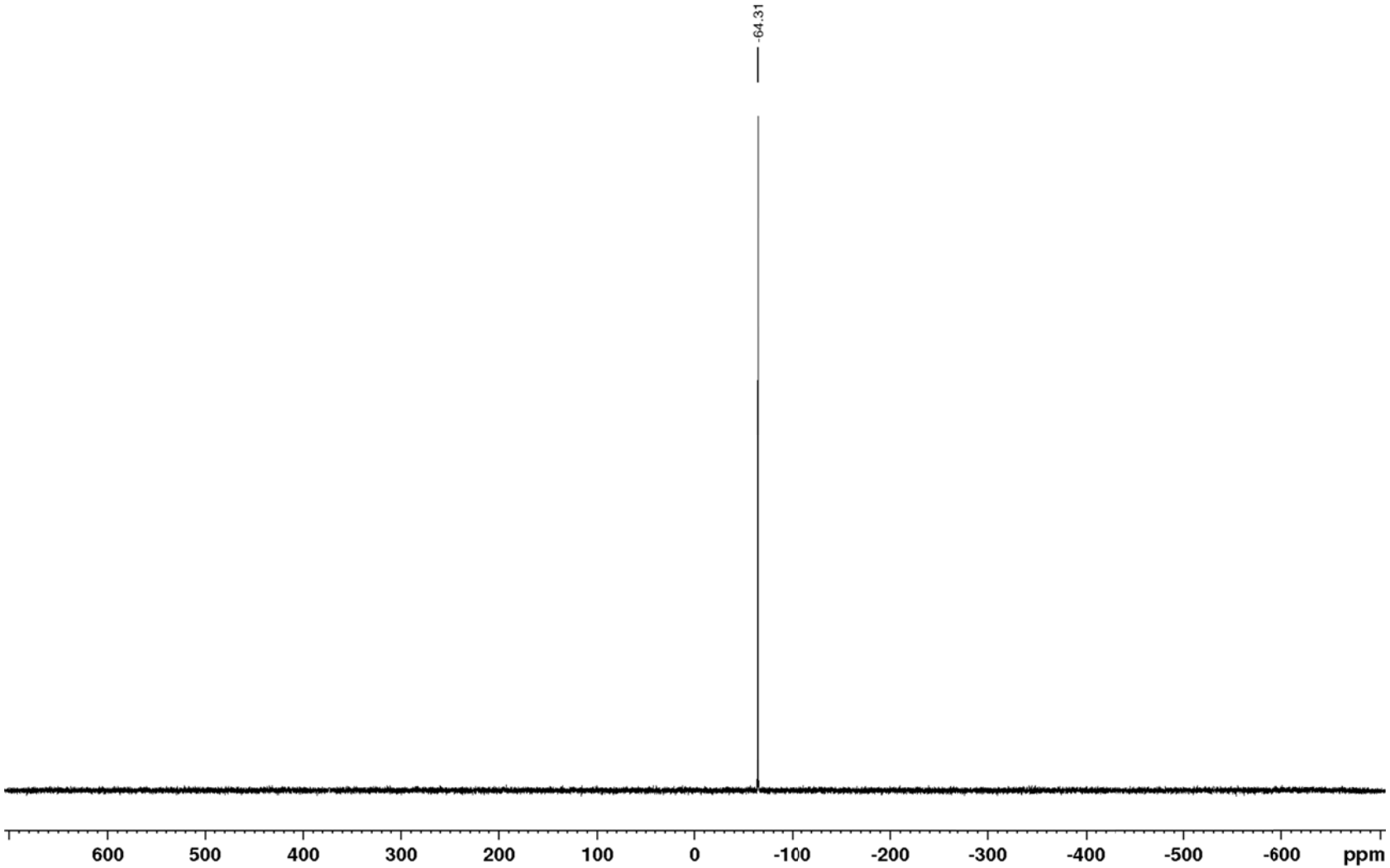


Figure S14 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl((4-(trifluoromethyl)phenyl)ethynyl)stannane (**3ac**)

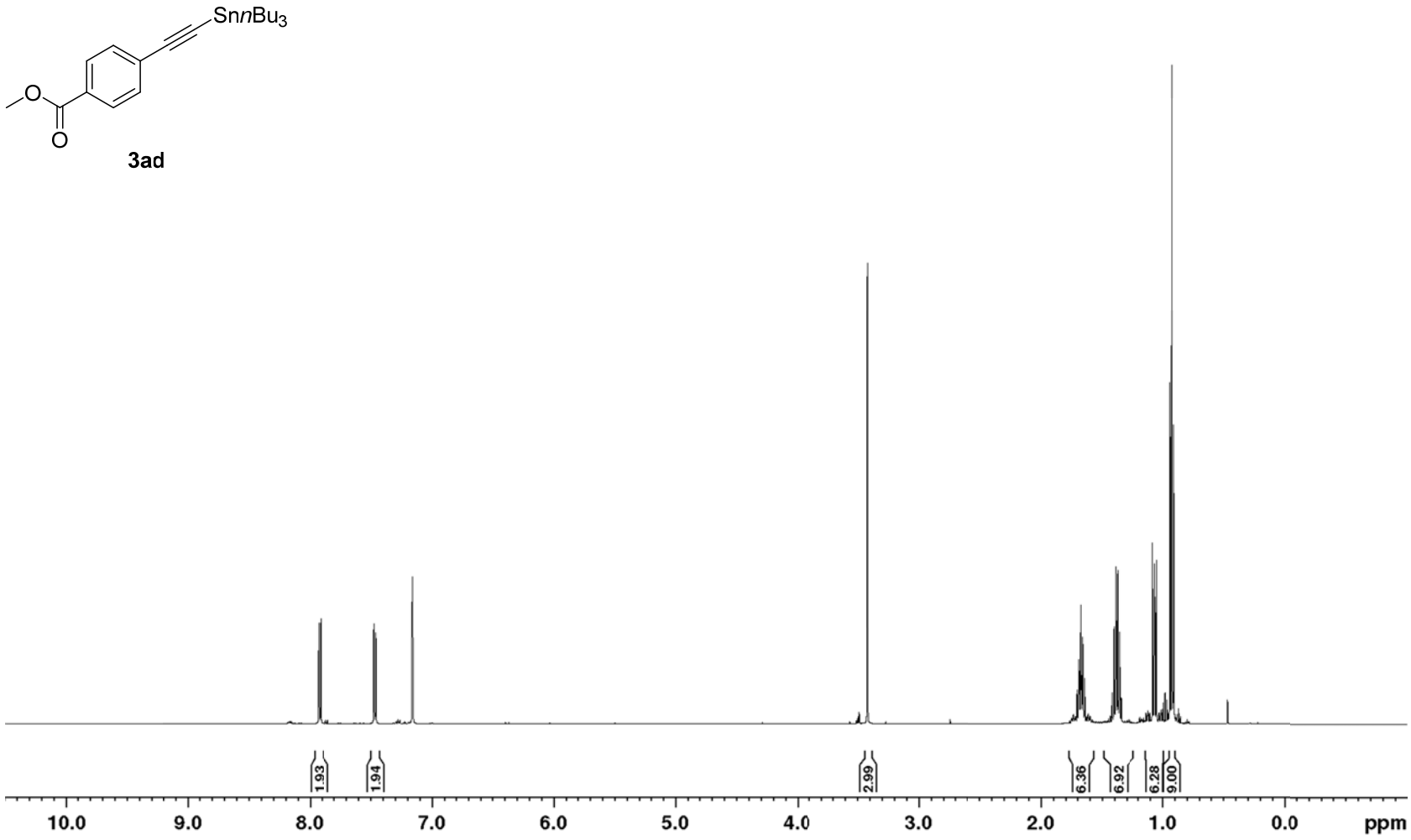


Figure S15 ^{1}H NMR (500 MHz, C_6D_6): Methyl 4-((tributylstannyl)ethynyl)benzoate (**3ad**)

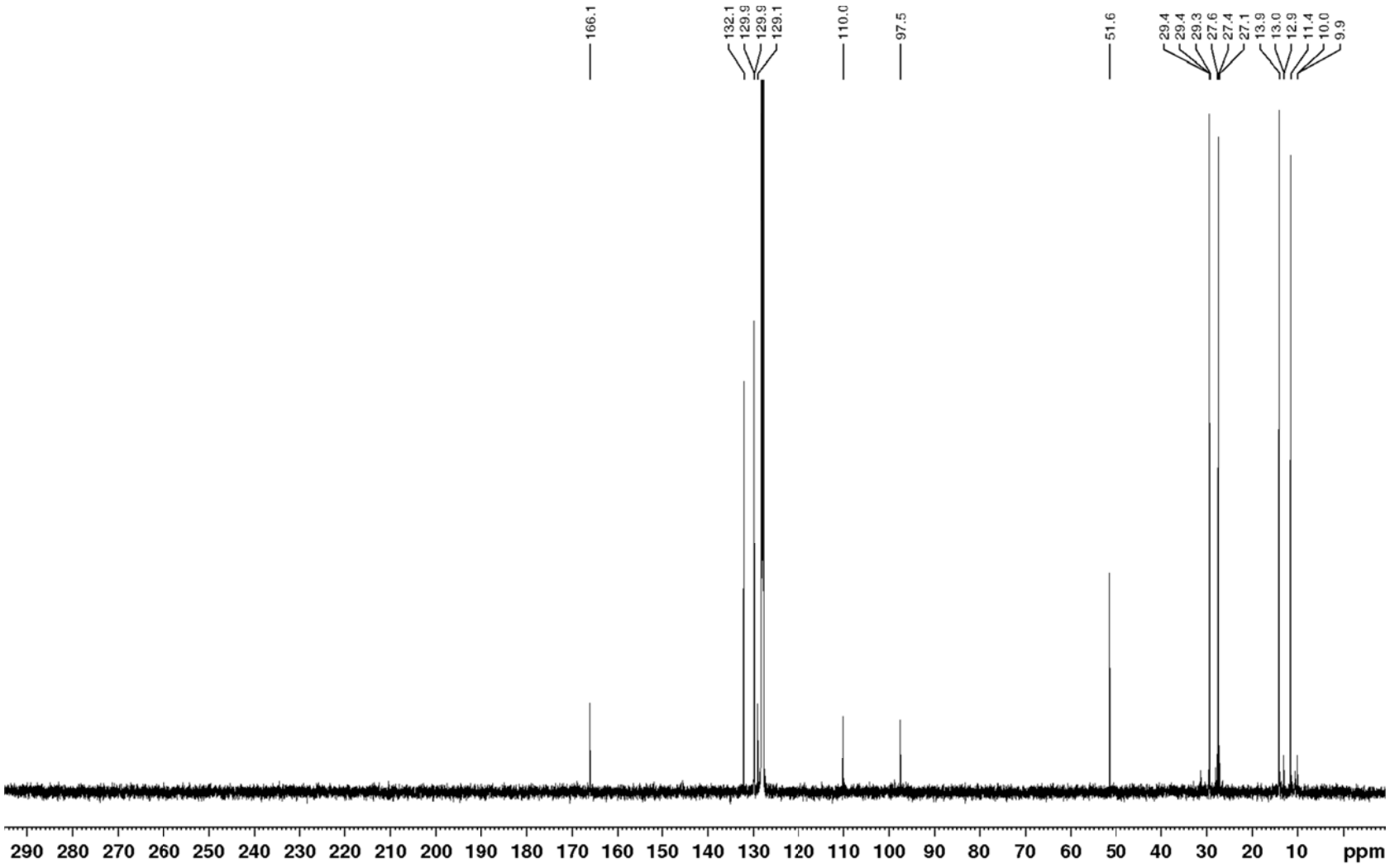


Figure S16 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Methyl 4-((tributylstannyl)ethynyl)benzoate (**3ad**)

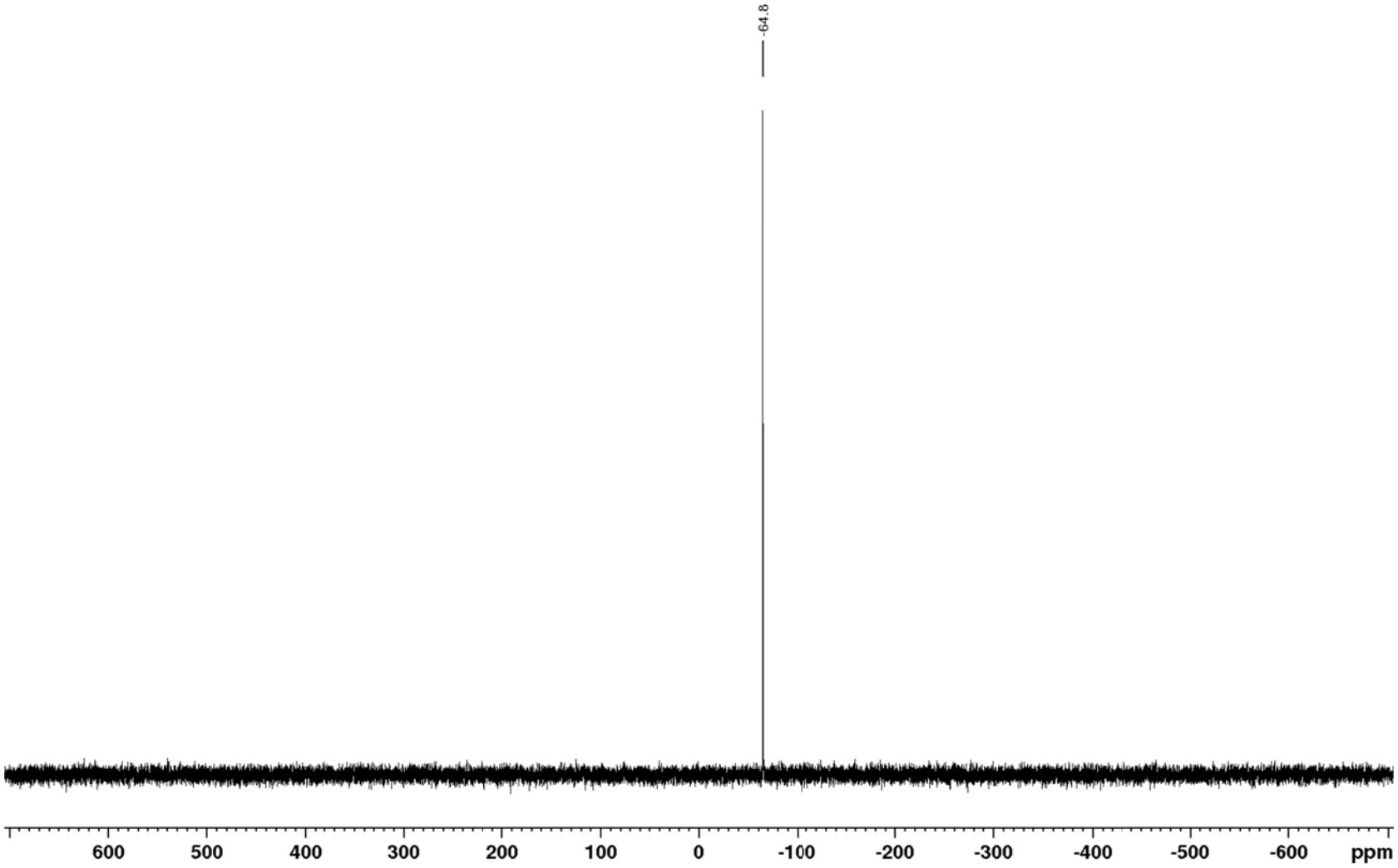


Figure S17 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Methyl 4-((tributylstannyl)ethynyl)benzoate (**3ad**)

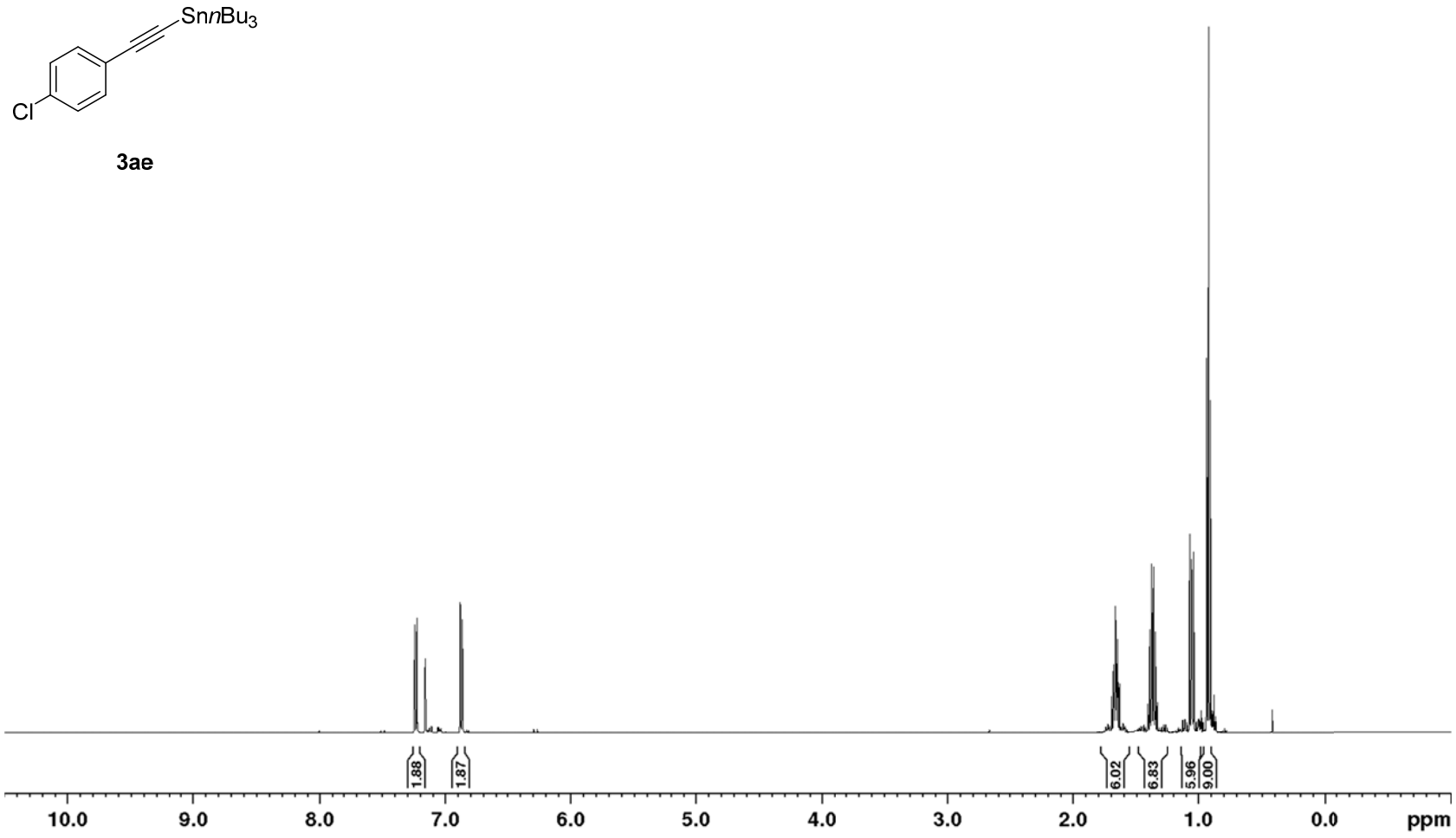


Figure S18 ^{1}H NMR (500 MHz, C_6D_6): Tributyl((4-chlorophenyl)ethynyl)stannane (**3ae**)

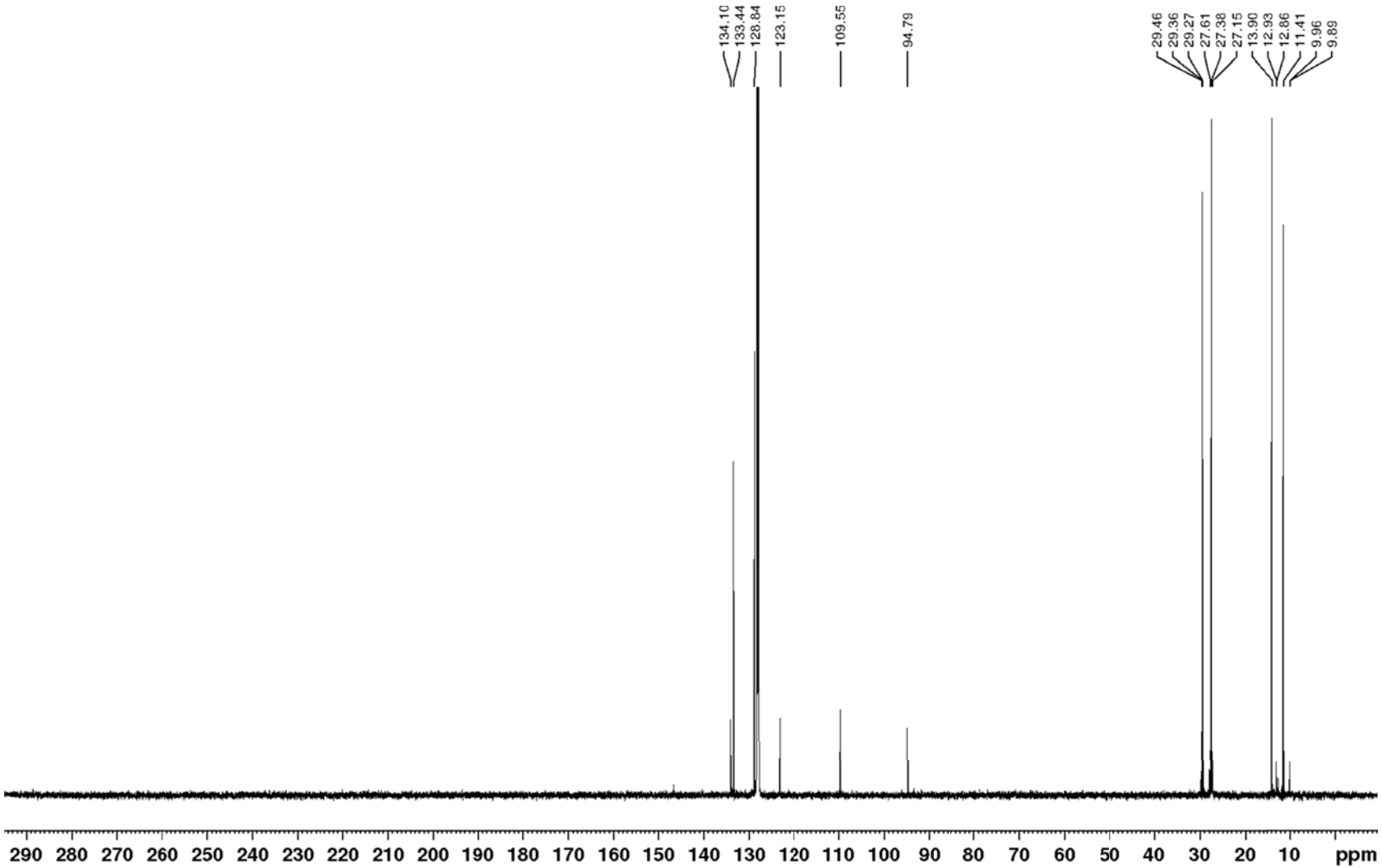


Figure S19 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl((4-chlorophenyl)ethynyl)stannane (**3ae**)

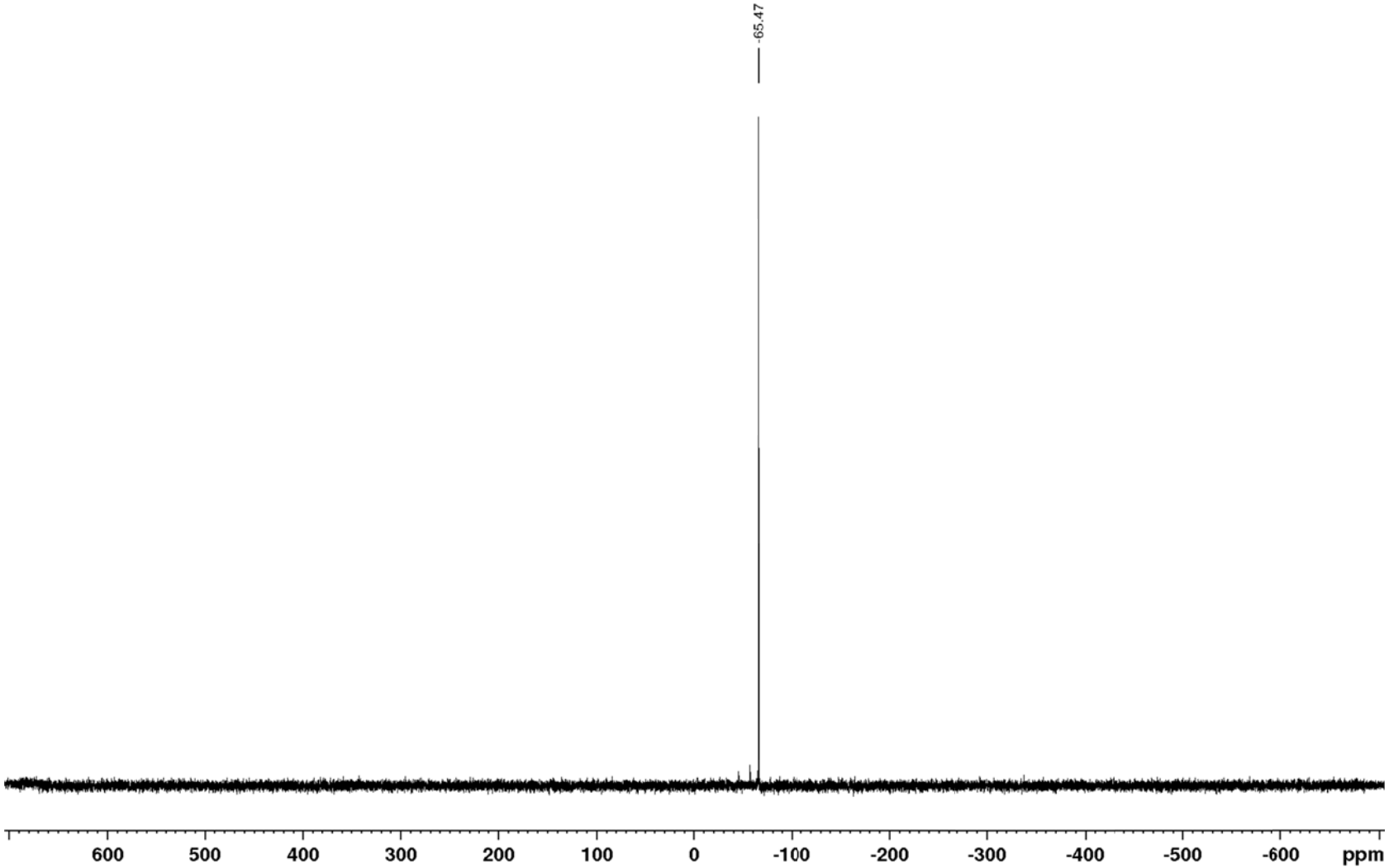


Figure S20 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl((4-chlorophenyl)ethynyl)stannane (**3ae**)

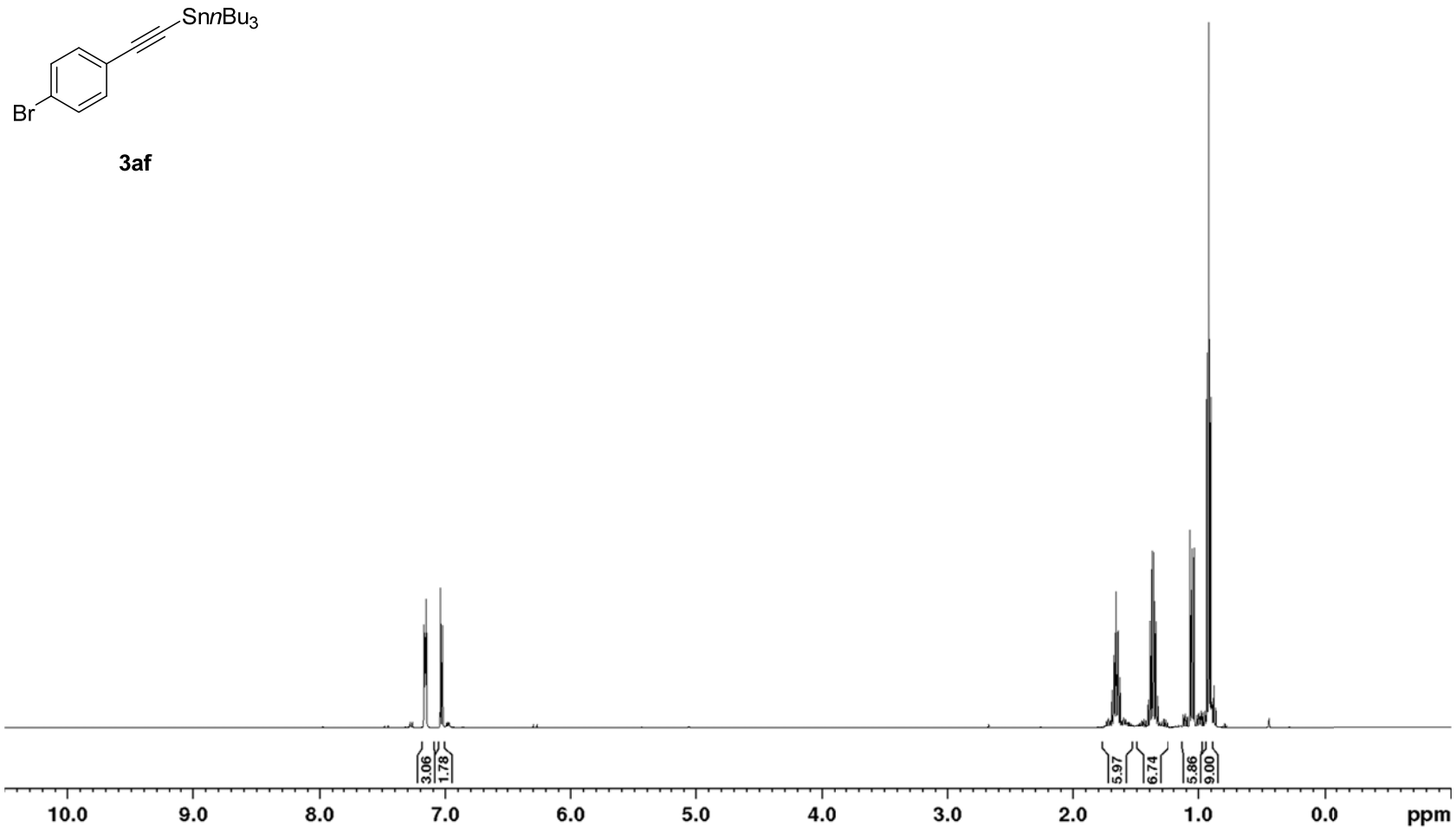


Figure S21 ^{1}H NMR (500 MHz, C_6D_6): ((4-bromophenyl)ethynyl)tributylstannane (**3af**)

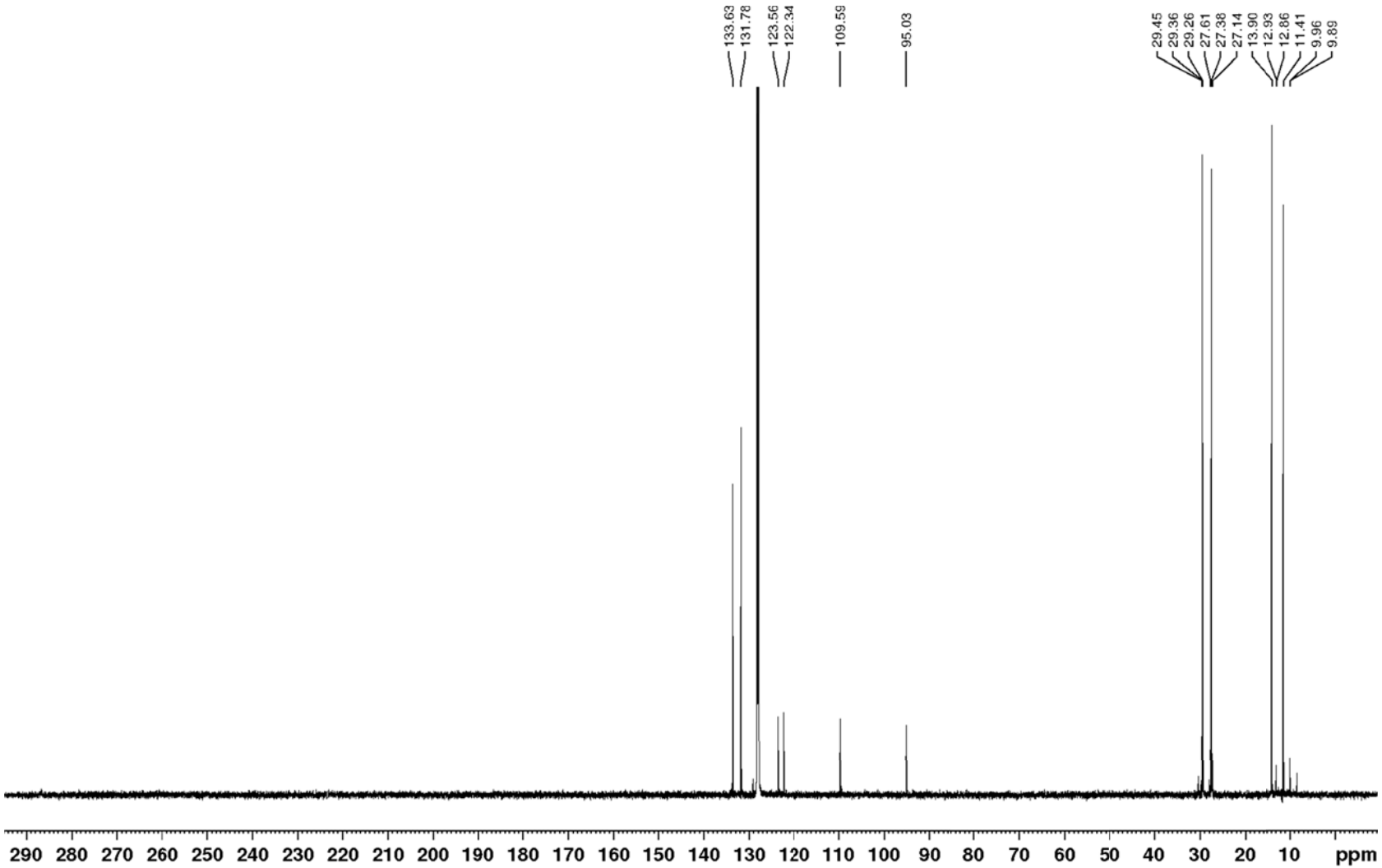


Figure S22 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): ((4-bromophenyl)ethynyl)tributylstannane (**3af**)

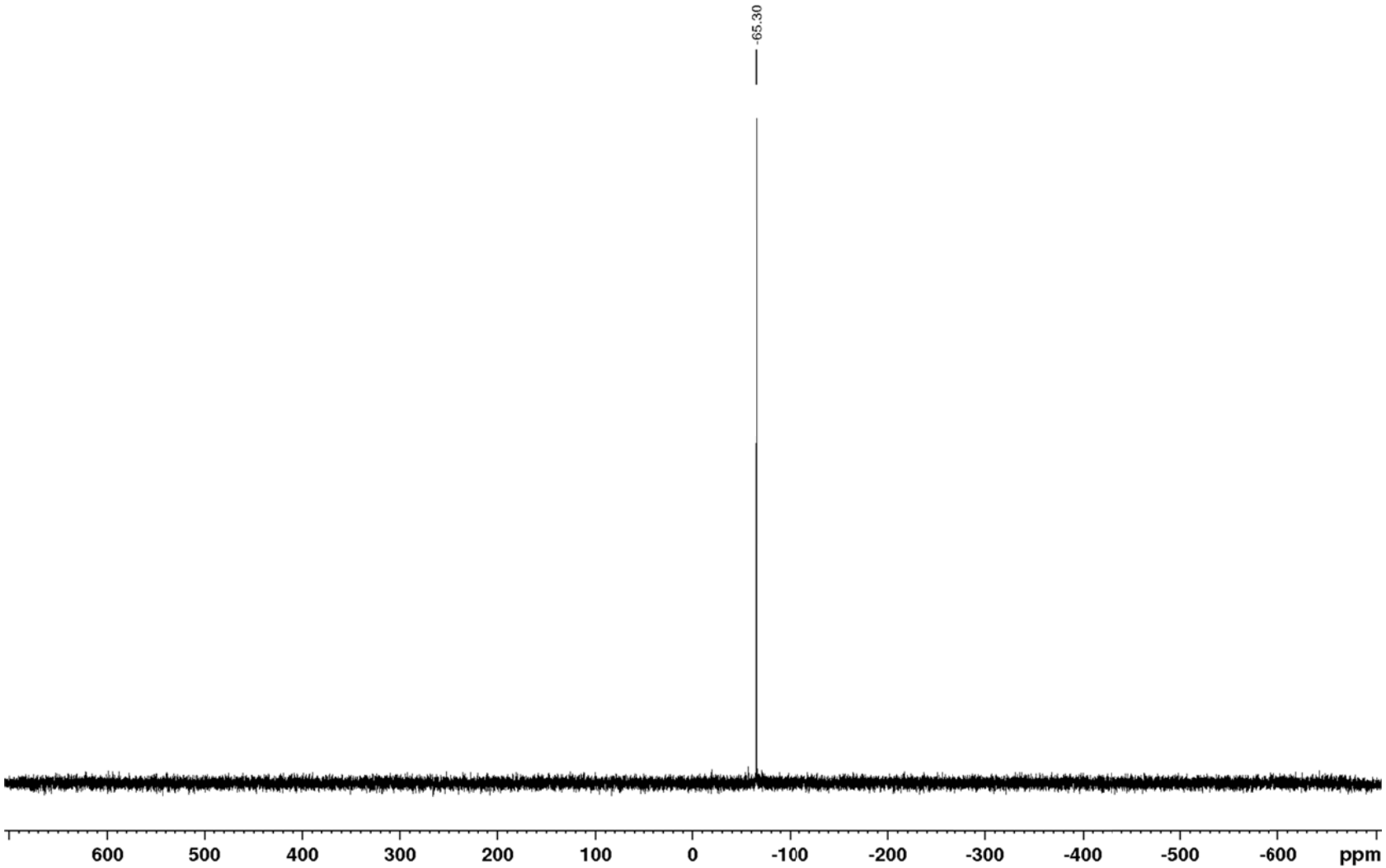


Figure S23 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): ((4-bromophenyl)ethynyl)tributylstannane (**3af**)

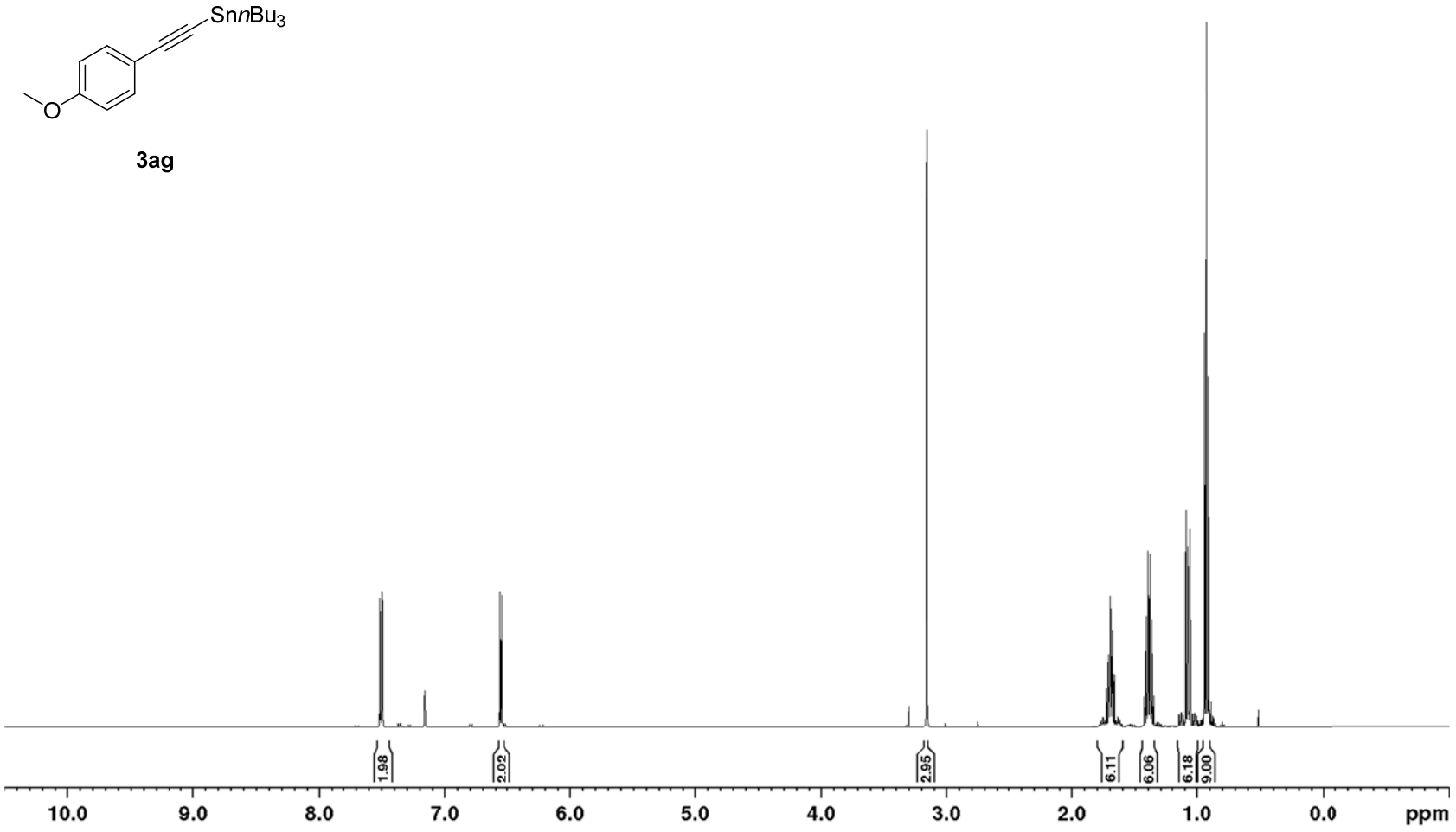


Figure S24 ^{1}H NMR (500 MHz, C_6D_6): Tributyl((4-methoxyphenyl)ethynyl)stannane (**3ag**)

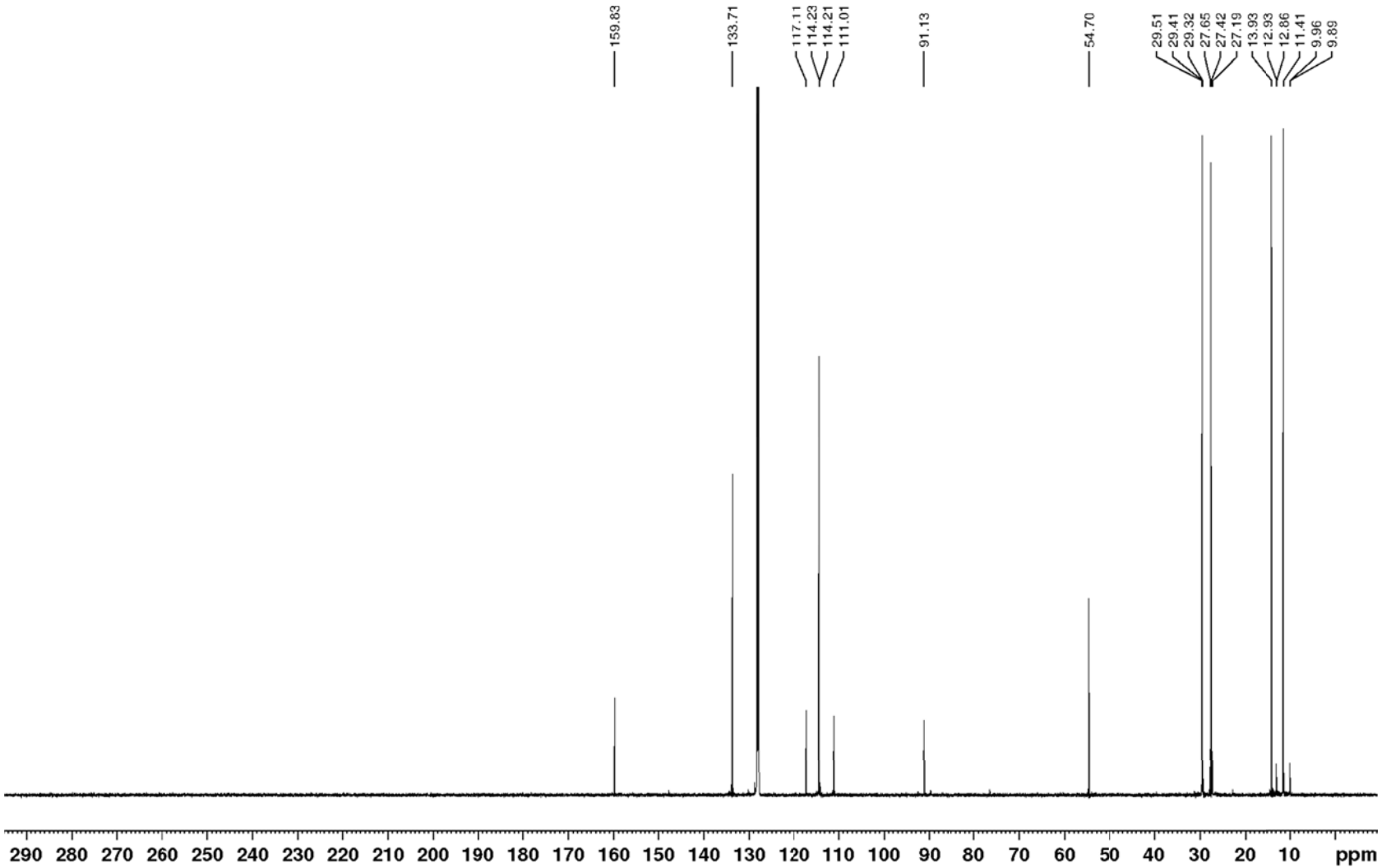


Figure S25 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl((4-methoxyphenyl)ethynyl)stannane (**3ag**)

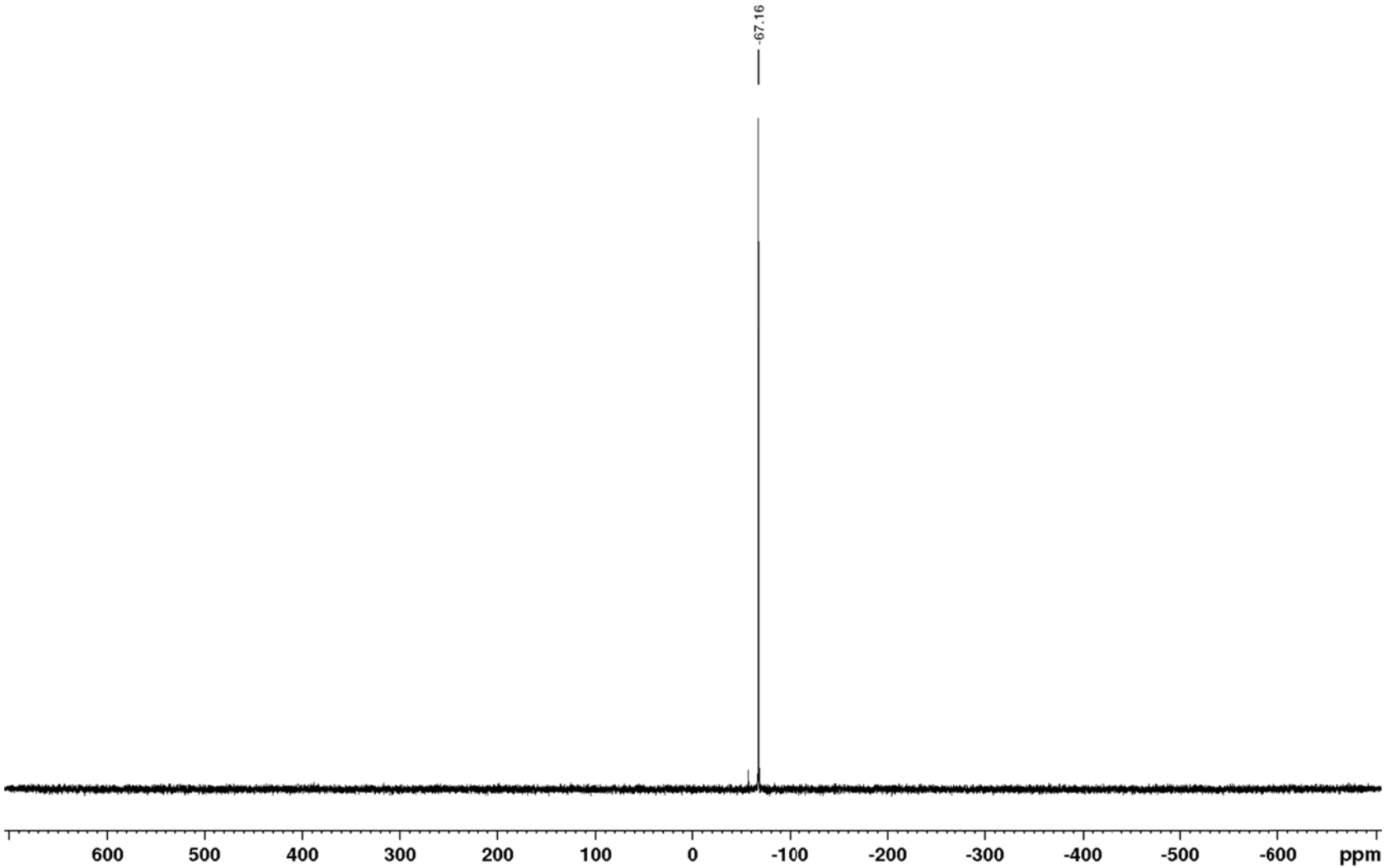


Figure S26 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl((4-methoxyphenyl)ethynyl)stannane (**3ag**)

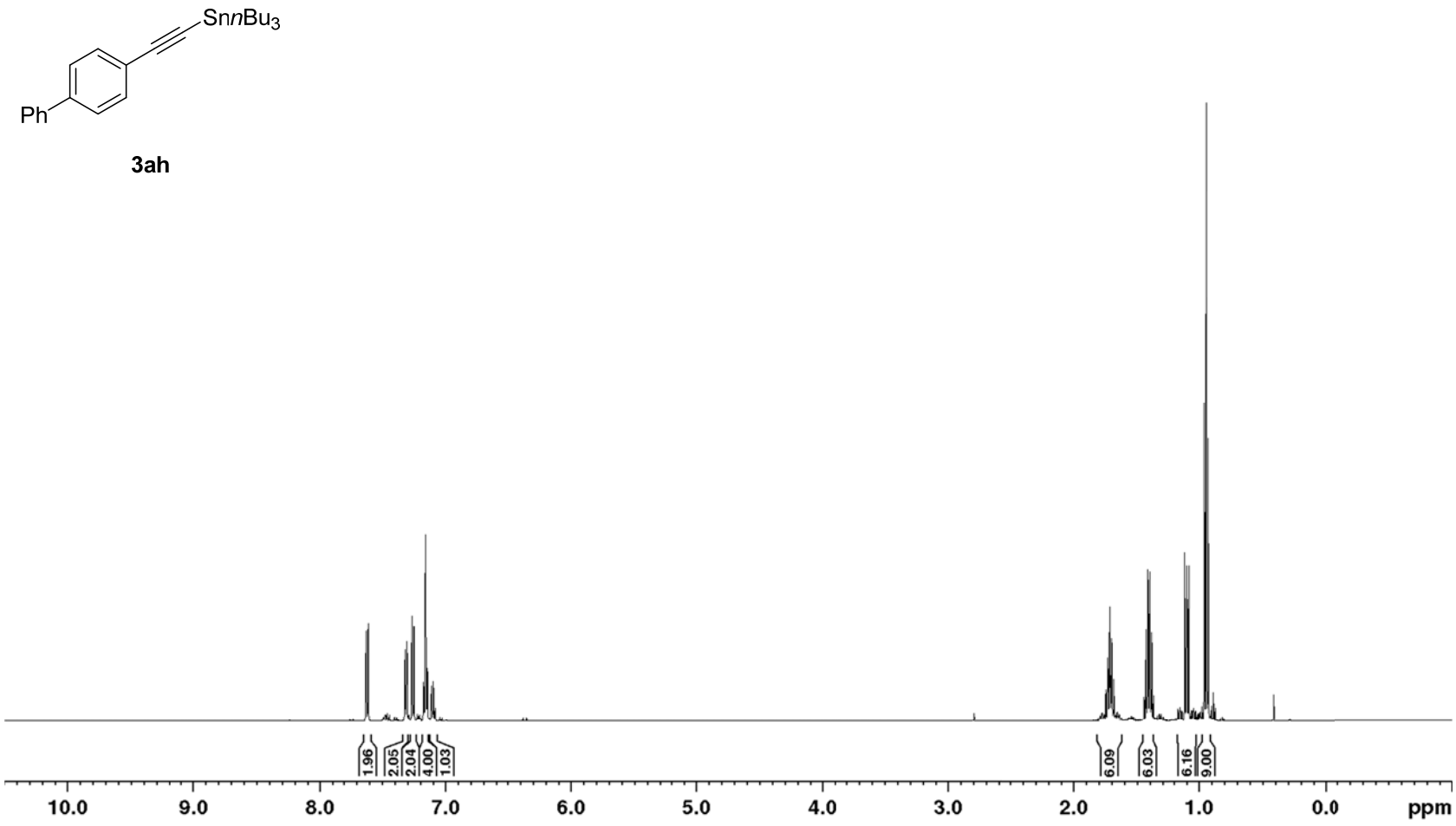


Figure S27 ^{1}H NMR (500 MHz, C_6D_6): ([1,1'-biphenyl]-4-ylethynyl)tributylstannane (**3ah**)

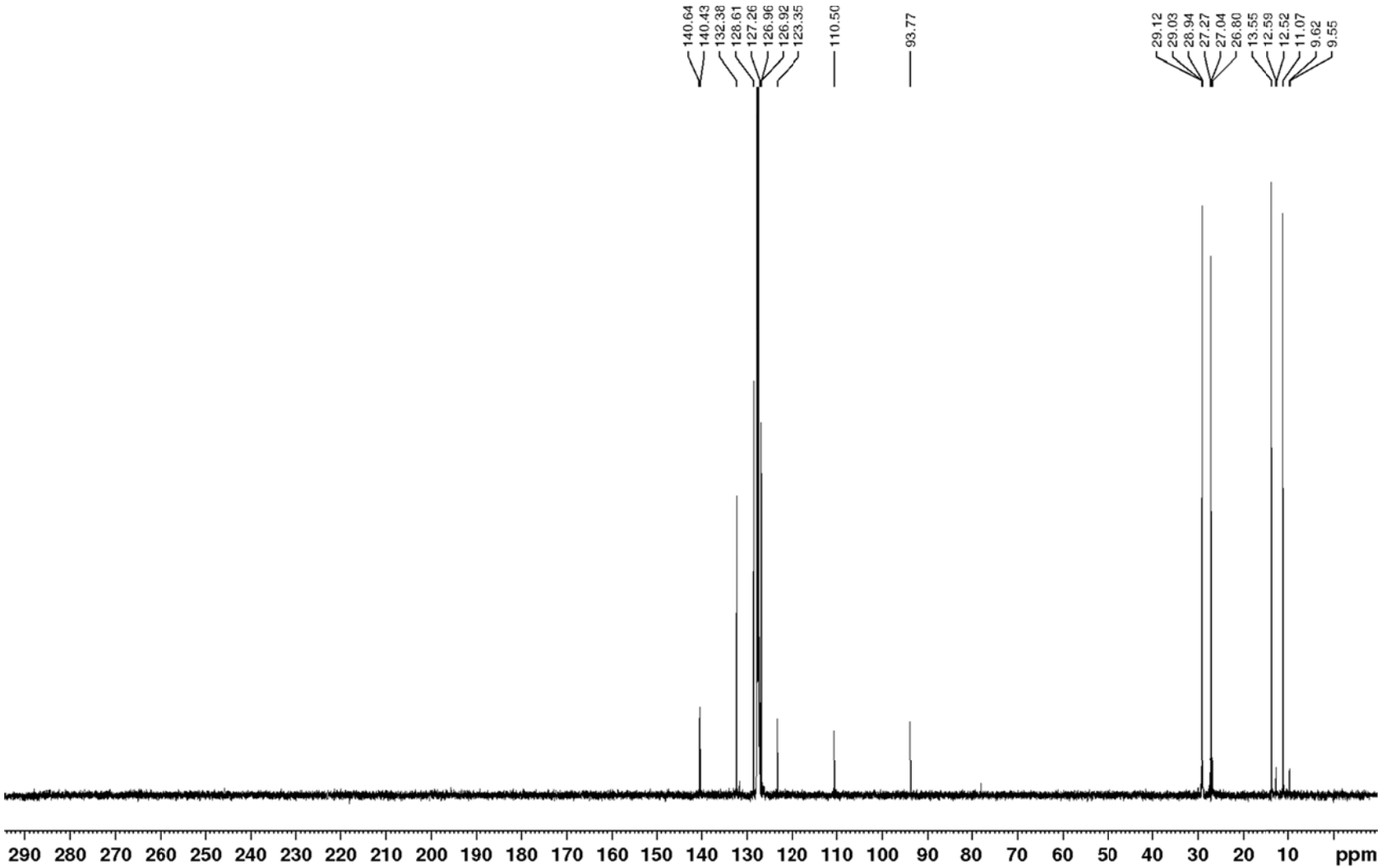


Figure S28 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): ([1,1'-biphenyl]-4-ylethynyl)tributylstannane (**3ah**)

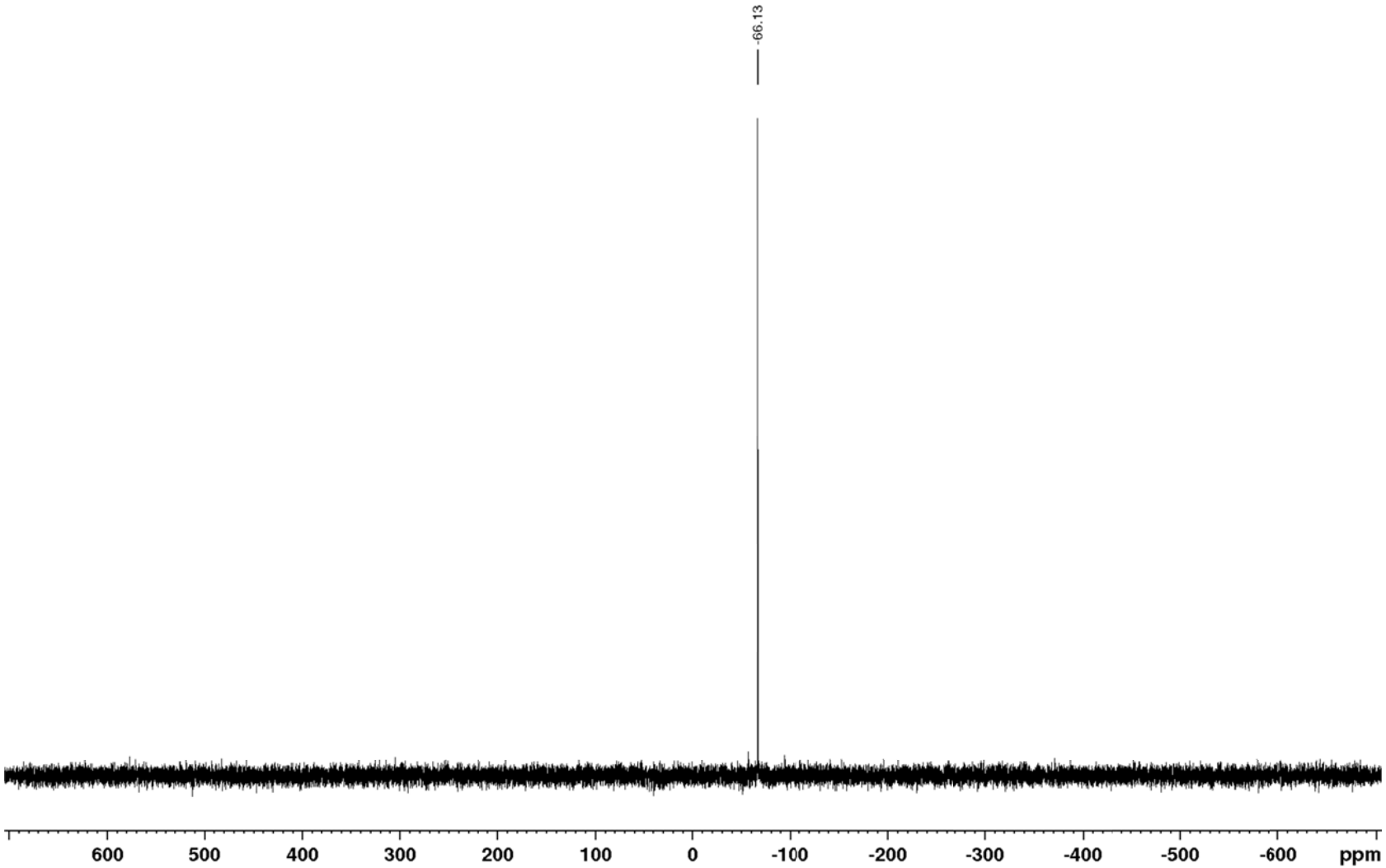


Figure S29 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): ([1,1'-biphenyl]-4-ylethynyl)tributylstannane (**3ah**)

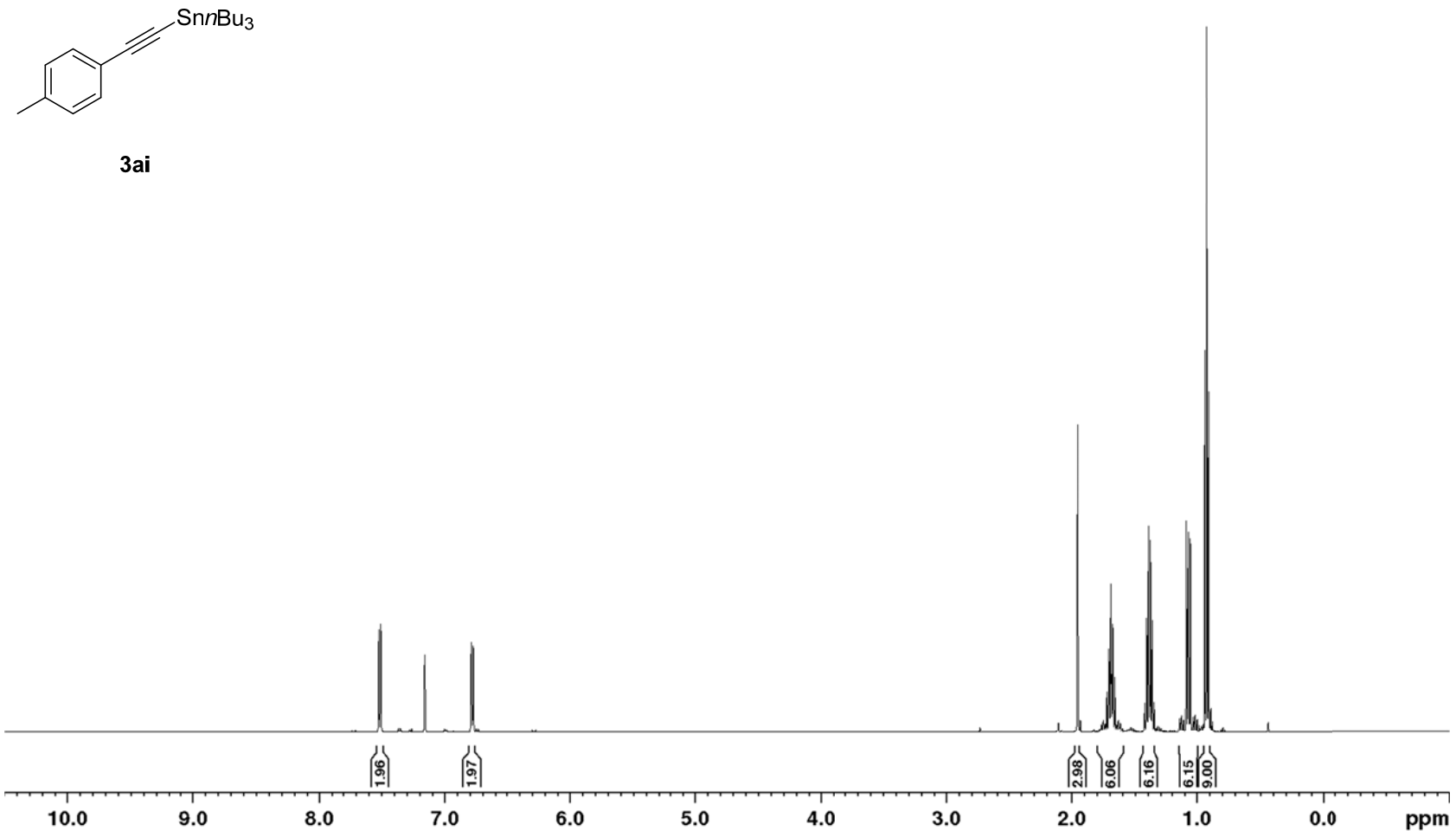


Figure S30 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(4-tolylethynyl)stannane (**3ai**)

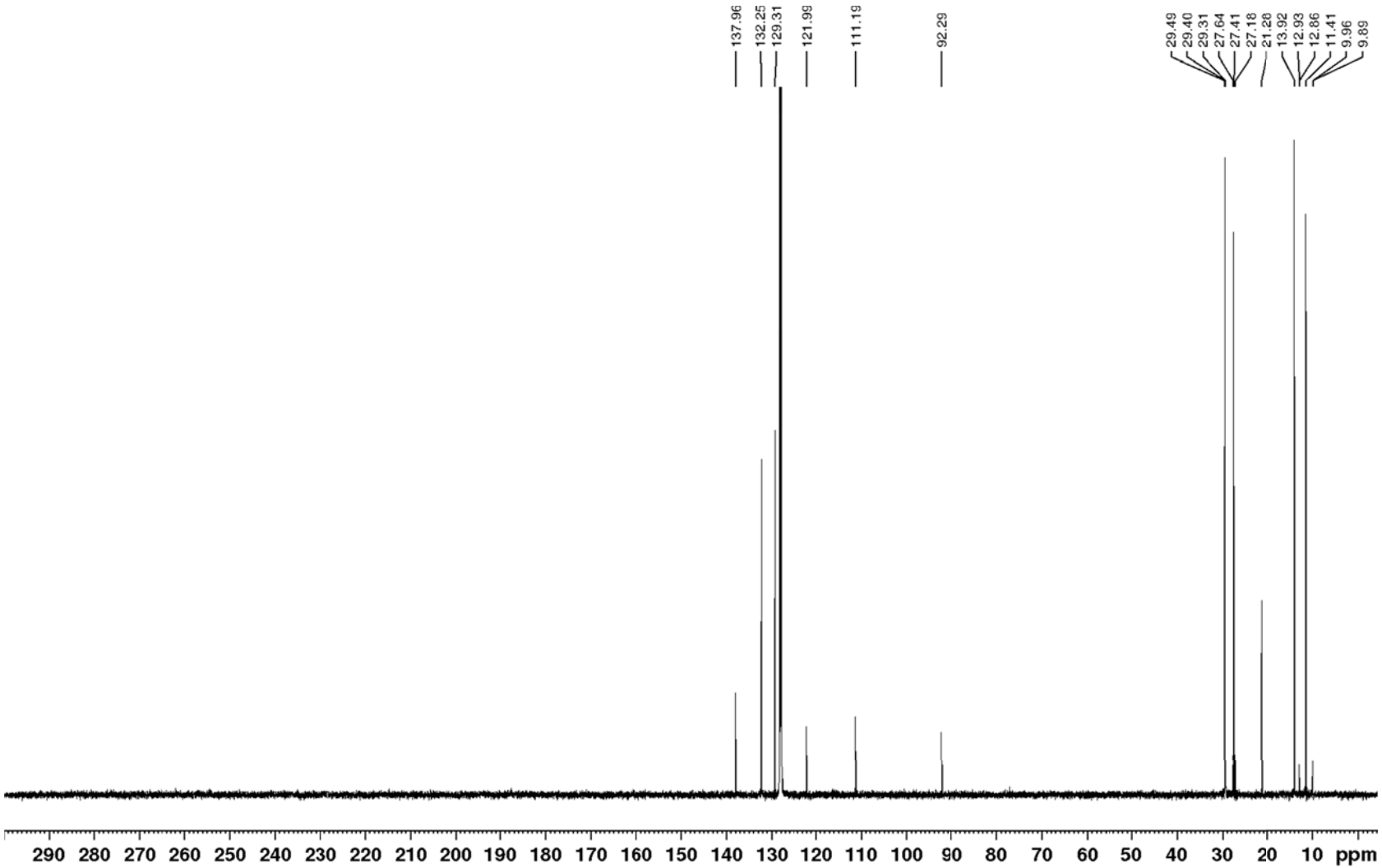


Figure S31 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(4-tolylethynyl)stannane (**3ai**)

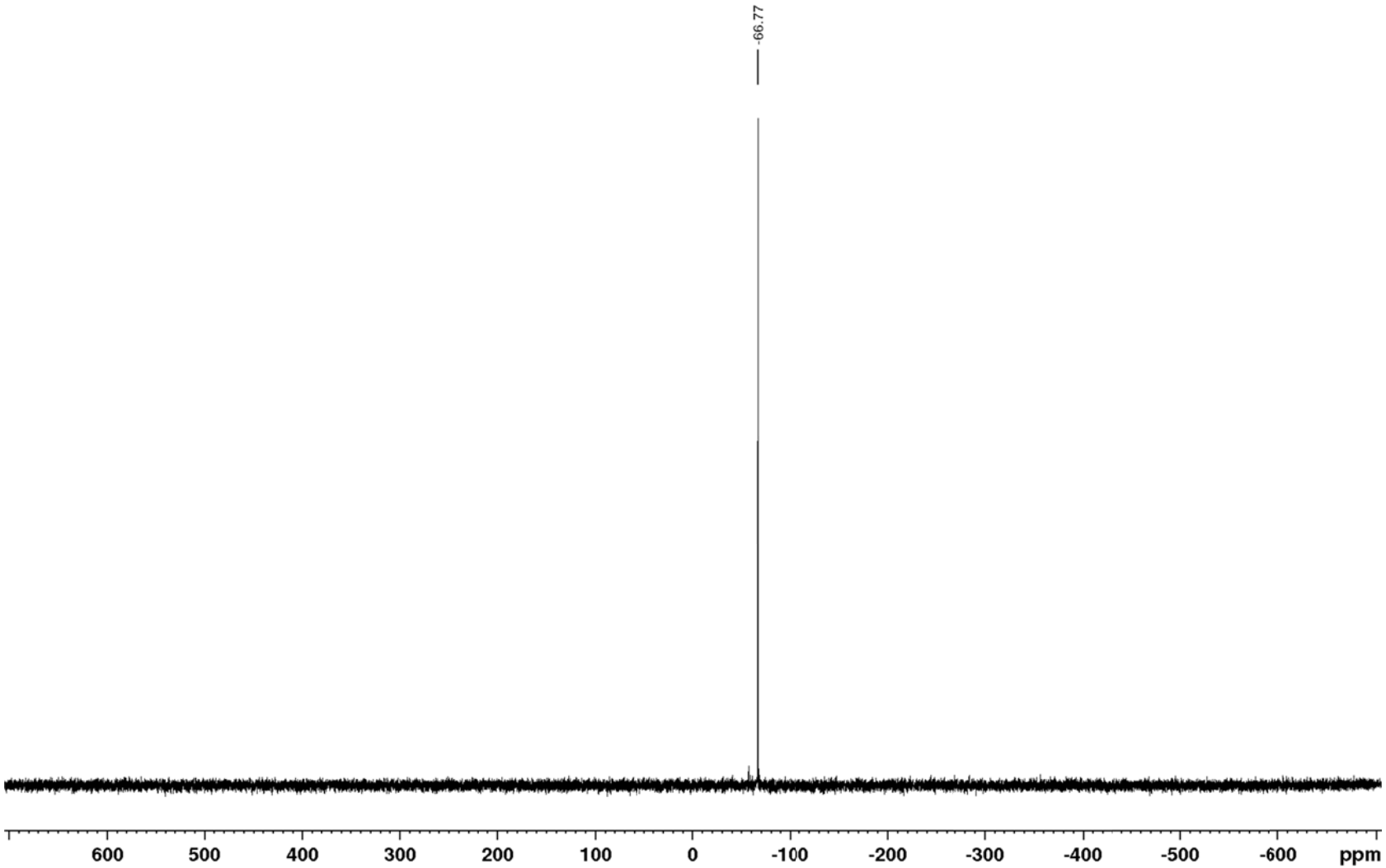


Figure S32 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(4-tolylethynyl)stannane (**3ai**)

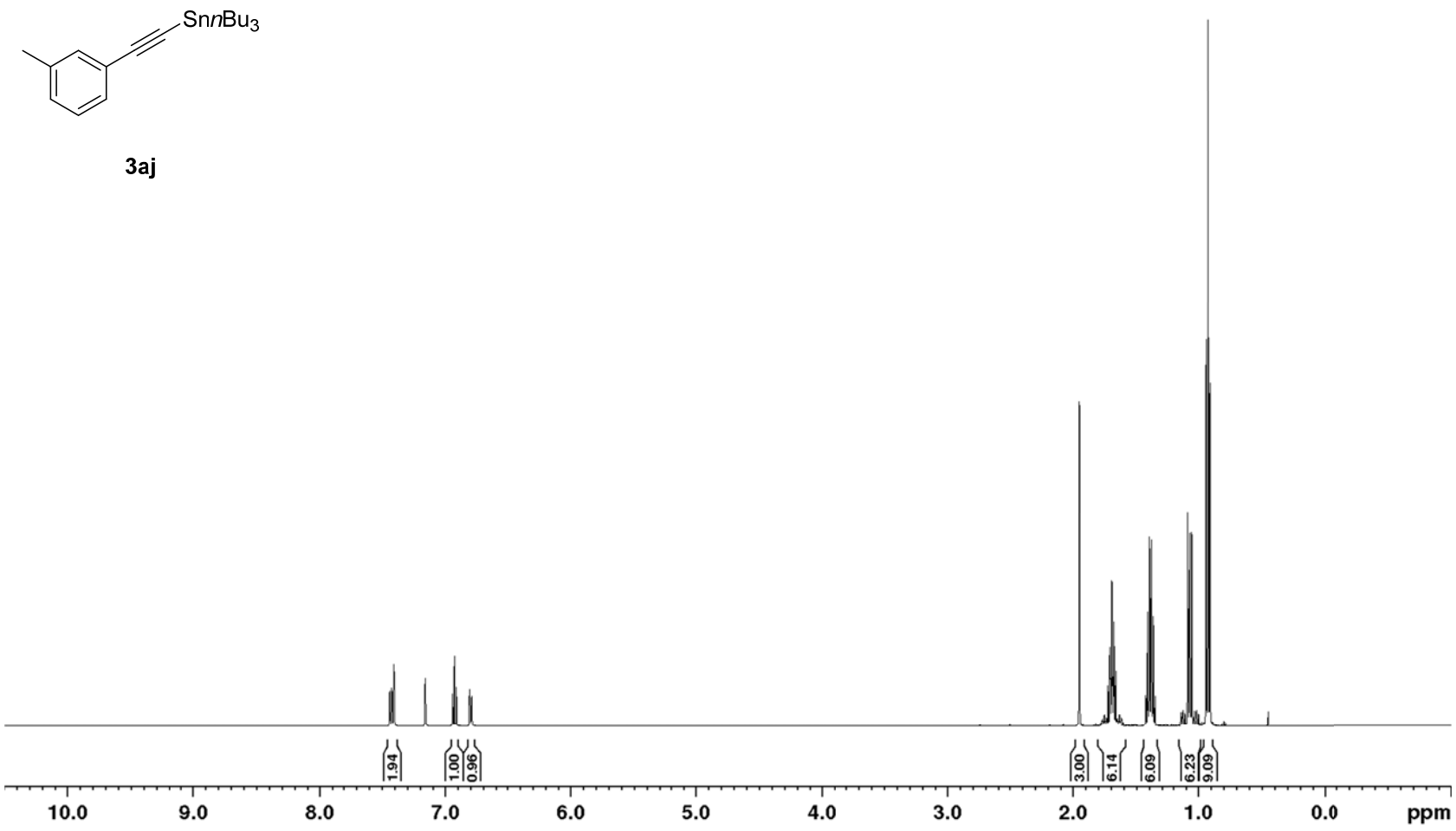


Figure S33 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(3-tolylethynyl)stannane (**3aj**)

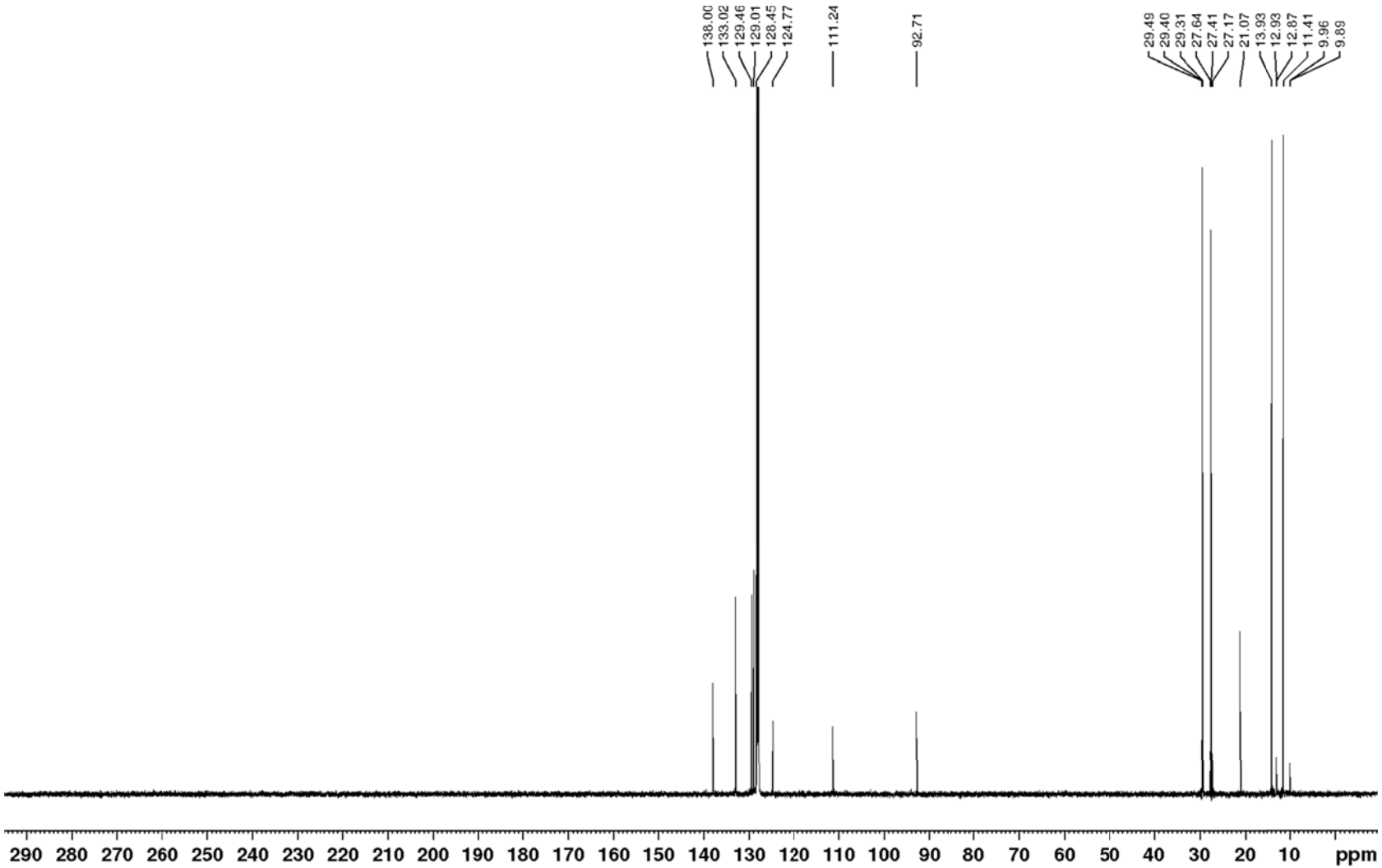


Figure S34 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(3-tolylethynyl)stannane (**3aj**)

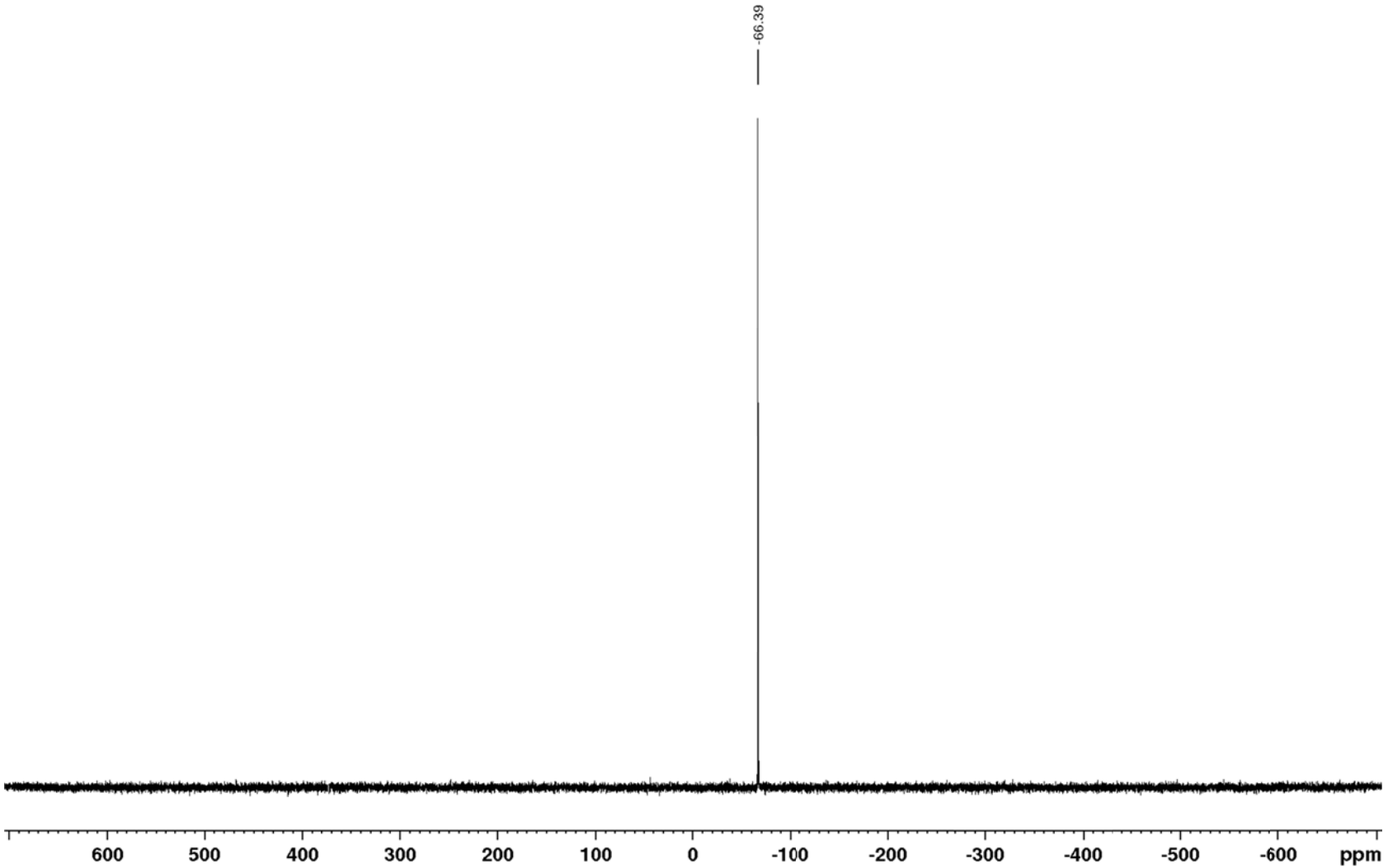


Figure S35 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(3-tolylethynyl)stannane (**3aj**)

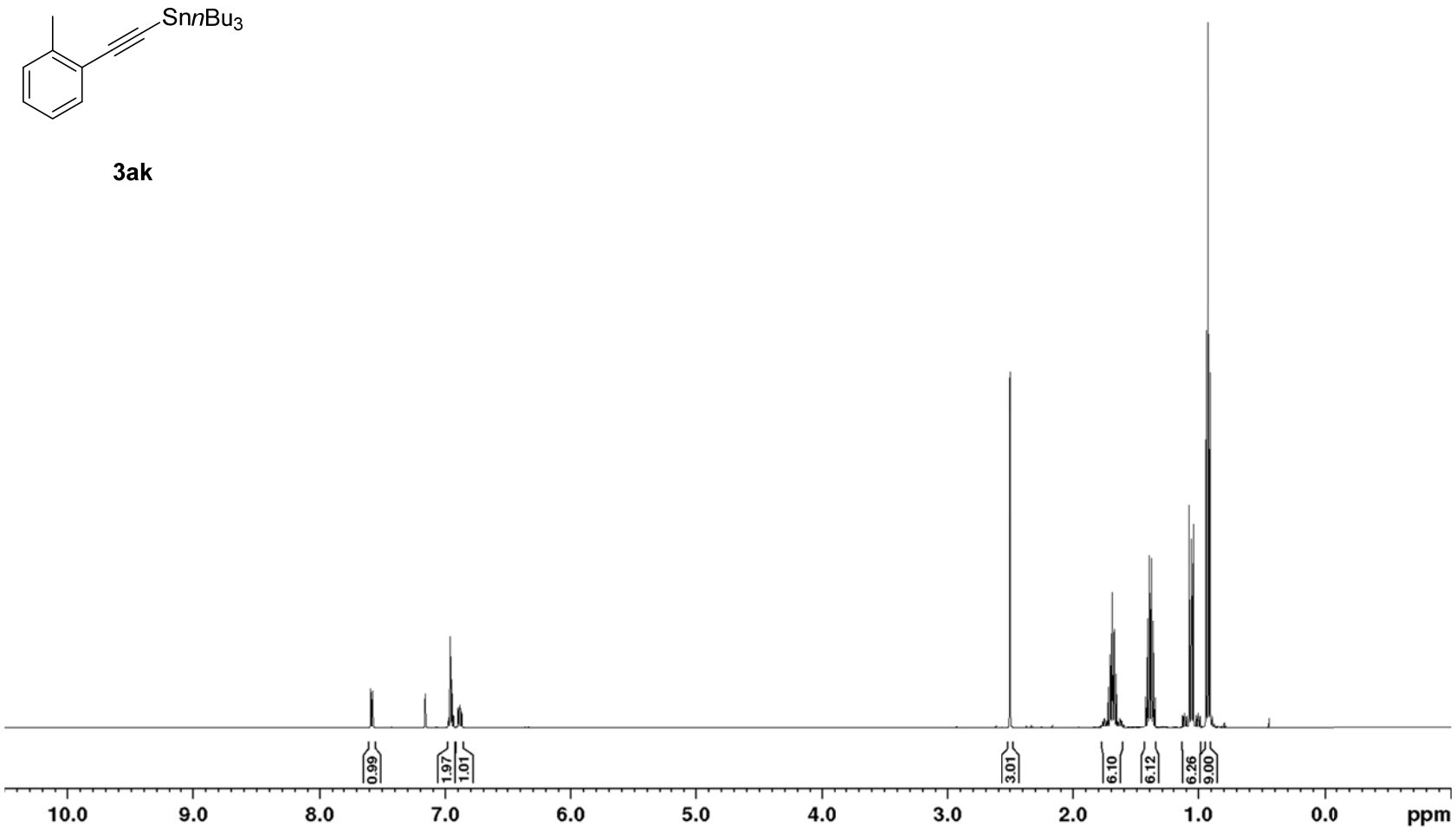


Figure S36 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(2-tolylethynyl)stannane (**3ak**)

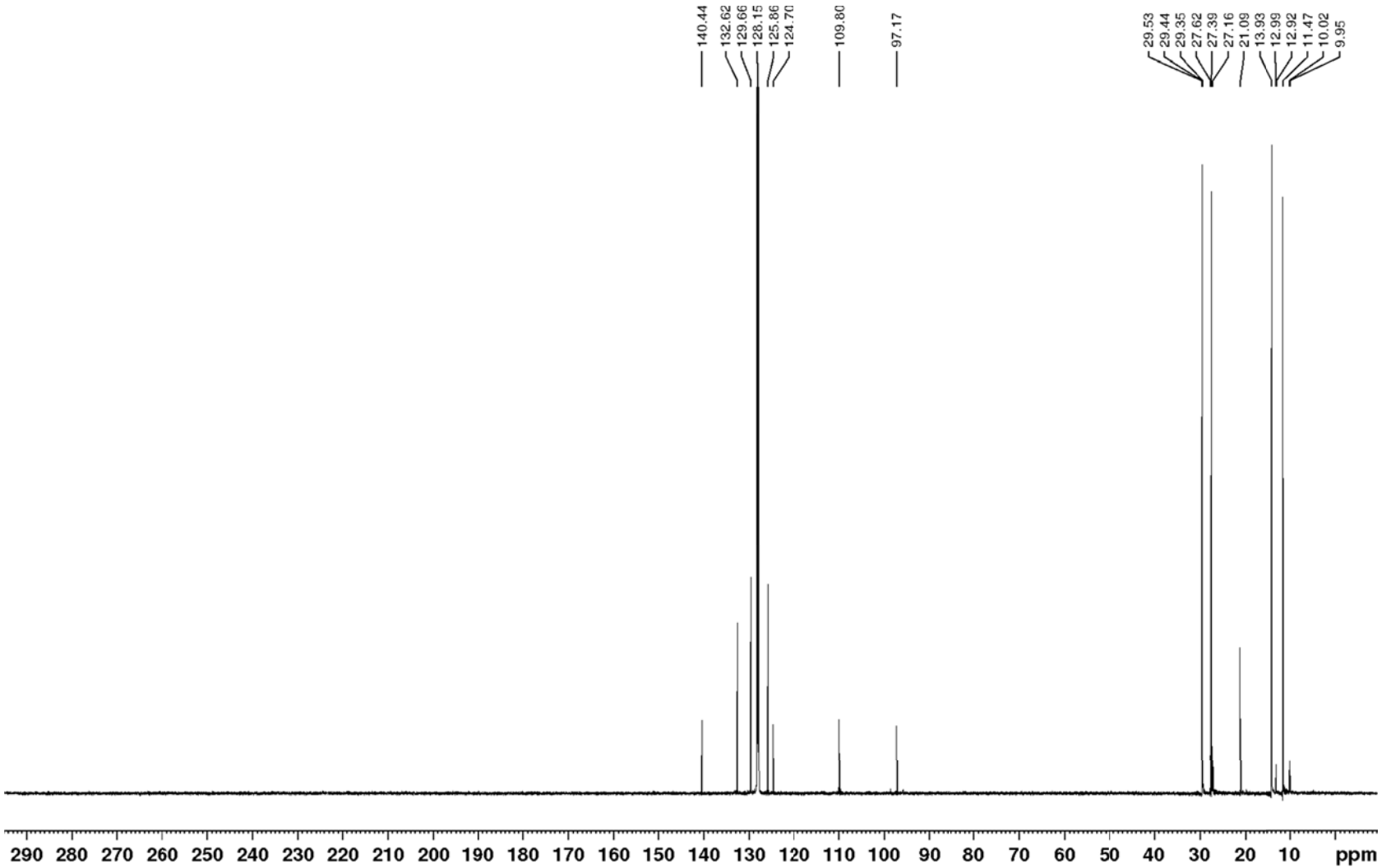


Figure S37 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(2-tolylethynyl)stannane (**3ak**)

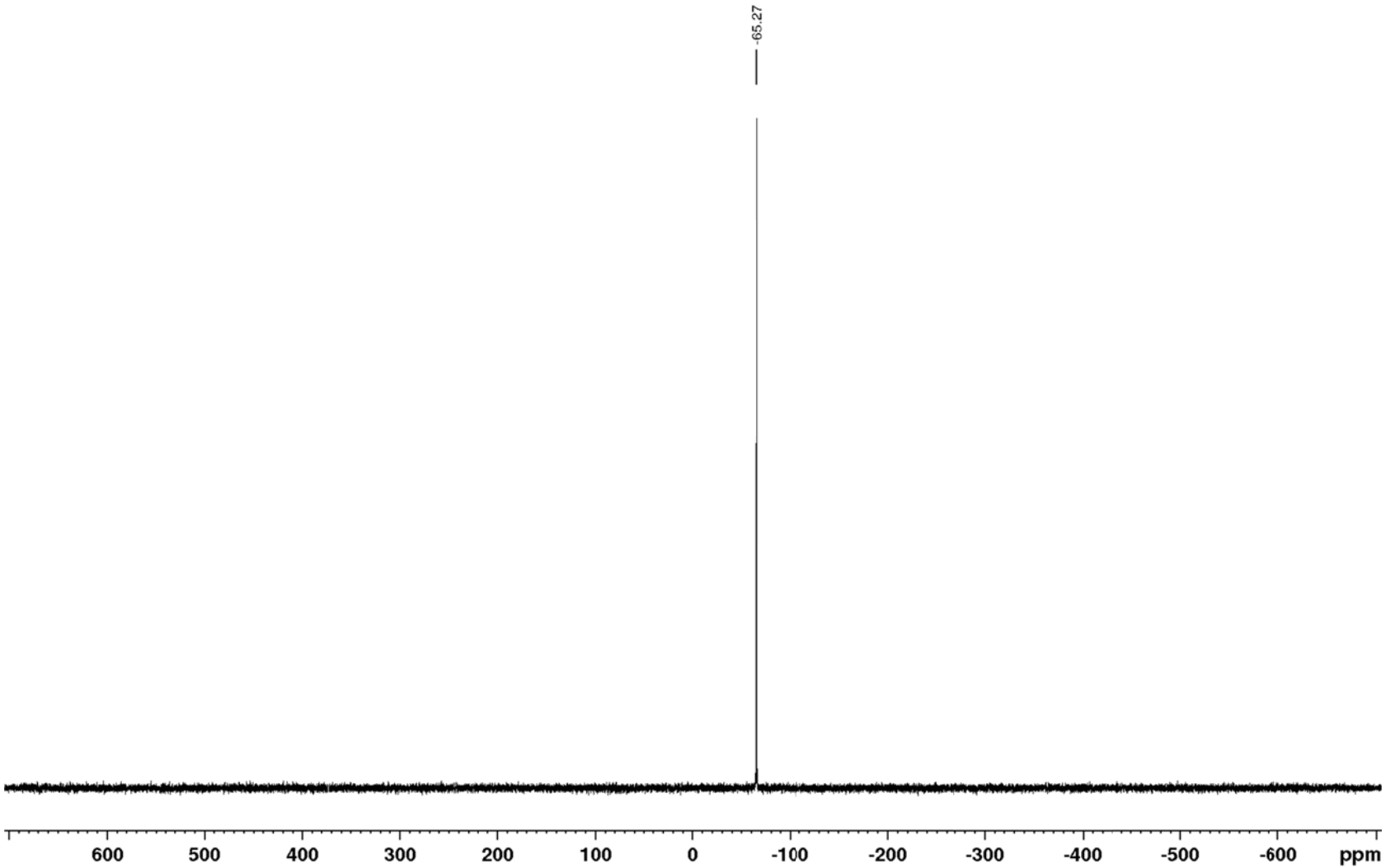
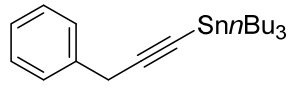


Figure S38 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(2-tolylethynyl)stannane (**3ak**)



3al

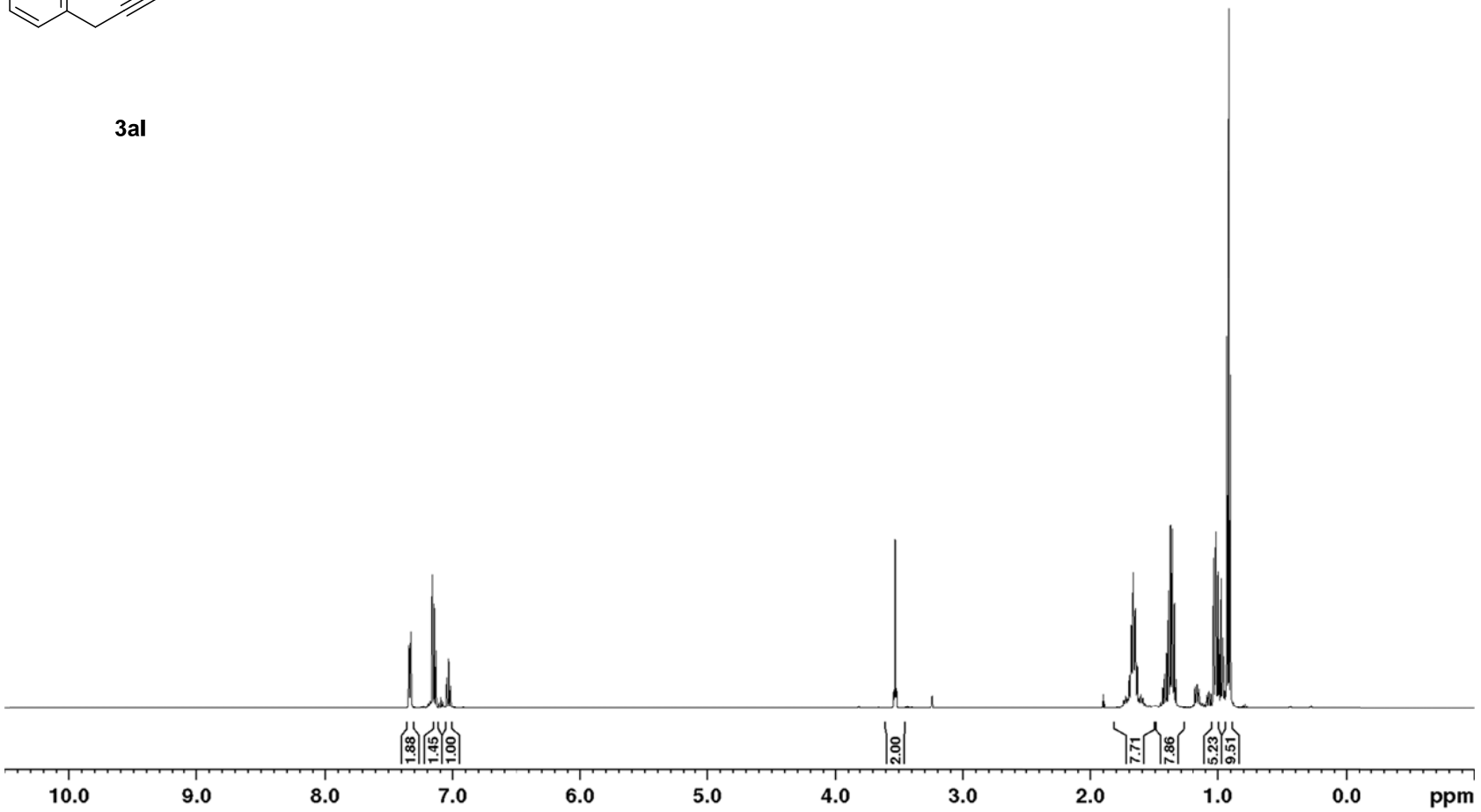


Figure S39 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(3-phenylprop-1-yn-1-yl)stannane (**3al**)

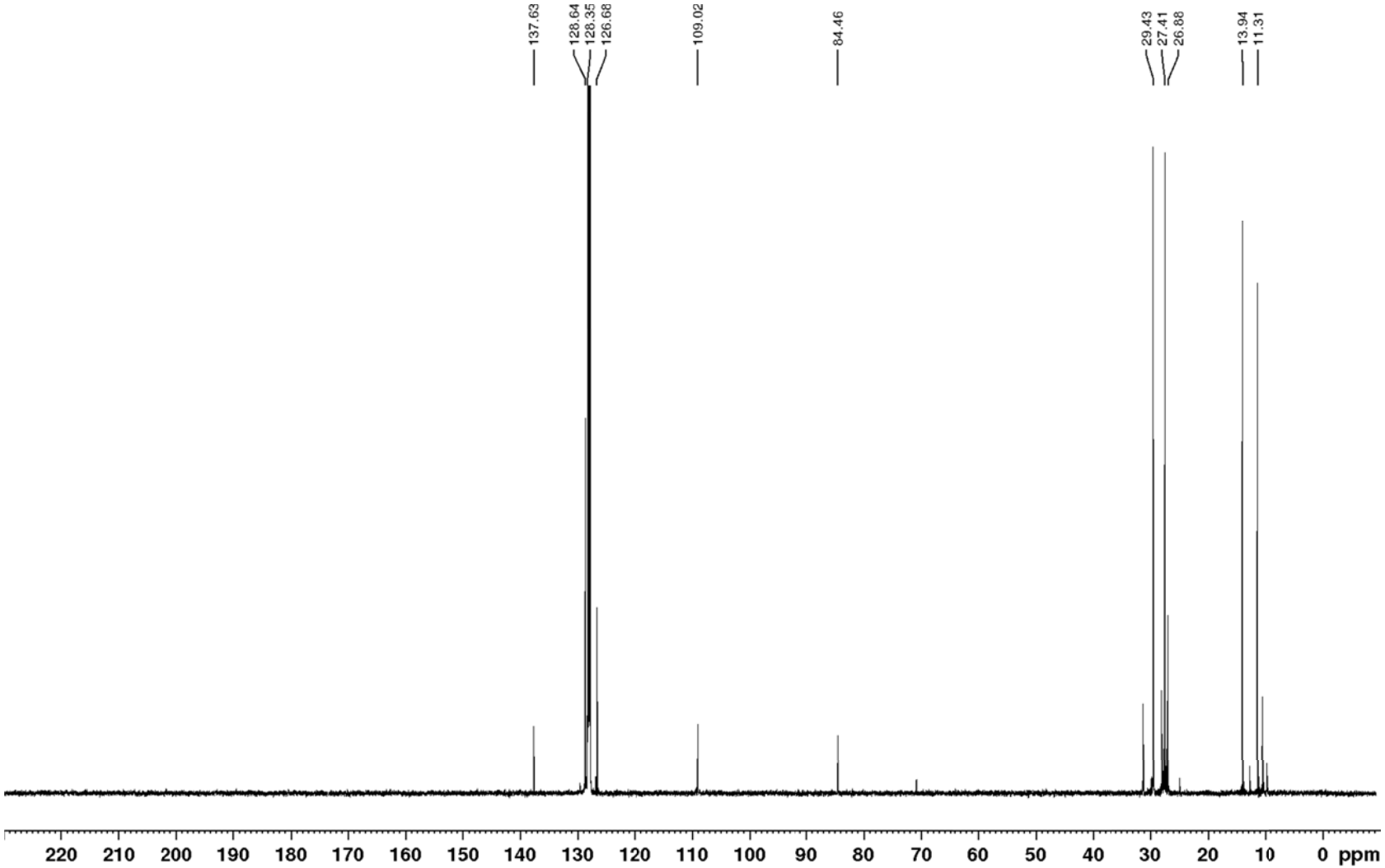


Figure S40 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(3-phenylprop-1-yn-1-yl)stannane (**3al**)

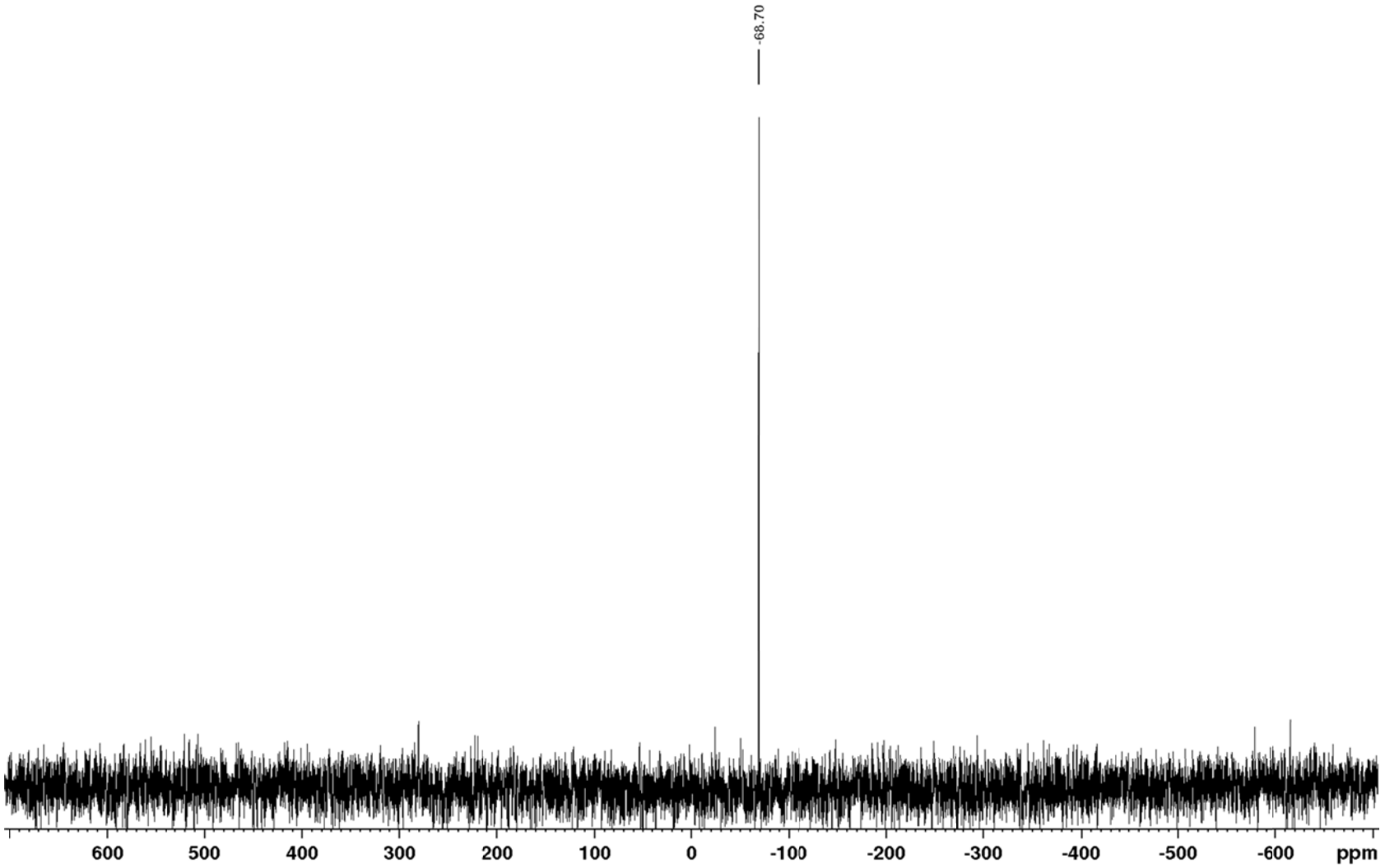
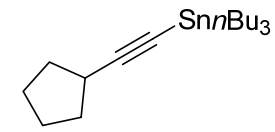


Figure S41 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(3-phenylprop-1-yn-1-yl)stannane (**3al**)



3am

Figure S42 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(cyclopentylethynyl)stannane (**3am**)

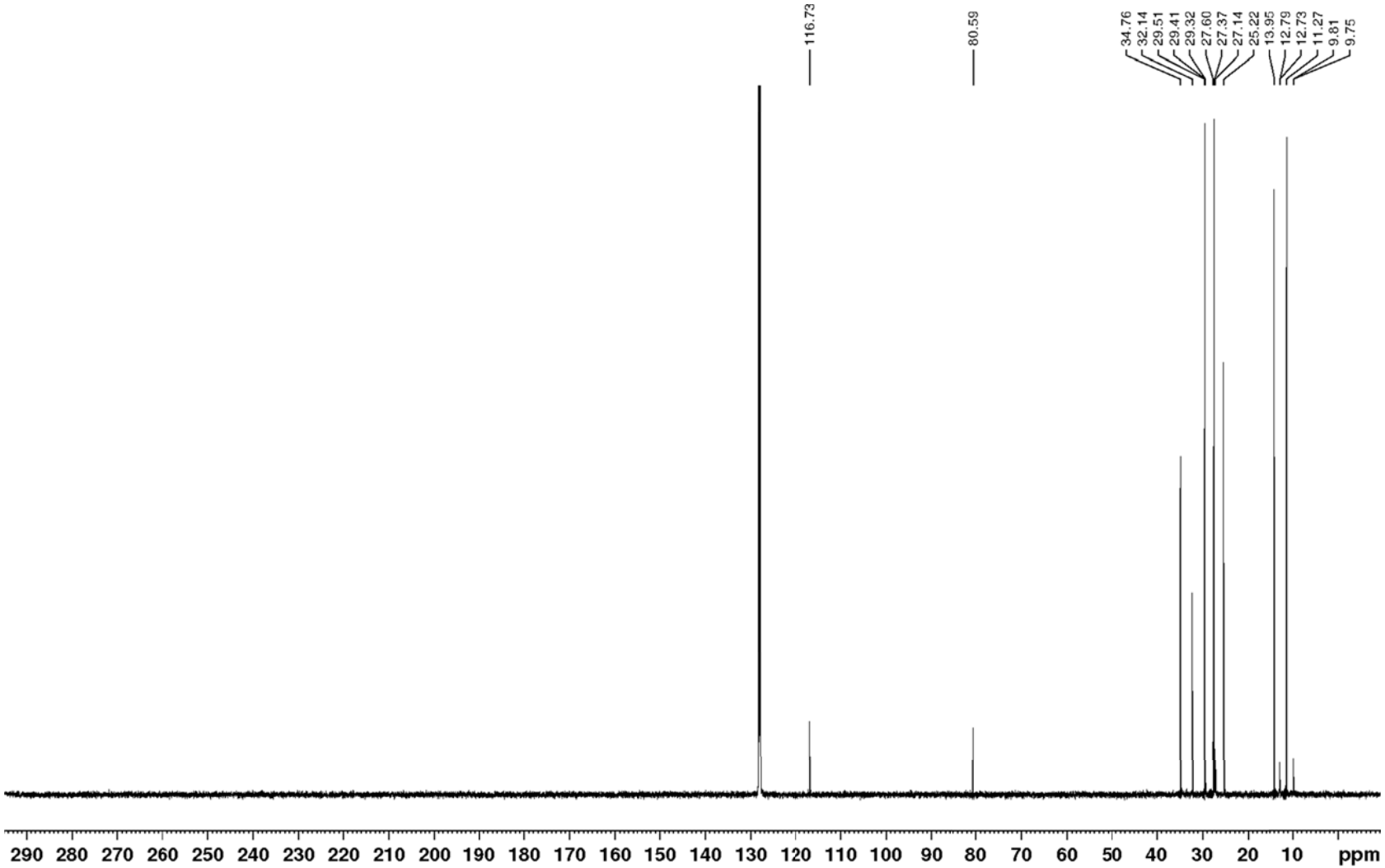


Figure S43 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(cyclopentylethynyl)stannane (**3am**)

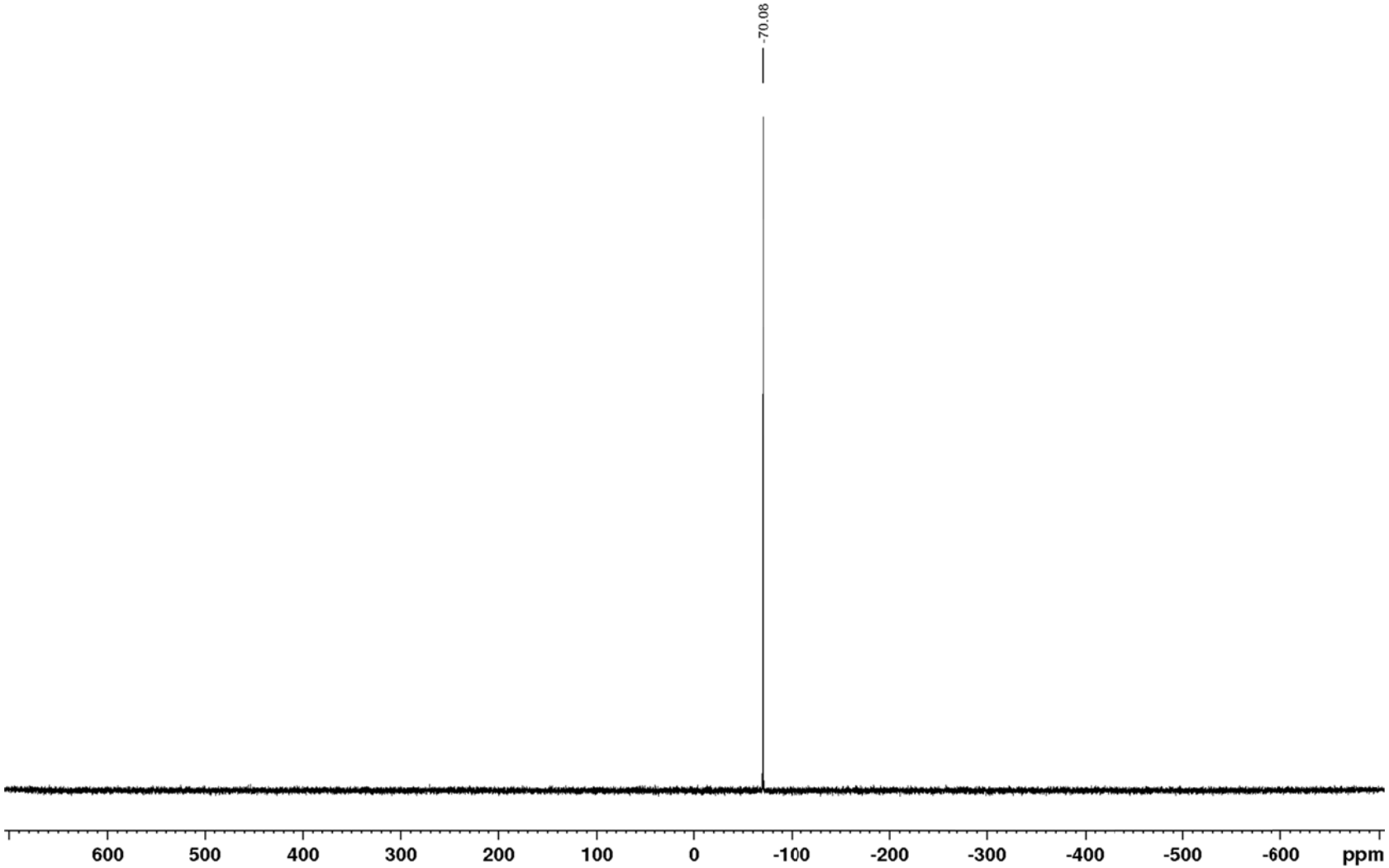


Figure S44 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(cyclopentylethynyl)stannane (**3am**)

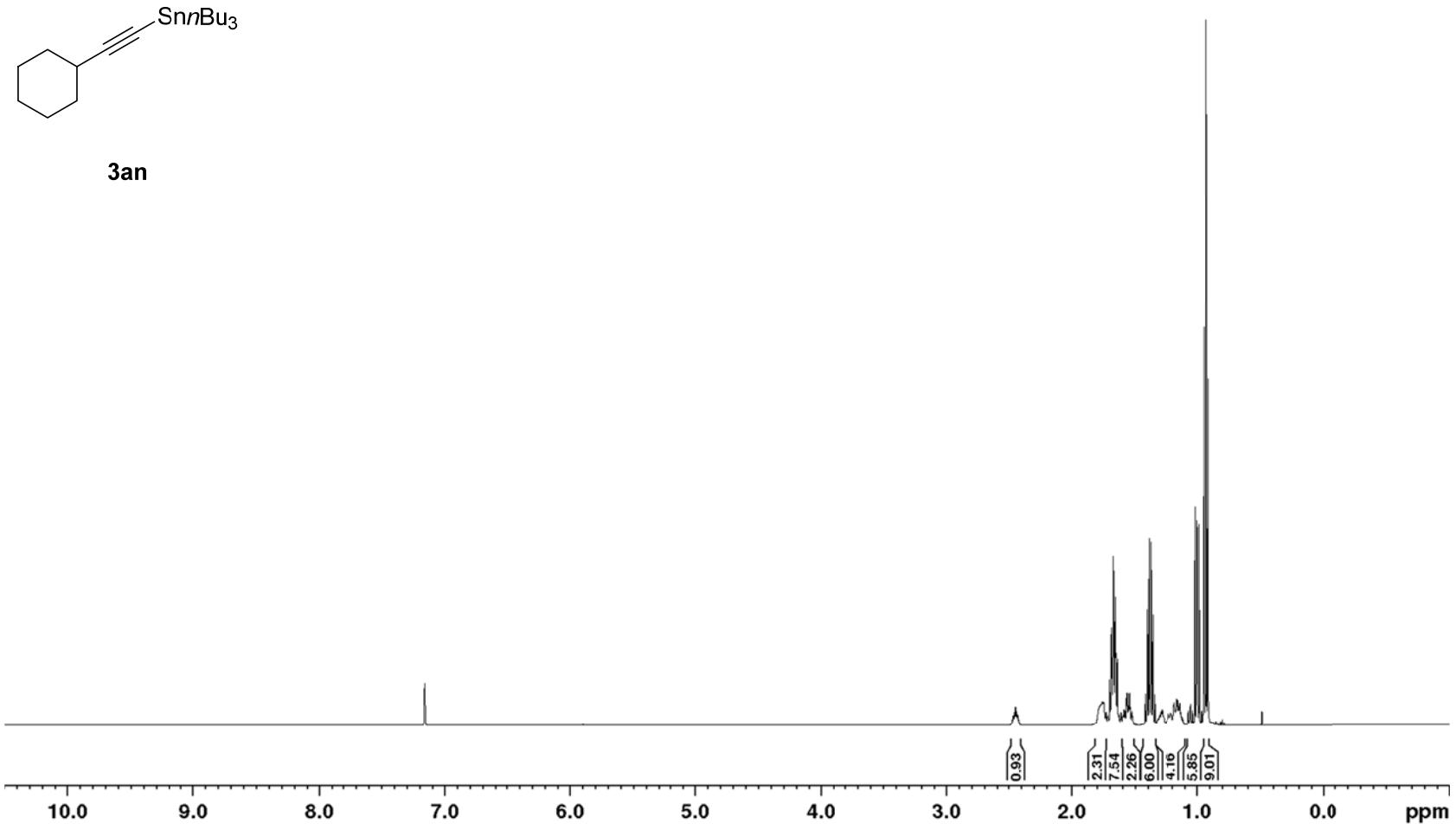


Figure S45 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(cyclohexylethynyl)stannane (**3an**)

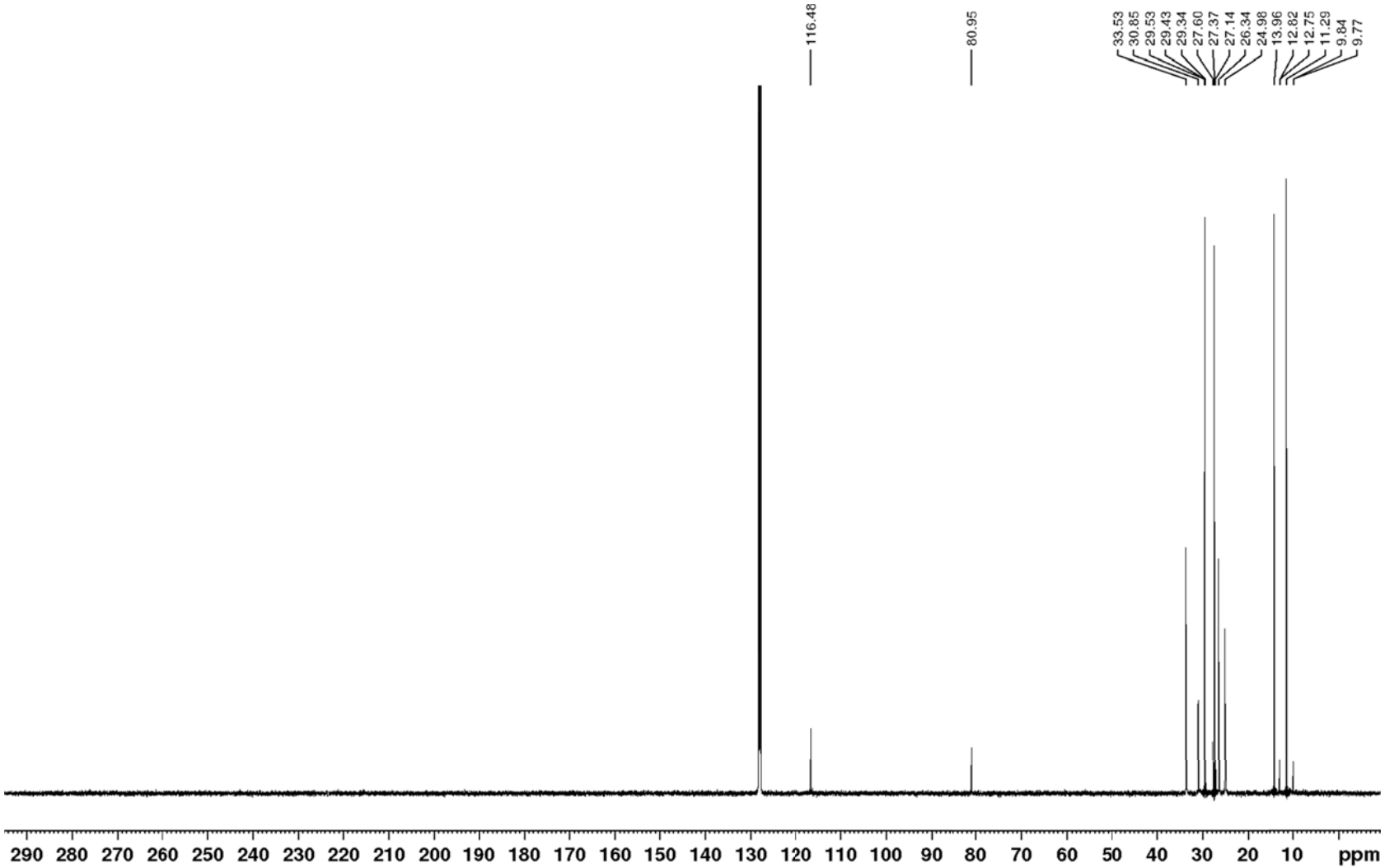


Figure S46 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(cyclohexylethynyl)stannane (**3an**)

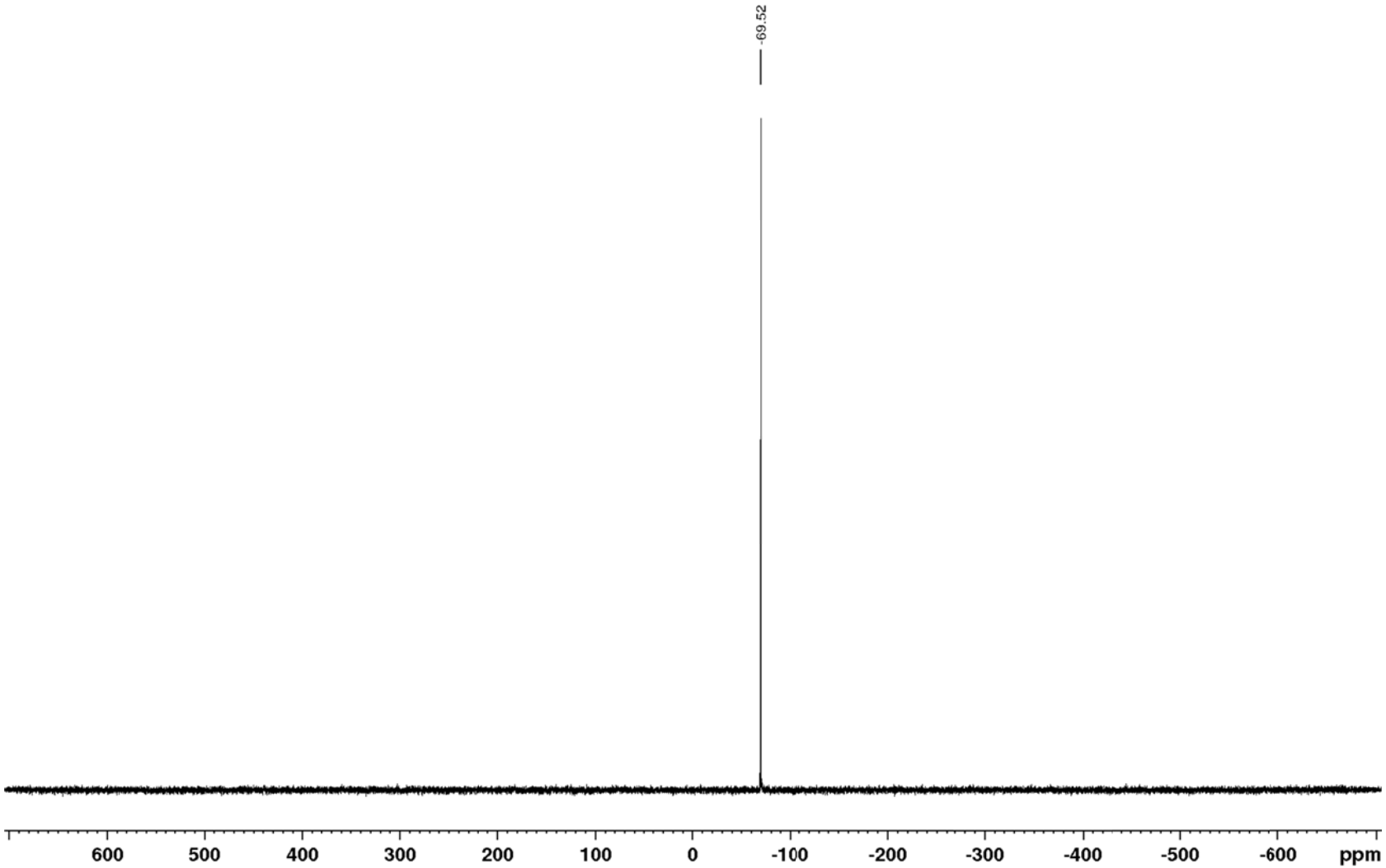


Figure S47 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(cyclohexylethynyl)stannane (**3an**)

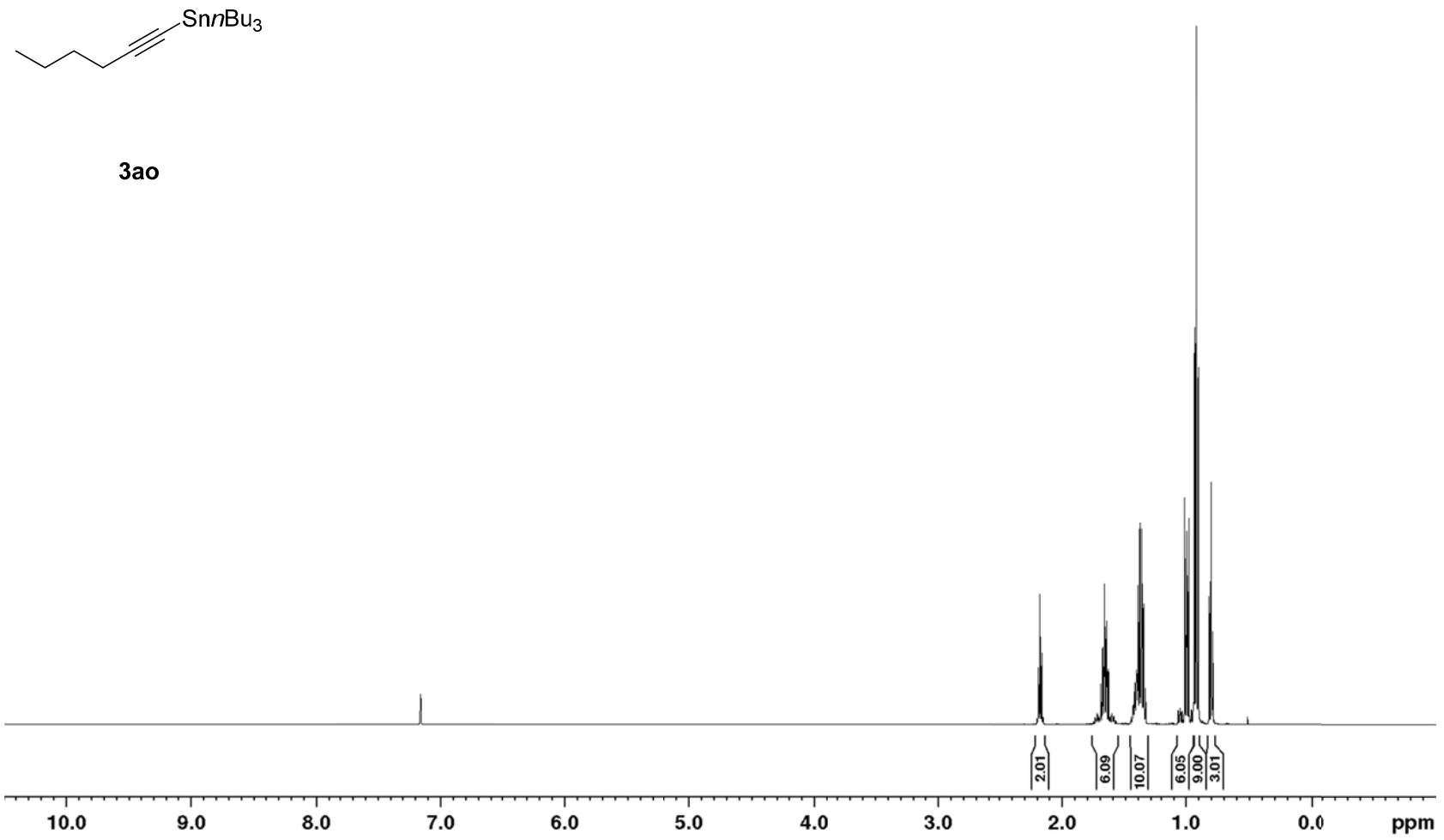


Figure S48 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(hex-1-yn-1-yl)stannane (**3ao**)

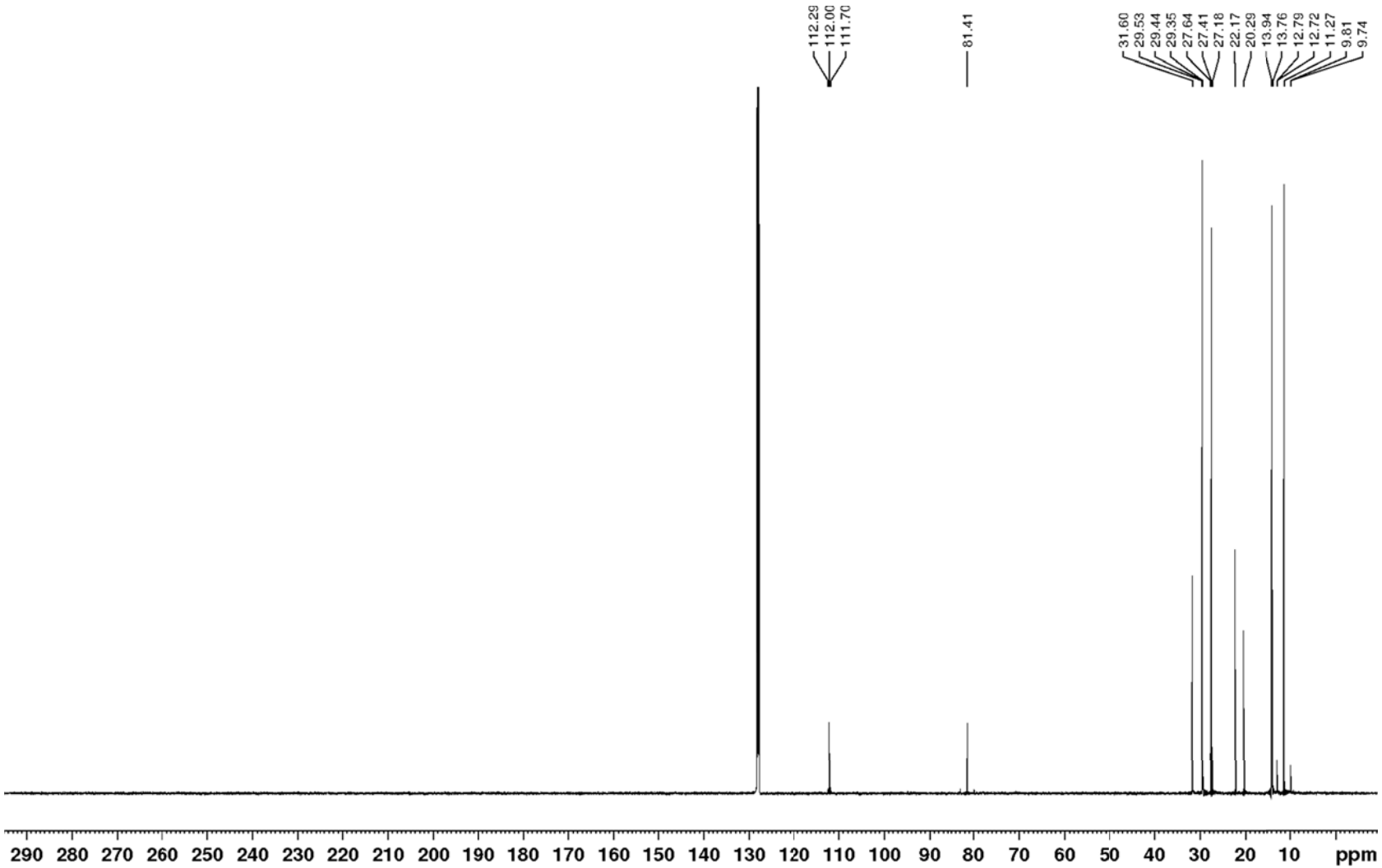


Figure S49 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(hex-1-yn-1-yl)stannane (**3ao**)

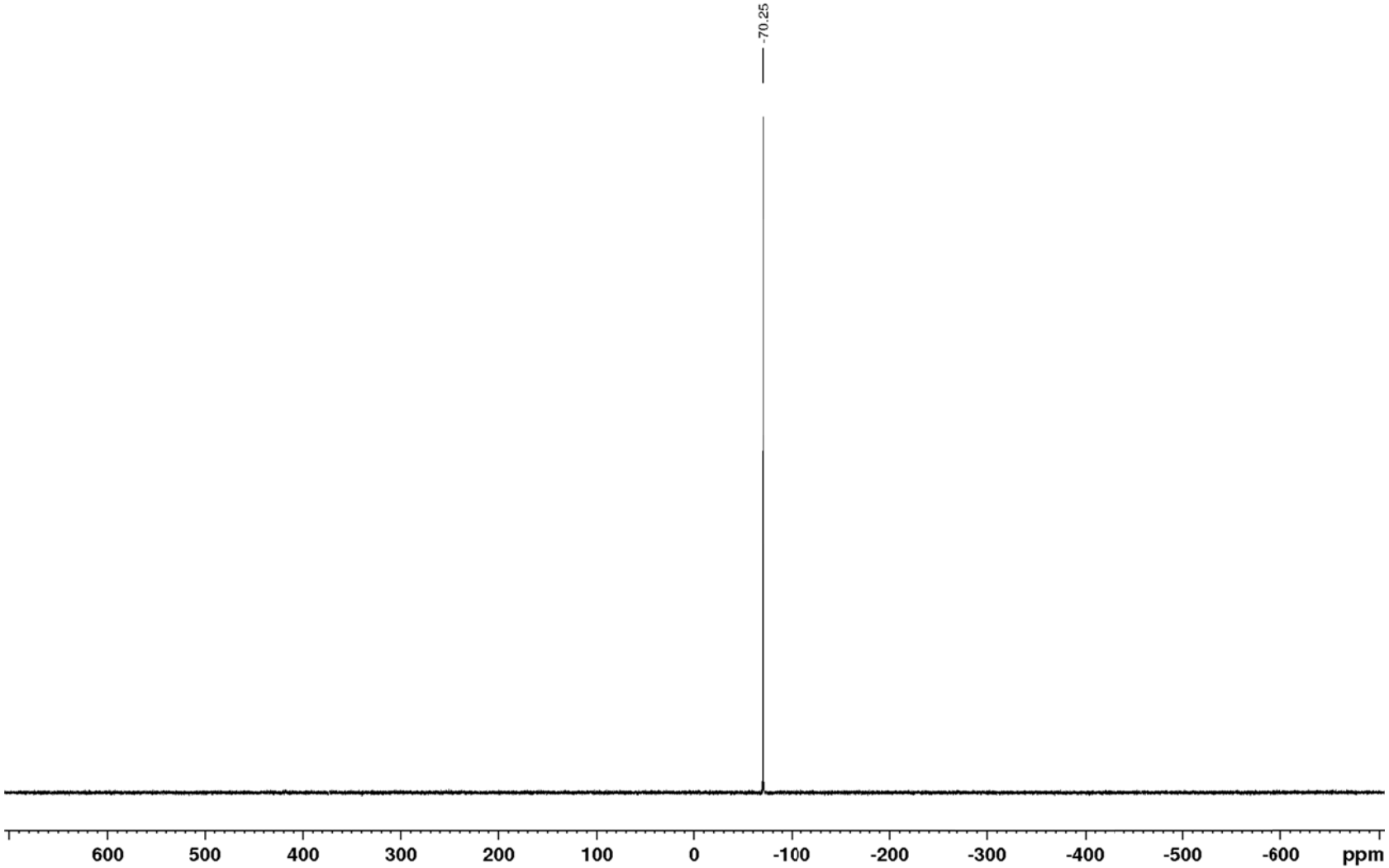


Figure S50 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(hex-1-yn-1-yl)stannane (**3ao**)

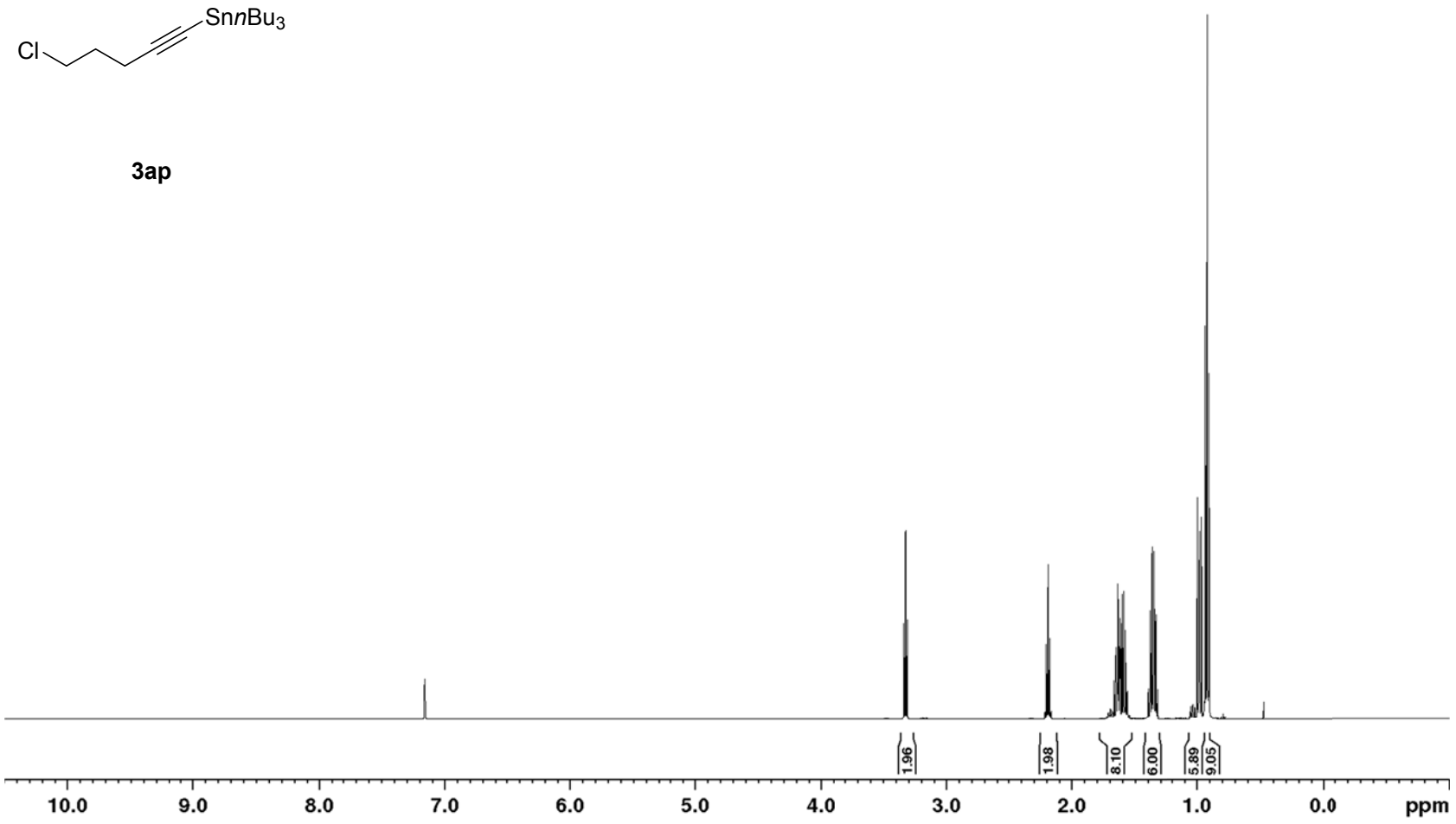


Figure S51 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(5-chloropent-1-yn-1-yl)stannane (**3ap**)

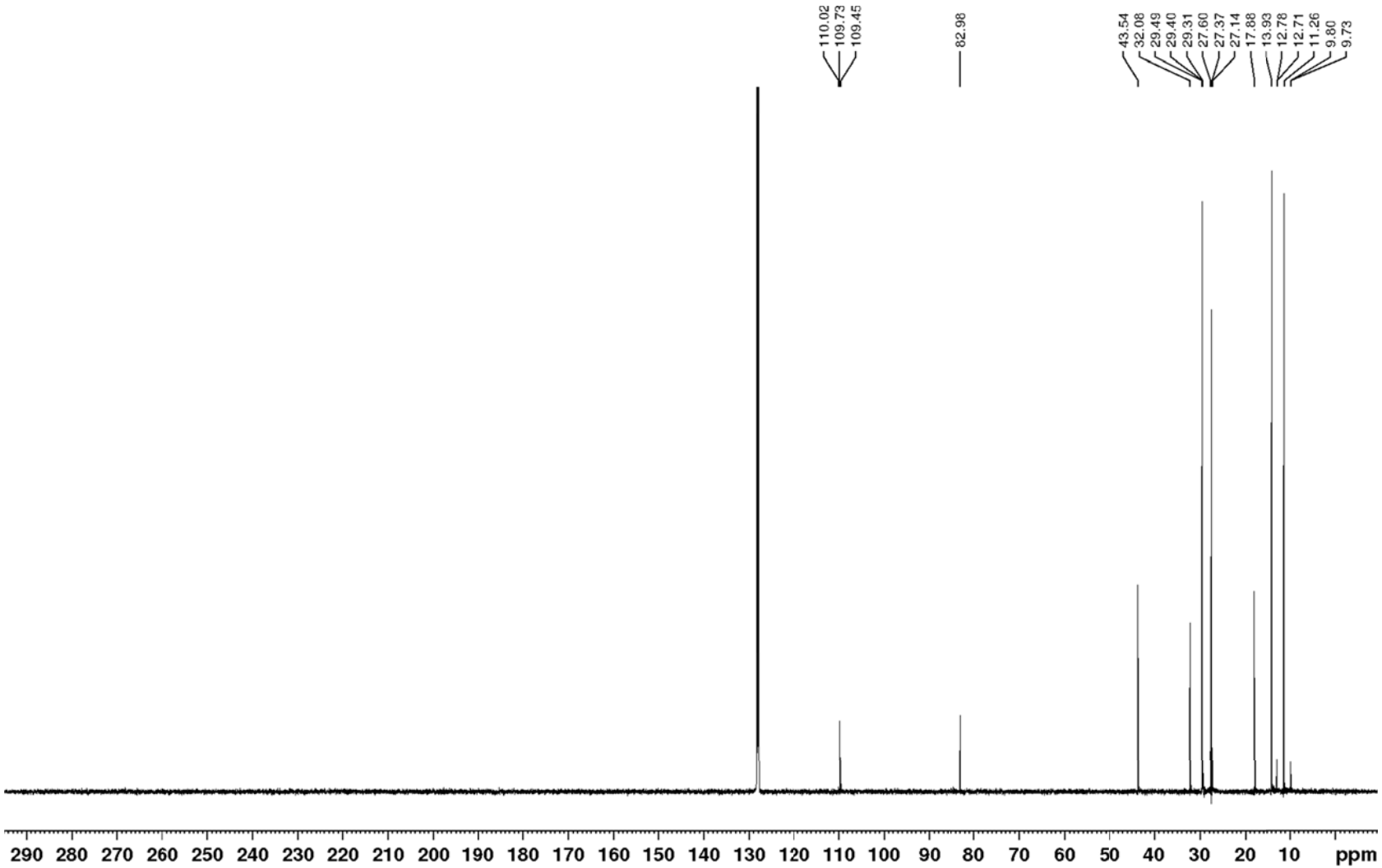


Figure S52 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(5-chloropent-1-yn-1-yl)stannane (**3ap**)

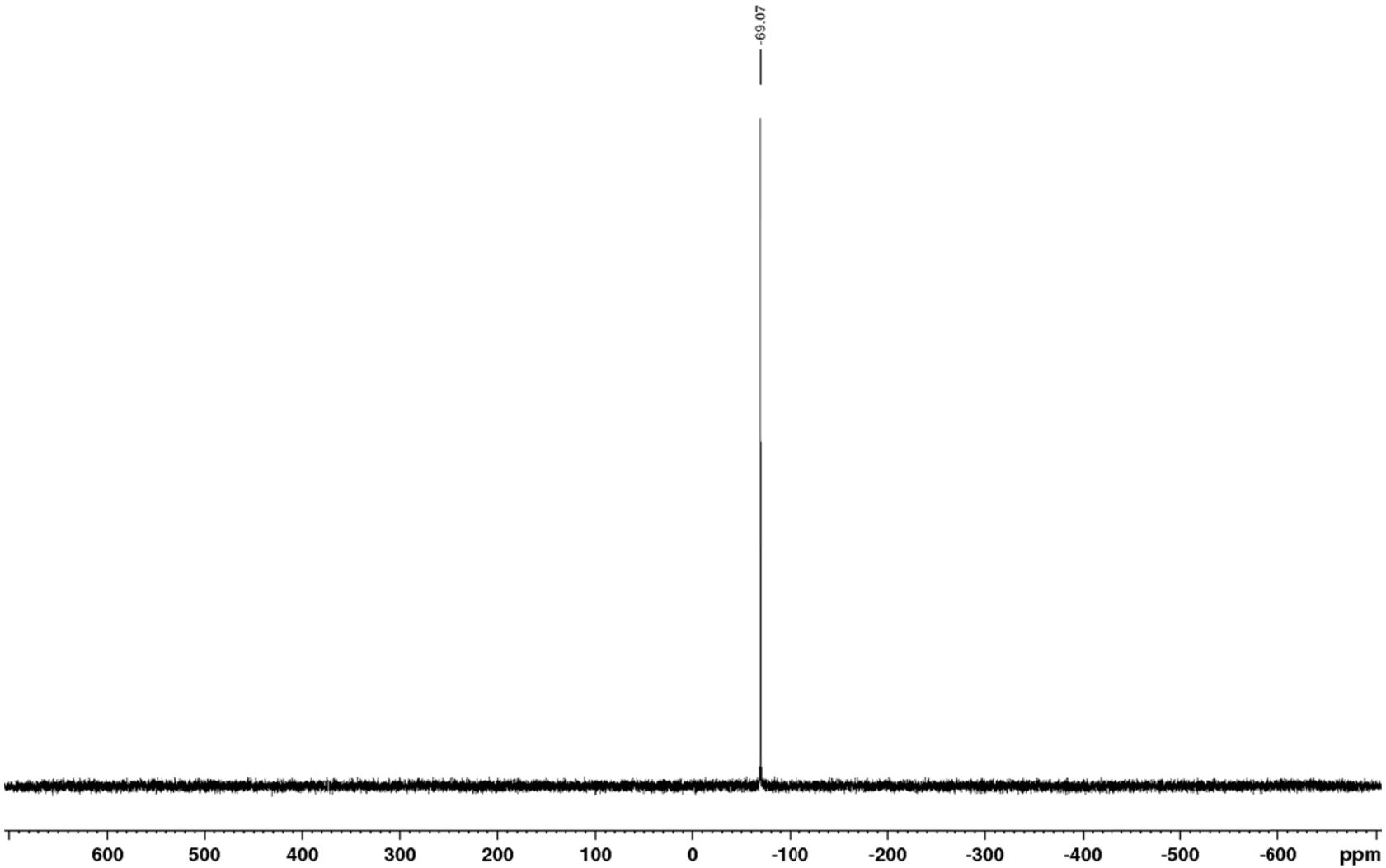


Figure S53 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(5-chloropent-1-yn-1-yl)stannane (**3ap**)

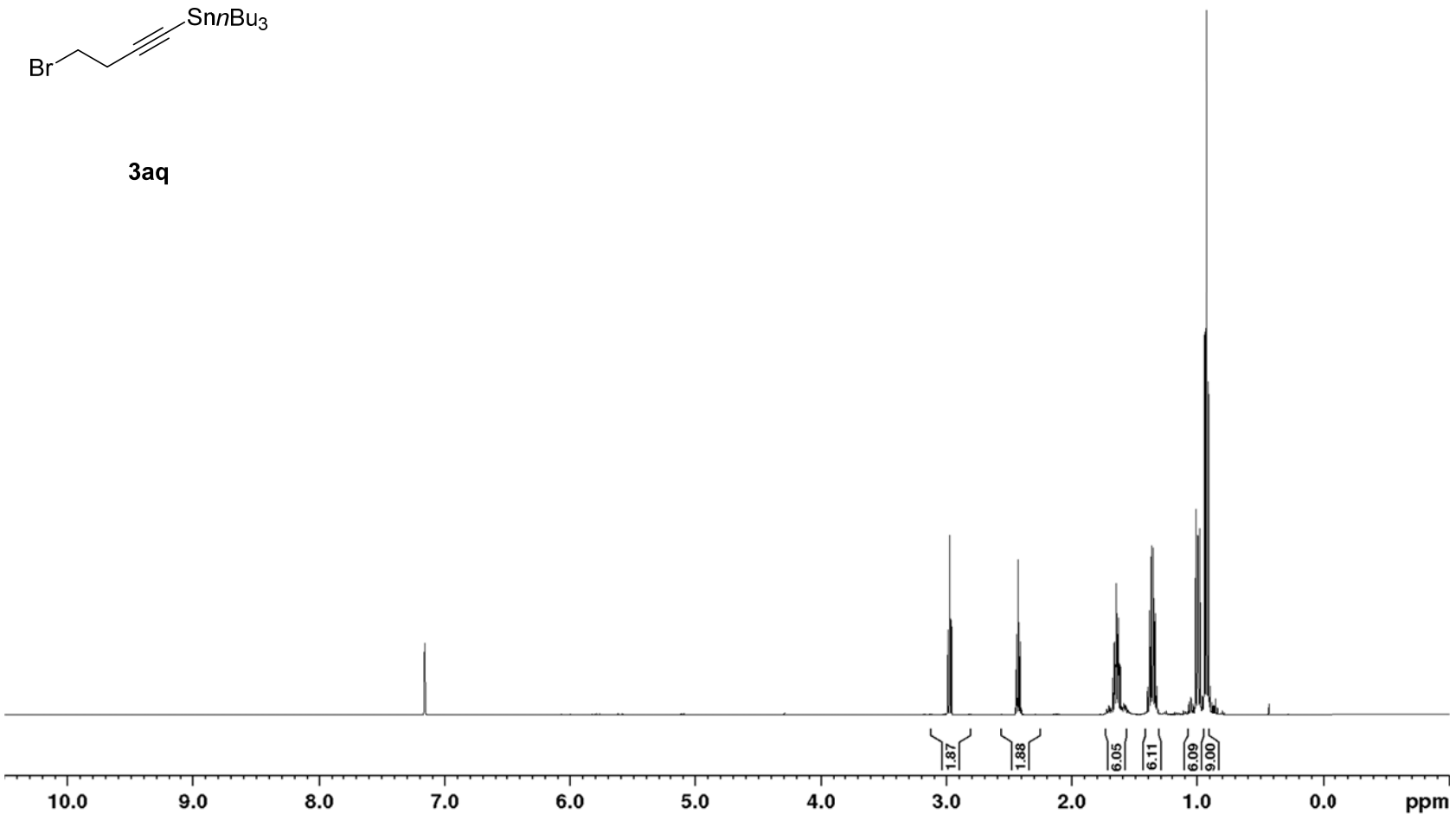


Figure S54 ^{1}H NMR (500 MHz, C_6D_6): (4-bromobut-1-yn-1-yl)tributylstannane (**3aq**)

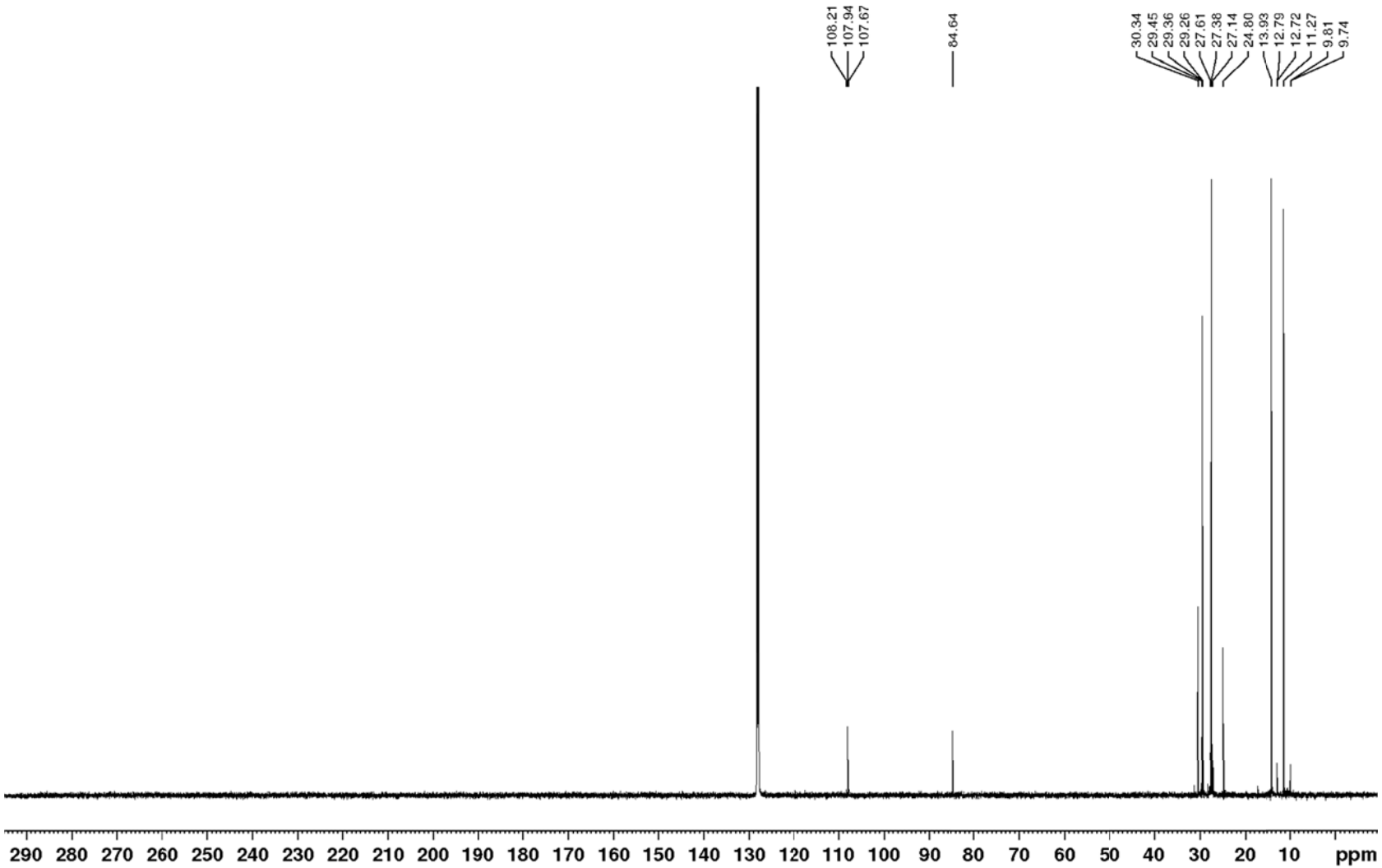


Figure S55 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): (4-bromobut-1-yn-1-yl)tributylstannane (**3aq**)

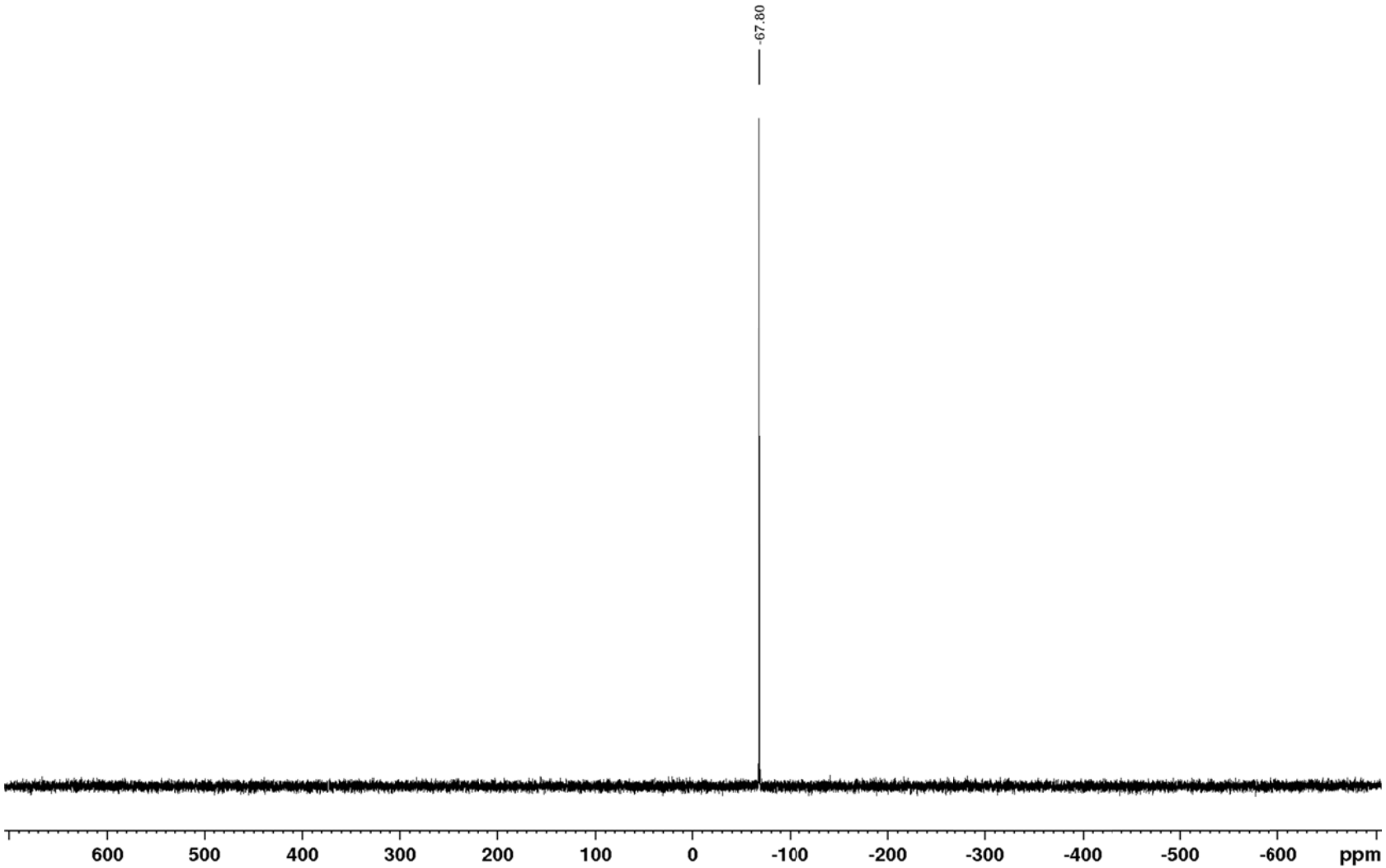


Figure S56 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): (4-bromobut-1-yn-1-yl)tributylstannane (**3aq**)

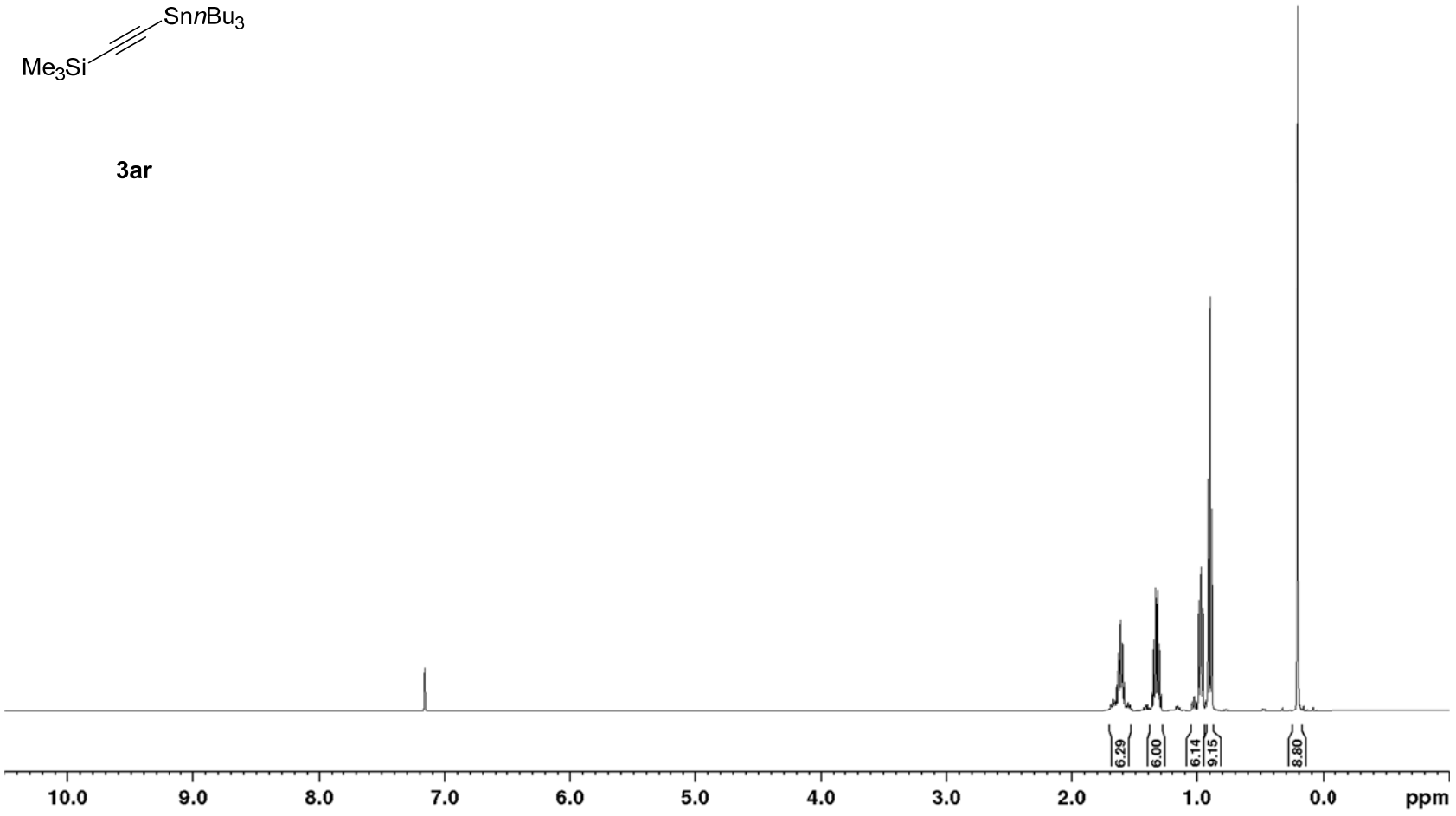


Figure S57 ^{1}H NMR (500 MHz, C_6D_6): Trimethyl((tributylstannyl)ethynyl)silane (**3ar**)

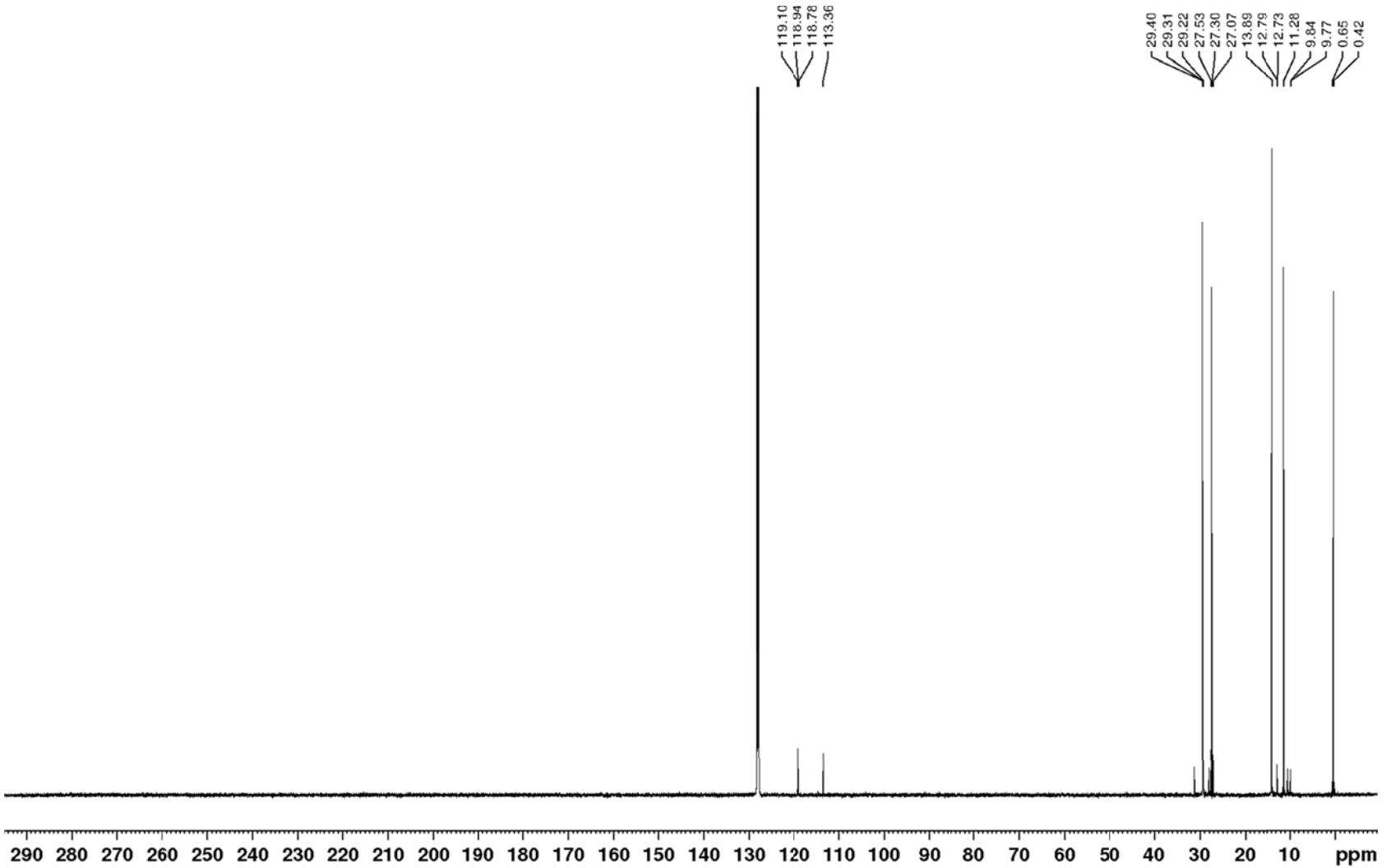


Figure S58 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Trimethyl((tributylstannyl)ethynyl)silane (**3ar**)

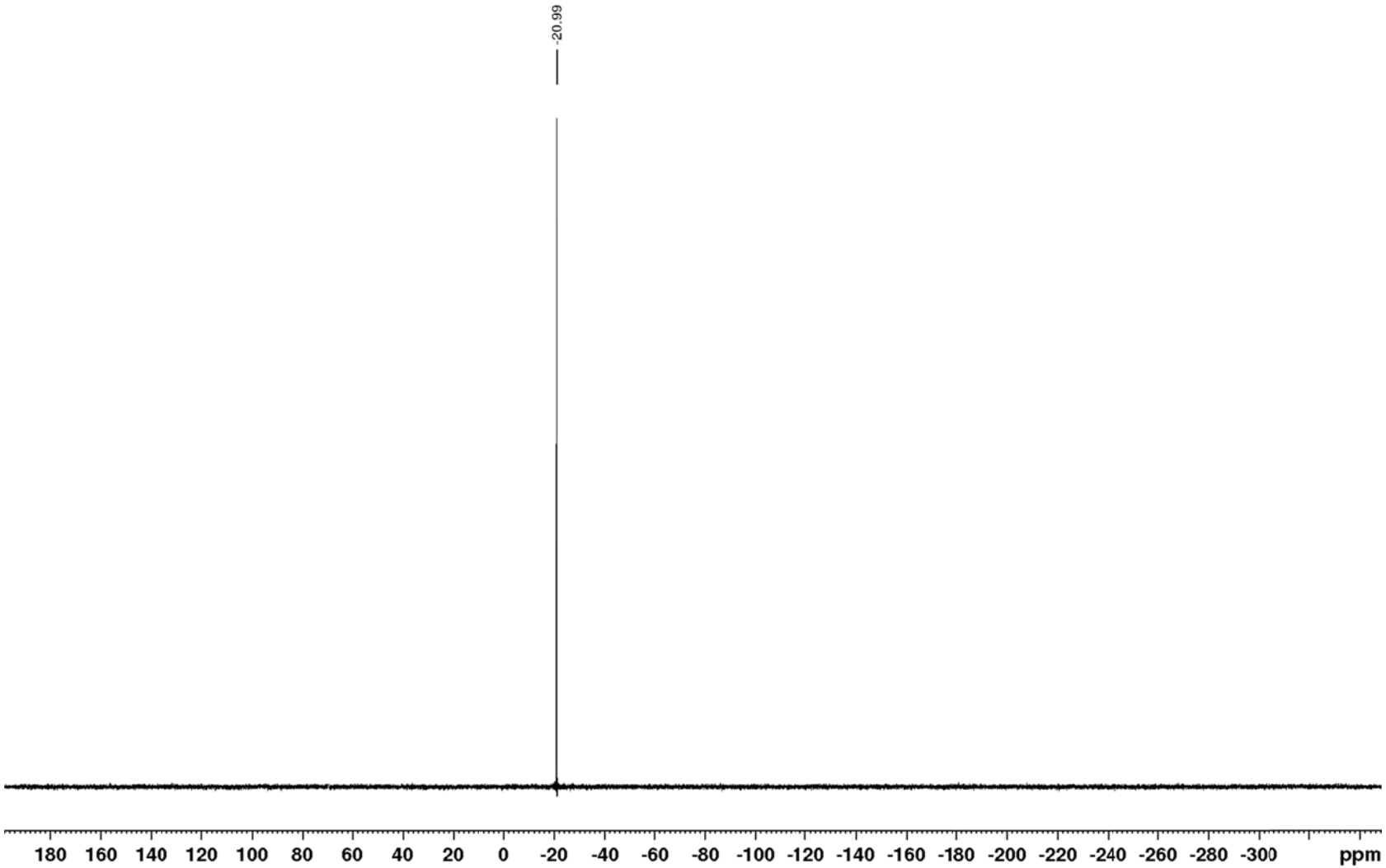


Figure S59 ^{29}Si-DEPT NMR (99 MHz, C_6D_6, optimized for J = 8 Hz): Trimethyl((tributylstannyl)ethynyl)silane (**3ar**)

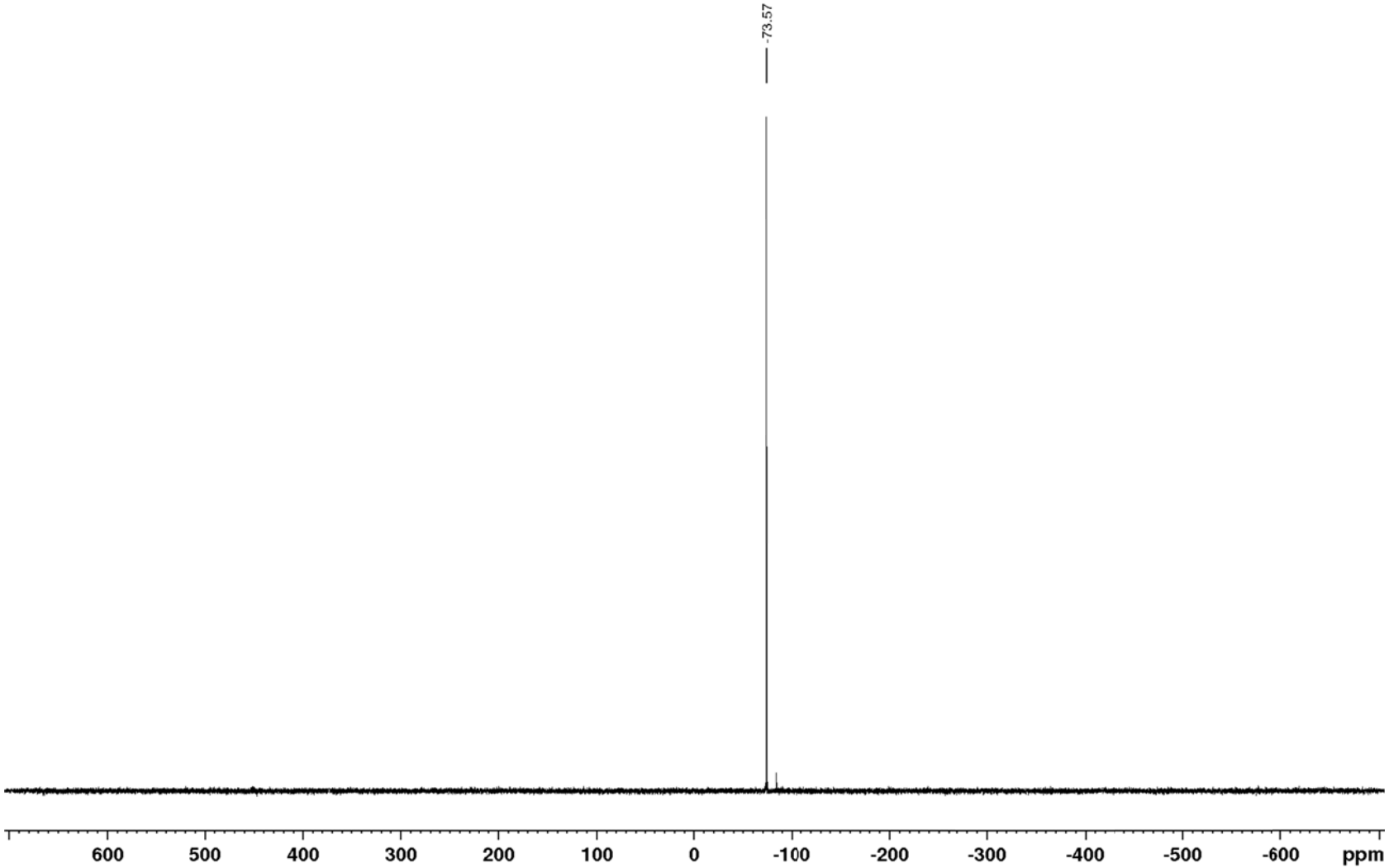


Figure S60 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Trimethyl((tributylstannyl)ethynyl)silane (**3ar**)

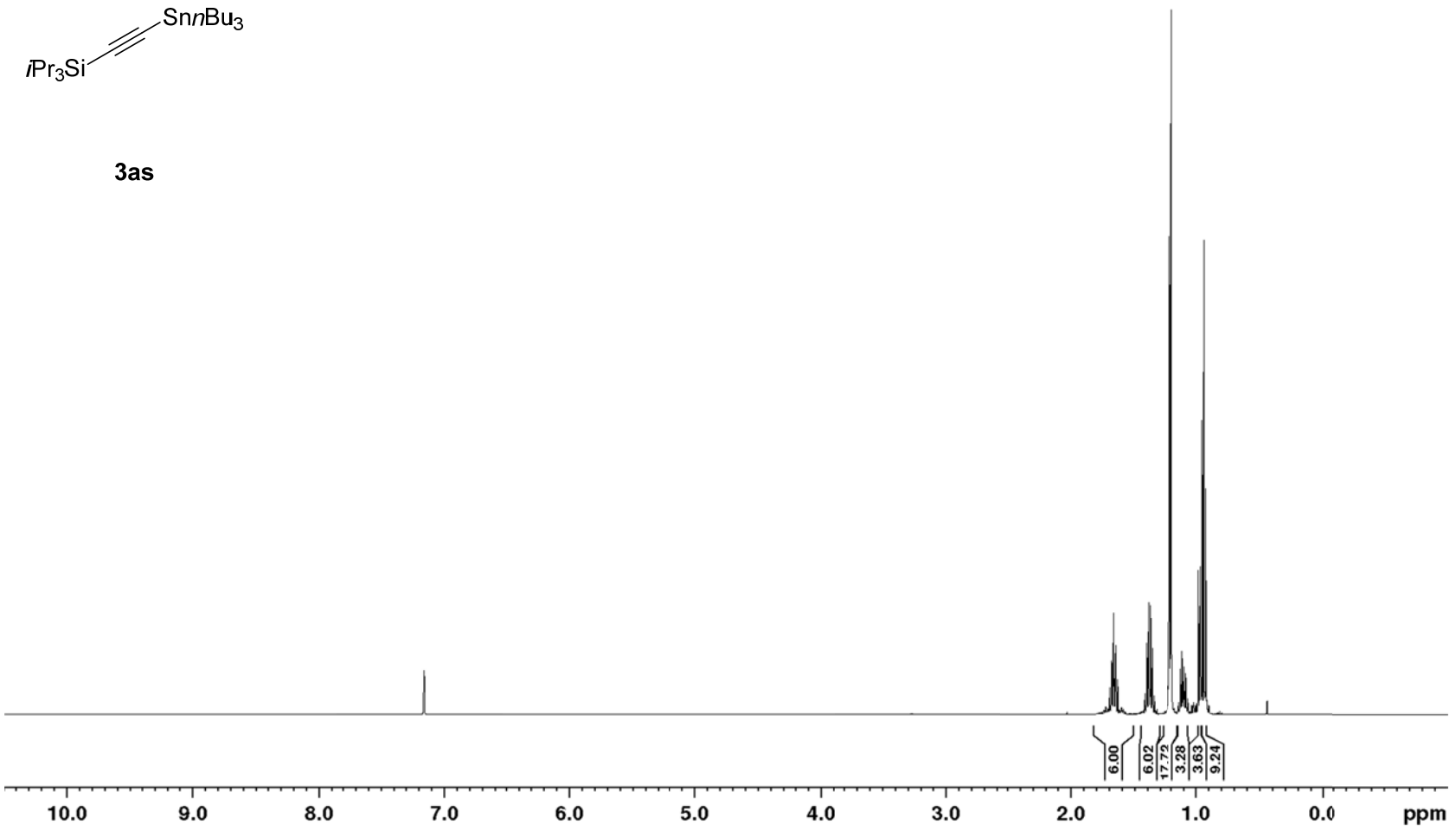


Figure S61 ^{1}H NMR (500 MHz, C_6D_6): Triisopropyl((tributylstannyl)ethynyl)silane (**3as**)

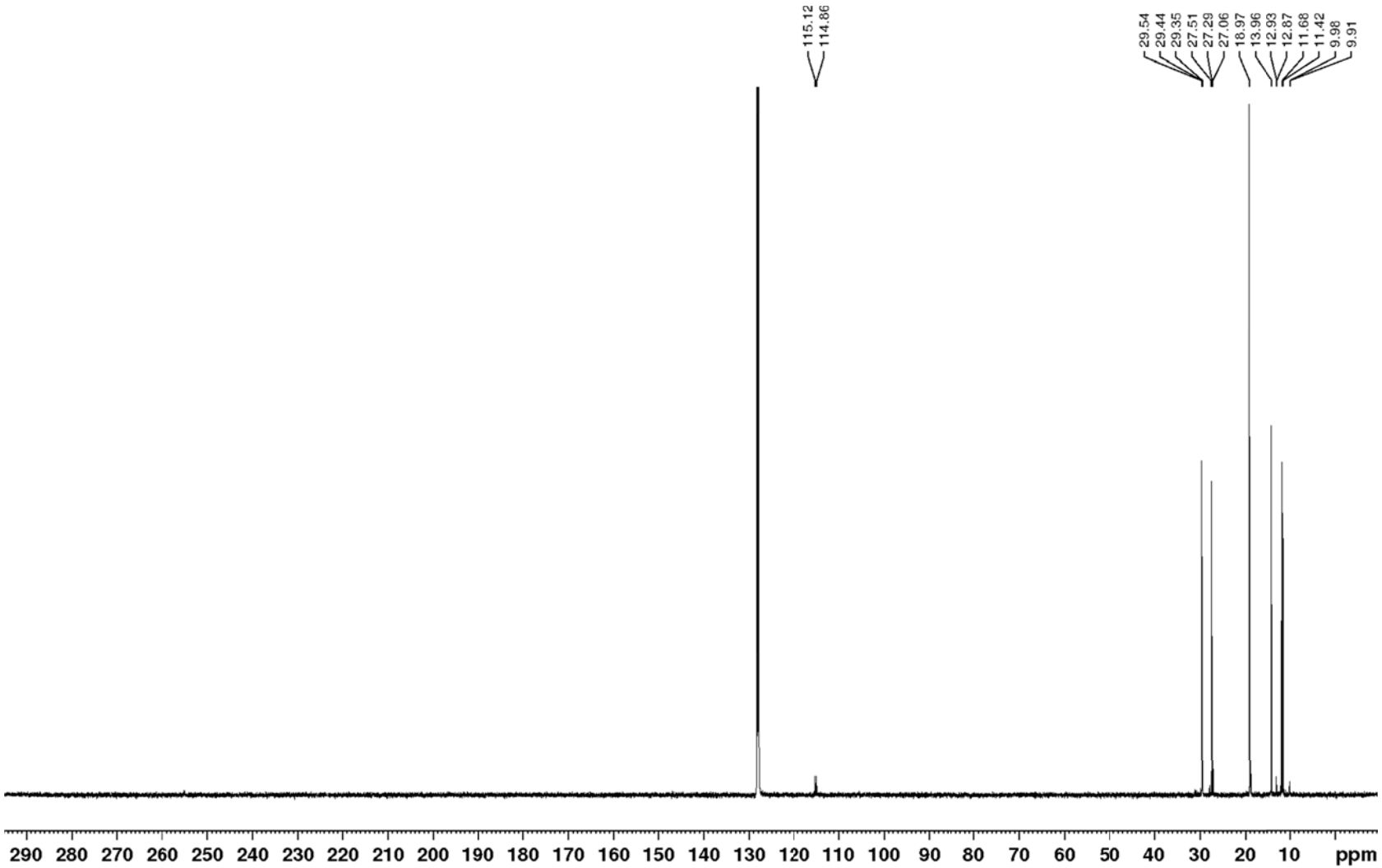


Figure S62 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Triisopropyl((tributylstannyl)ethynyl)silane (**3as**)

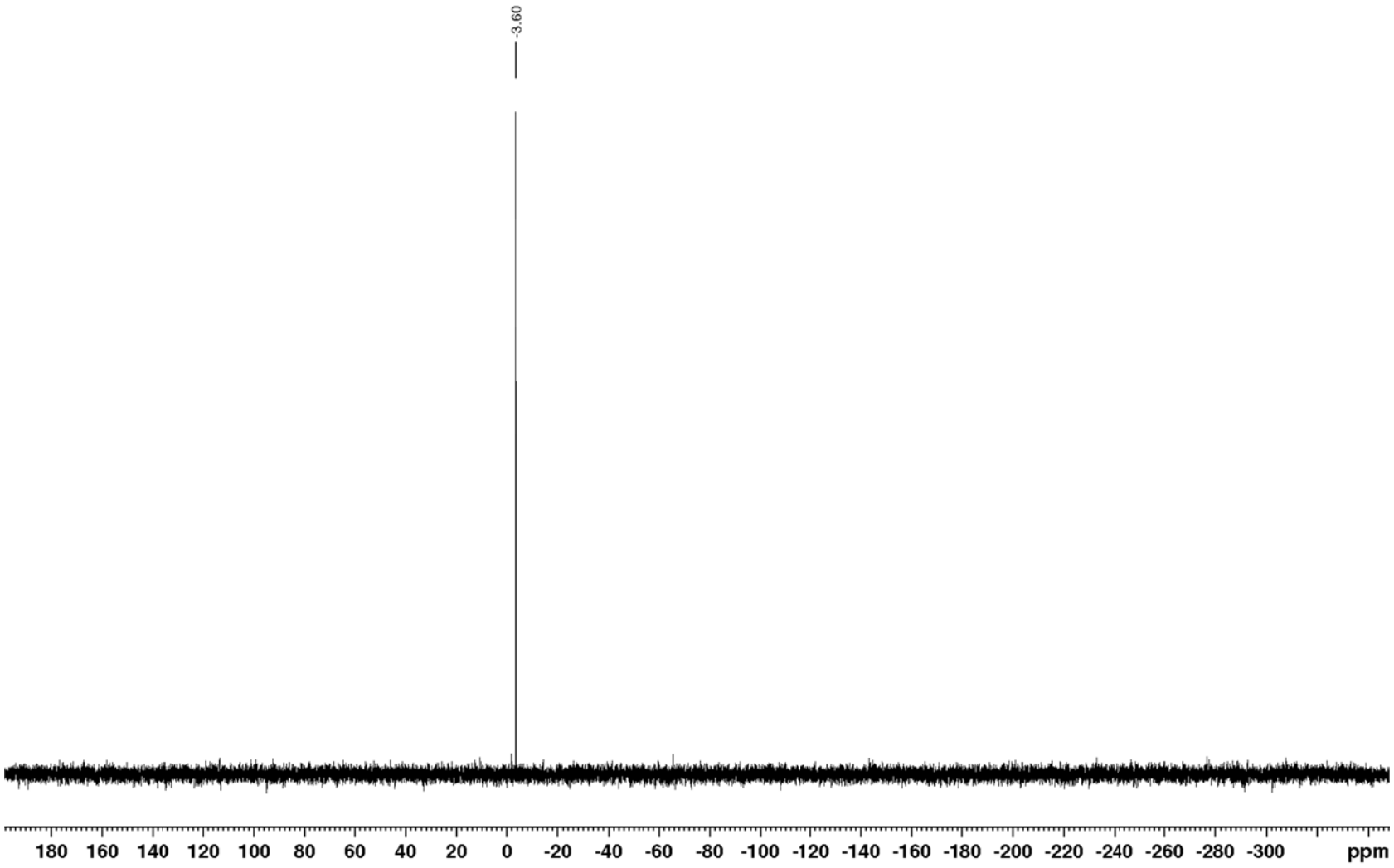


Figure S63 ^{29}Si-DEPT NMR (99 MHz, C_6D_6, optimized for J = 8 Hz): Triisopropyl((tributylstannyl)ethynyl)silane (**3as**)

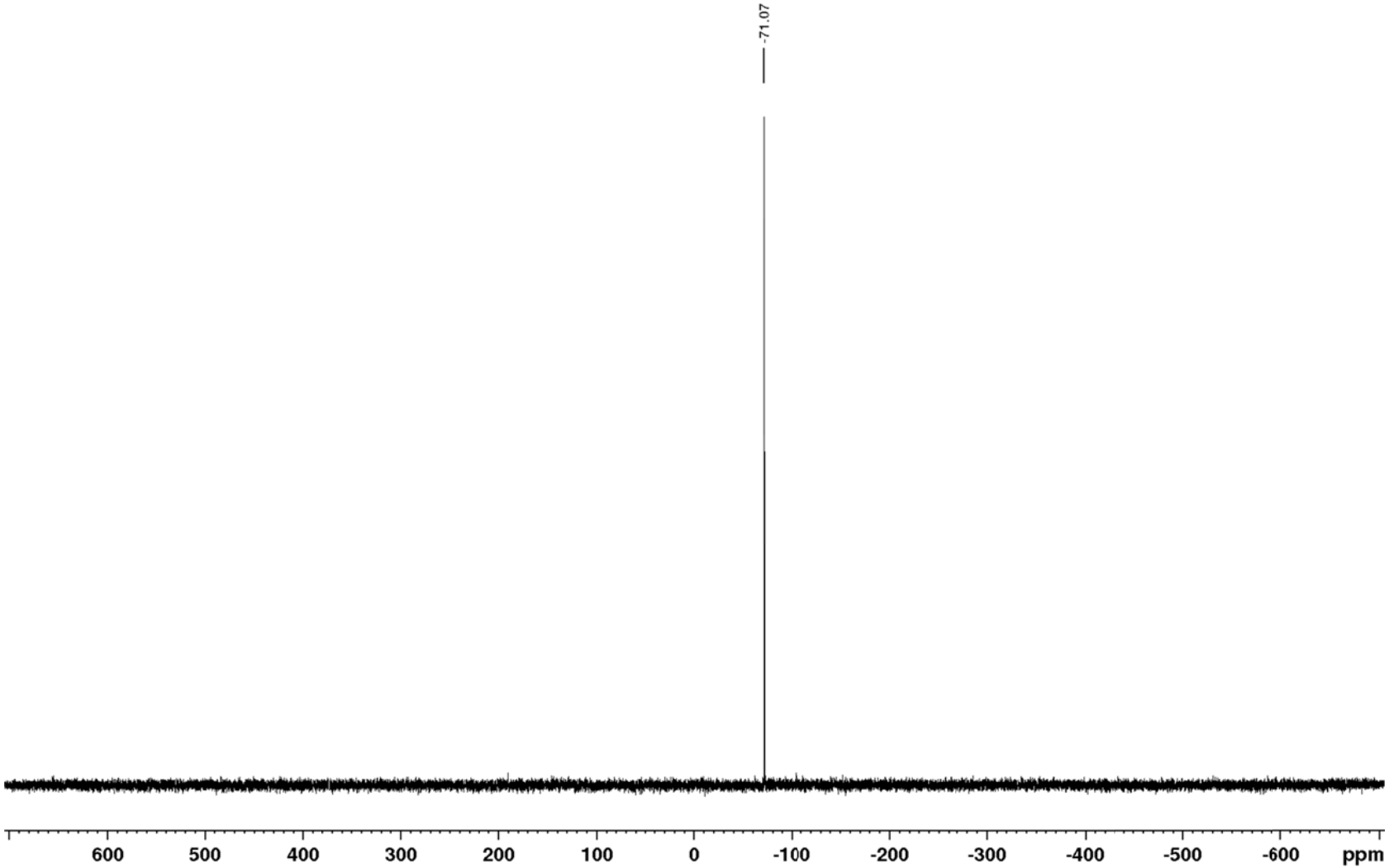


Figure S64 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Triisopropyl((tributylstannyl)ethynyl)silane (**3as**)

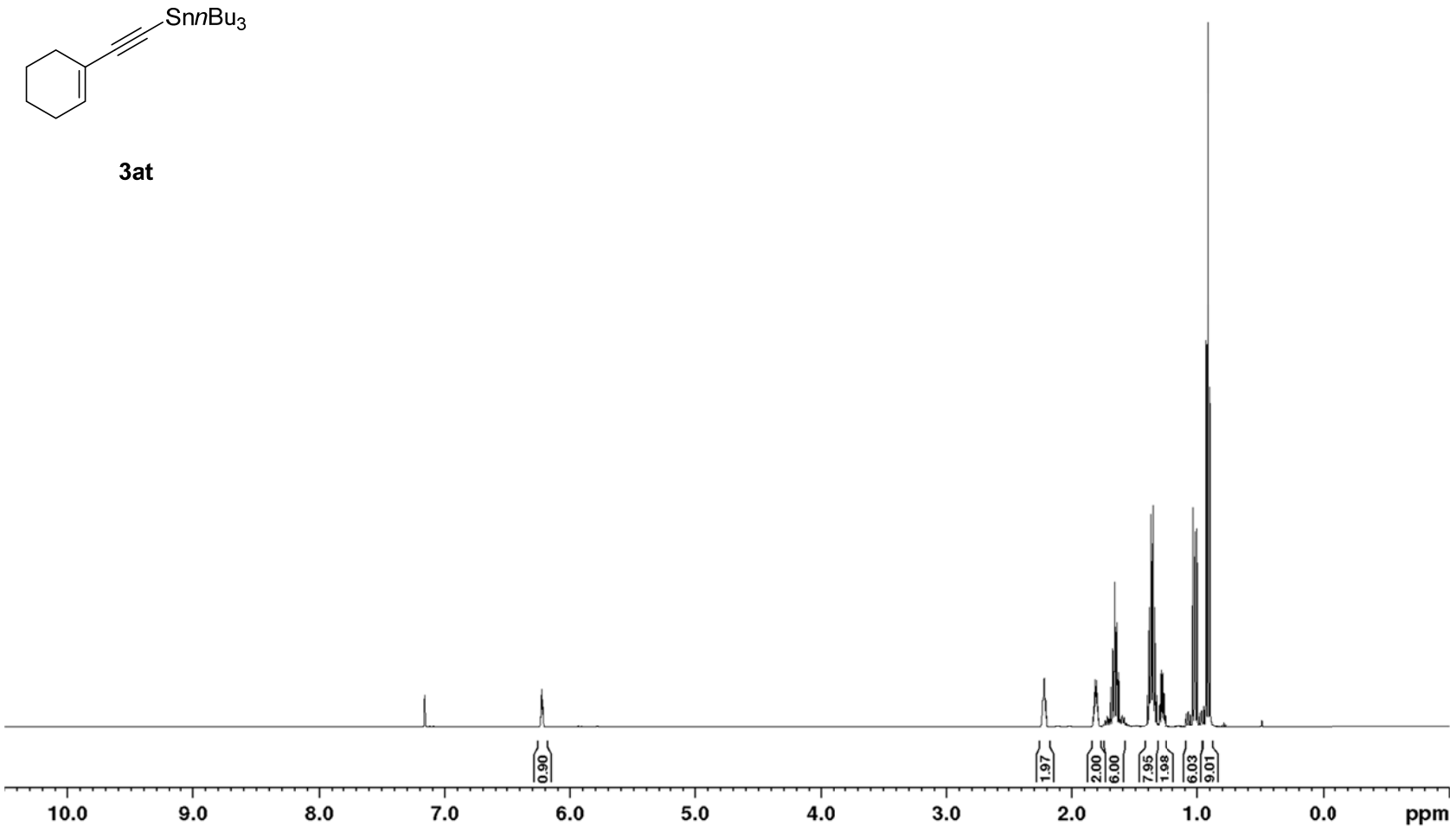


Figure S65 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(cyclohex-1-en-1-ylethynyl)stannane (**3at**)

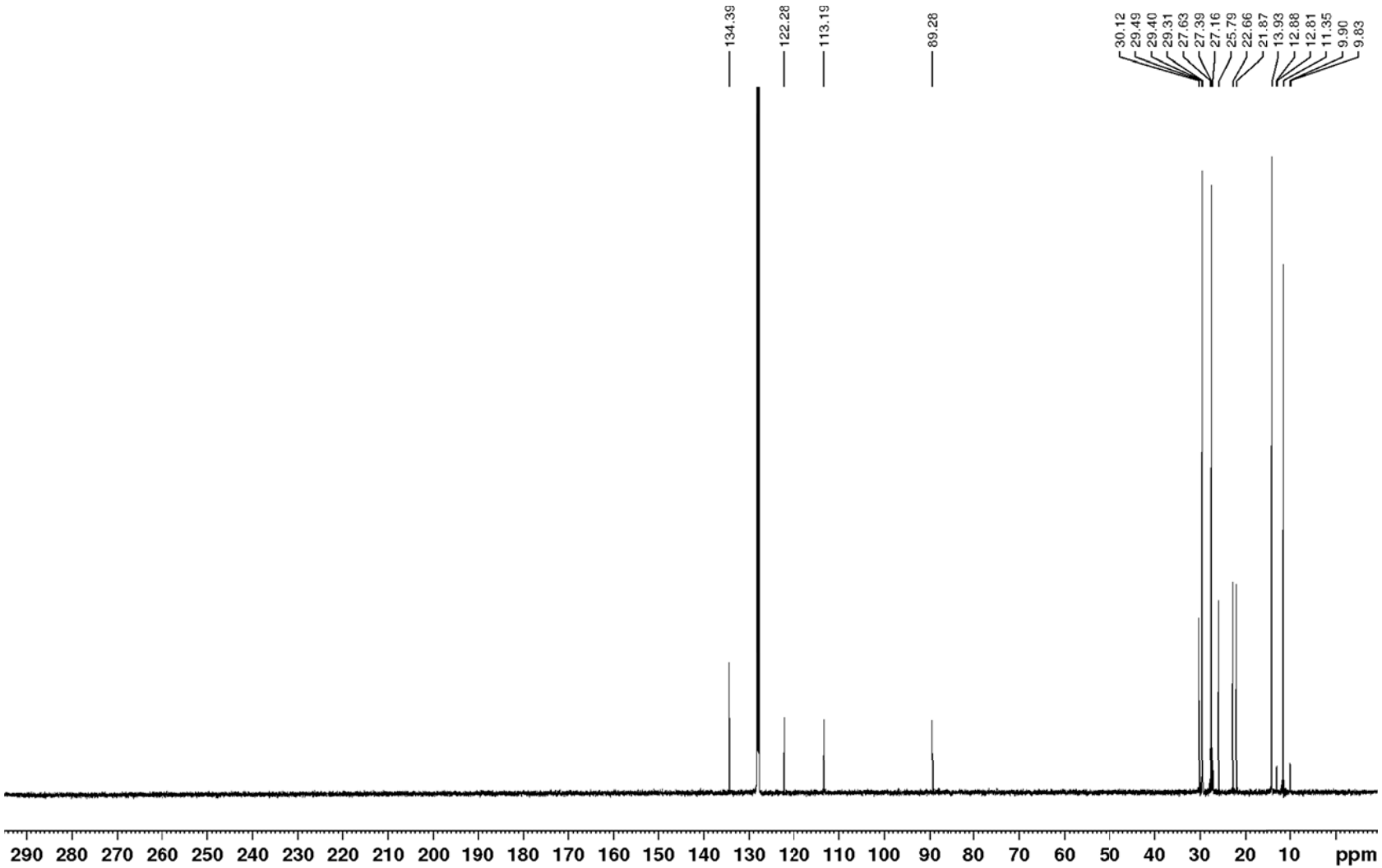


Figure S66 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(cyclohex-1-en-1-ylethynyl)stannane (**3at**)

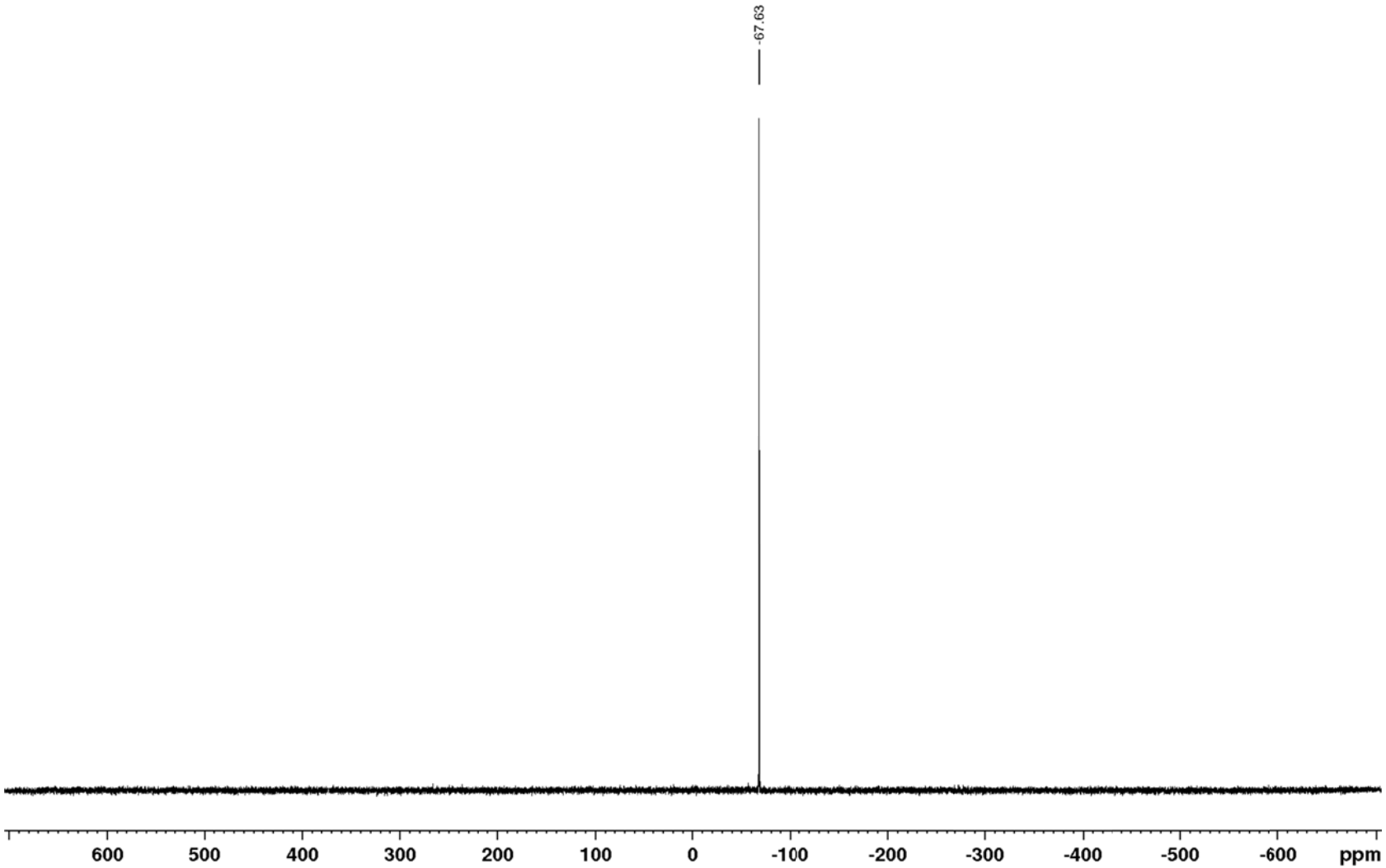


Figure S67 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(cyclohex-1-en-1-ylethynyl)stannane (**3at**)

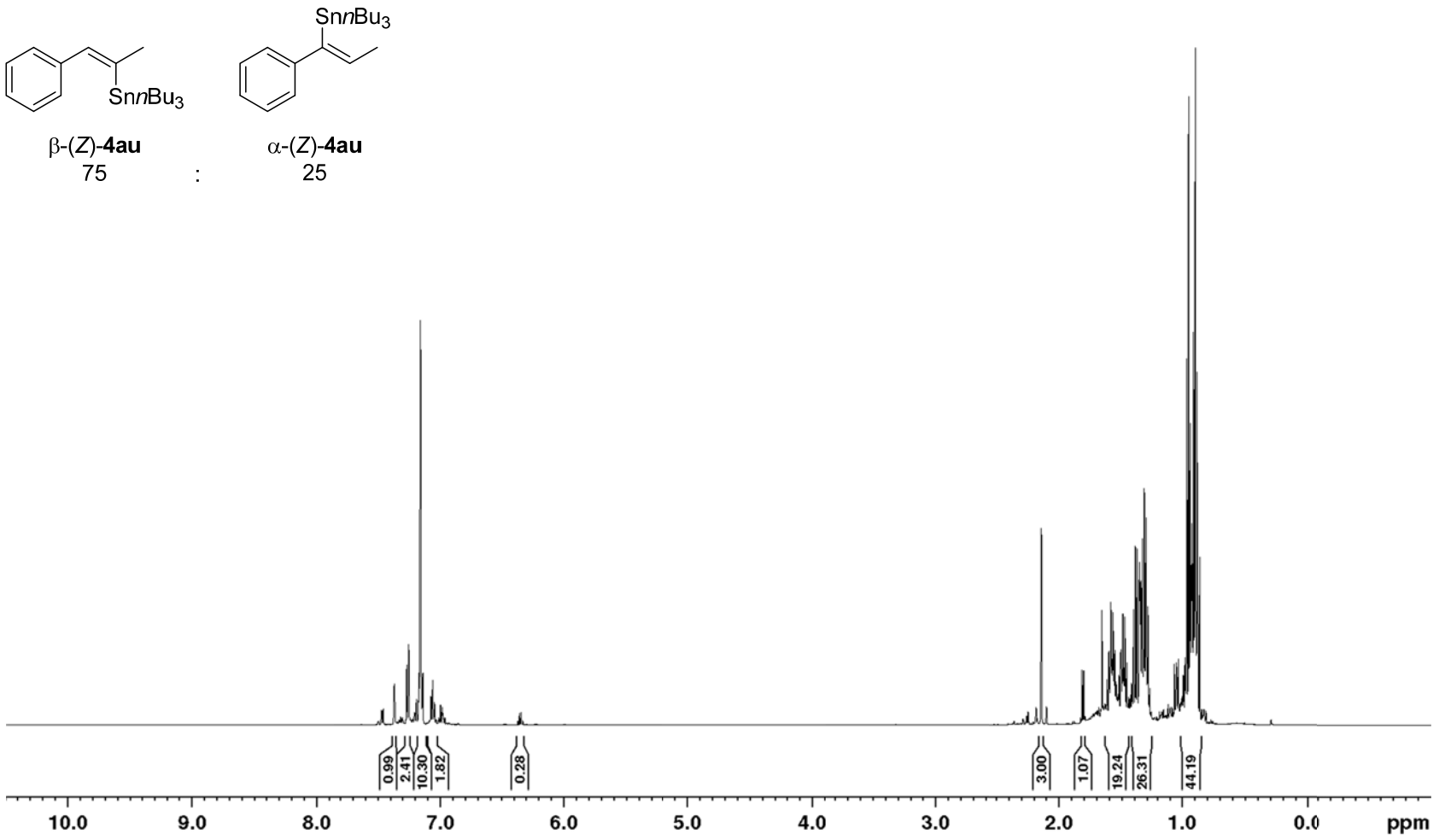


Figure S68 ^{1}H NMR (500 MHz, C_6D_6): Tributyl(1-phenylprop-1-en-2-yl)stannane (β-(*Z*)-**4au**) and Tributyl(1-phenylprop-1-en-1-yl)stannane (α-(*Z*)-**4au**)

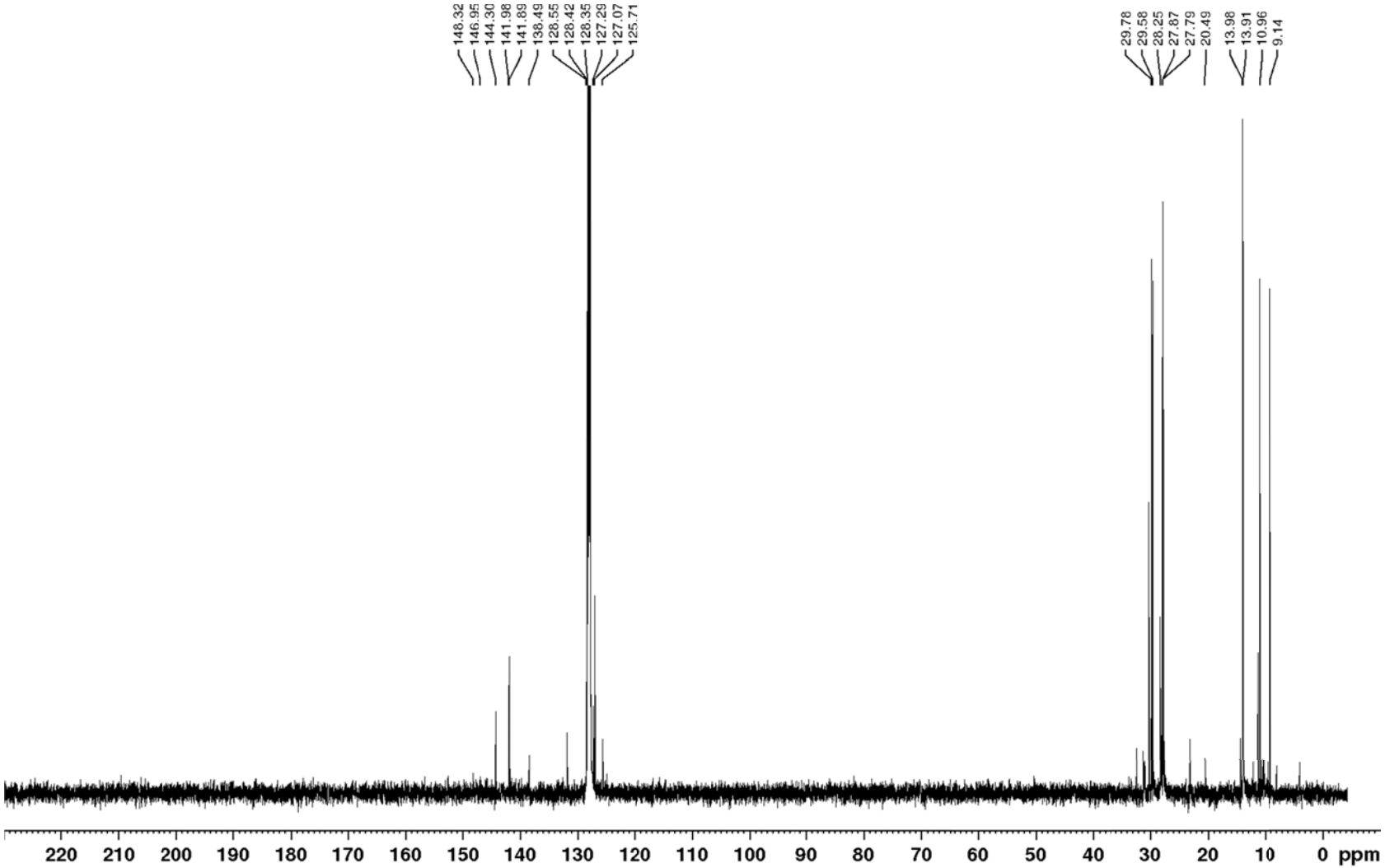


Figure S69 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): Tributyl(1-phenylprop-1-en-2-yl)stannane (β-(*Z*)-**4au**) and Tributyl(1-phenylprop-1-en-1-yl)stannane (α-(*Z*)-**4au**)

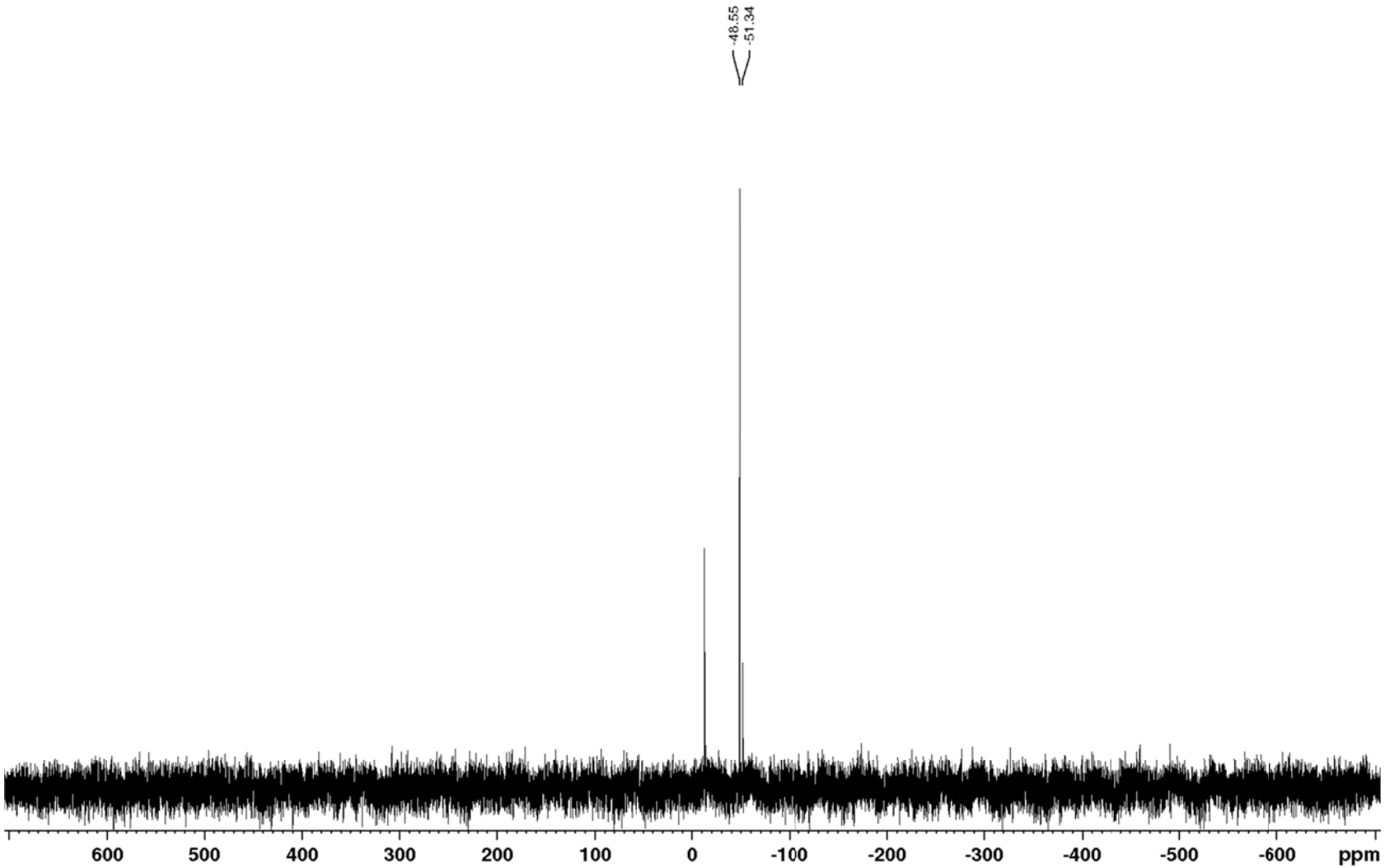


Figure S70 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, C_6D_6): Tributyl(1-phenylprop-1-en-2-yl)stannane (β-(*Z*)-**4au**) and Tributyl(1-phenylprop-1-en-1-yl)stannane (α-(*Z*)-**4au**)

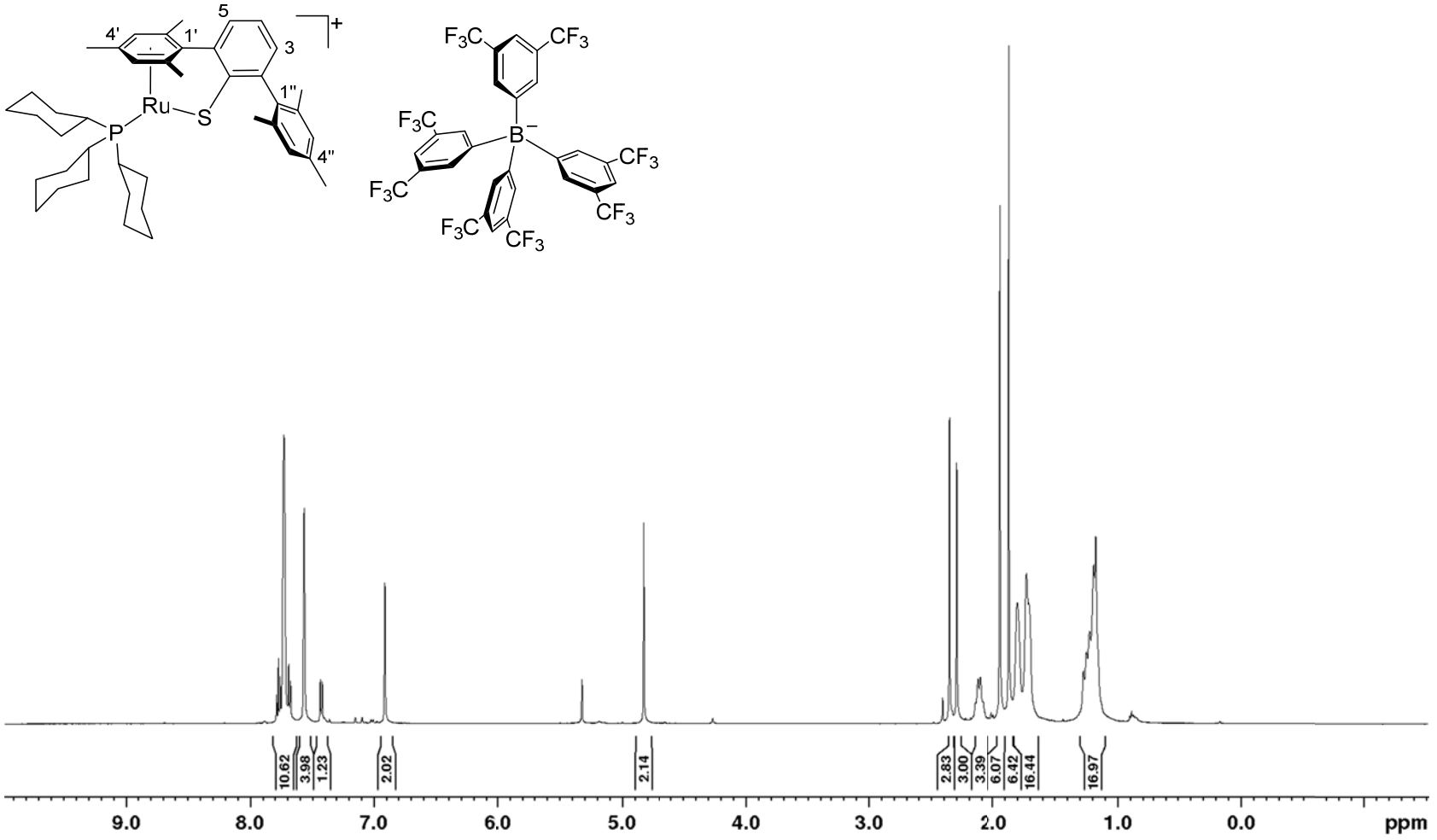


Figure S71 ^{1}H NMR (500 MHz, CD_2Cl_2): [**5c**]$^{+}$[BAr^{F}_{4}]$^{-}$

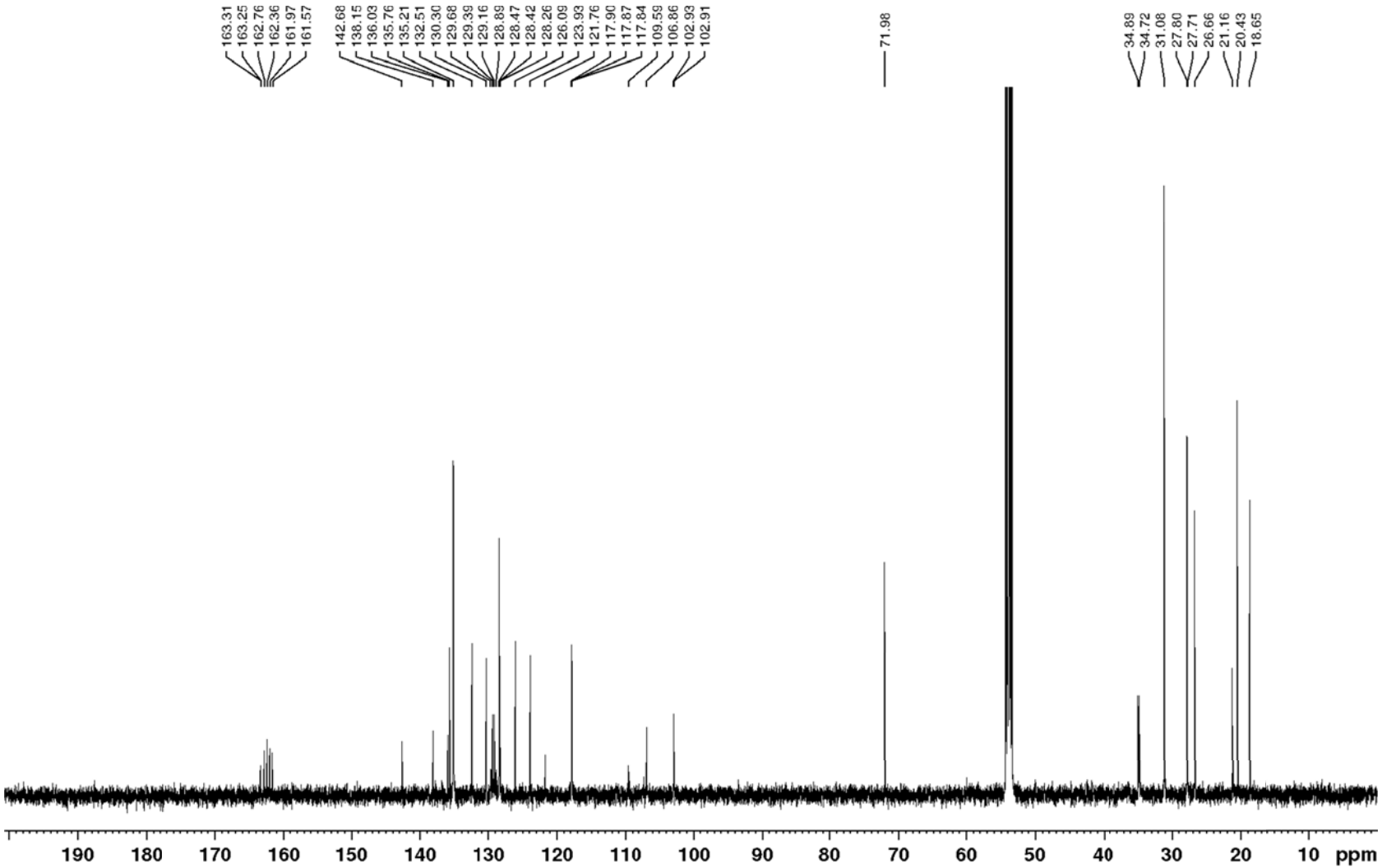


Figure S72 $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): [**5c**]$^{+}$[BAr^{F}_{4}]$^{-}$

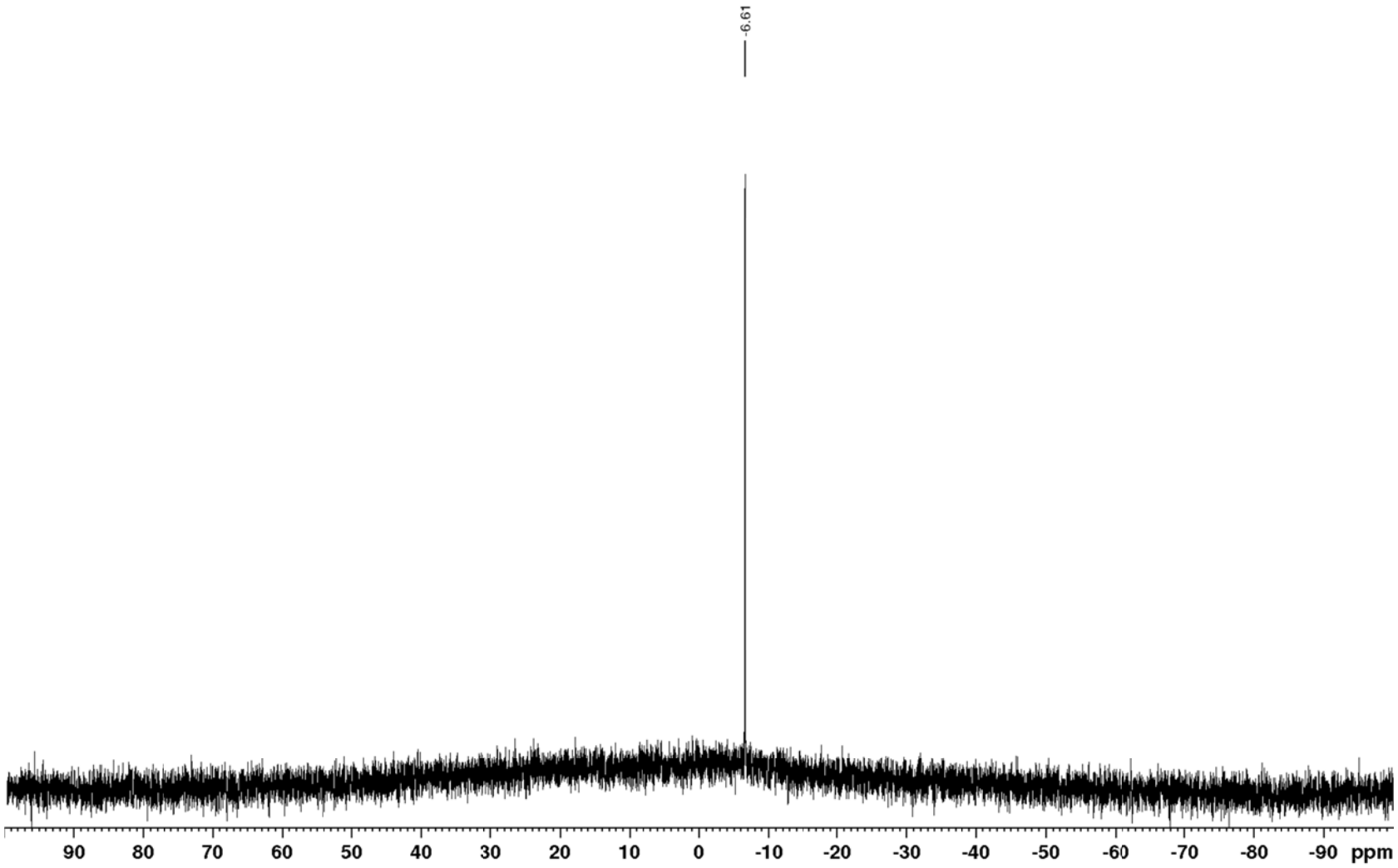


Figure S73 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2): [**5c**]$^{+}$[BAr^{F}_{4}]$^{-}$

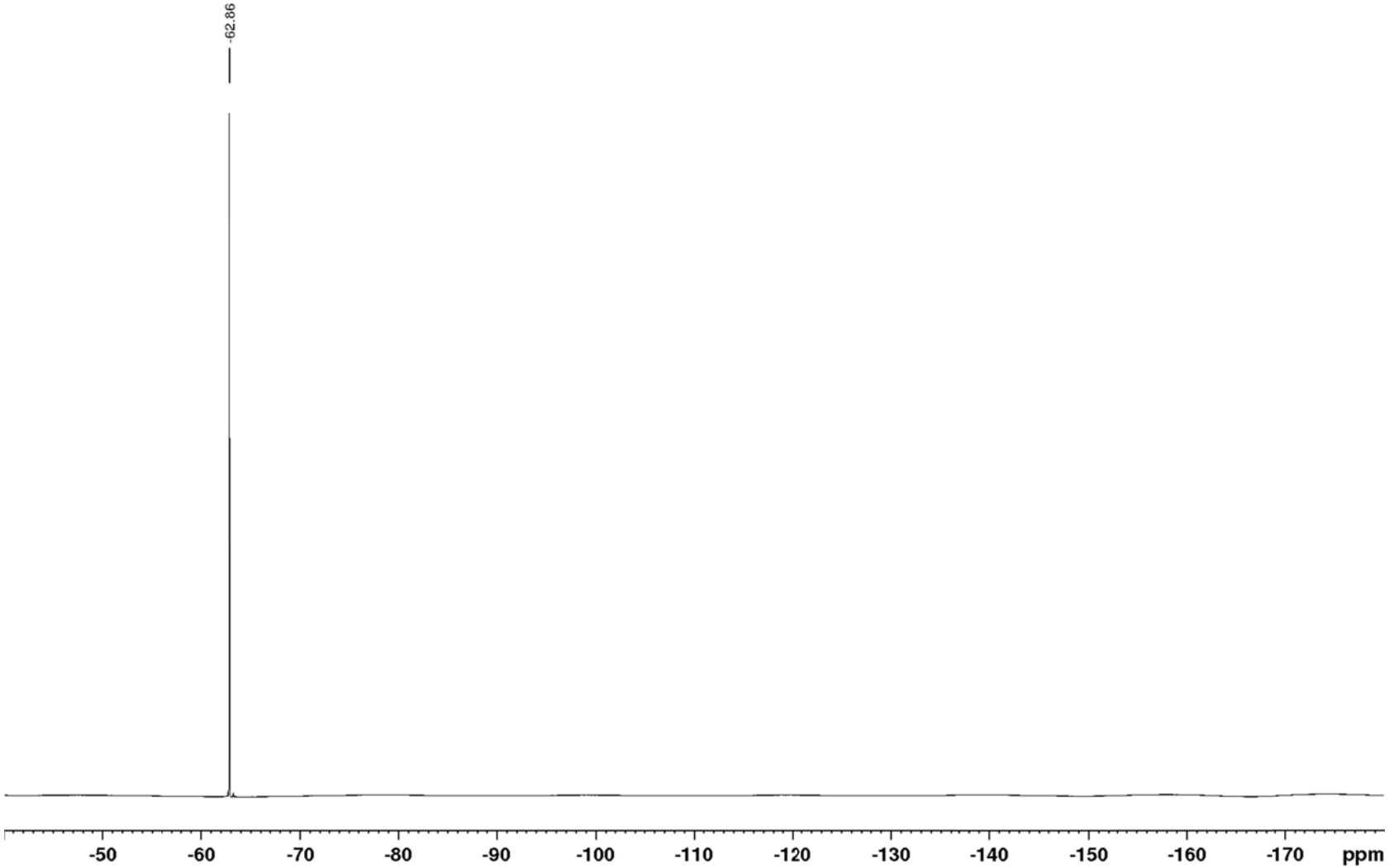


Figure S74 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2): [**5c**]$^{+}$[BAr^{F}_{4}]$^{-}$

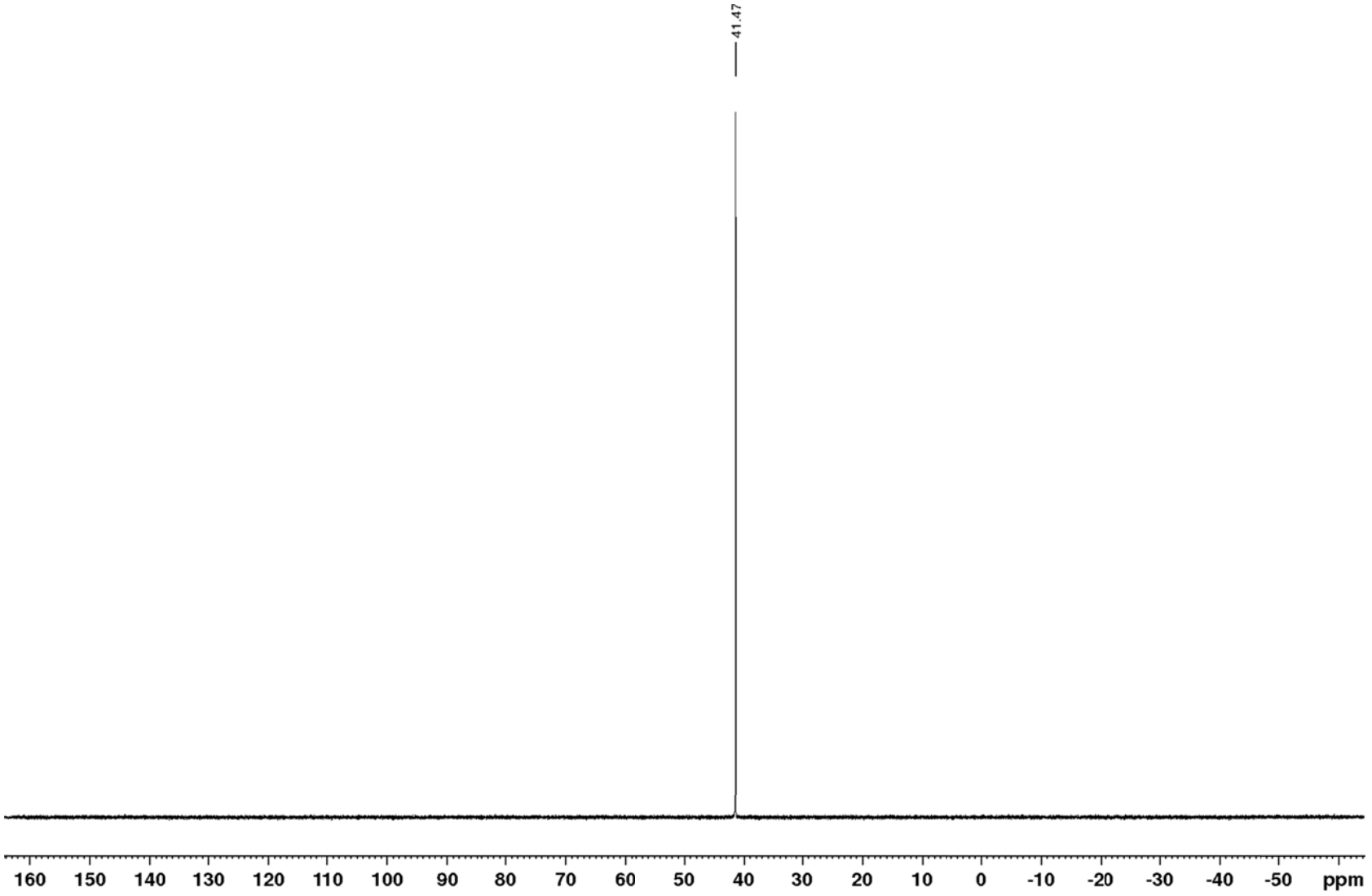


Figure S75 $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2): [**5c**]$^{+}$[BAr^{F}_{4}]$^{-}$

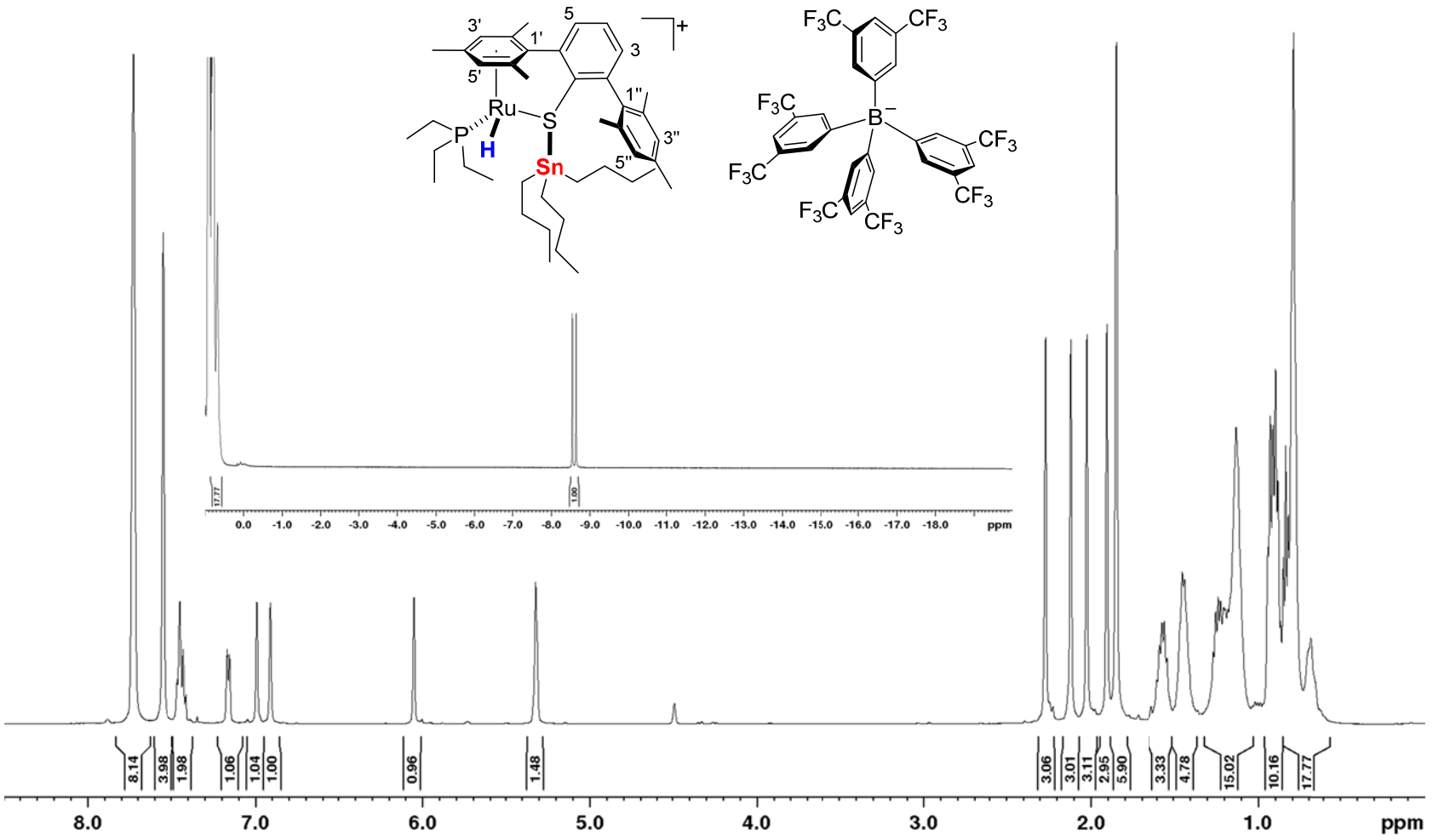


Figure S76 ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): [**5a**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

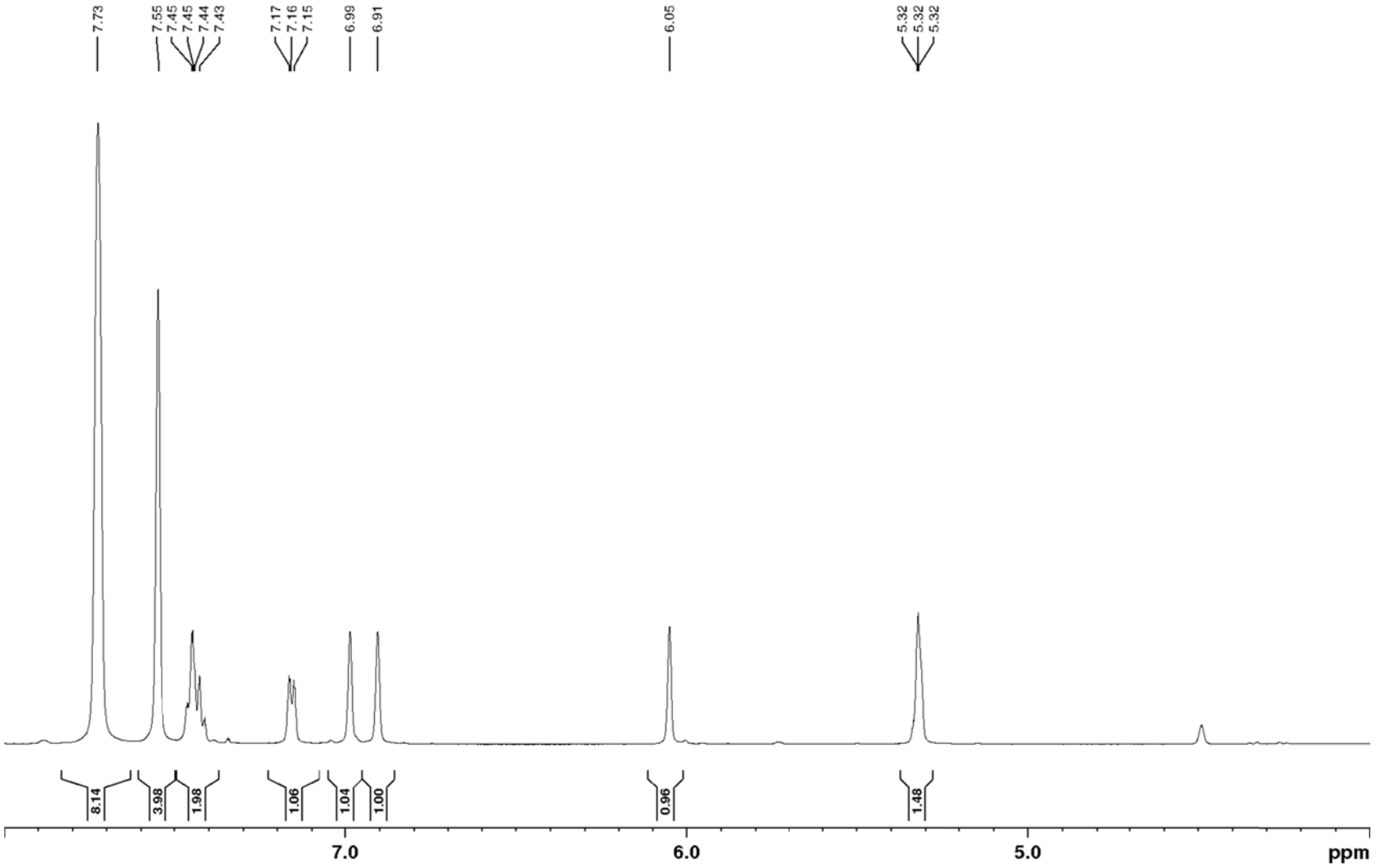


Figure S77 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): Aromatic region of [**5a**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

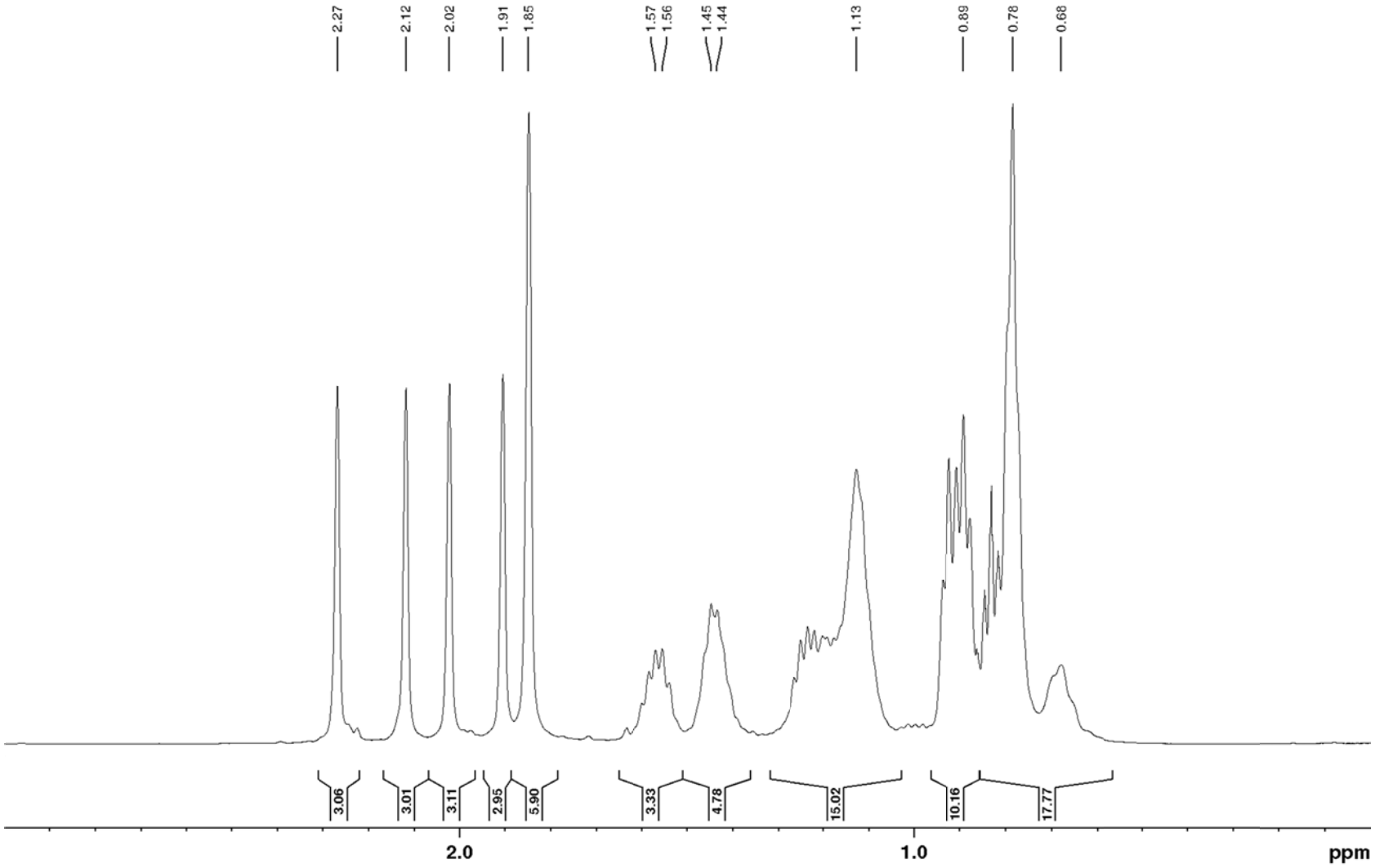


Figure S78 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): Aliphatic region of [**5a**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

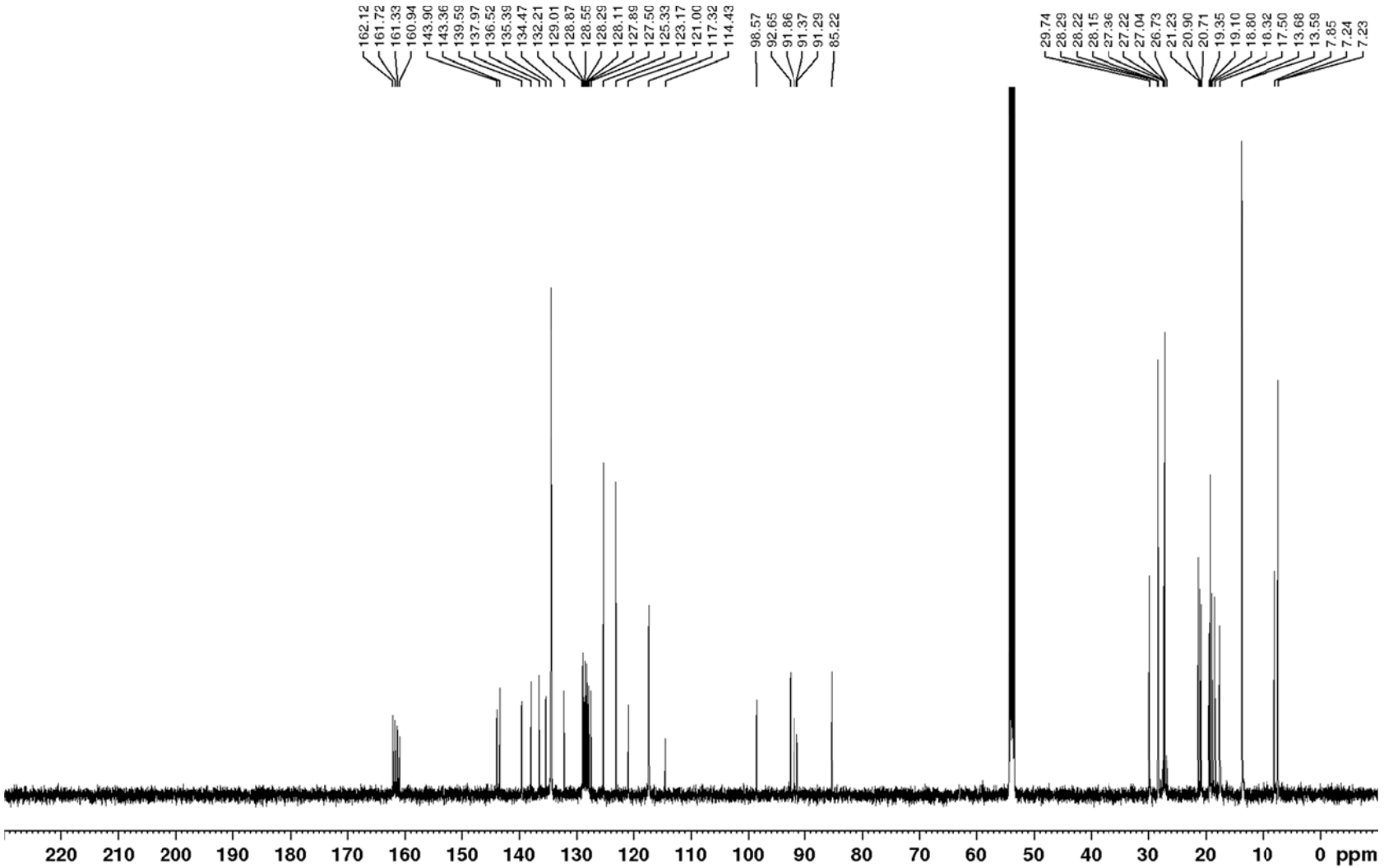


Figure S79 $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, 213 K): [**5a**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

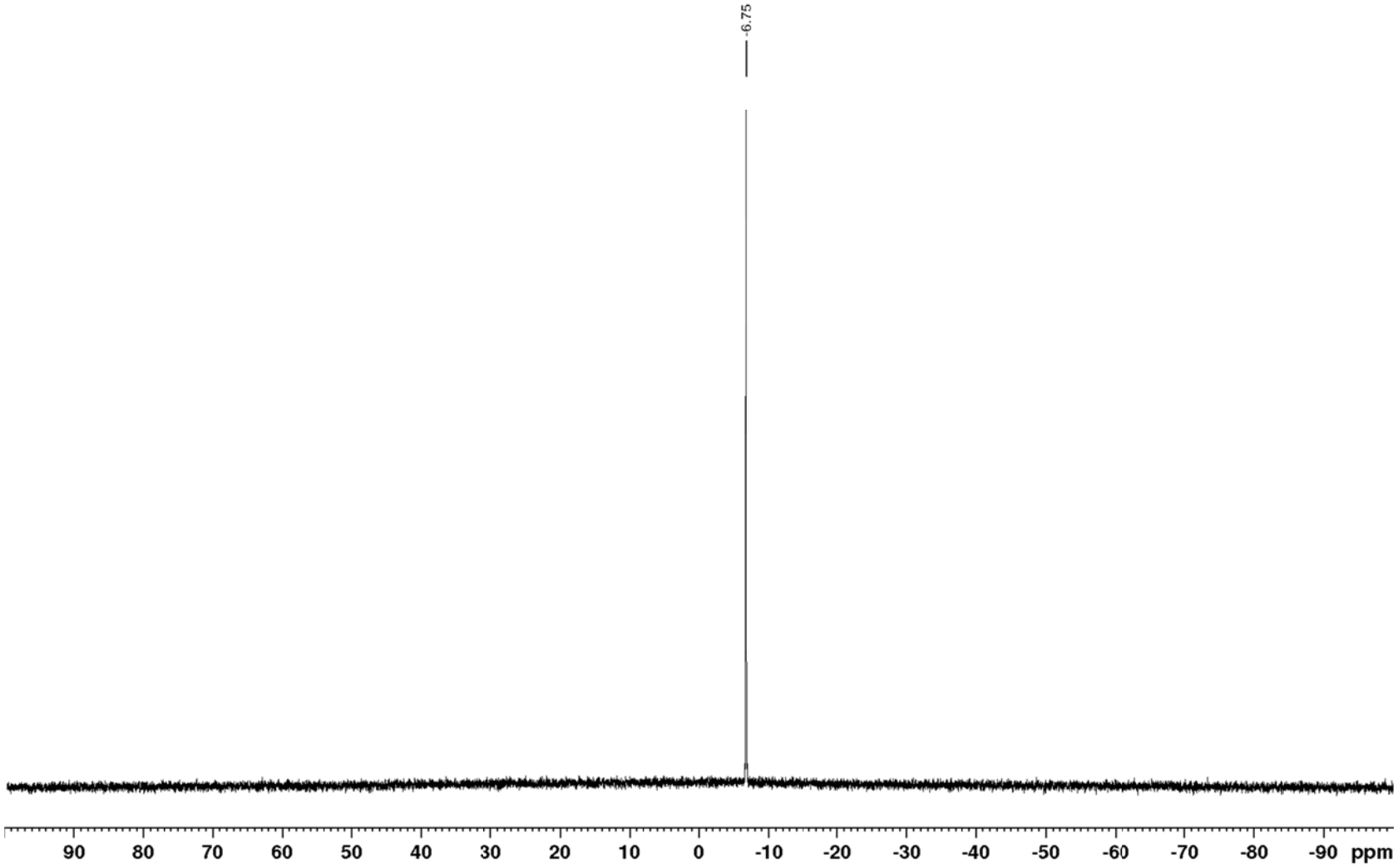


Figure S80 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 213 K): [**5a**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

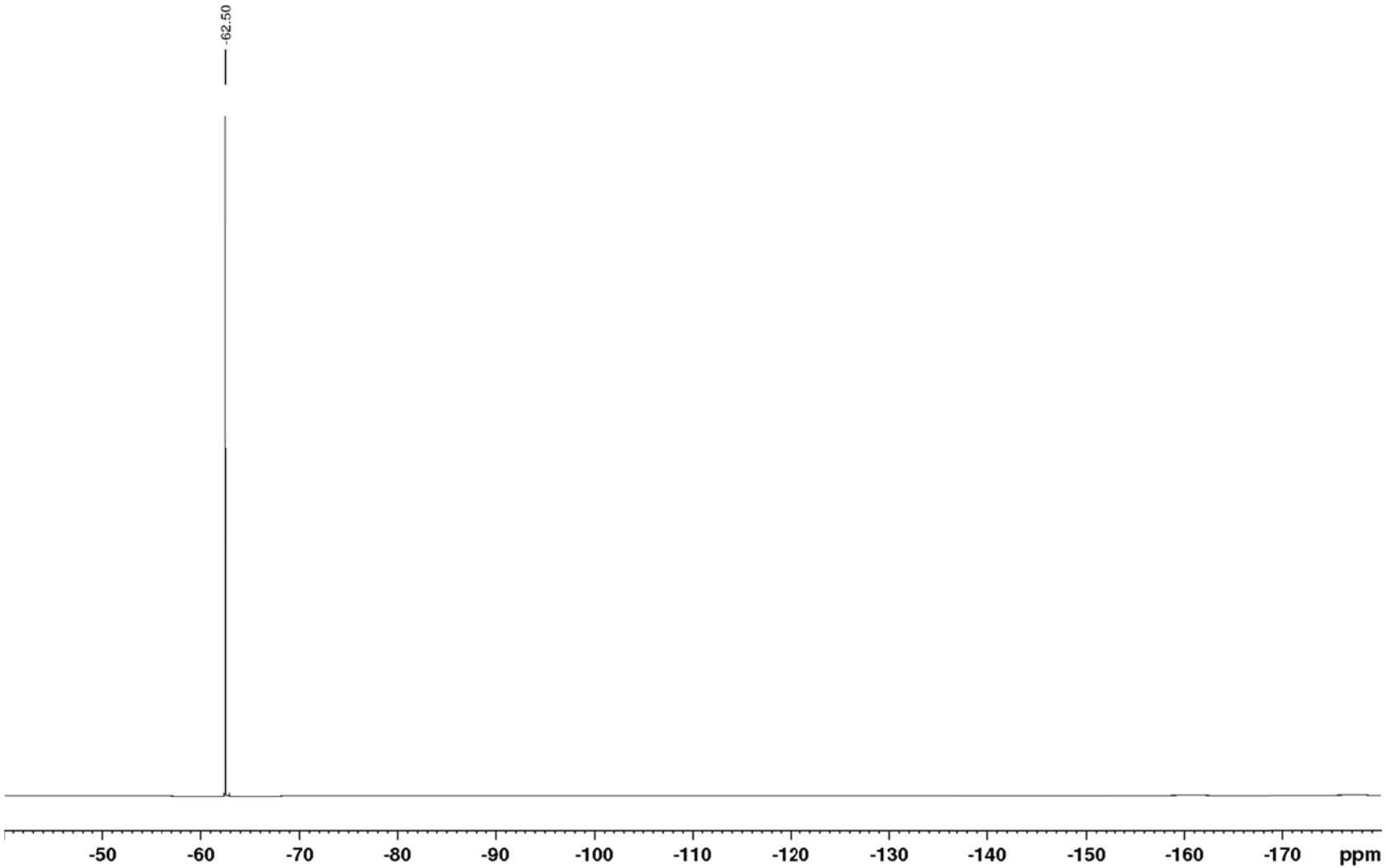


Figure S81 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2, 213 K): [**5a**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

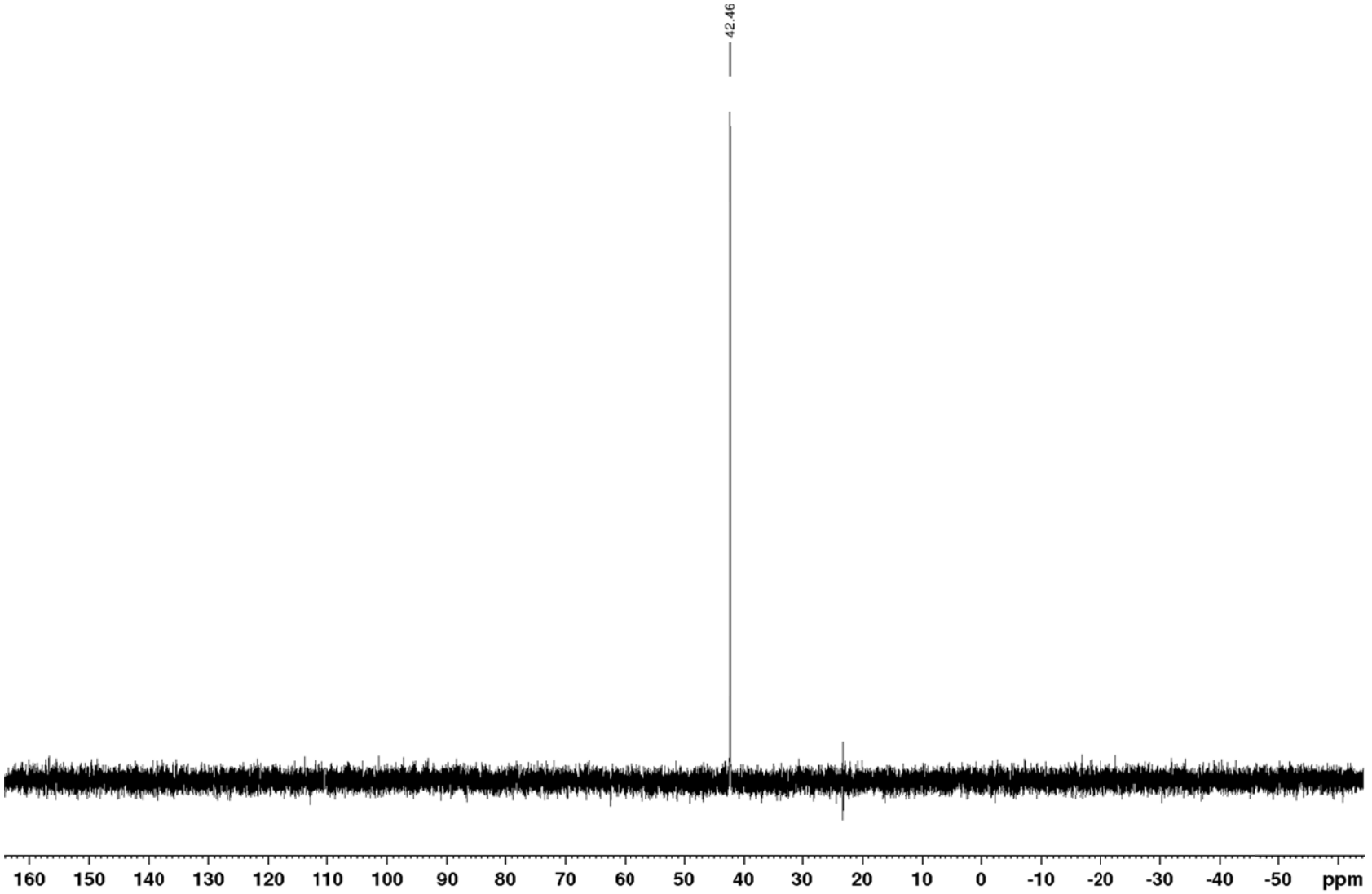


Figure S82 $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2, 213 K): [**5a**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

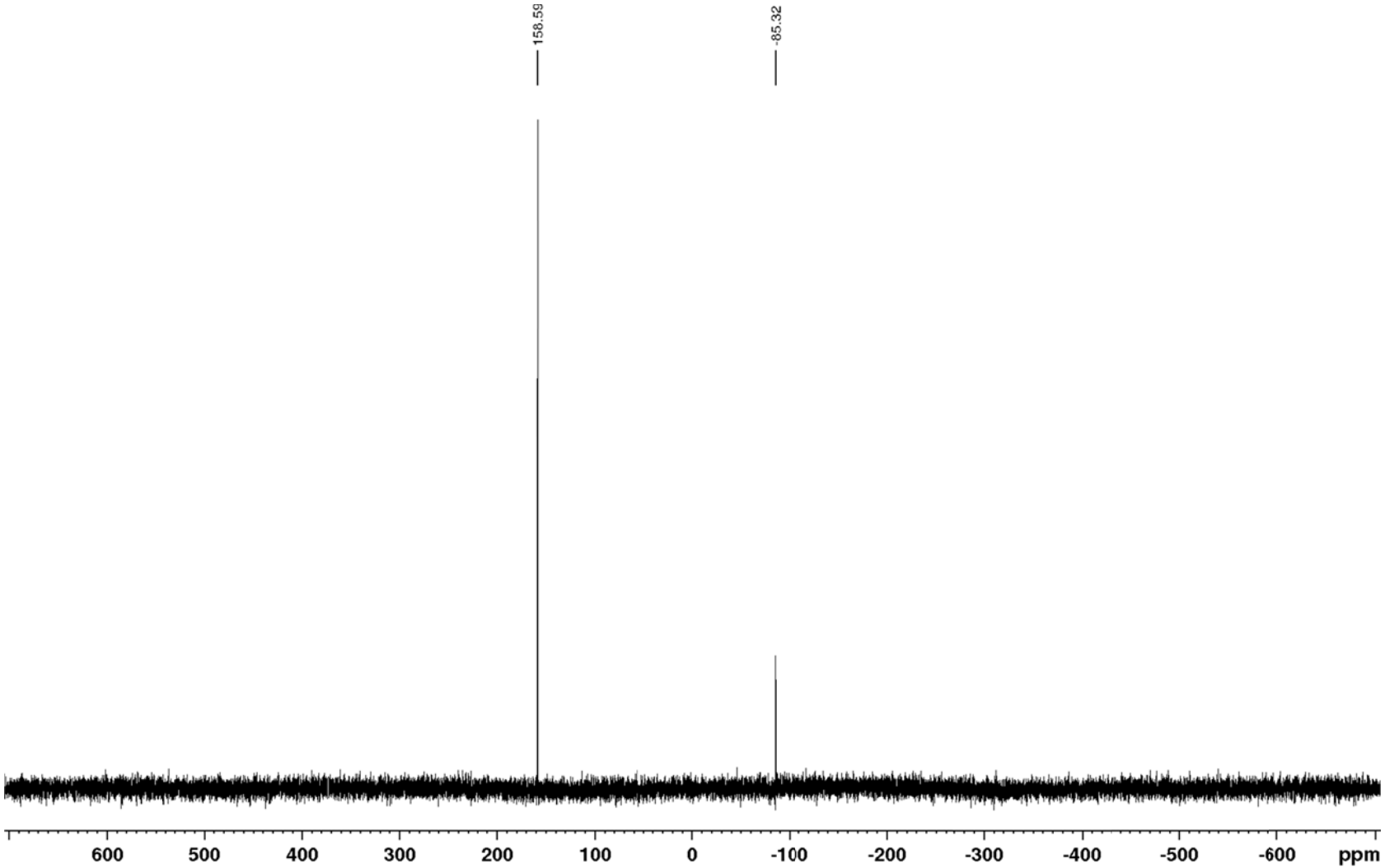


Figure S83 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, CD_2Cl_2, 213 K): [**5a**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

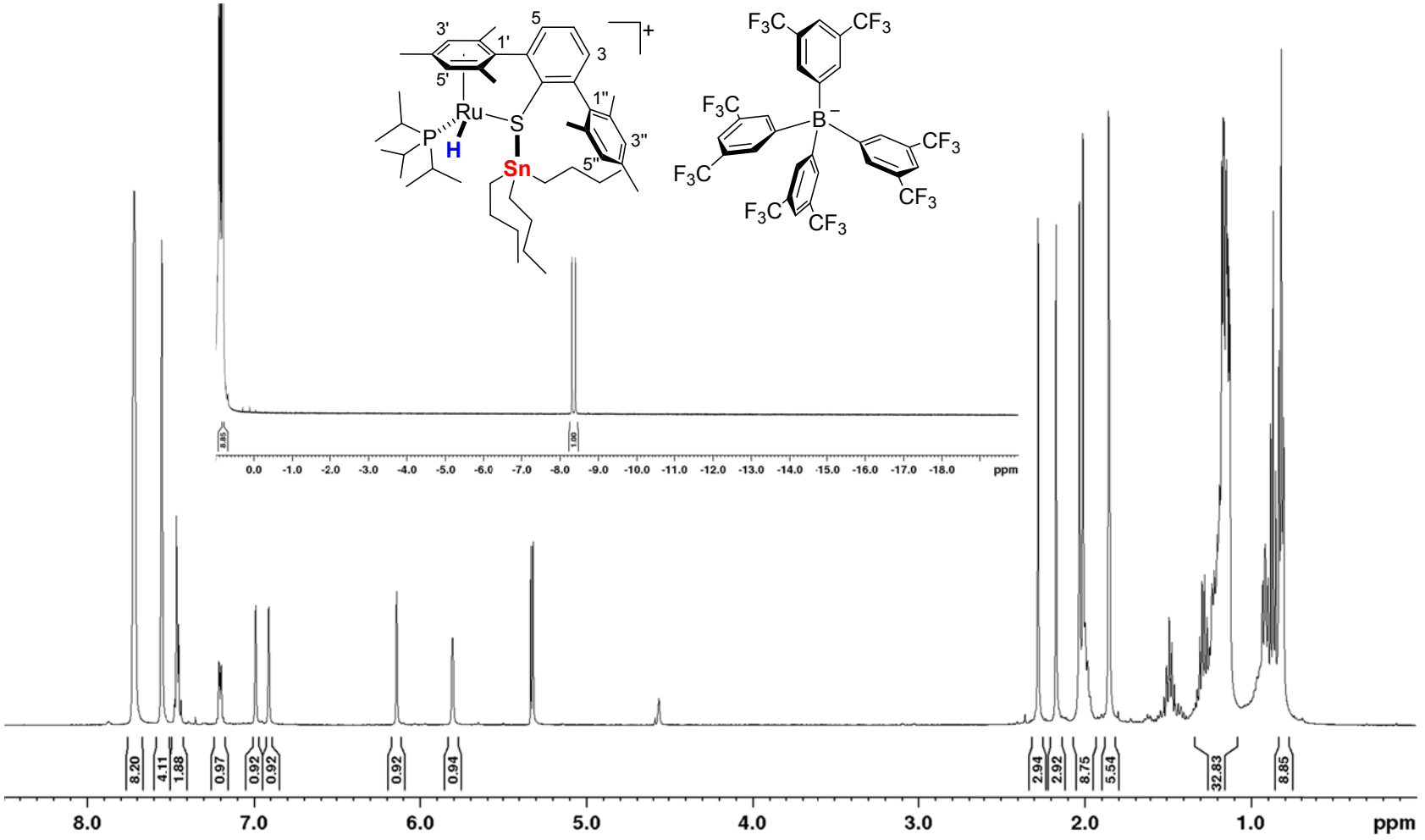


Figure S84 ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): [**5b**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$

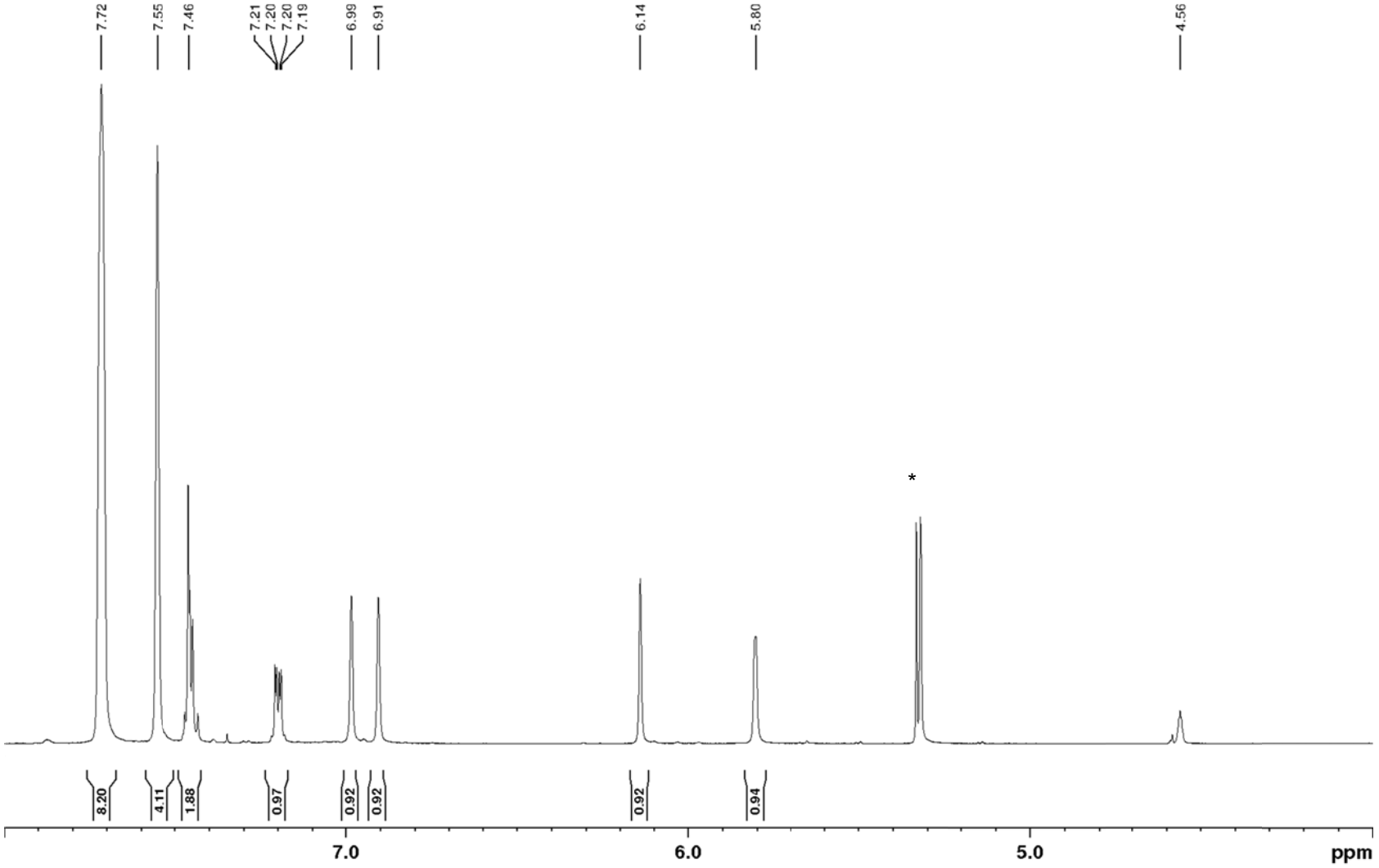


Figure S85 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): Aromatic region of [**5b**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$ (* = CH_2Cl_2)

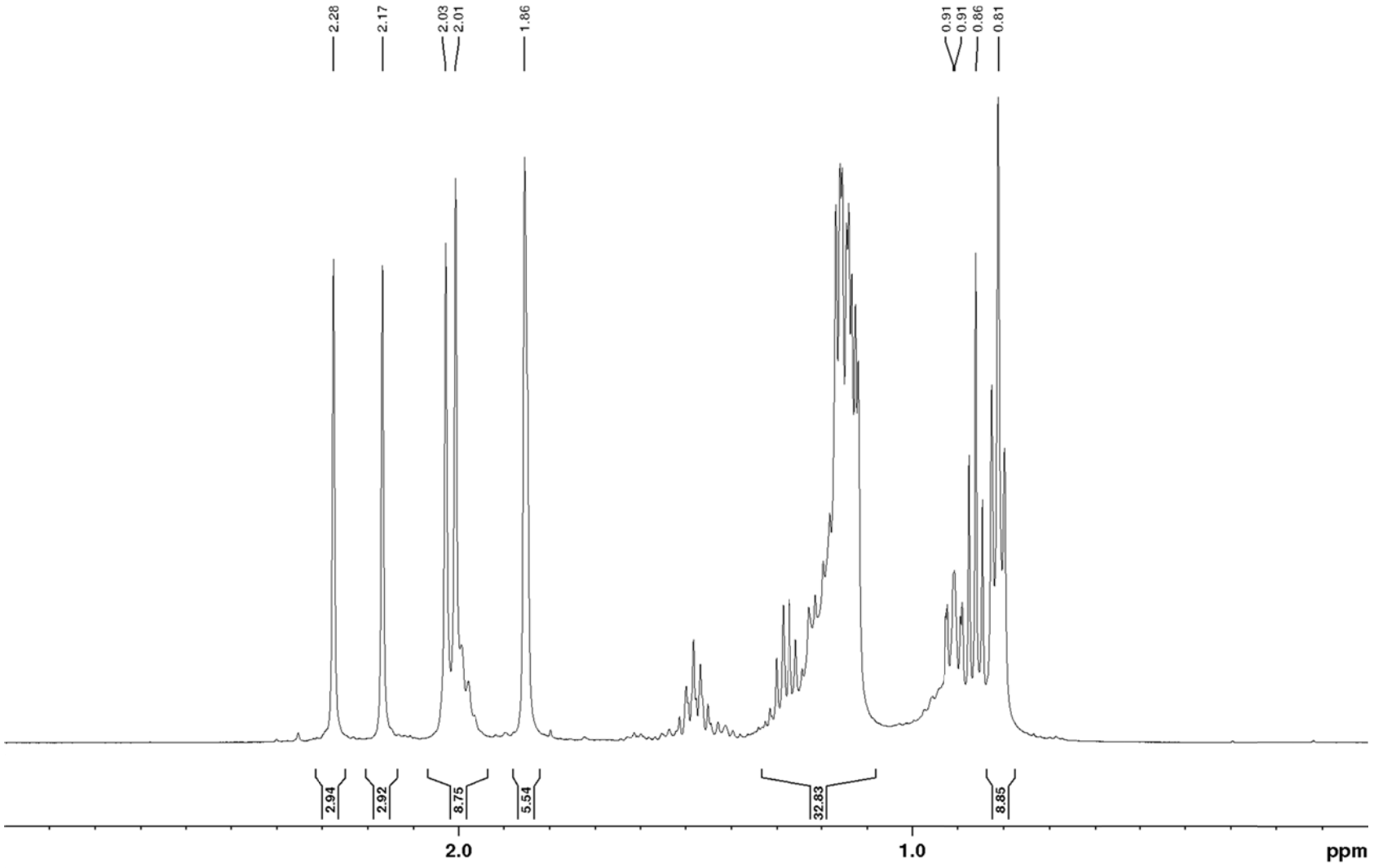


Figure S86 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): Aliphatic region of [**5b**·nBu$_3$SnH]$^+$[BAr$^F_4$]$^-$

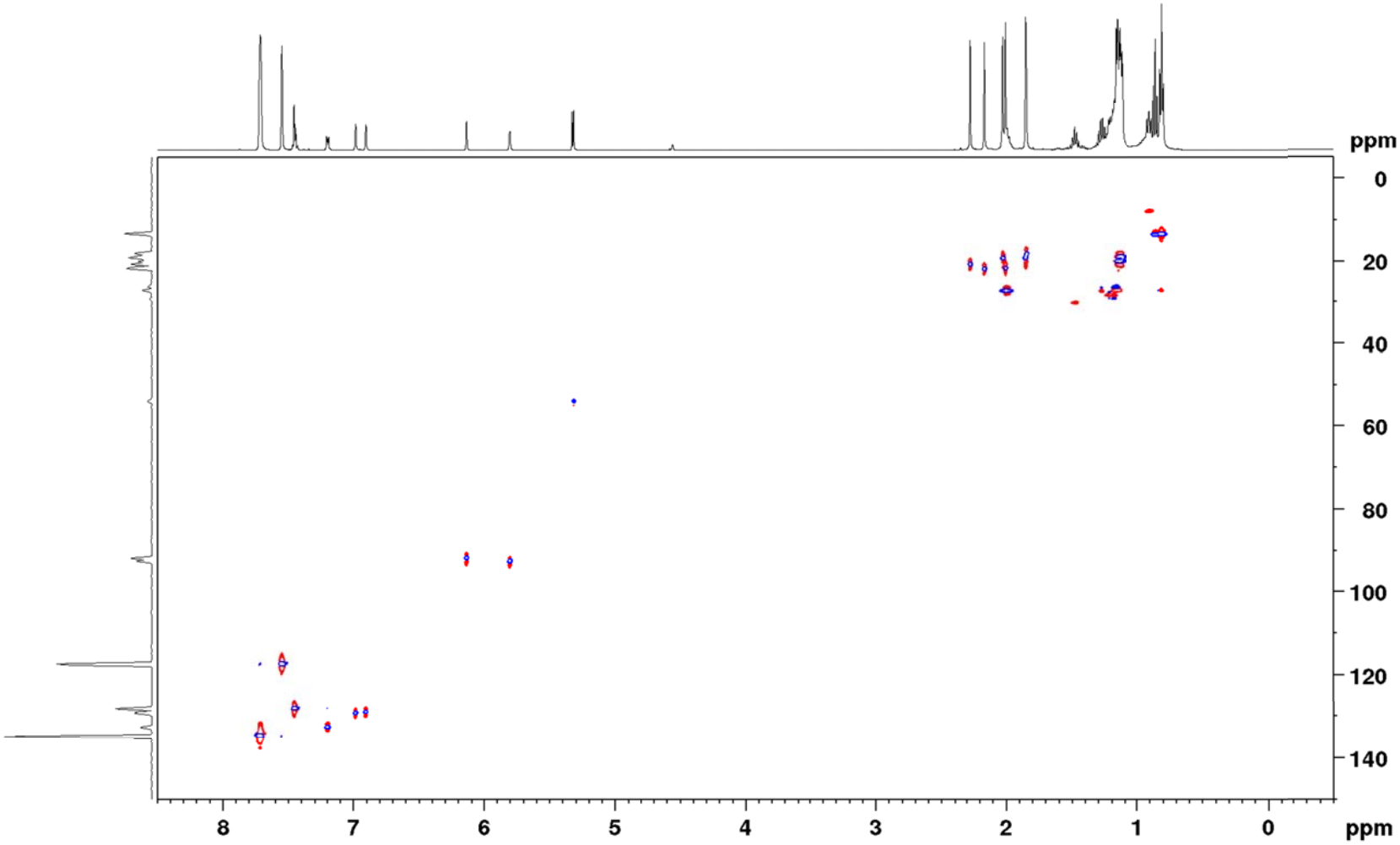


Figure S87 $^{1}H/^{13}C$ HSQC NMR (500/126 MHz, CD_2Cl_2, 253 K): [**5b**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

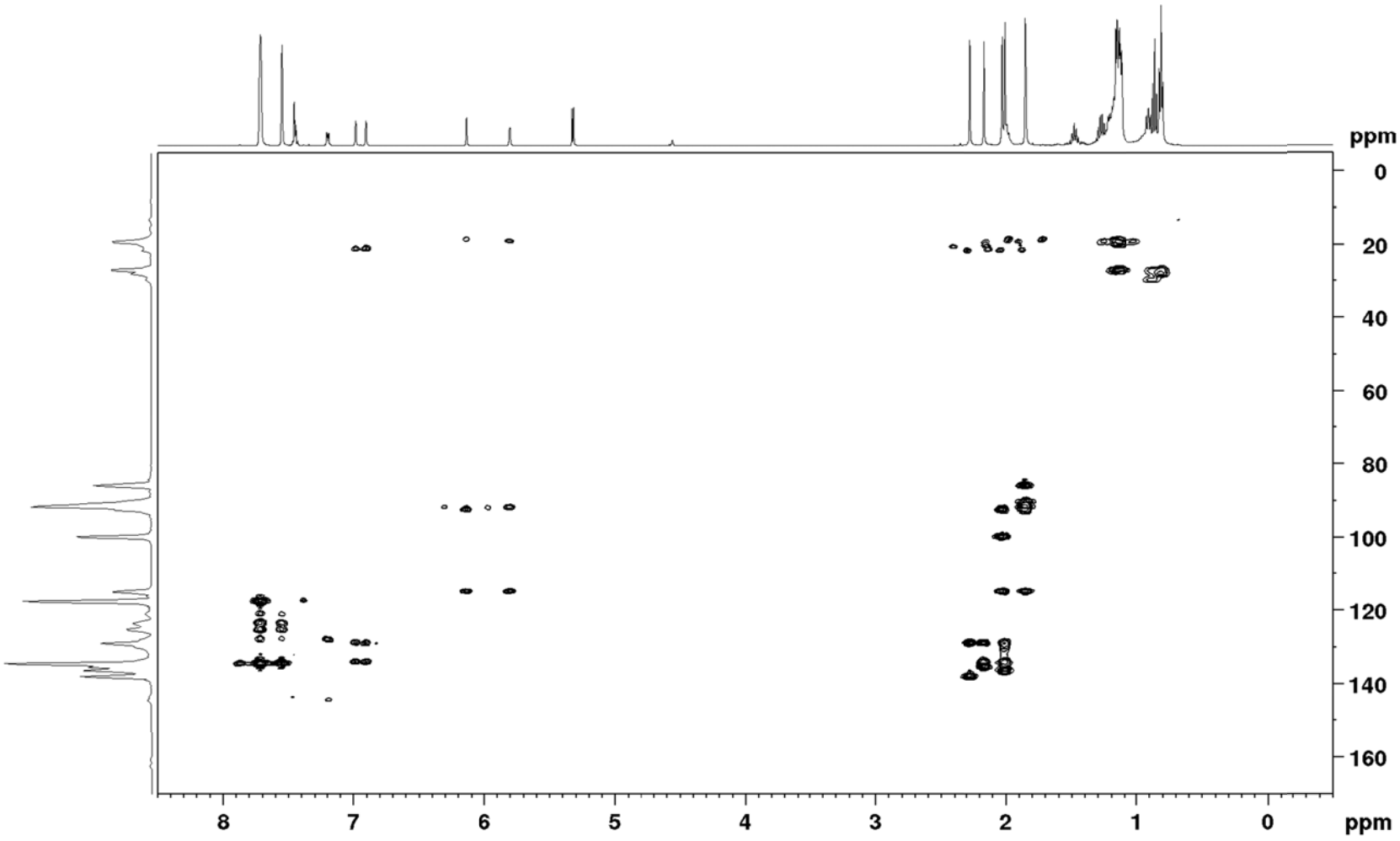


Figure S88 $^{1}H/^{13}C$ HMBC NMR (500/126 MHz, CD_2Cl_2, 253 K): [**5b**·*n*Bu_3SnH]$^+$[BAr^F_4]$^-$

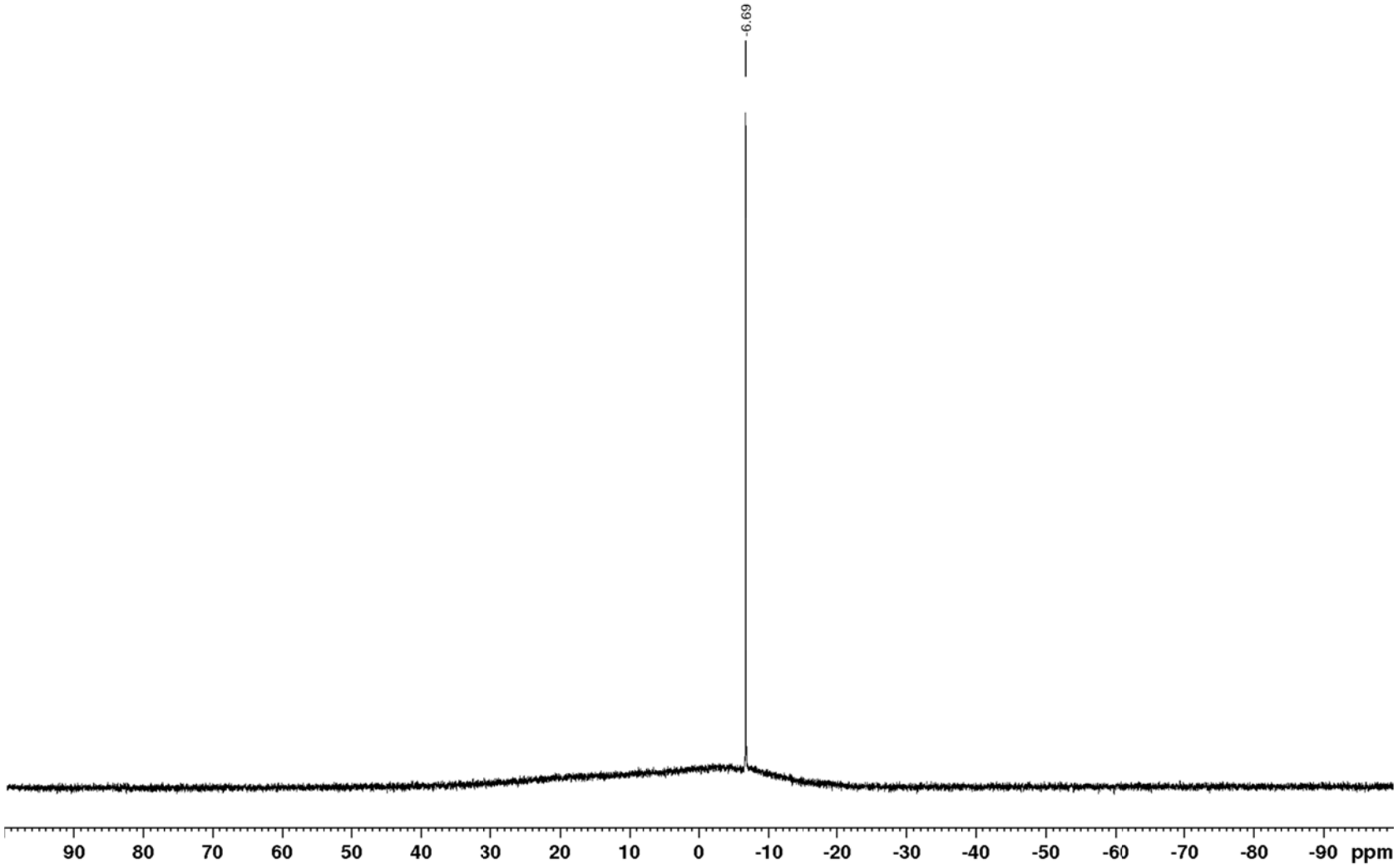


Figure S89 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 253 K): [**5b**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

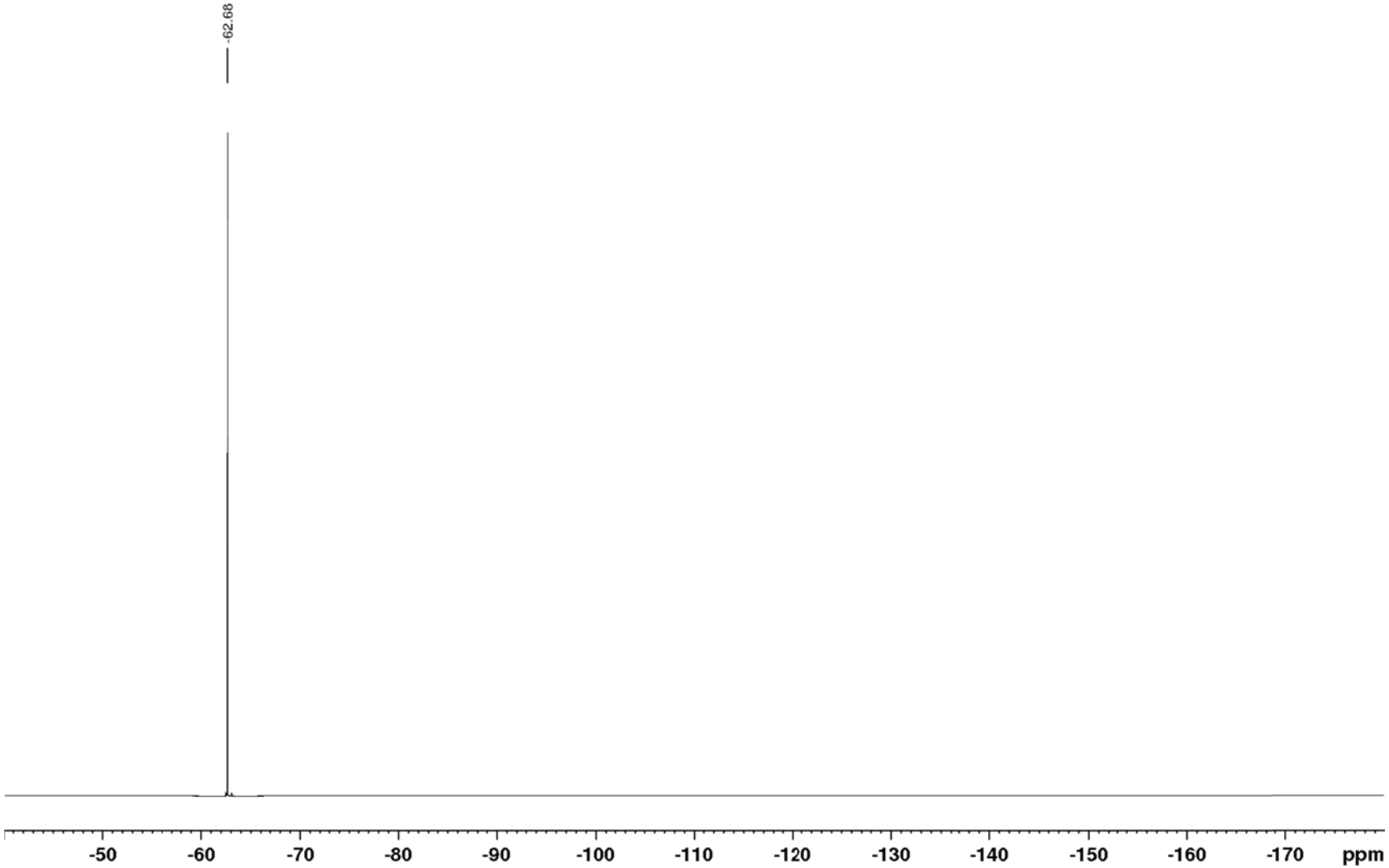


Figure S90 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2, 253 K): [**5b**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

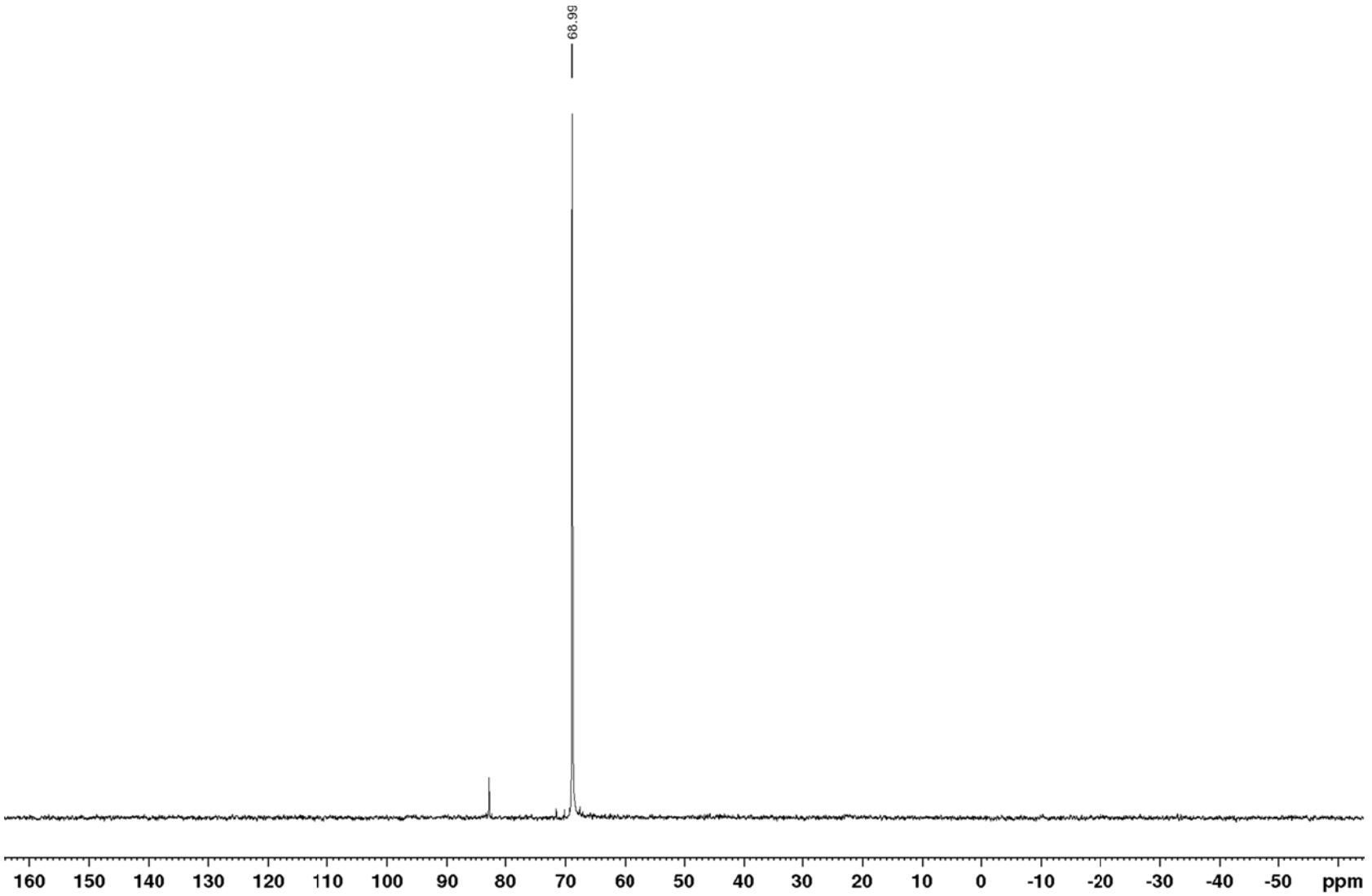


Figure S91 $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2, 253 K): [**5b**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

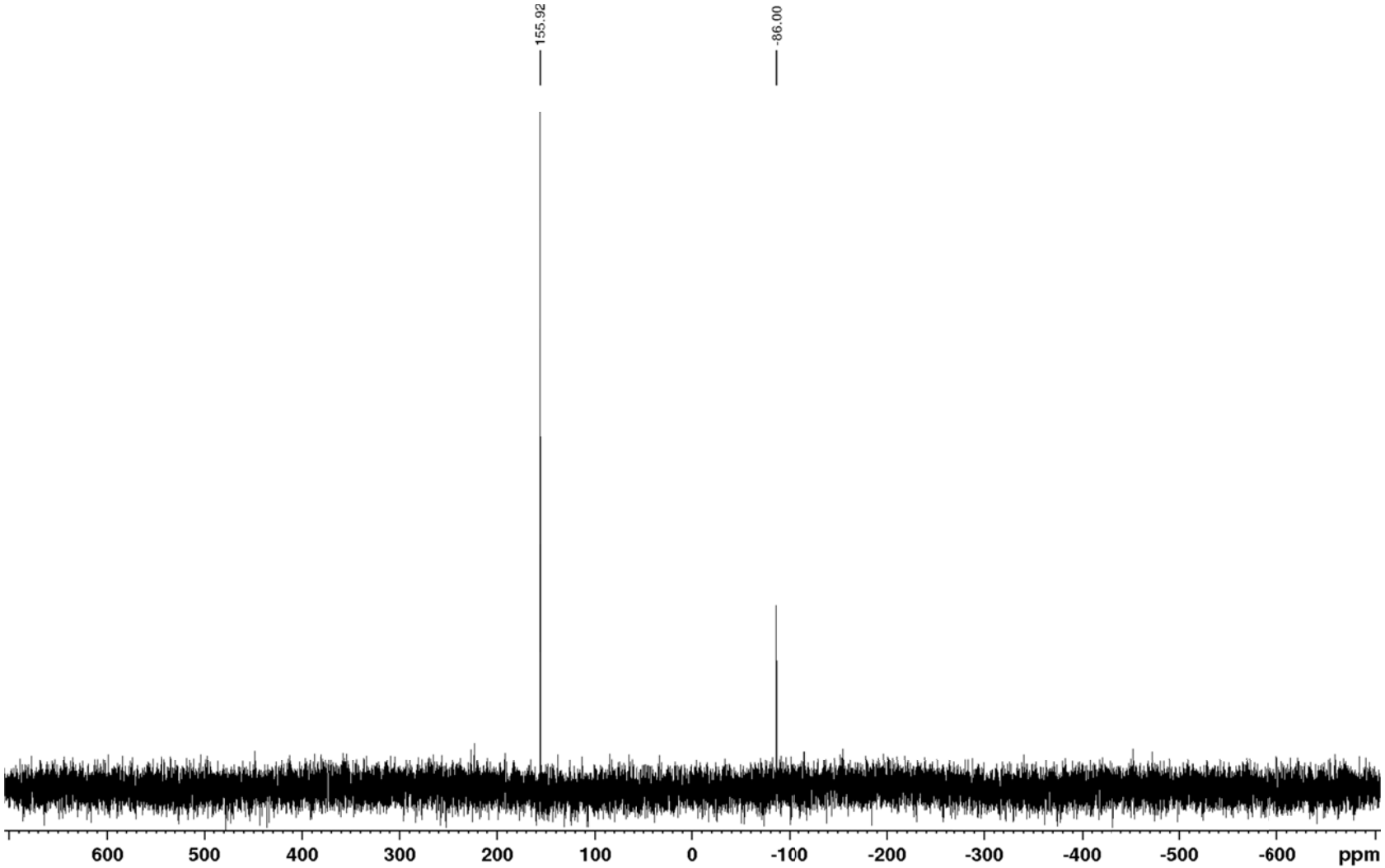


Figure S92 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, CD_2Cl_2, 253 K): [**5b**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

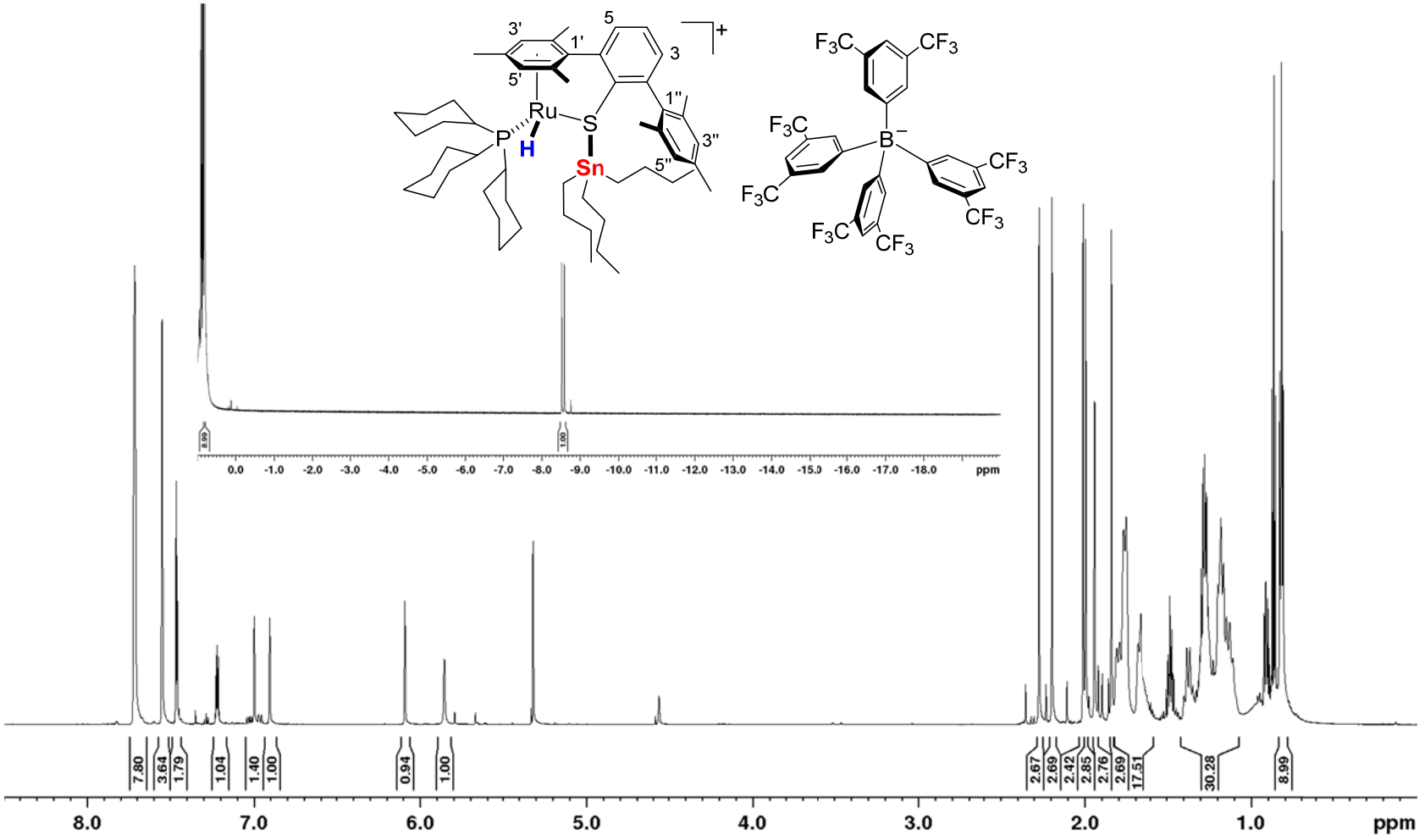


Figure S93 ^{1}H NMR (700 MHz, CD_2Cl_2, 253 K): [**5c**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

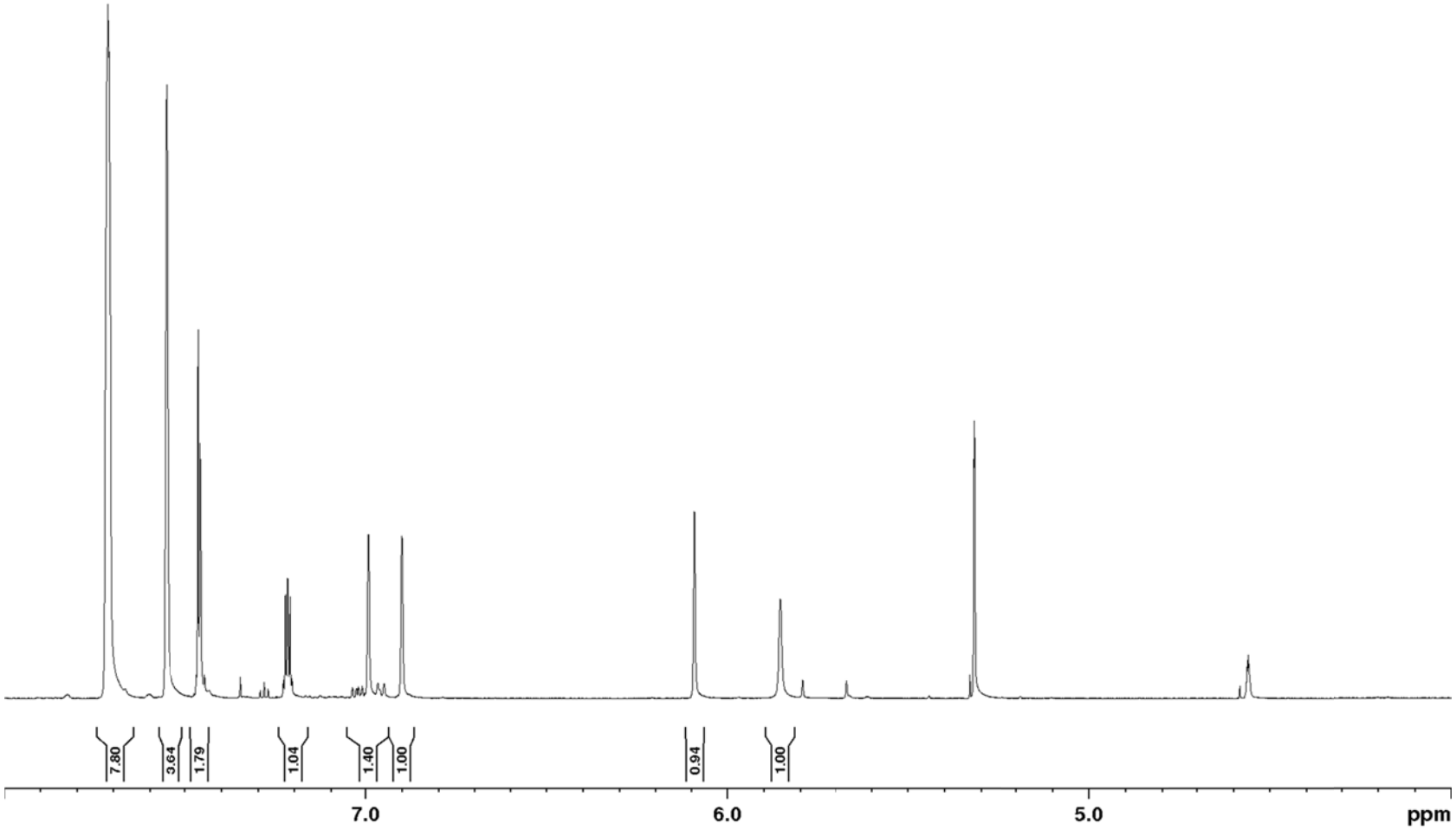


Figure S94 Expanded ^{1}H NMR (700 MHz, CD_2Cl_2, 253 K): Aromatic region of [**5c**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

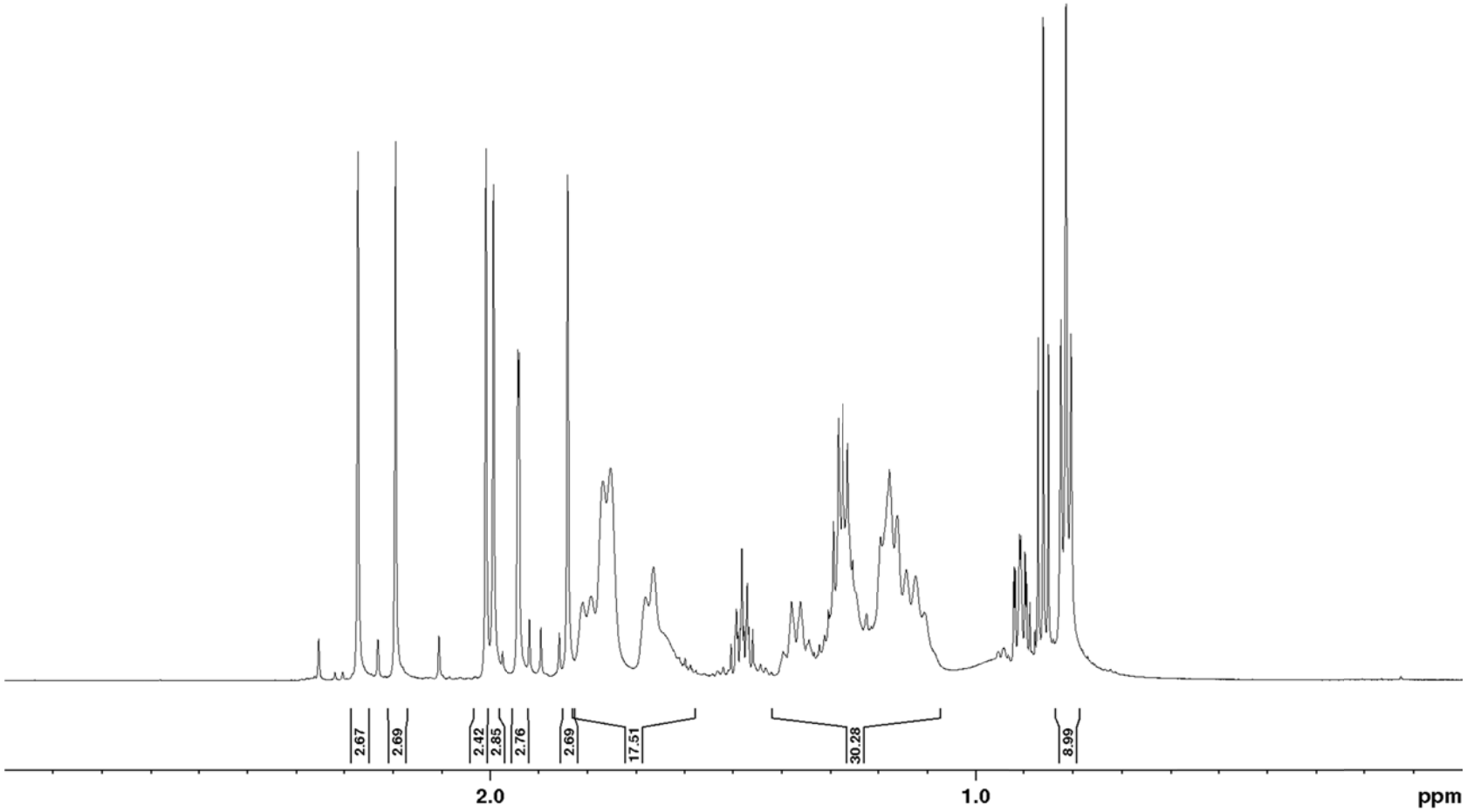


Figure S95 Expanded ^{1}H NMR (700 MHz, CD_2Cl_2, 253 K): Aromatic region of [**5c**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

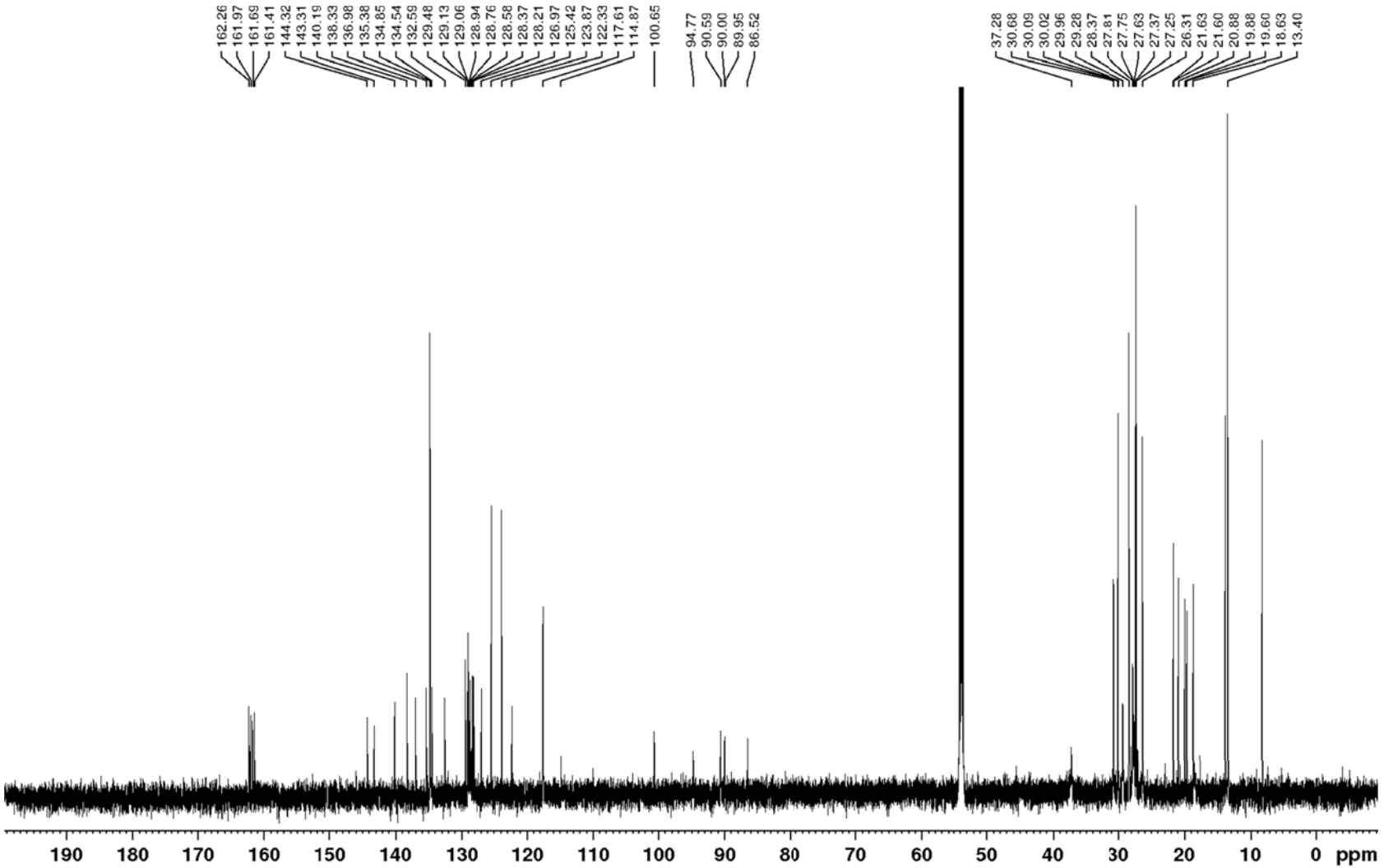


Figure S96 $^{13}C\{^{1}H\}$ NMR (175 MHz, CD_2Cl_2, 253 K): [**5c**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

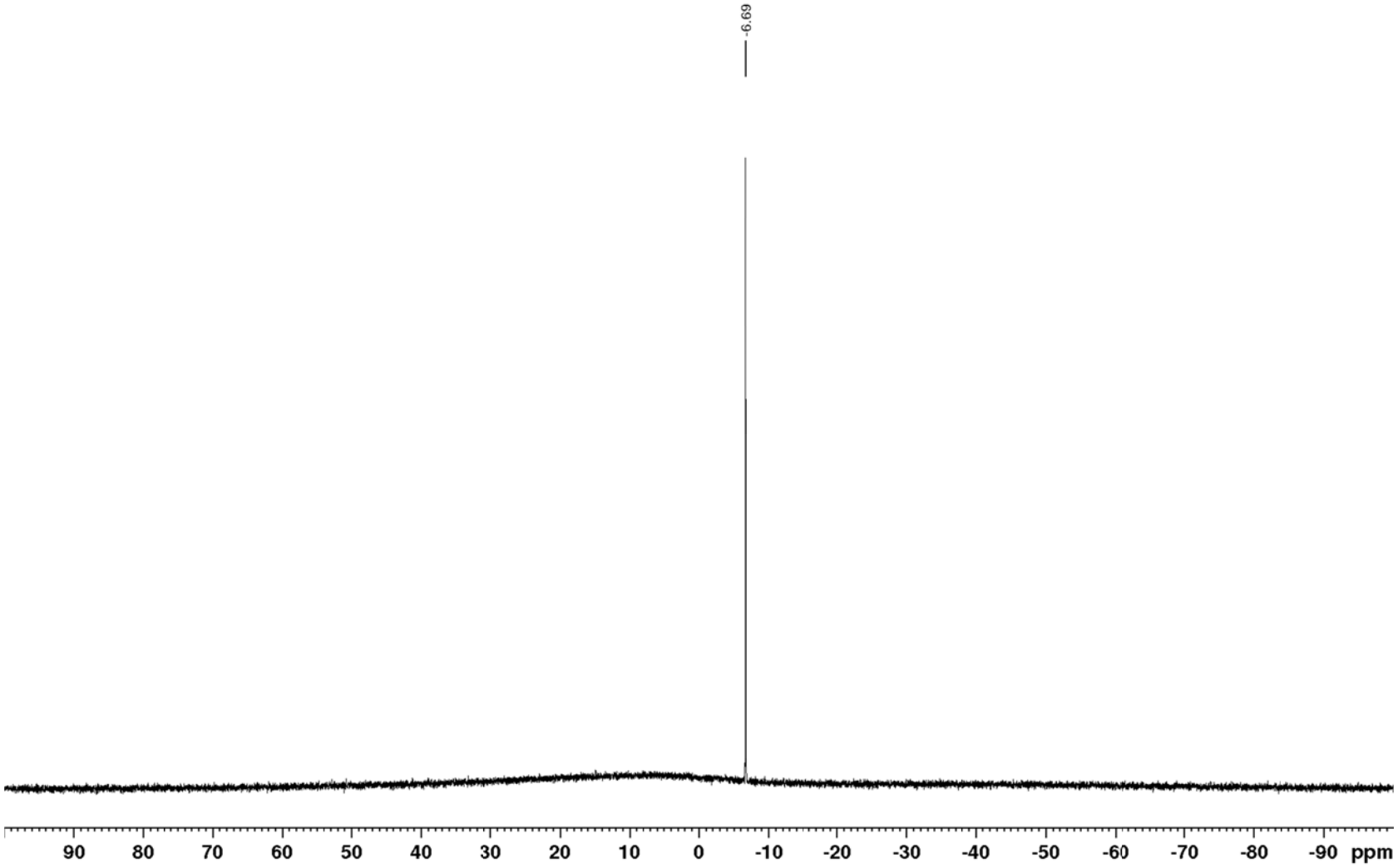


Figure S97 $^{11}B\{^{1}H\}$ NMR (224 MHz, CD_2Cl_2, 253 K): [**5c**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

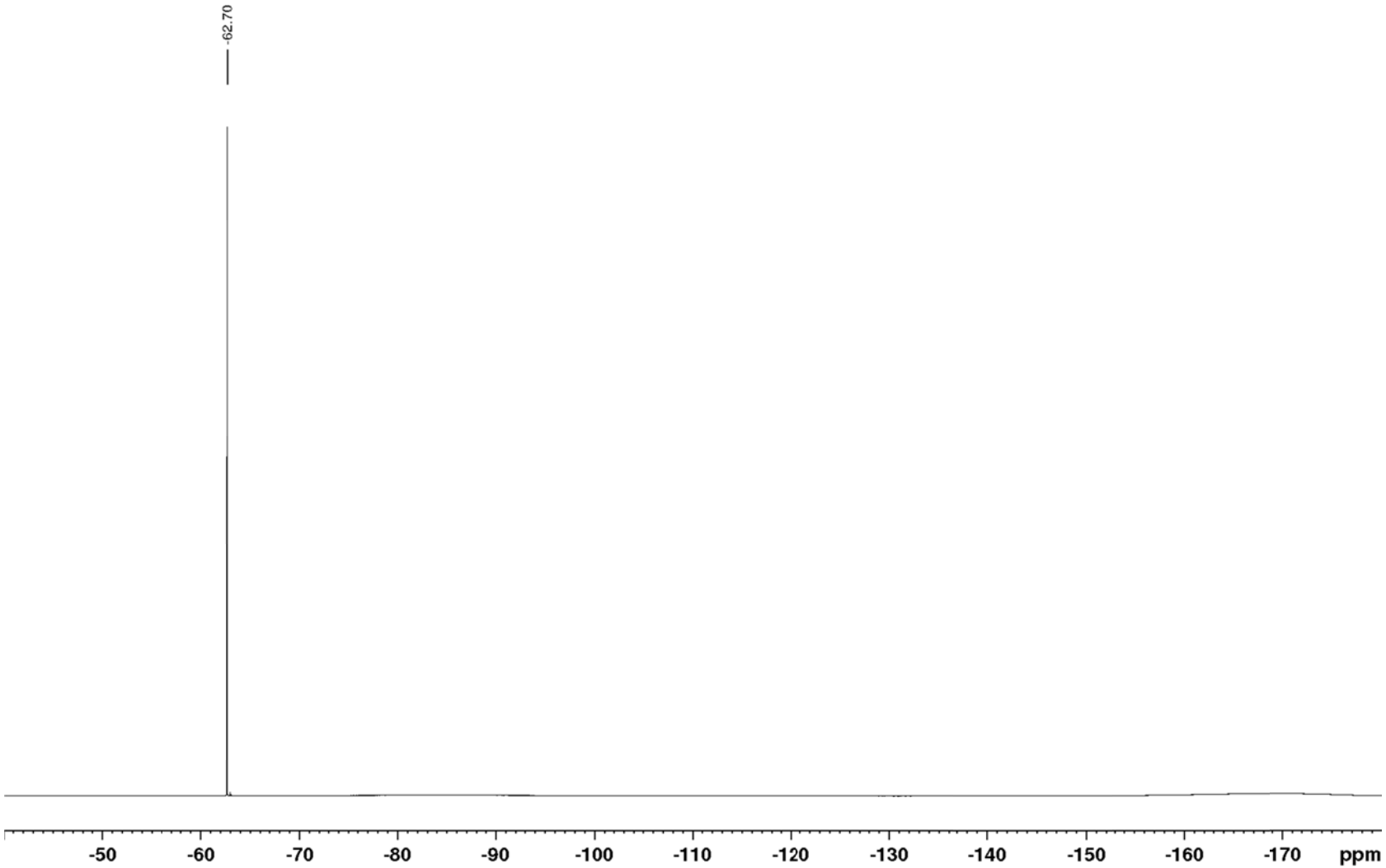


Figure S98 $^{19}F\{^{1}H\}$ NMR (659 MHz, CD_2Cl_2, 253 K): [**5c**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

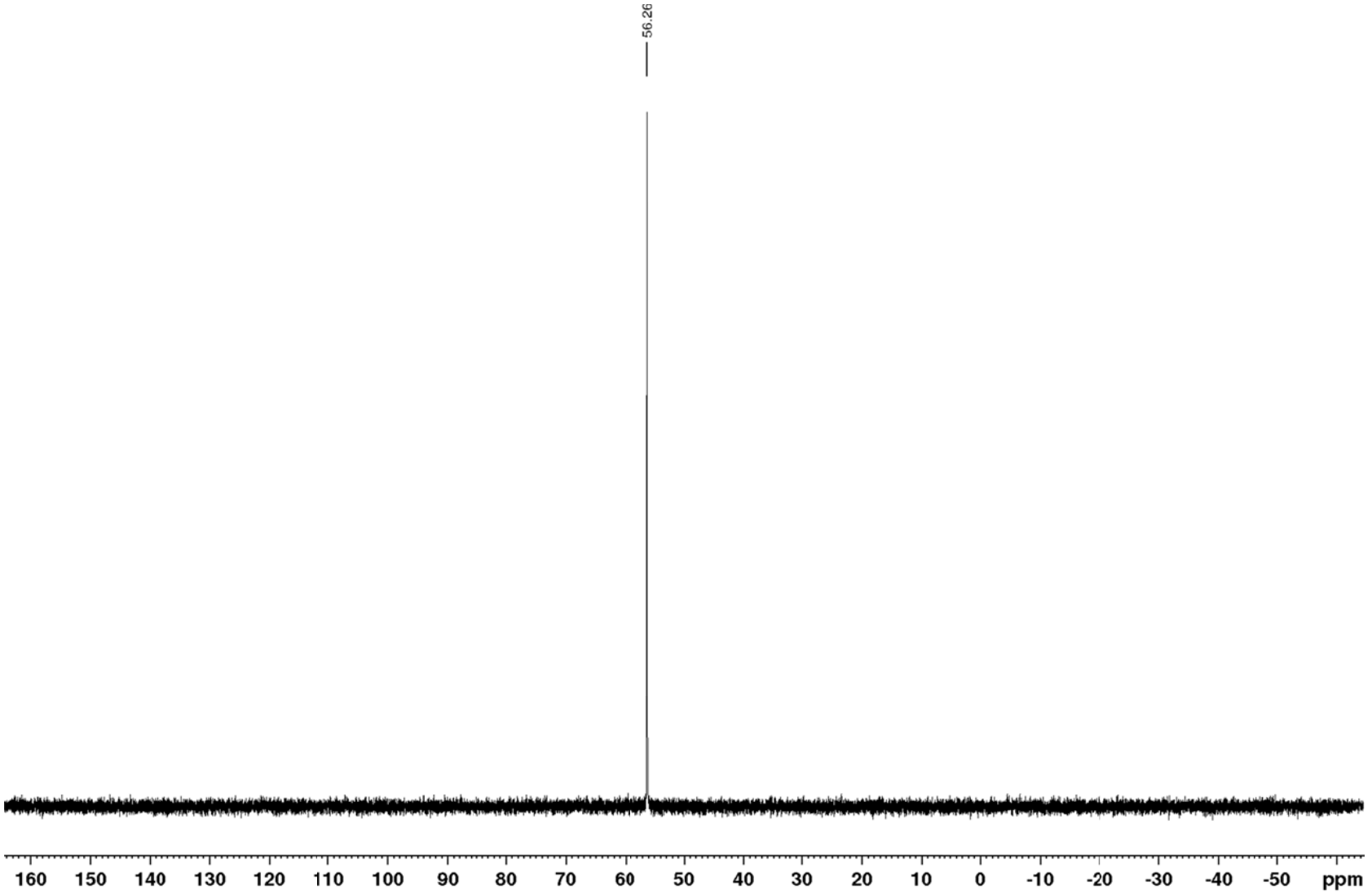


Figure S99 $^{31}P\{^{1}H\}$ NMR (283 MHz, CD_2Cl_2, 253 K): [**5c**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

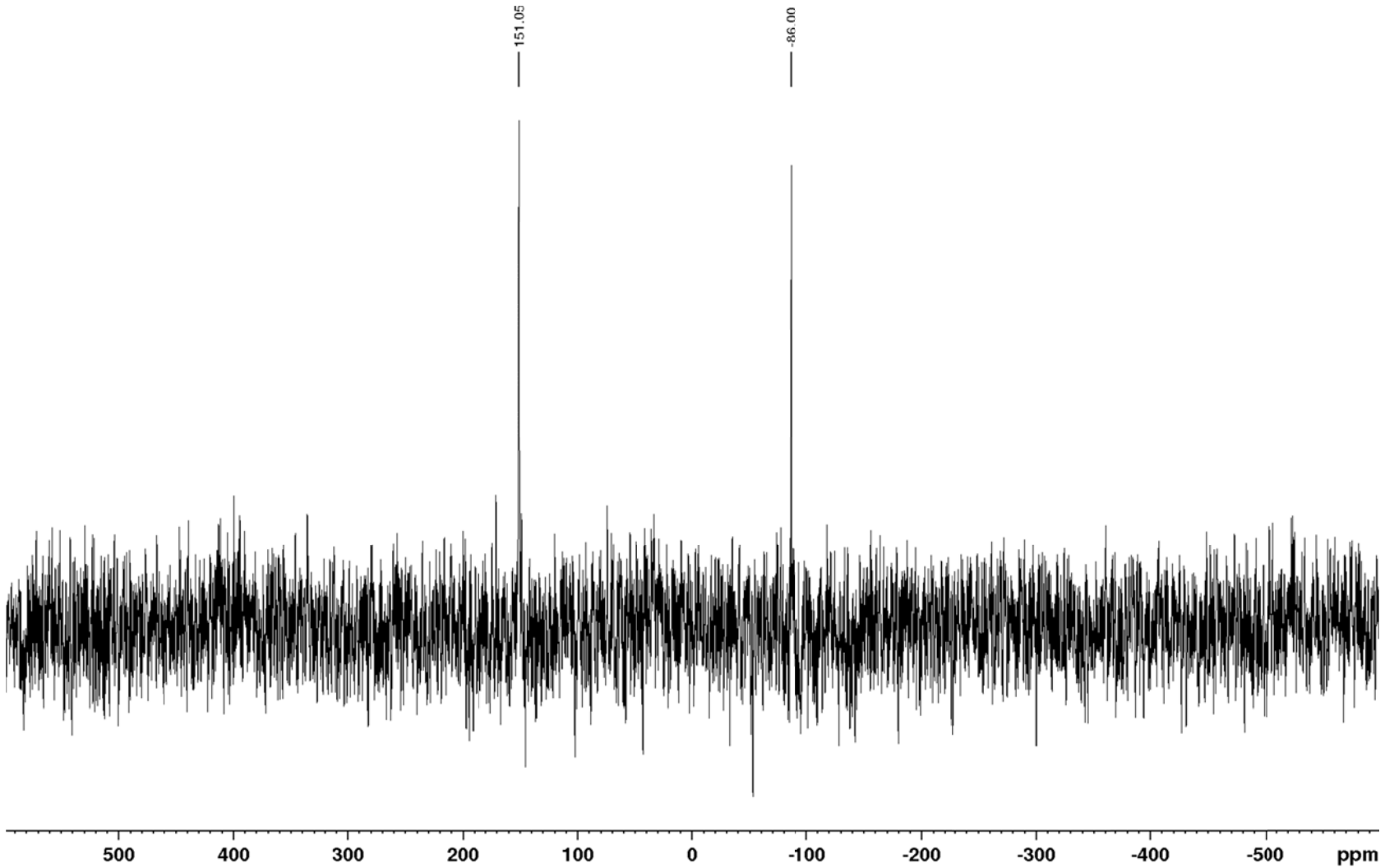


Figure S100 $^{119}Sn\{^{1}H\}$ NMR (261 MHz, CD_2Cl_2, 253 K): [**5c**·*n*Bu_3SnH]$^+$[BAr^F_4]$^-$

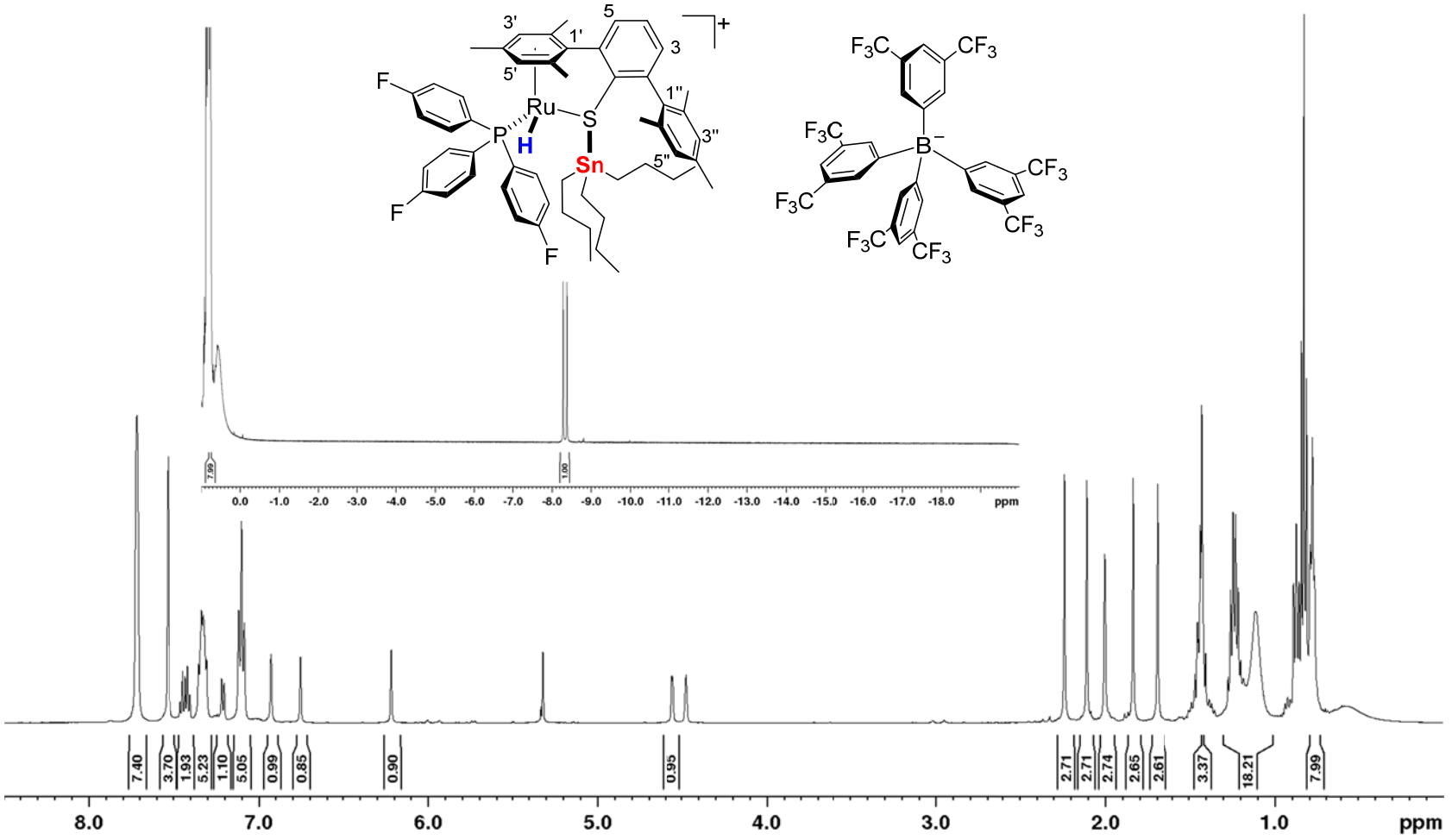


Figure S101 ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): [**5d**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

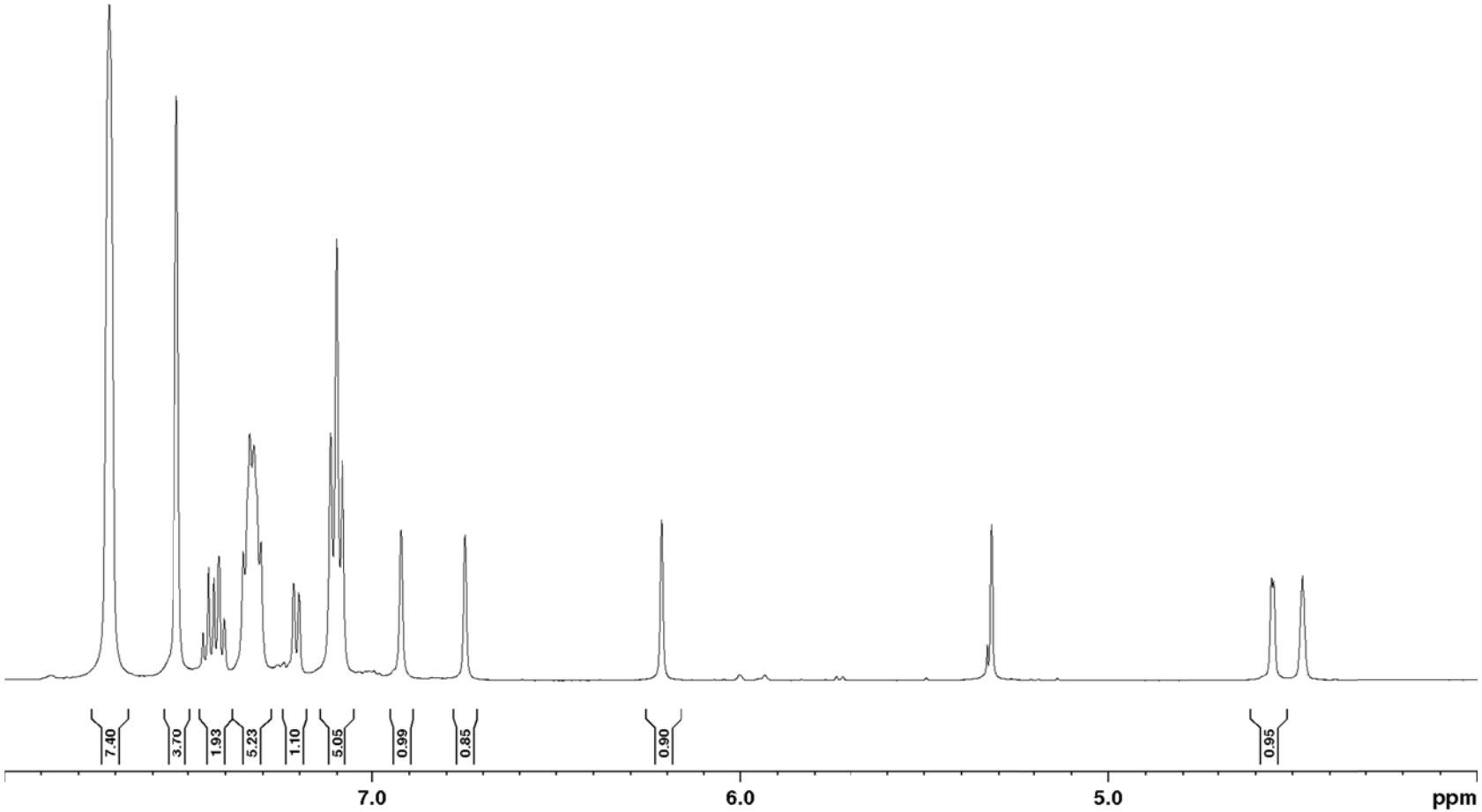


Figure S102 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): Arylarea of [**5d**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

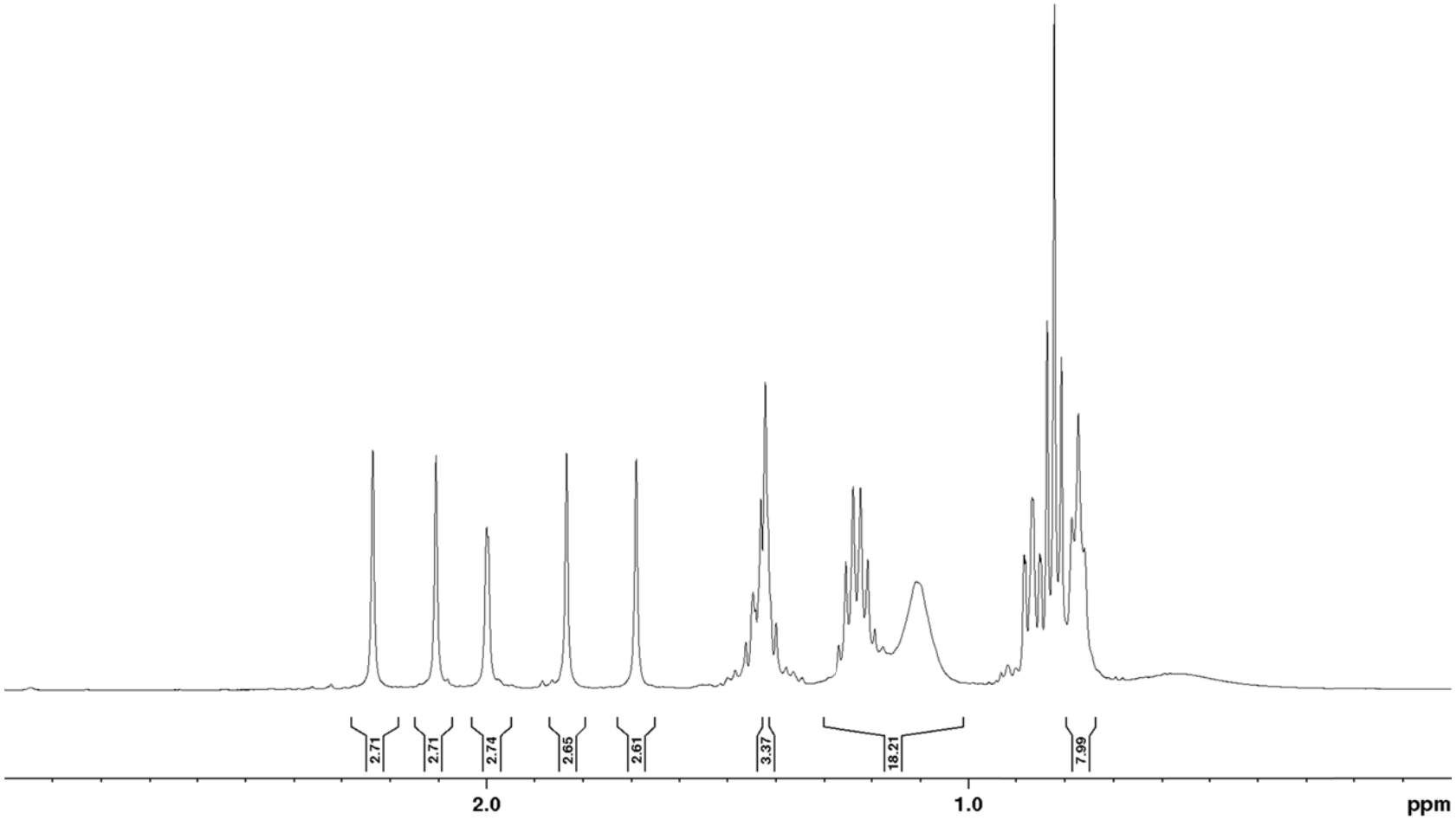


Figure S103 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): Aliphatic region of [**5d**·*n*Bu_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

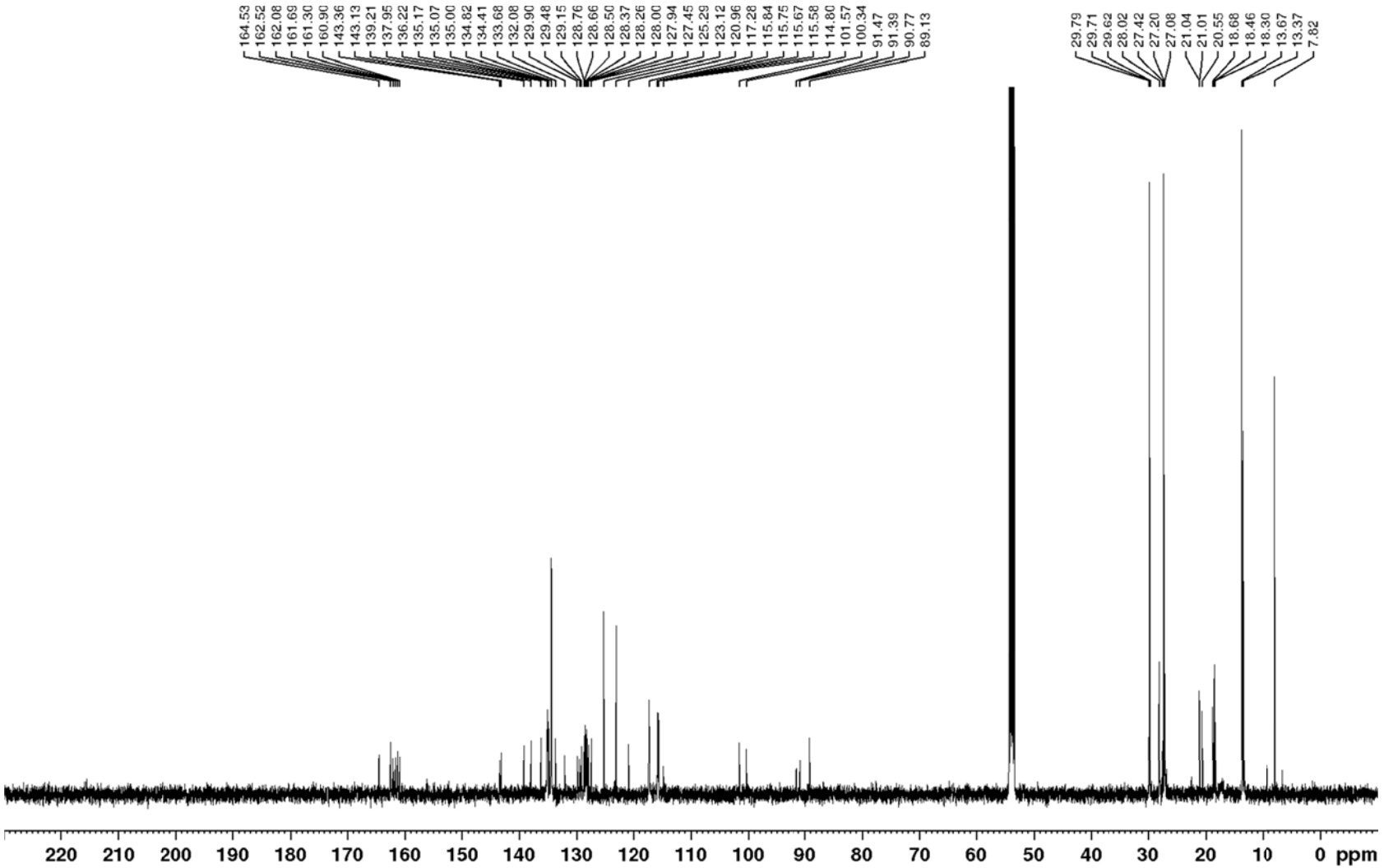


Figure S104 $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 213 K): [**5d**·*n*Bu_3SnH]$^+$[BAr^F_4]$^-$

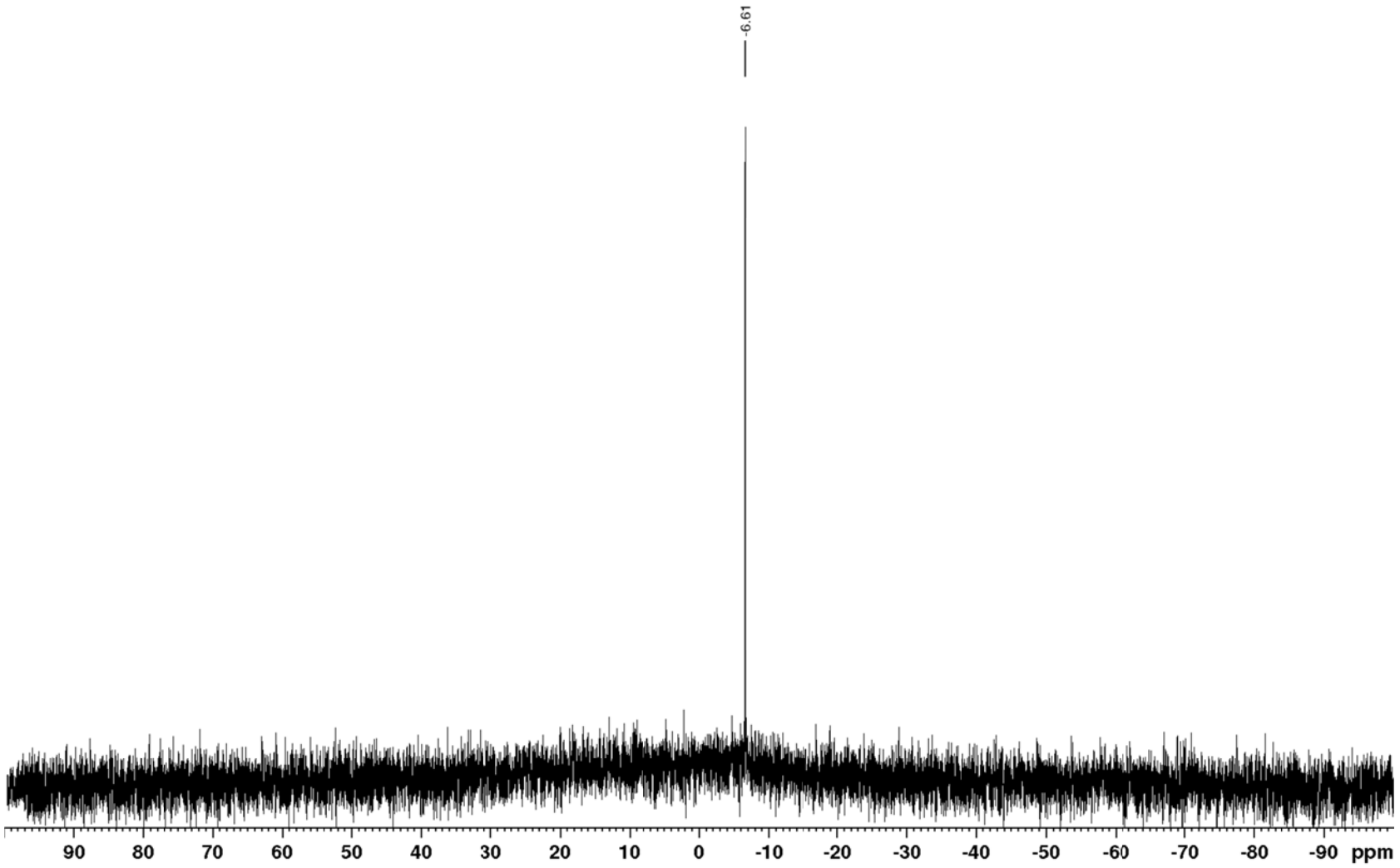


Figure S105 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 213 K): [**5d**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

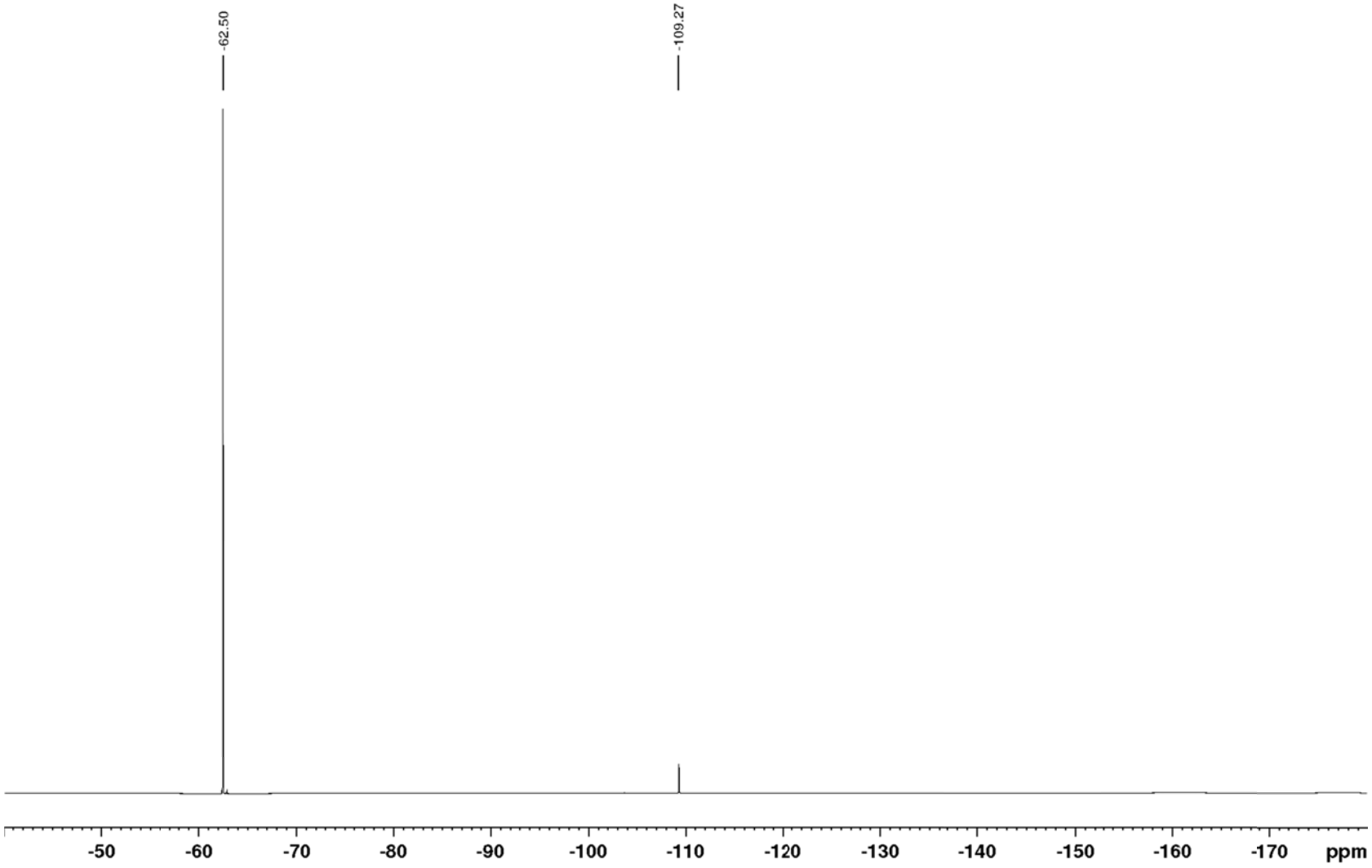


Figure S106 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2, 213 K): [**5d**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

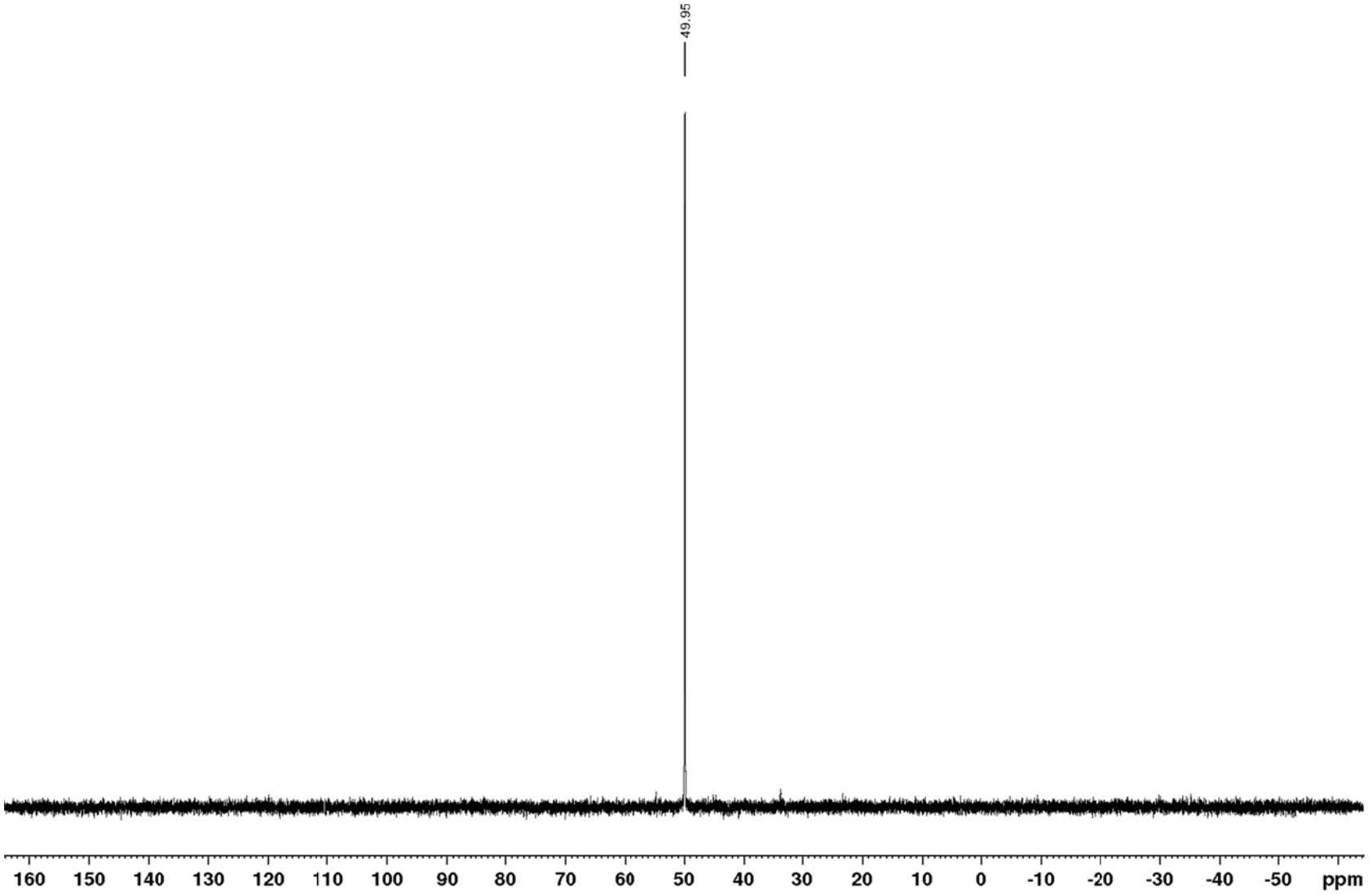


Figure S107 $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2, 213 K): [**5d**·*n*Bu_3SnH]$^+$[$BAr^F{}_4$]$^-$

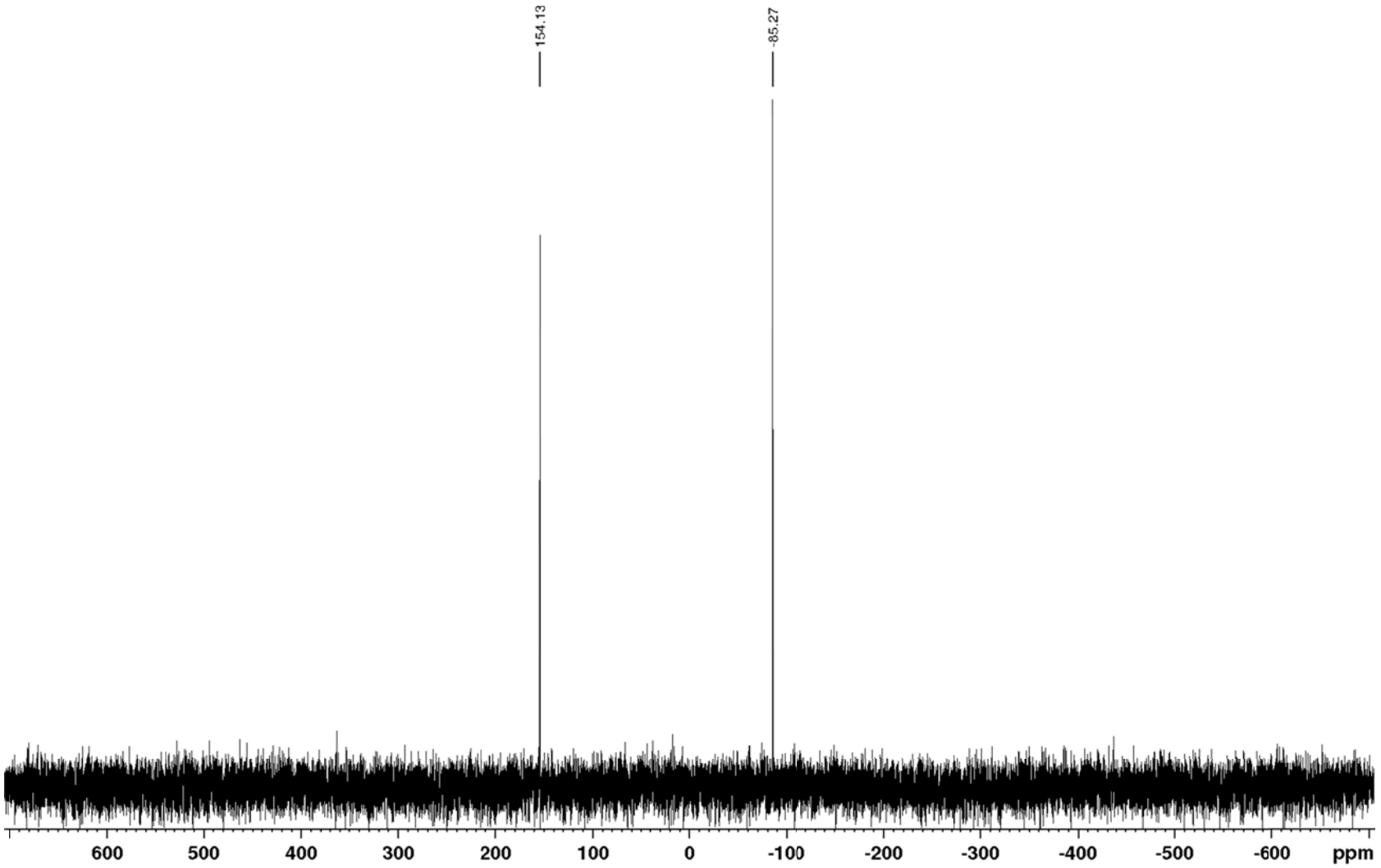


Figure S108 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, CD_2Cl_2, 213 K): [**5d**·*n*Bu_3SnH]$^+$[BAr^F_4]$^-$

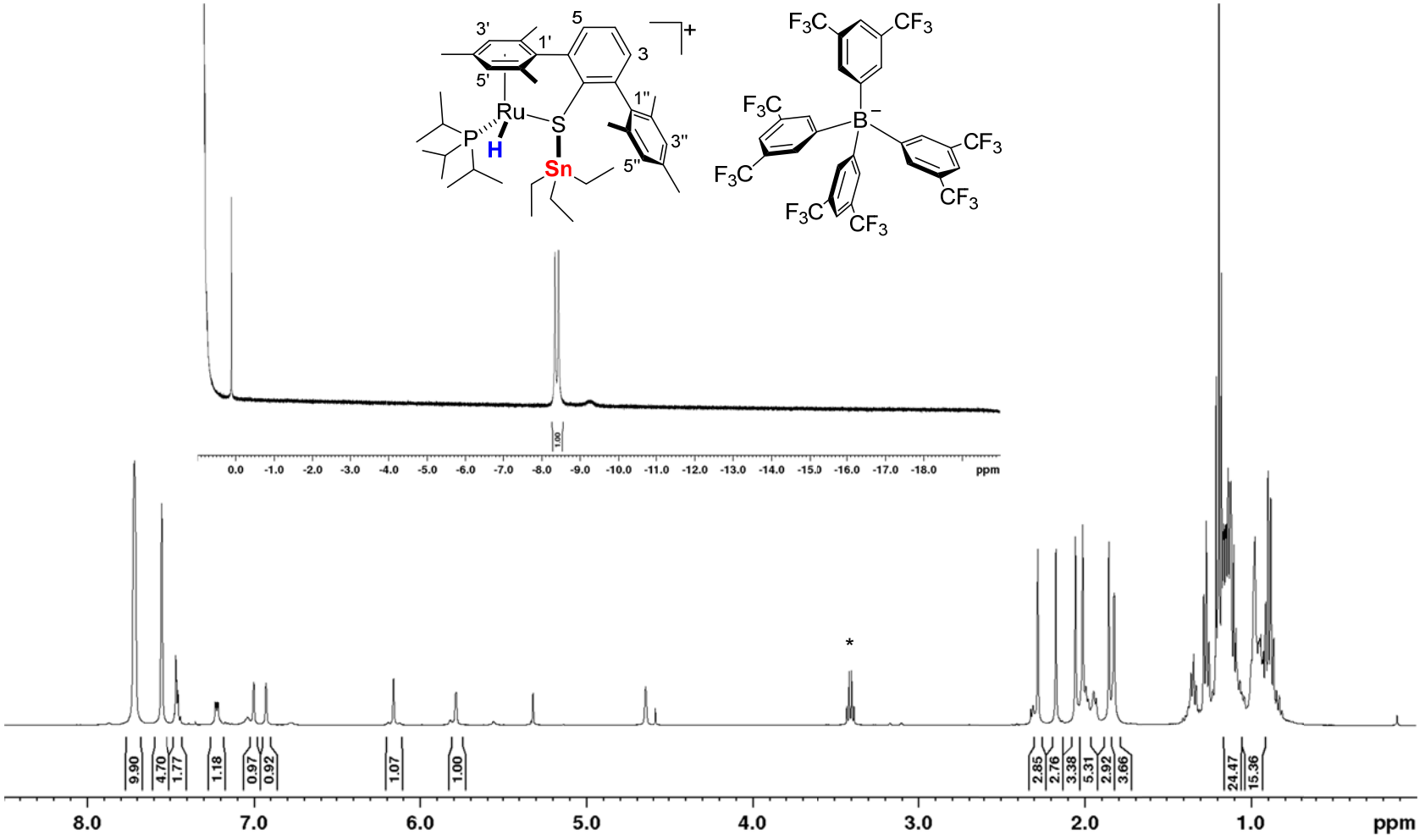


Figure S109 ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$ (* = Et_2O)

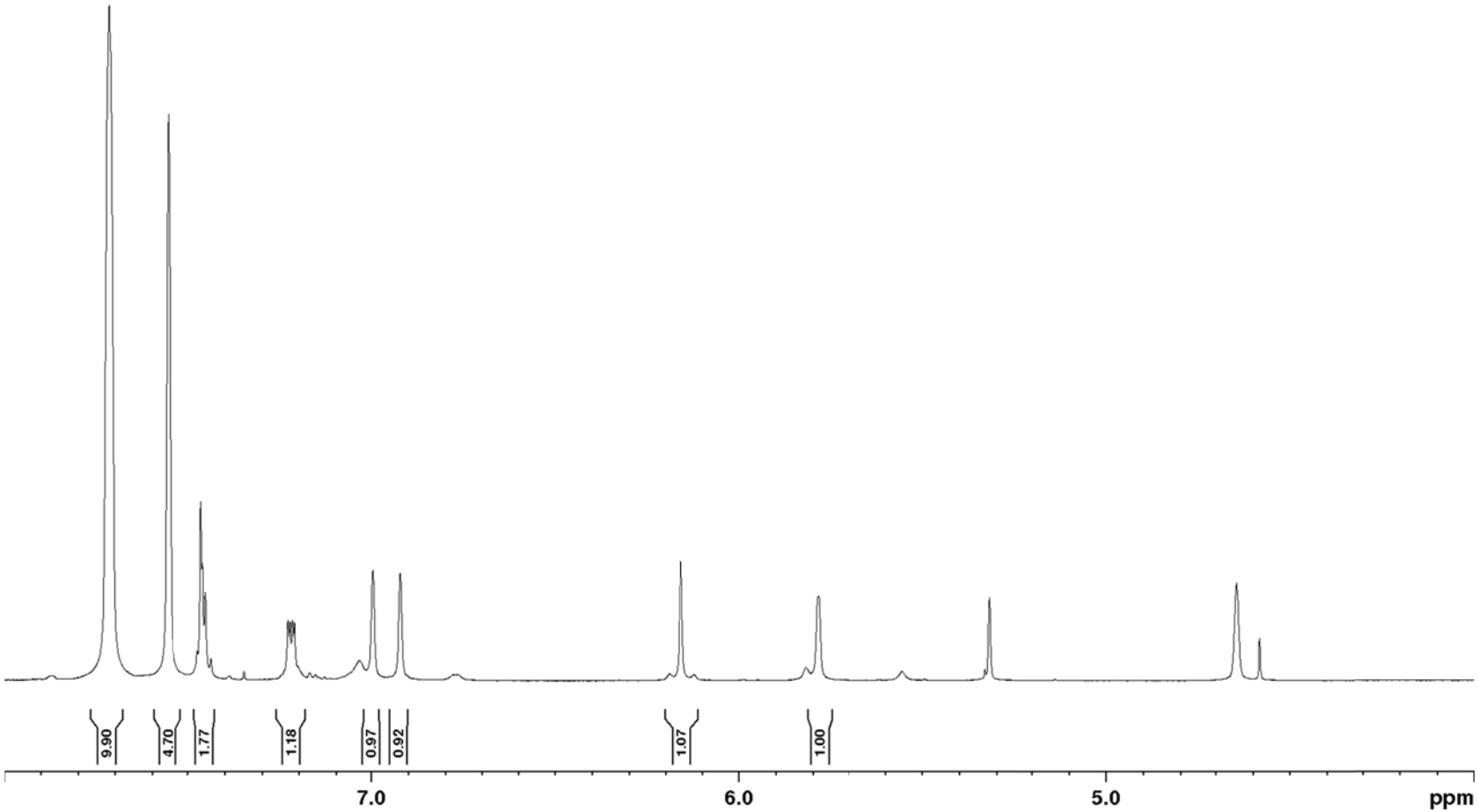


Figure S110 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): Aromatic region of [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

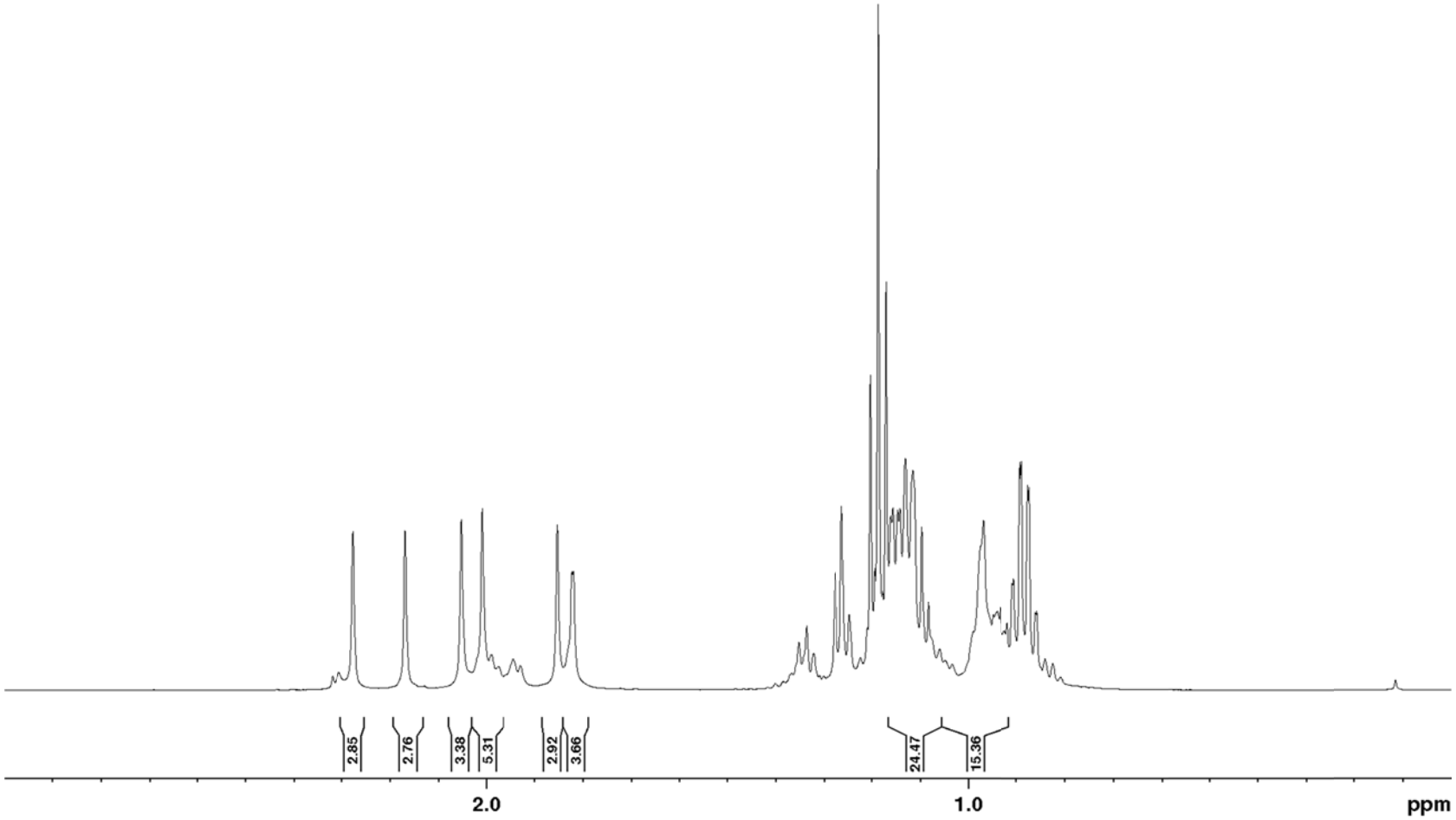


Figure S111 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 253 K): Aliphatic region of [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

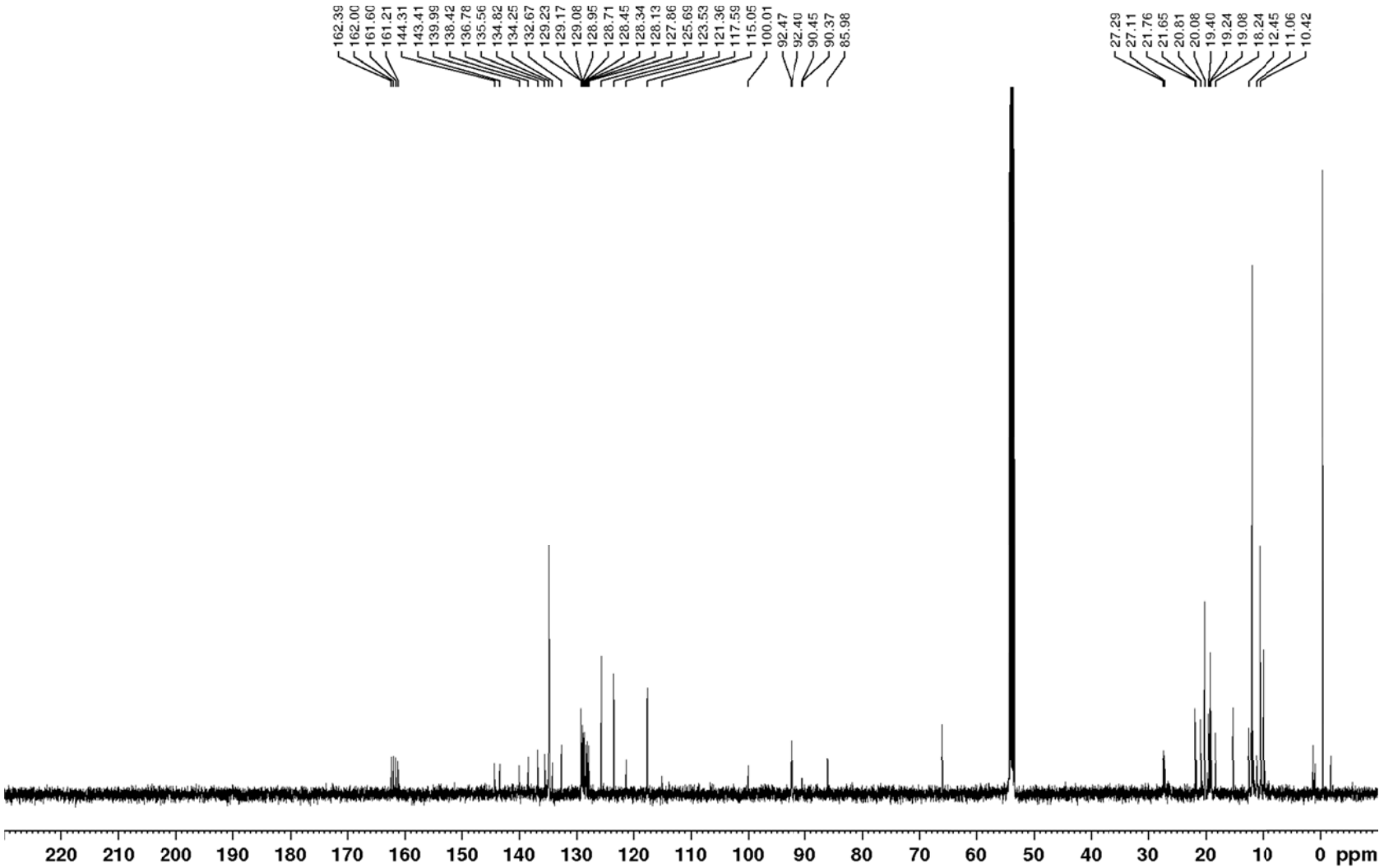


Figure S112 $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 253 K): [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

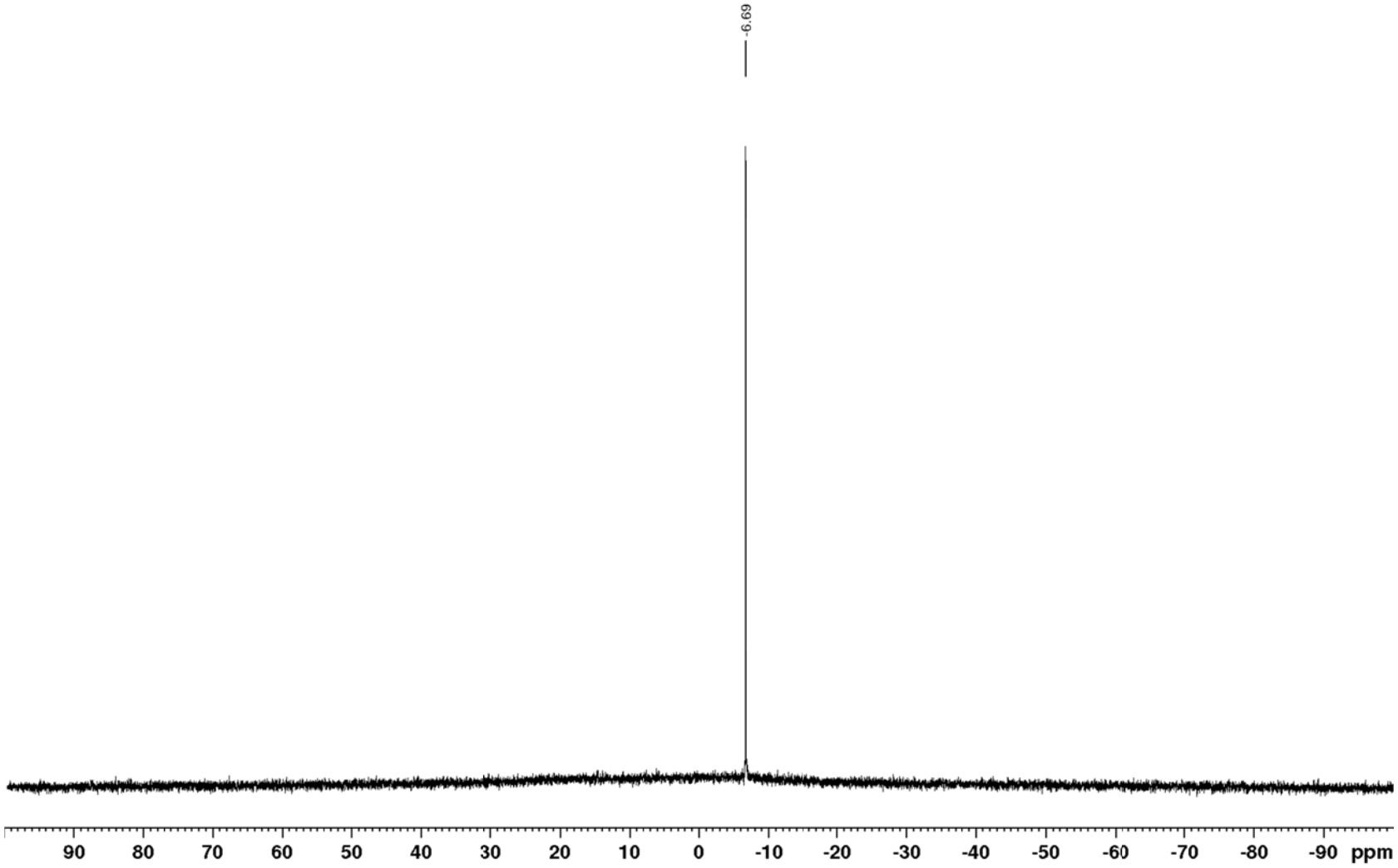


Figure S113 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 253 K): [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

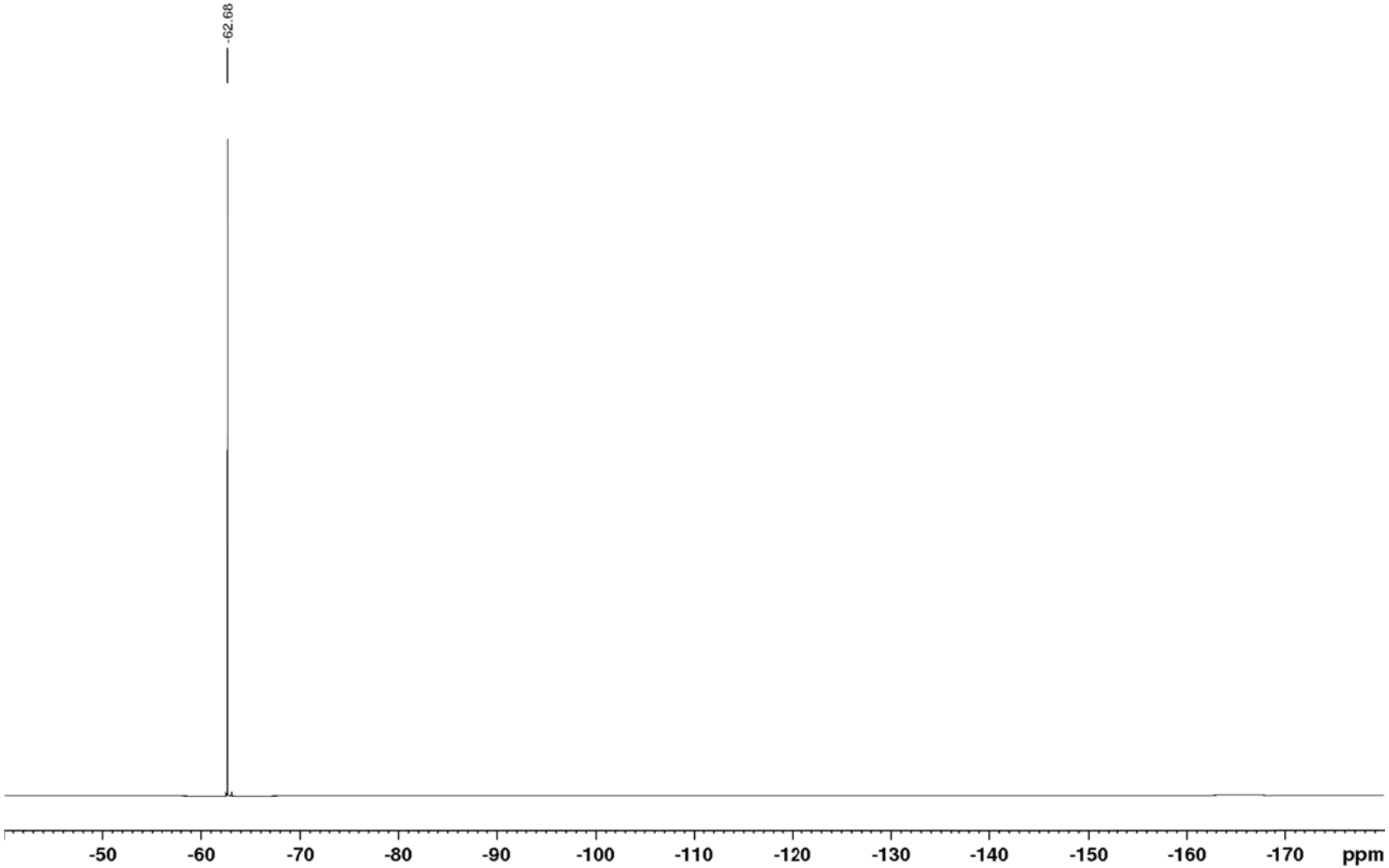


Figure S114 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2, 253 K): [**5b**·Et_3SnH]$^+$[$BAr^F{}_4$]$^-$

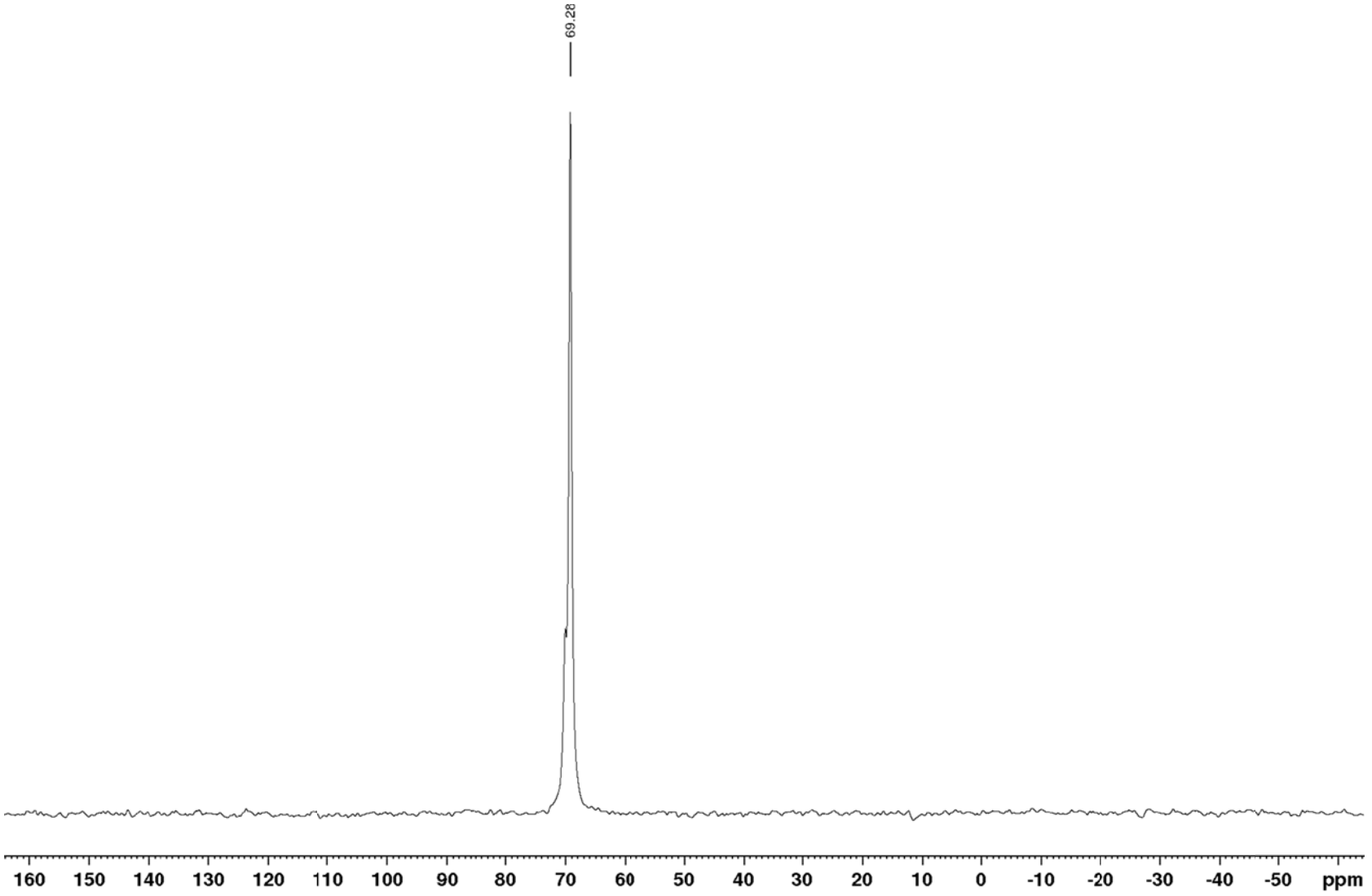


Figure S115 $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2, 253 K): [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

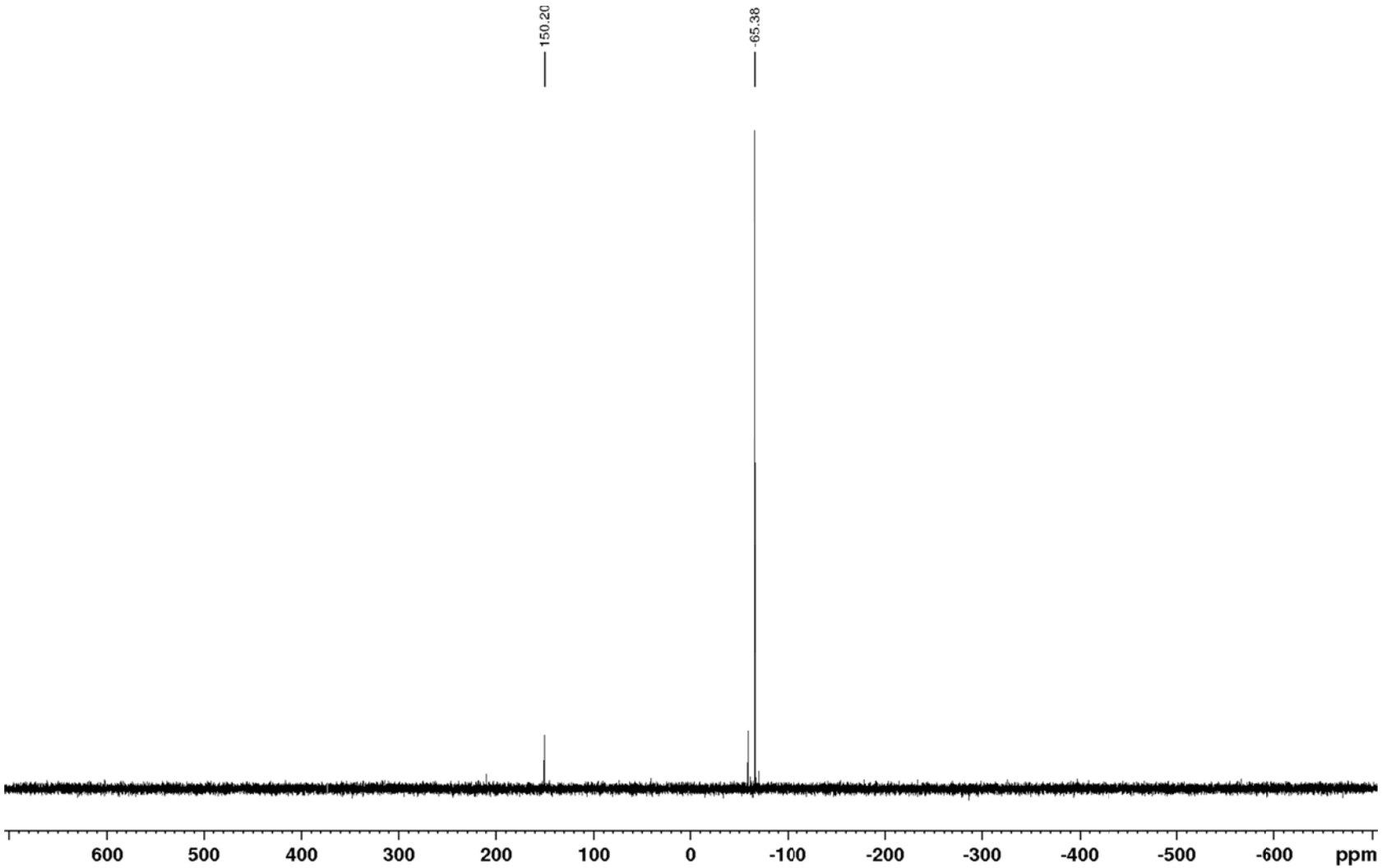


Figure S116 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, CD_2Cl_2, 253 K): [**5b**·Et_3SnH]$^{+}$[BAr^{F}_{4}]$^{-}$

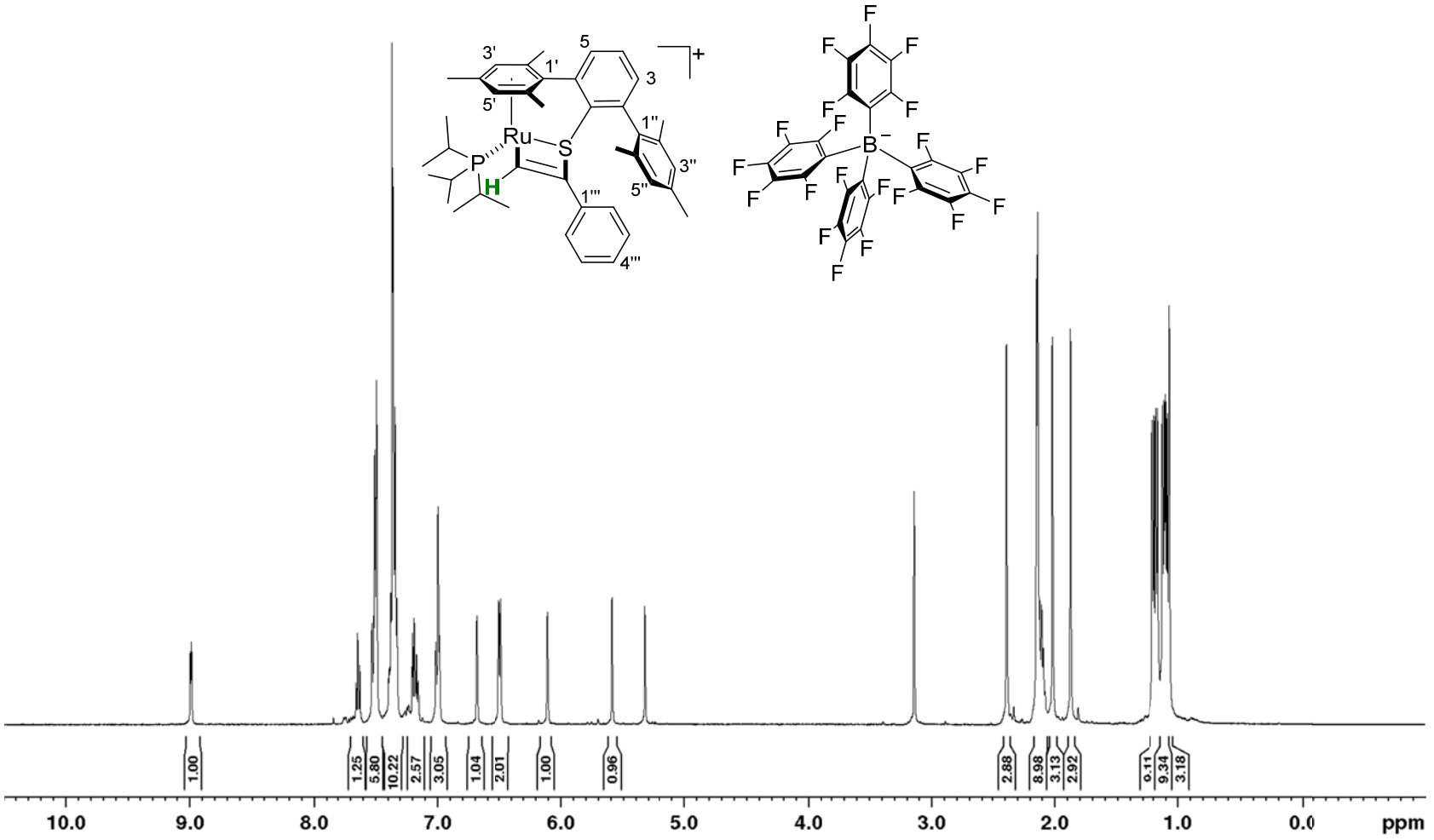


Figure S117 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

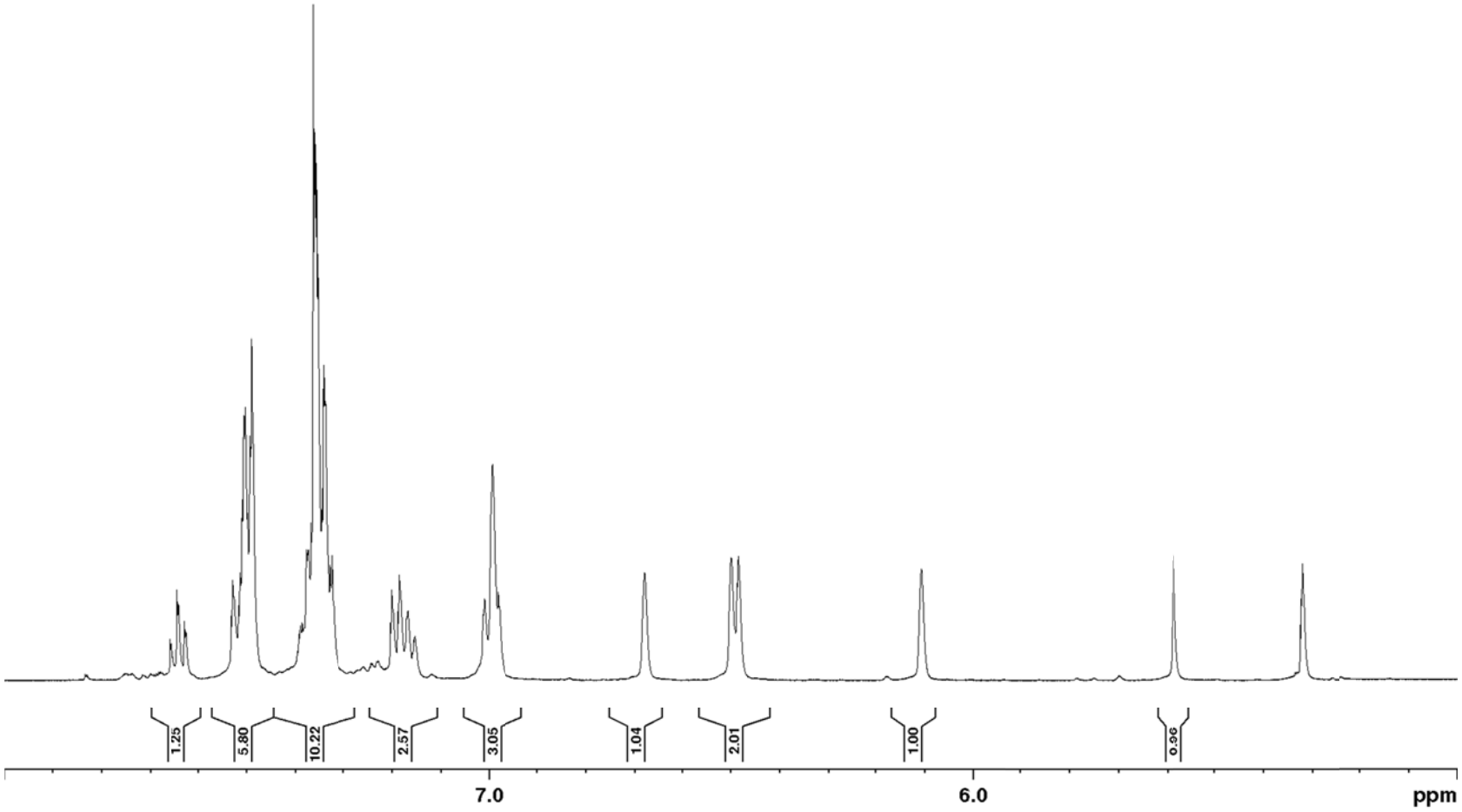


Figure S118 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Aromatic region of [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

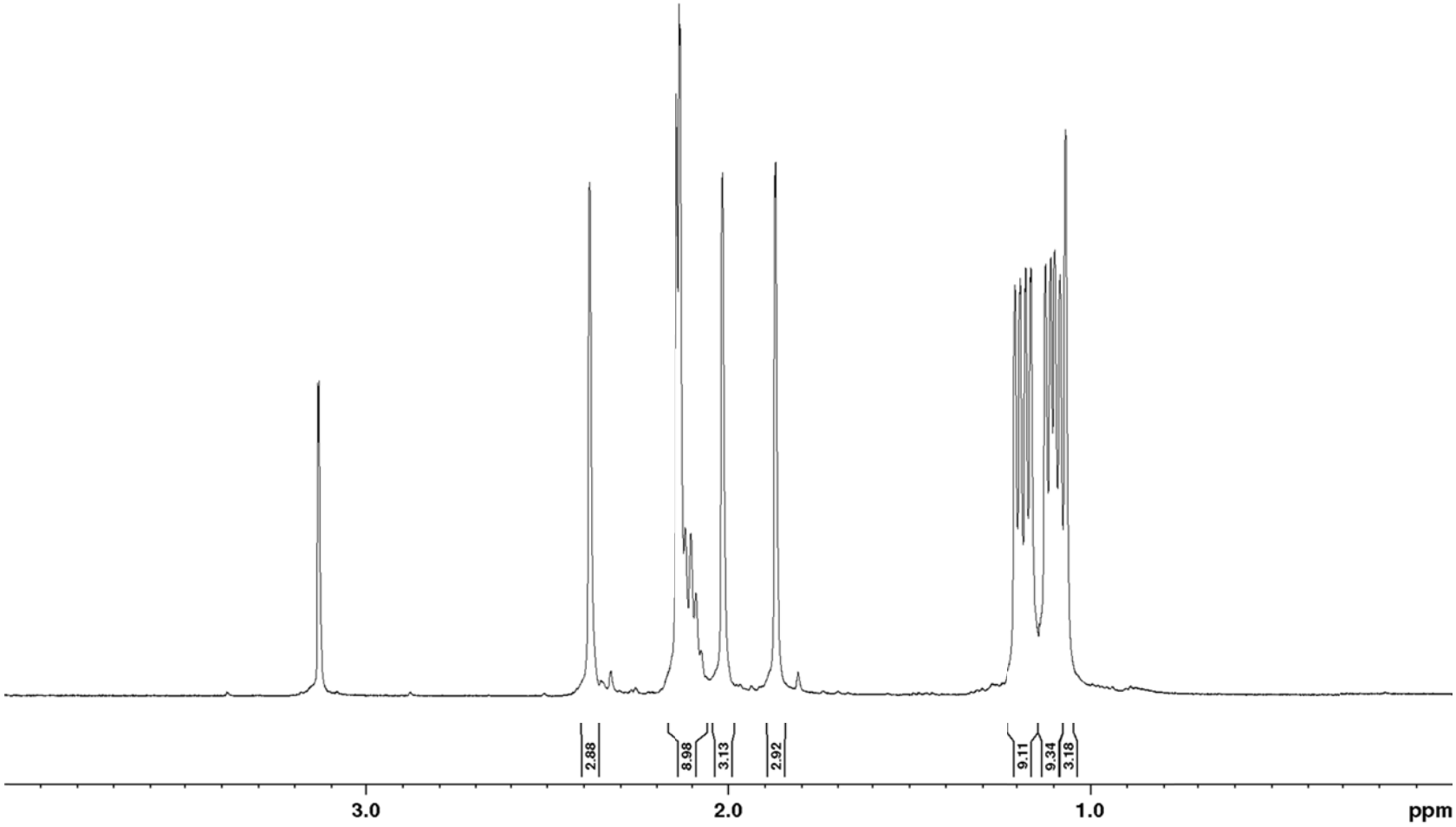


Figure S119 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Aliphatic region of [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

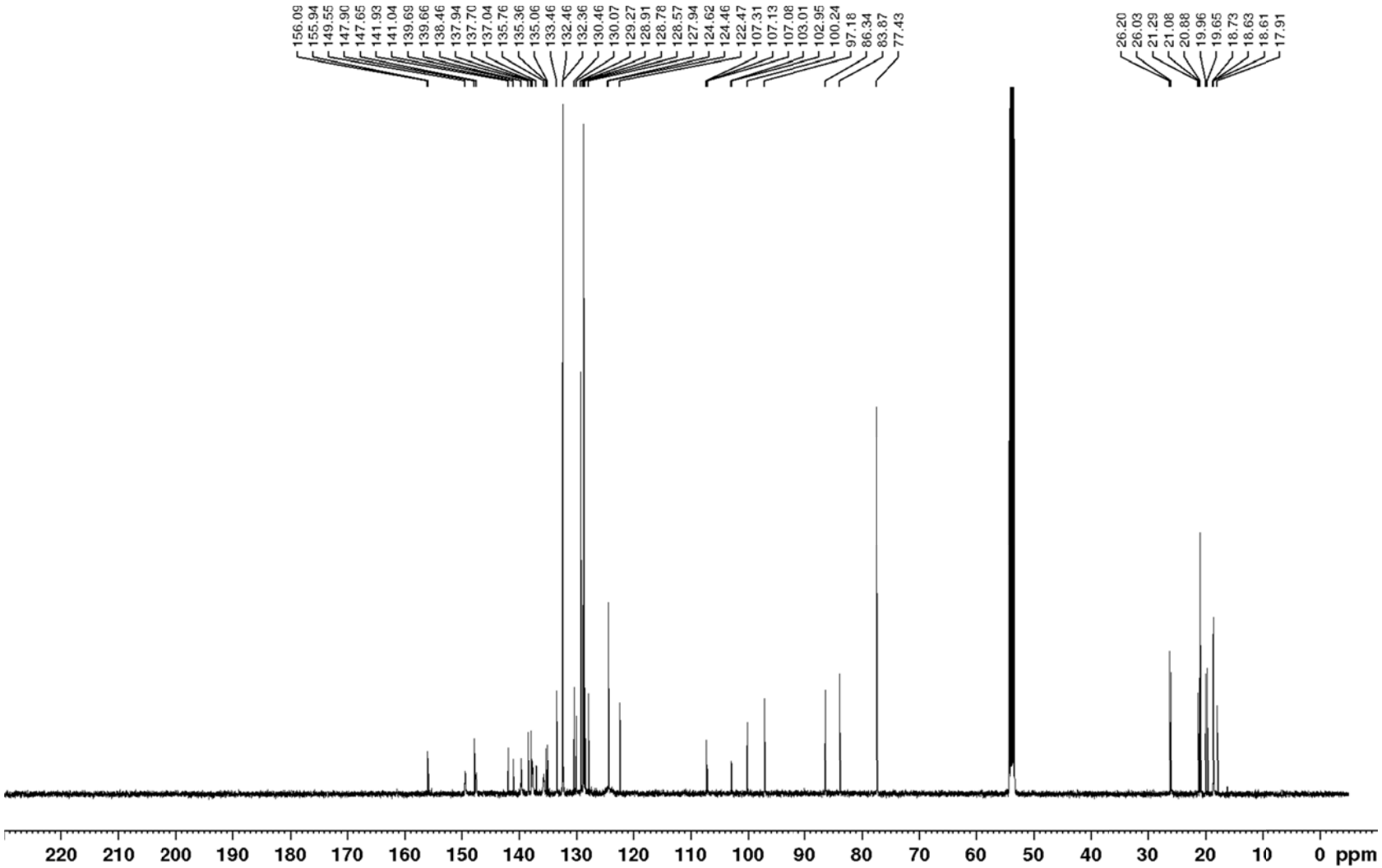


Figure S120 $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

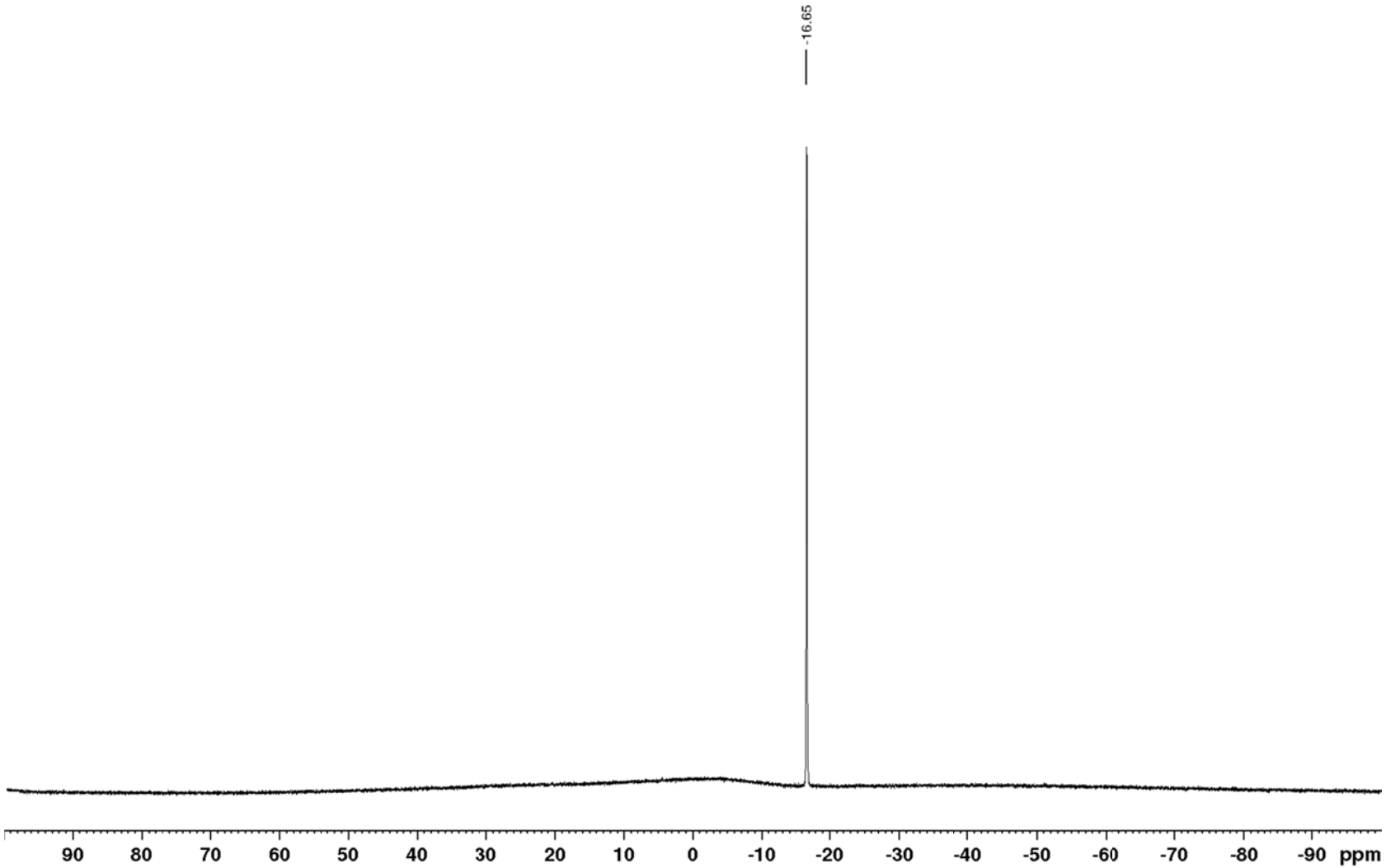


Figure S121 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 298 K): [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

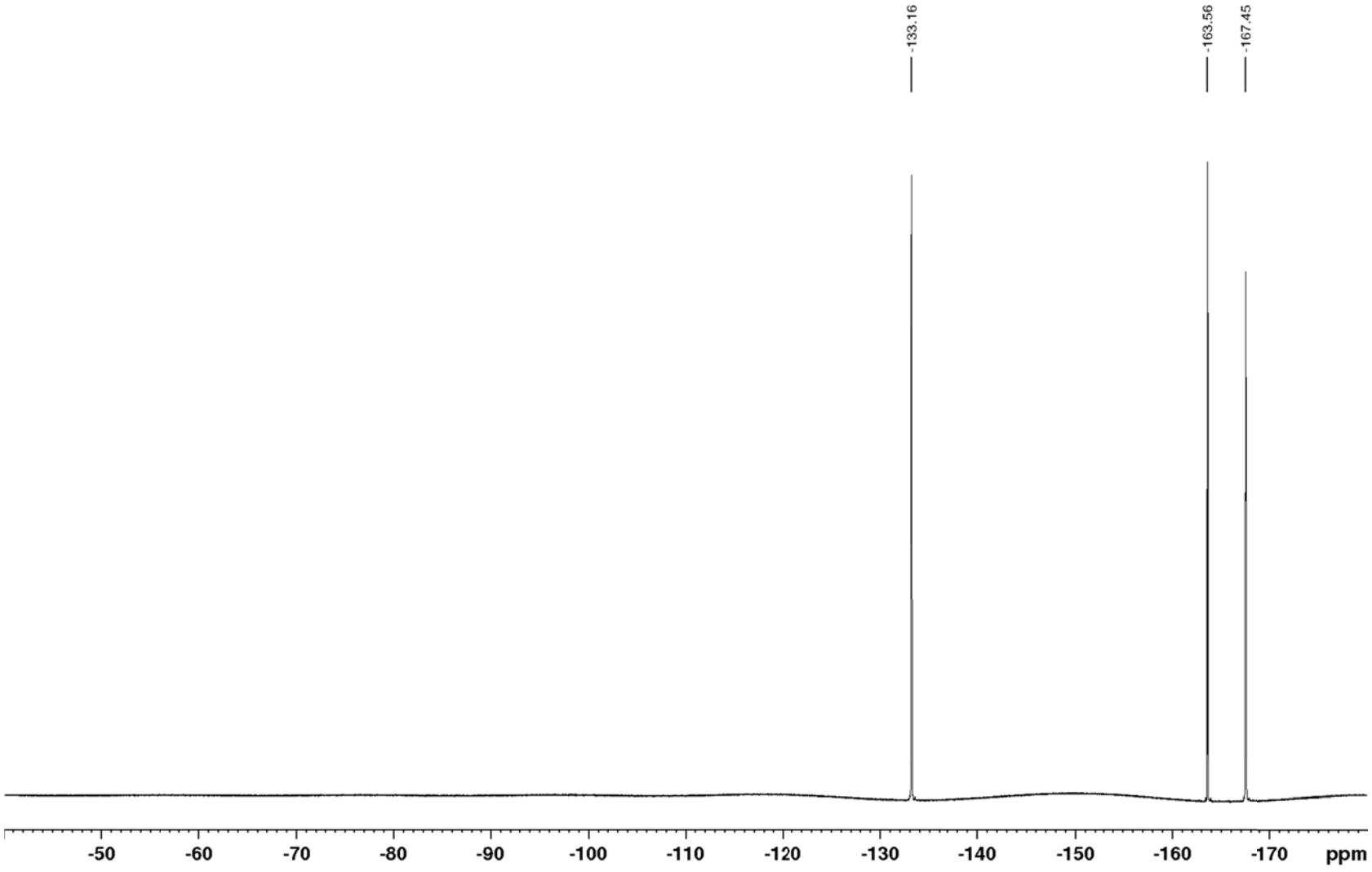


Figure S122 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2, 298 K): [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

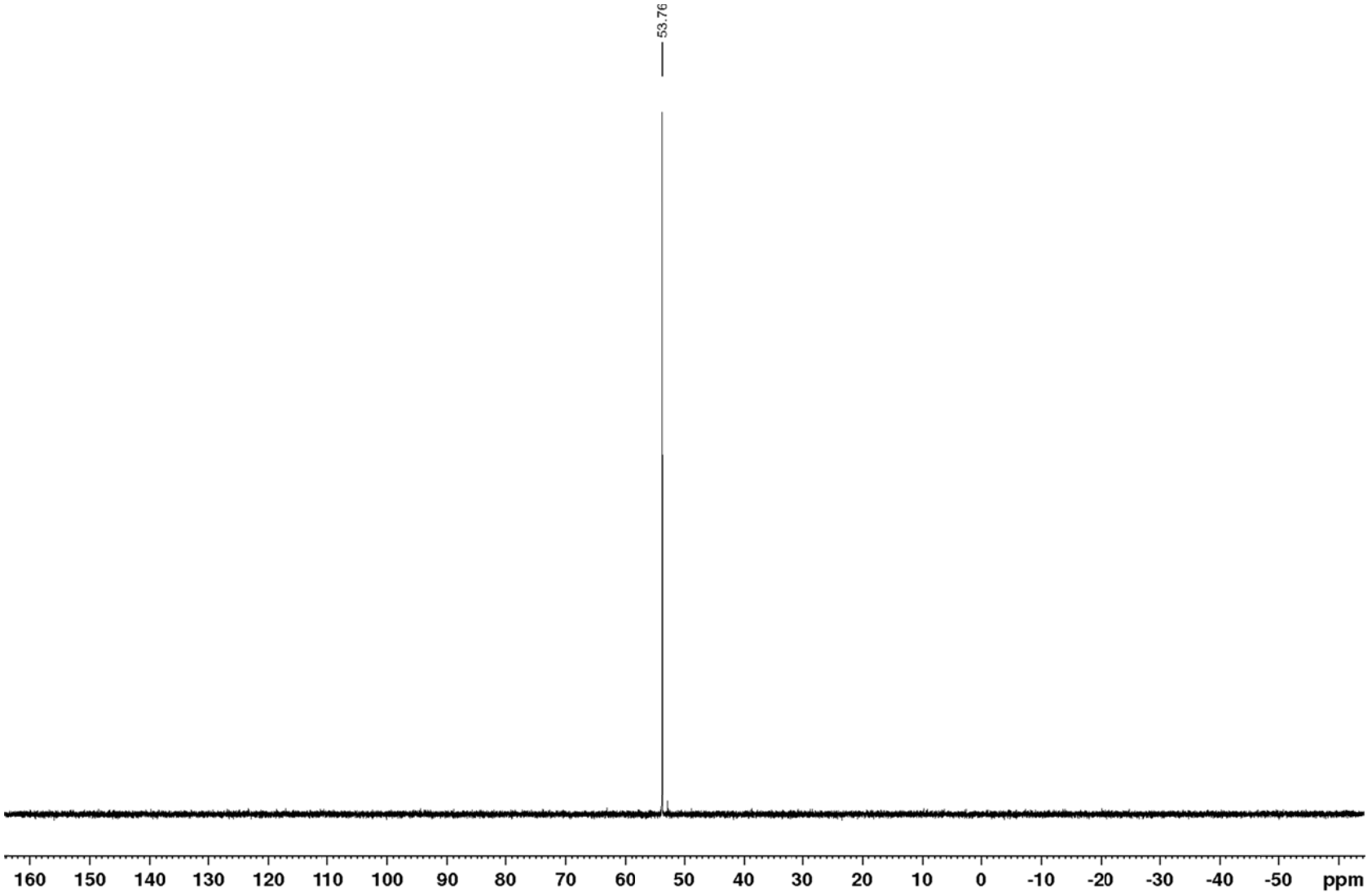


Figure S123 $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): [**5b**·PhCCH]$^{+}$[$B(C_6F_5)_4$]$^{-}$

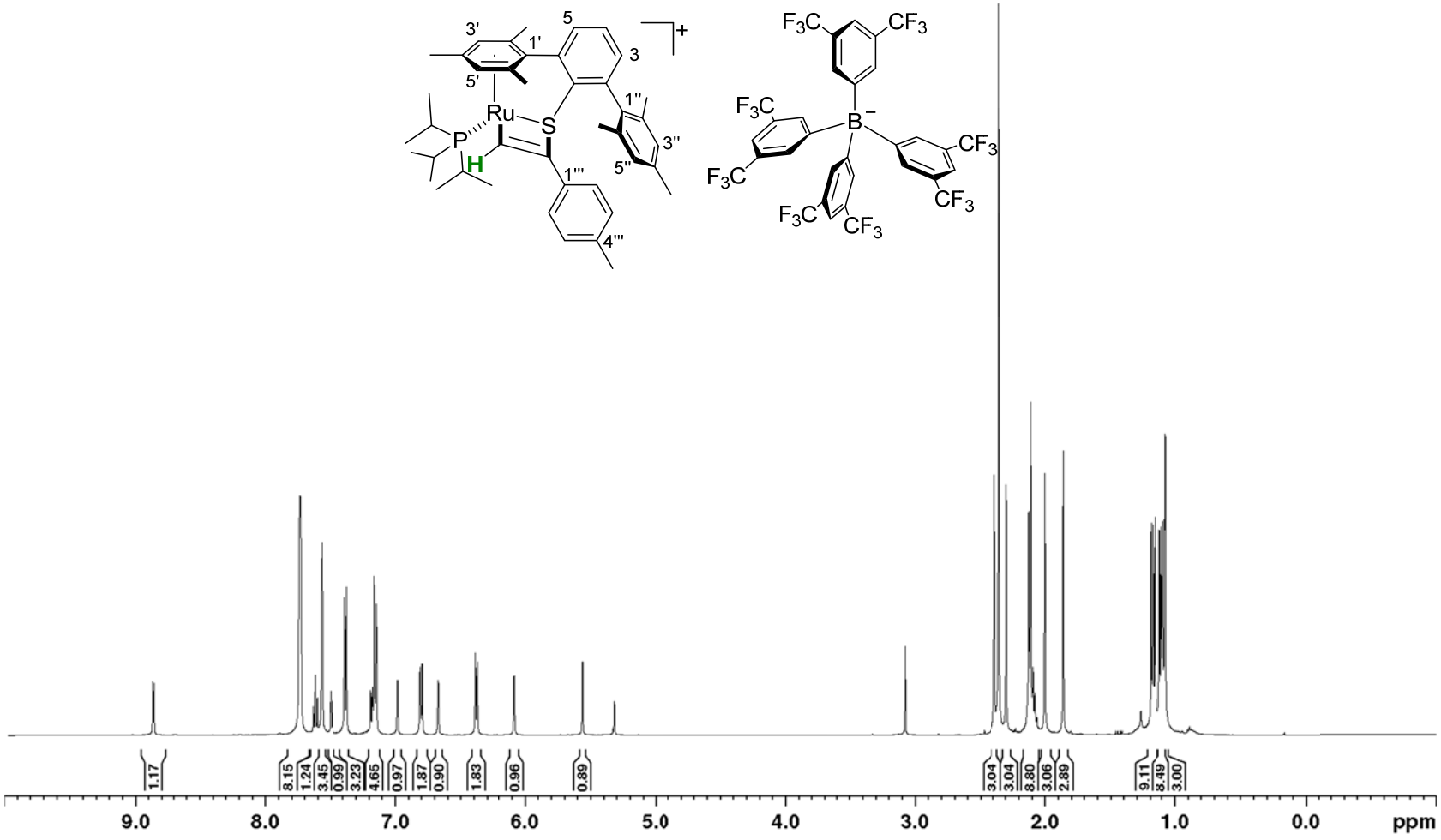


Figure S124 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

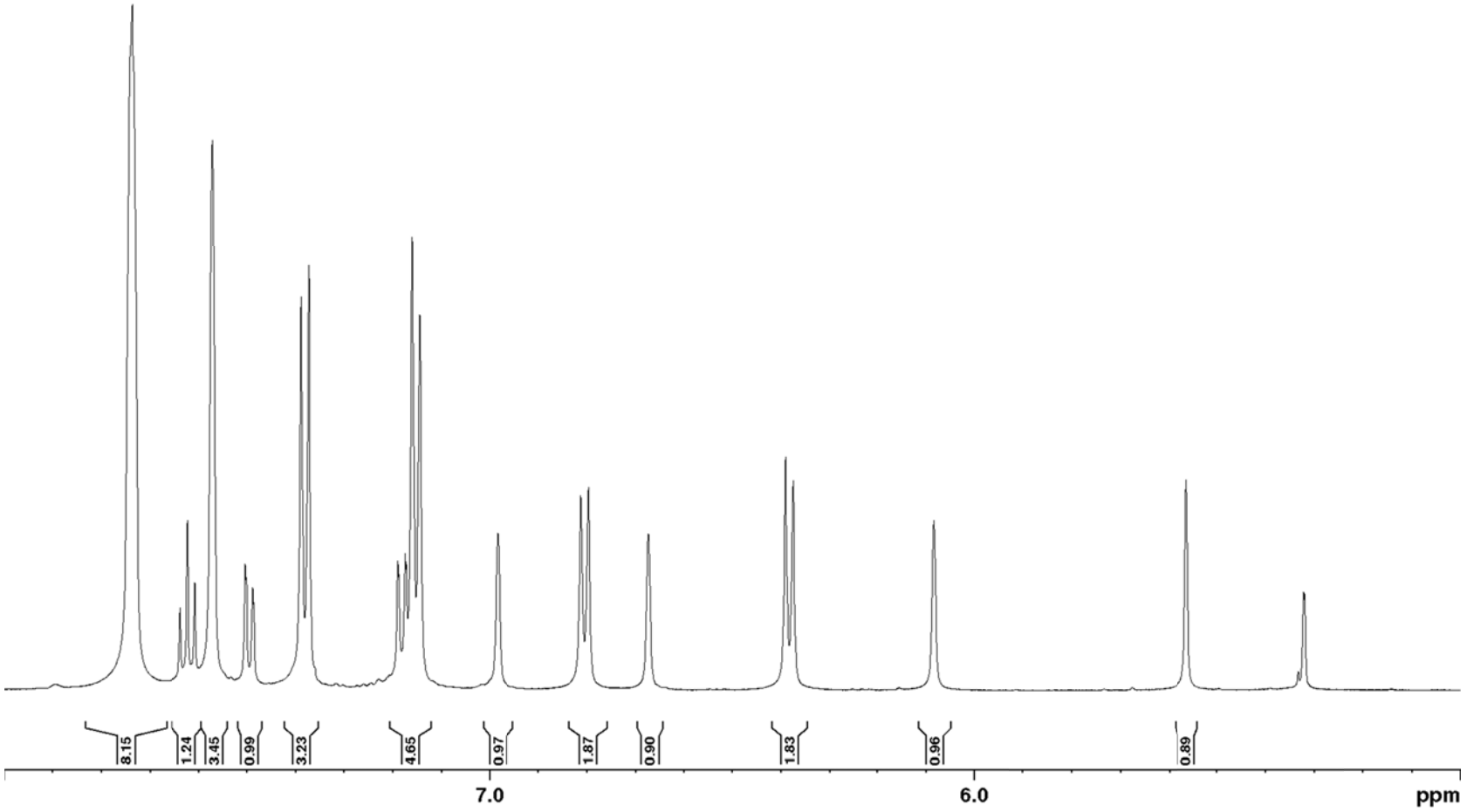


Figure S125 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Aromatic region of [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

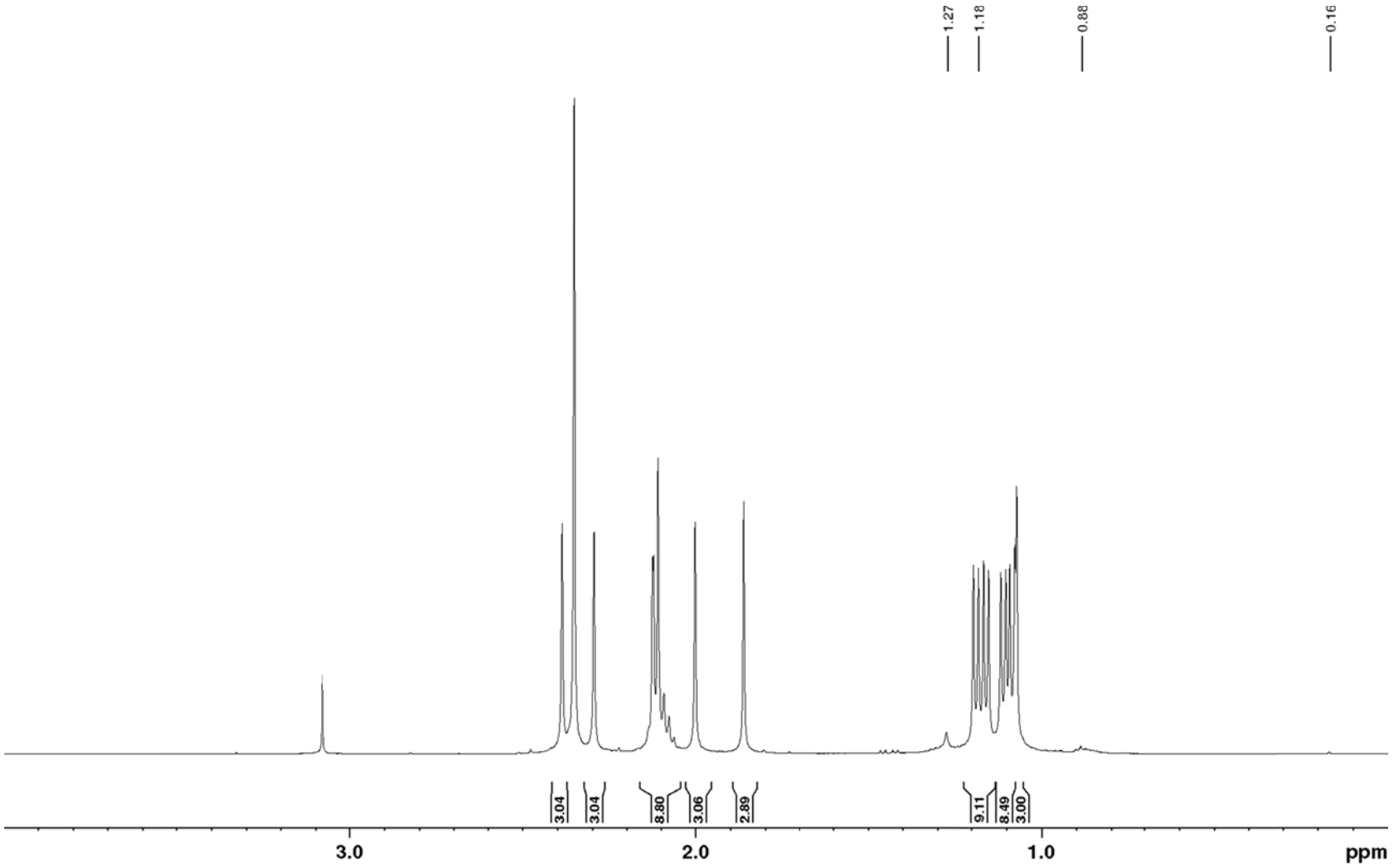


Figure S126 Expanded ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Aliphatic region of [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

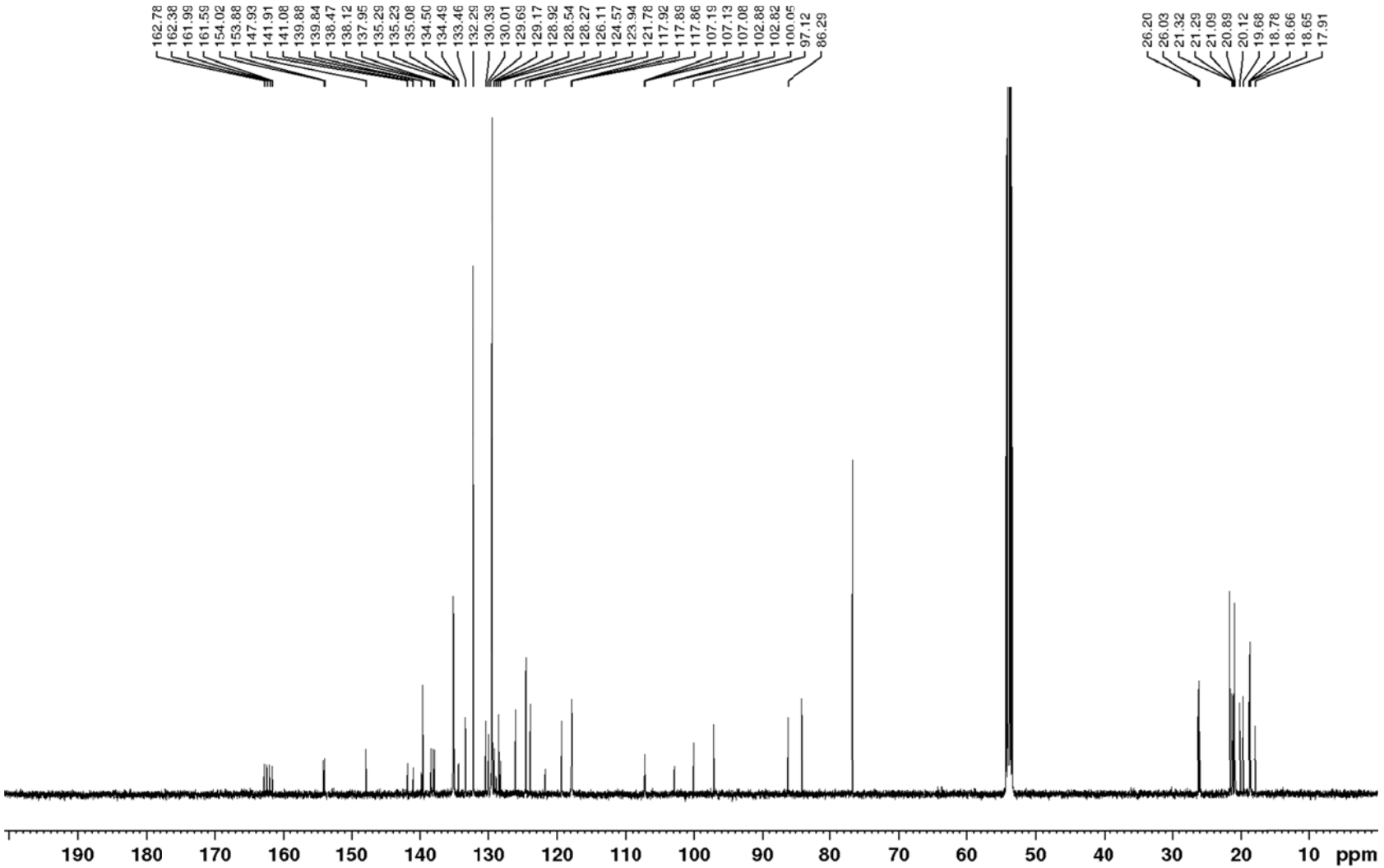


Figure S127 $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

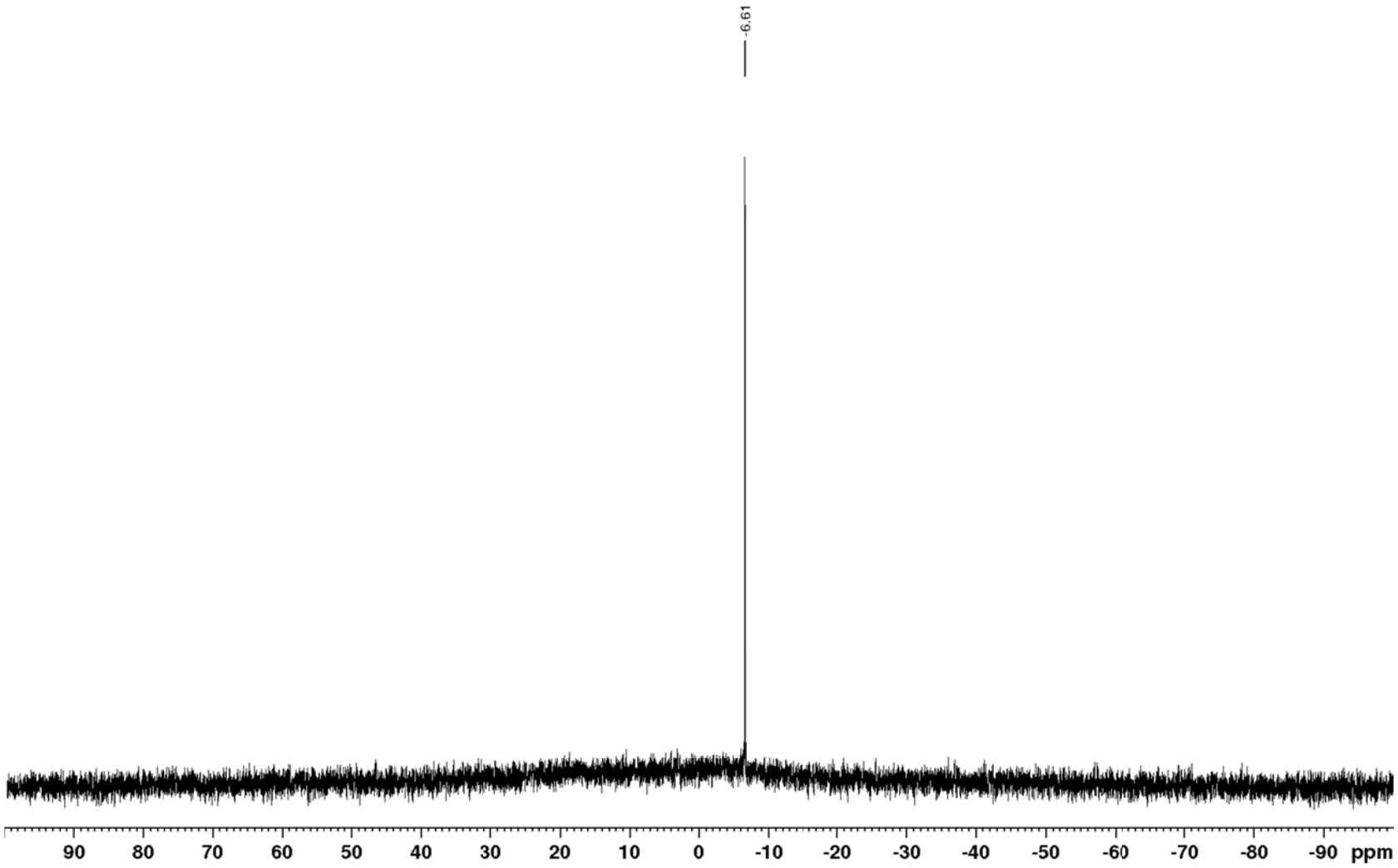


Figure S128 $^{11}B\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 298 K): [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

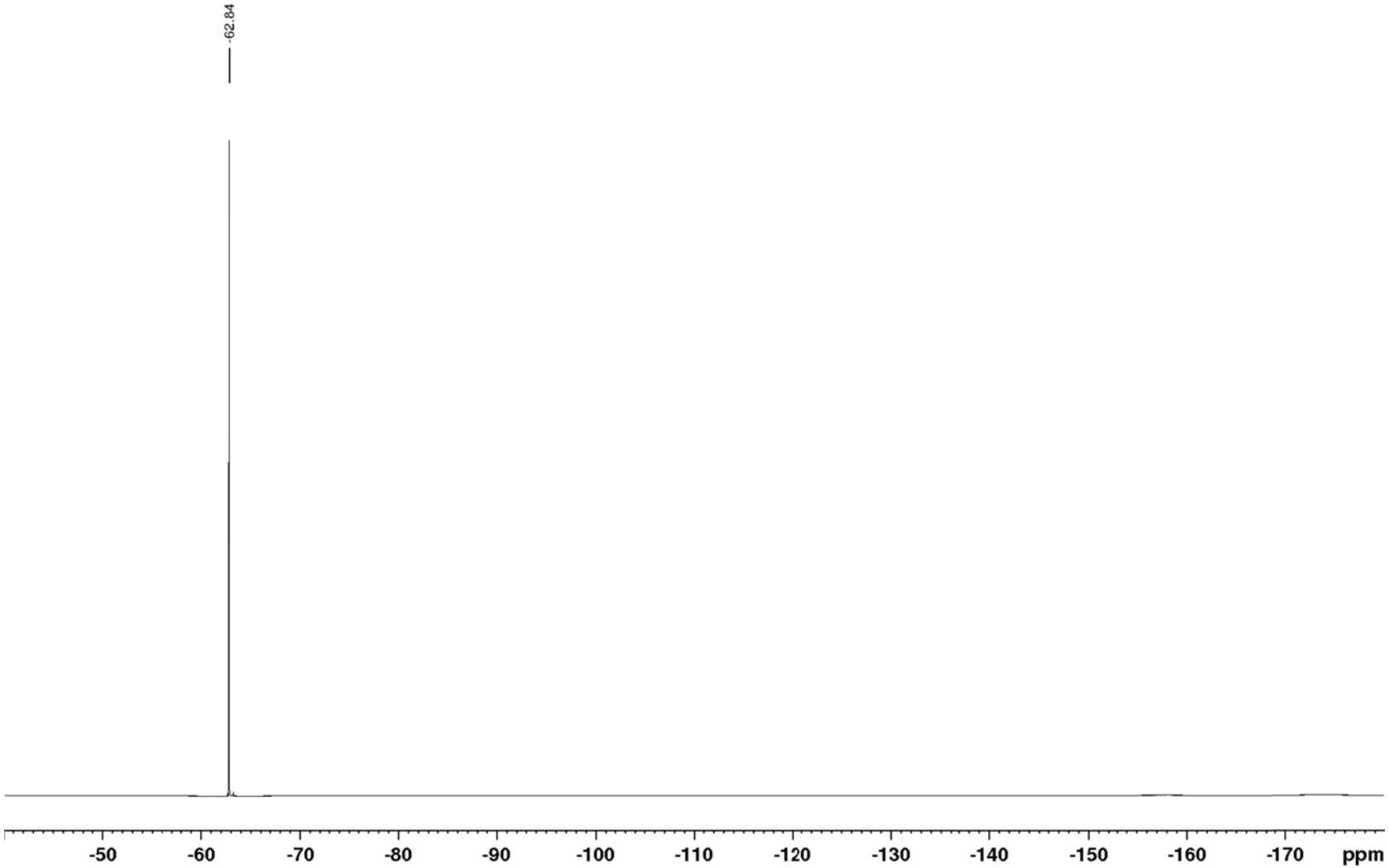


Figure S129 $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2, 298 K): [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

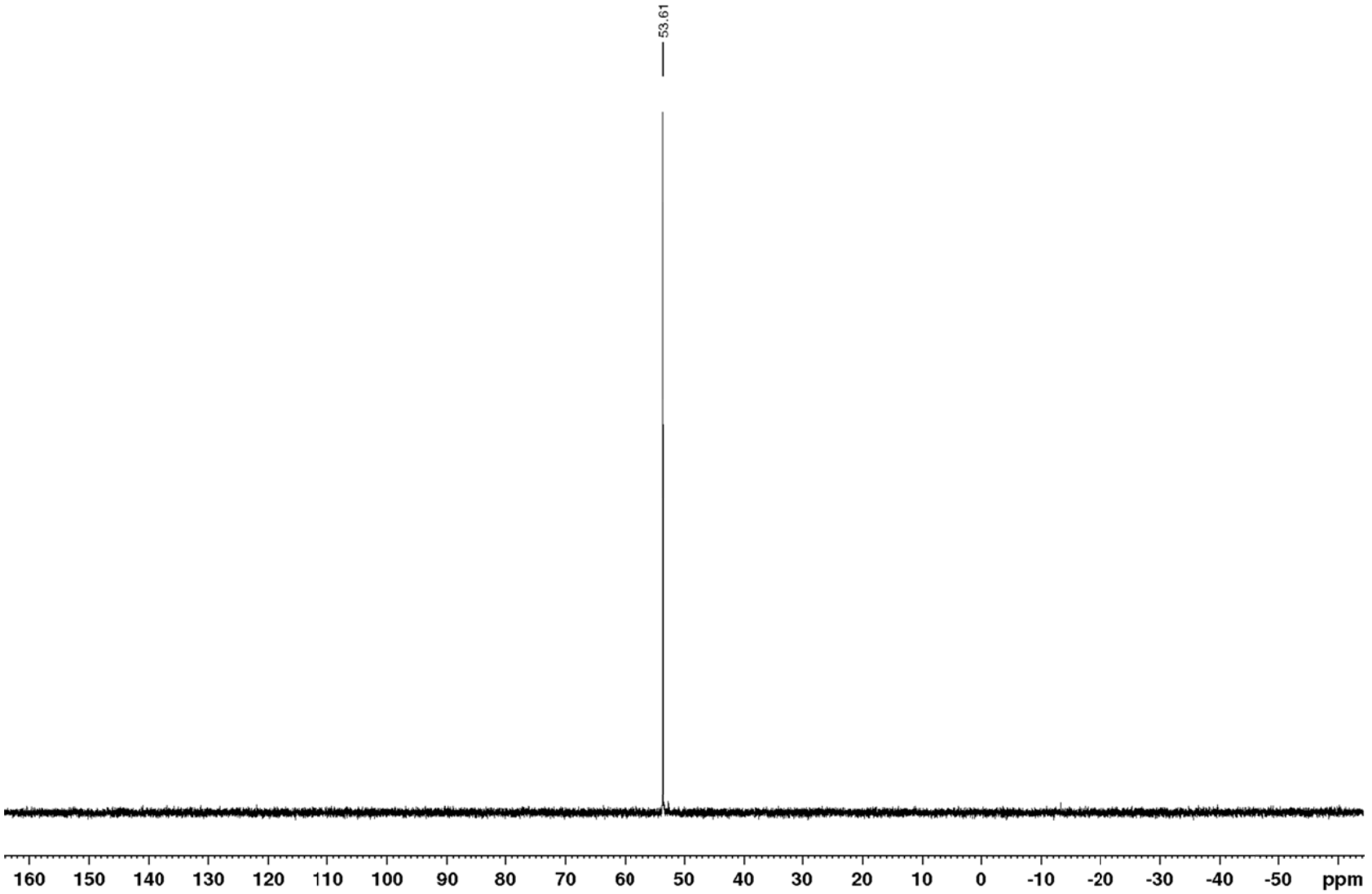


Figure S130 $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): [**5b**·4-TolCCH]$^{+}$[BAr^{F}_{4}]$^{-}$

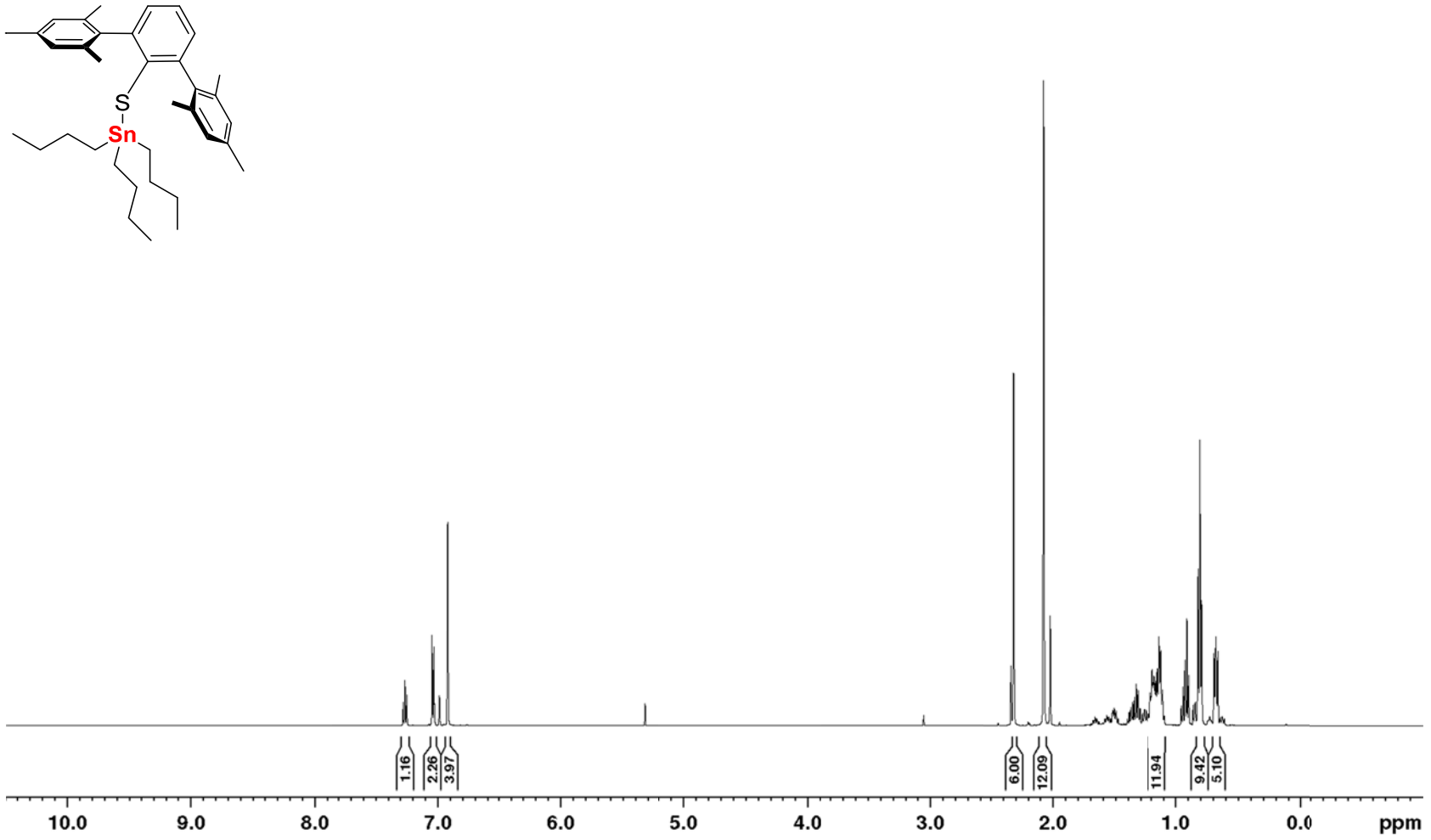


Figure S131 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): DmpSSn*n*Bu$_3$

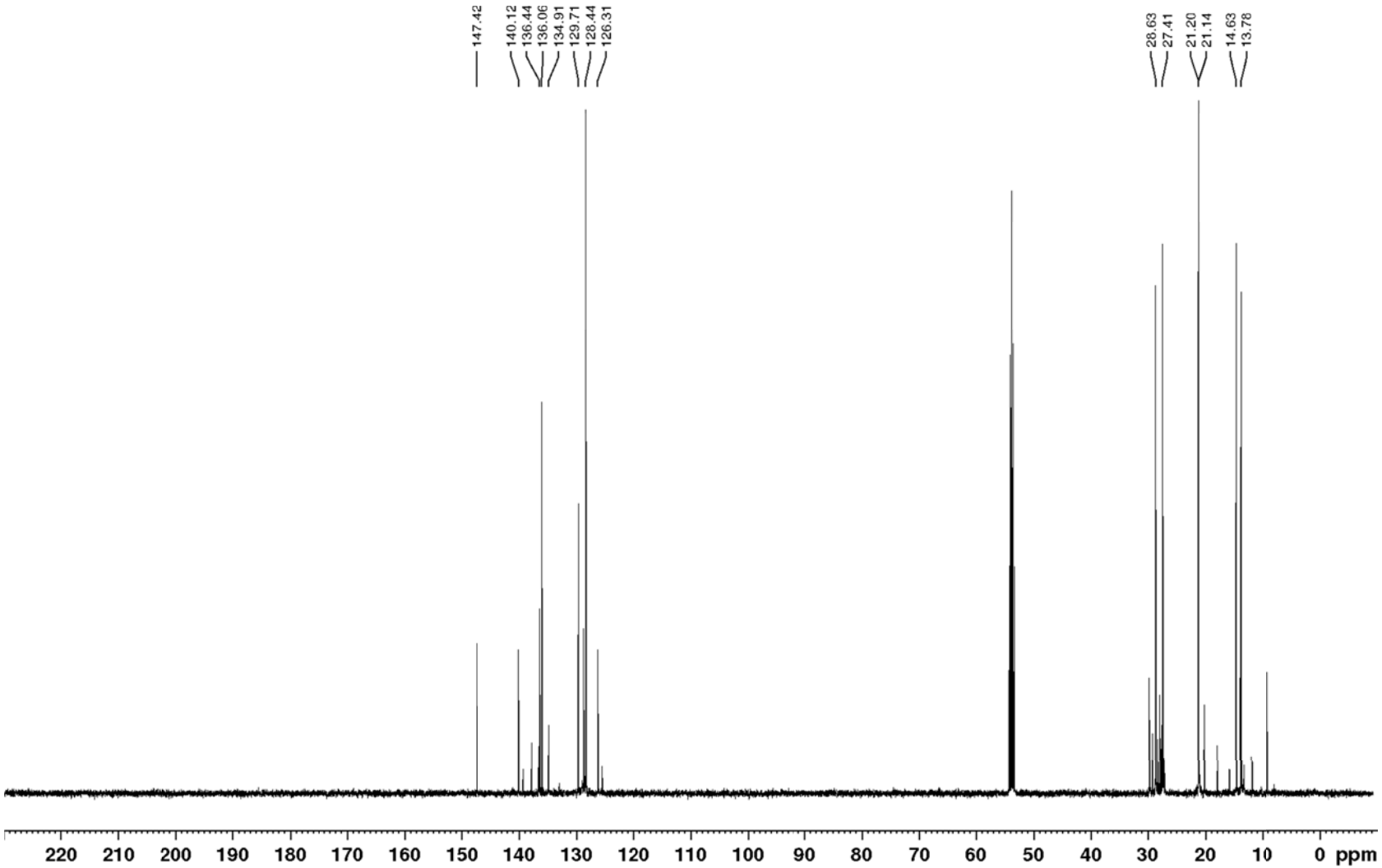


Figure S132 $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): DmpSSn*n*Bu_3

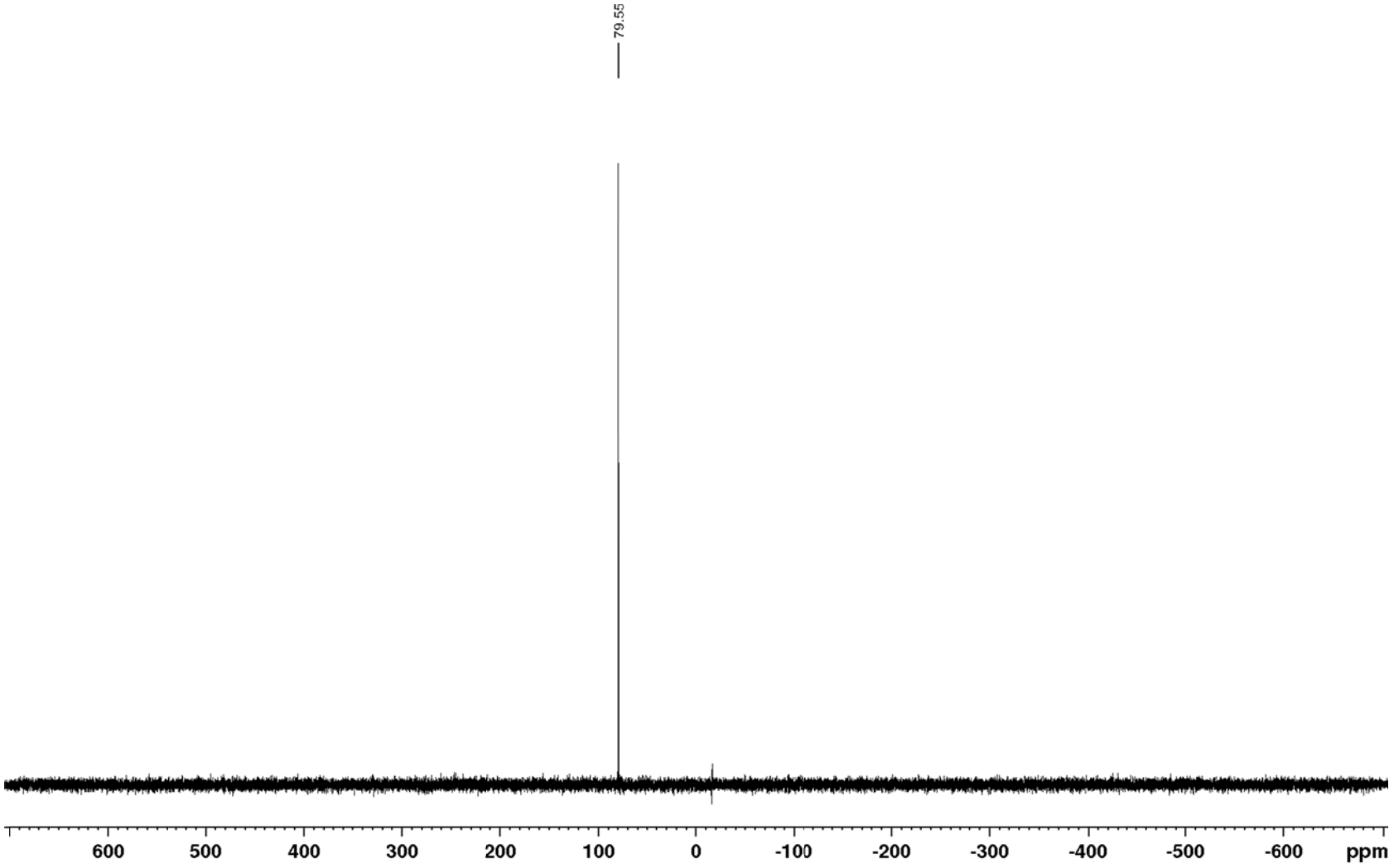


Figure S133 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, CD_2Cl_2, 298 K): DmpSSn*n*Bu_3

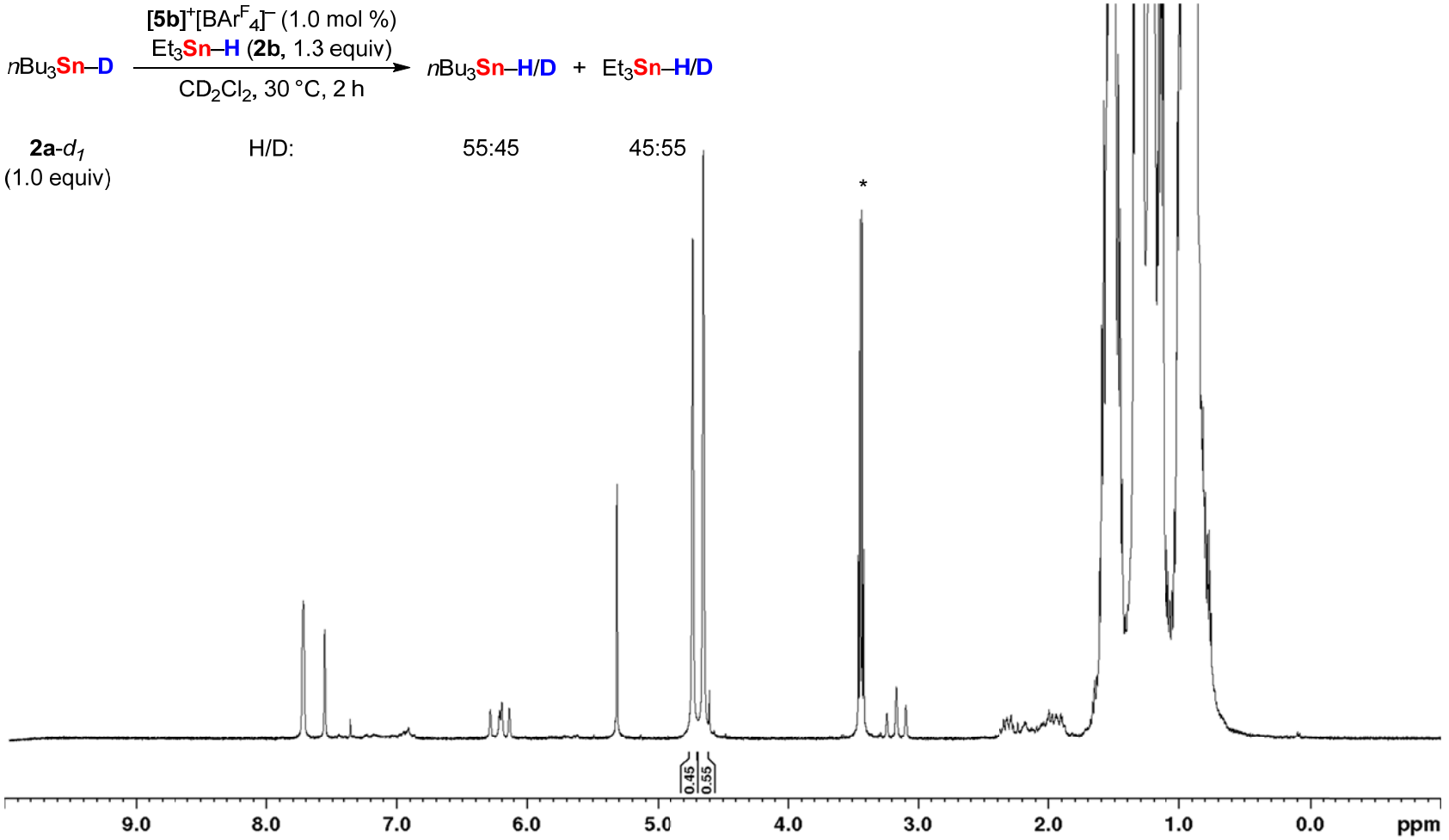


Figure S134 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Scrambling experiment of nBu$_3$SnD (**2a**-d_1) and Et$_3$SnH (**2b**) in the presence of catalyst [**5b**]$^+$[BAr$^F_4$]$^-$ (* = Et$_2$O)

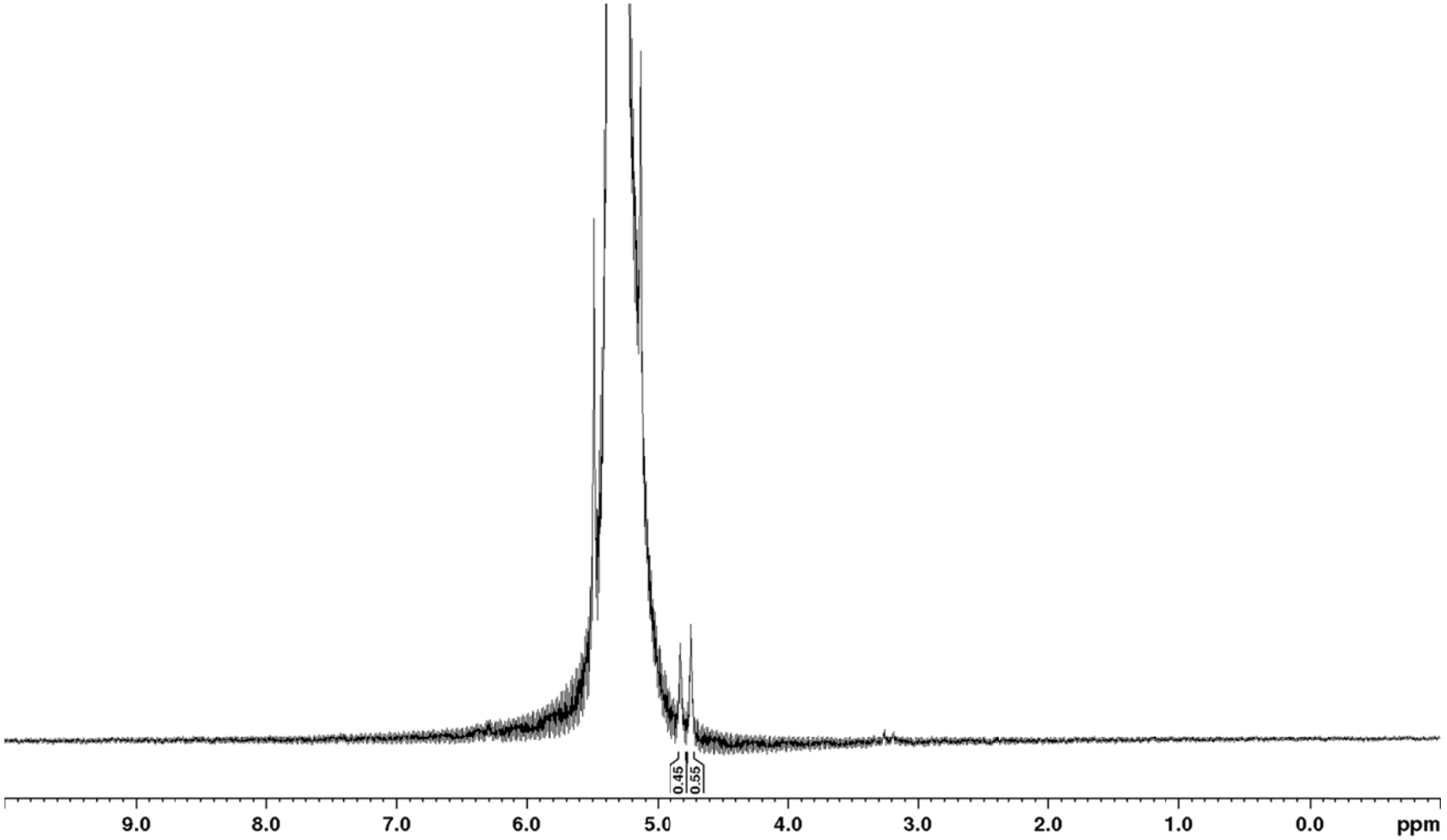


Figure S135 ^{2}H NMR (77 MHz, CD_2Cl_2, 298 K): Scrambling experiment of *n*Bu_3SnD (**2a**-*d*$_1$) and Et_3SnH (**2b**) in the presence of catalyst [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$

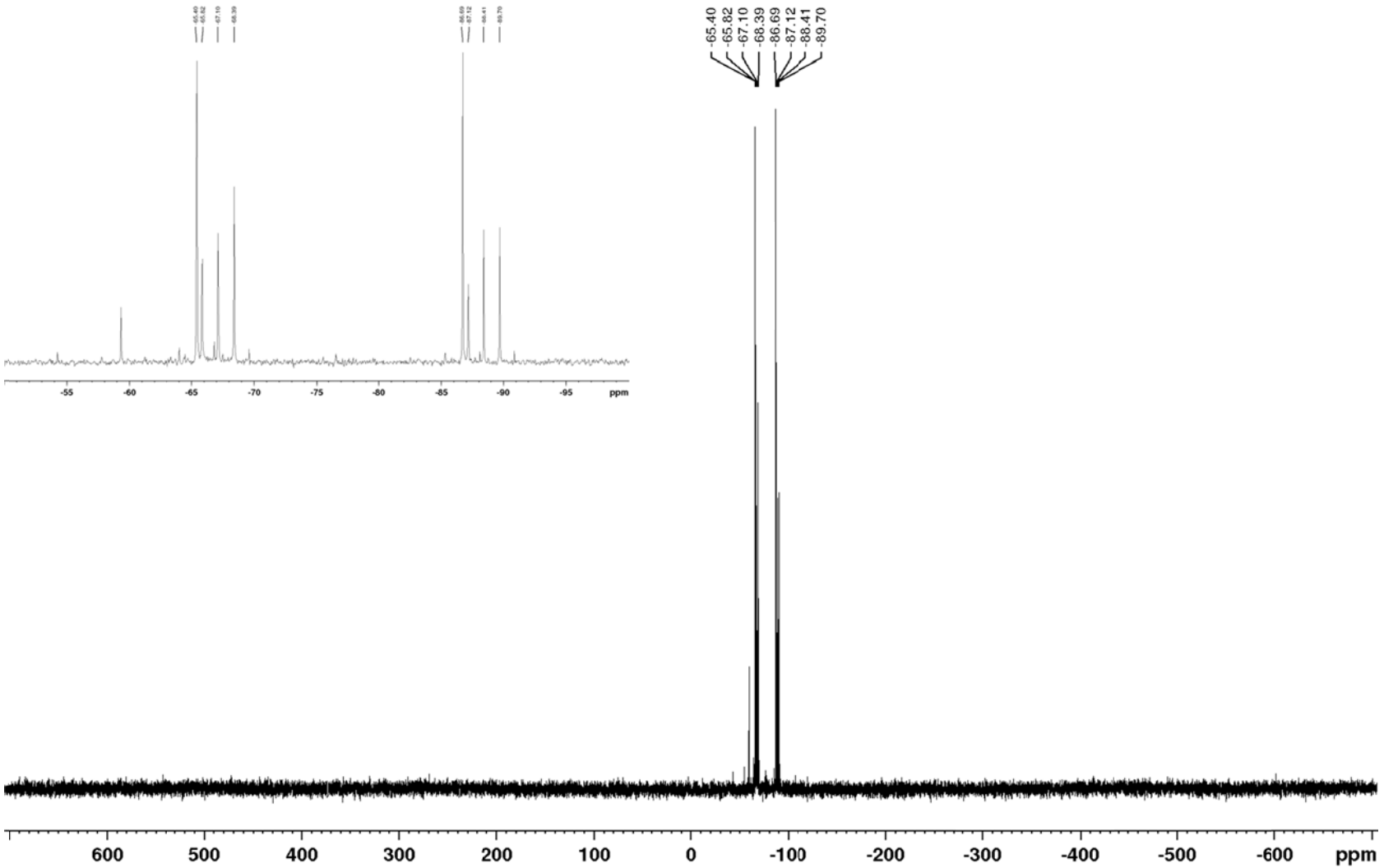


Figure S136 $^{119}Sn\{^{1}H\}$ NMR (186 MHz, CD_2Cl_2, 298 K): Scrambling experiment of *n*Bu_3SnD (**2a**-d_1) and Et_3SnH (**2b**) in the presence of catalyst [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$

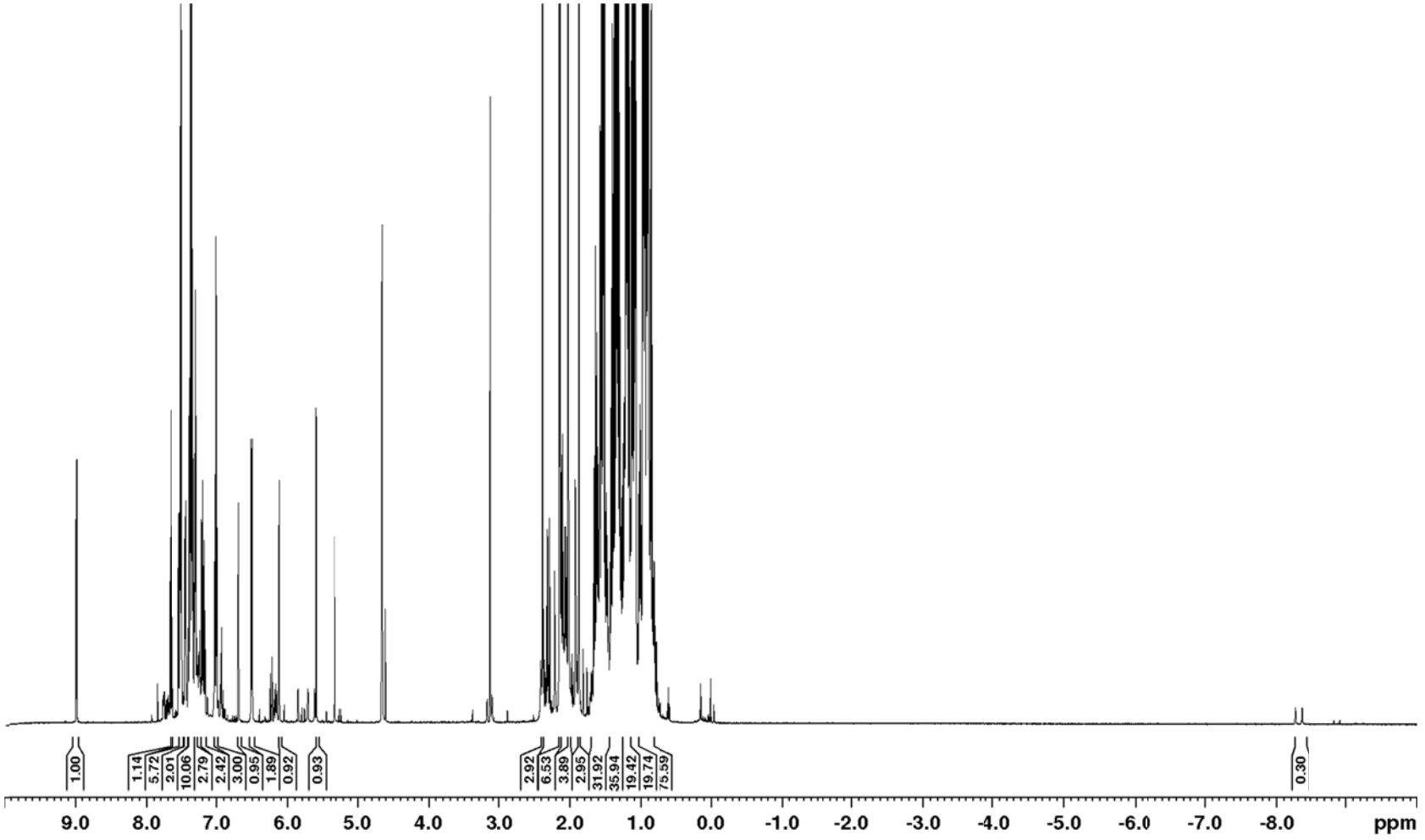


Figure S137 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Competition experiment: a) Premixing of [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ with phenyl acetylene (**1a**) and subsequent addition of *n*Bu_3SnH (**2a**)

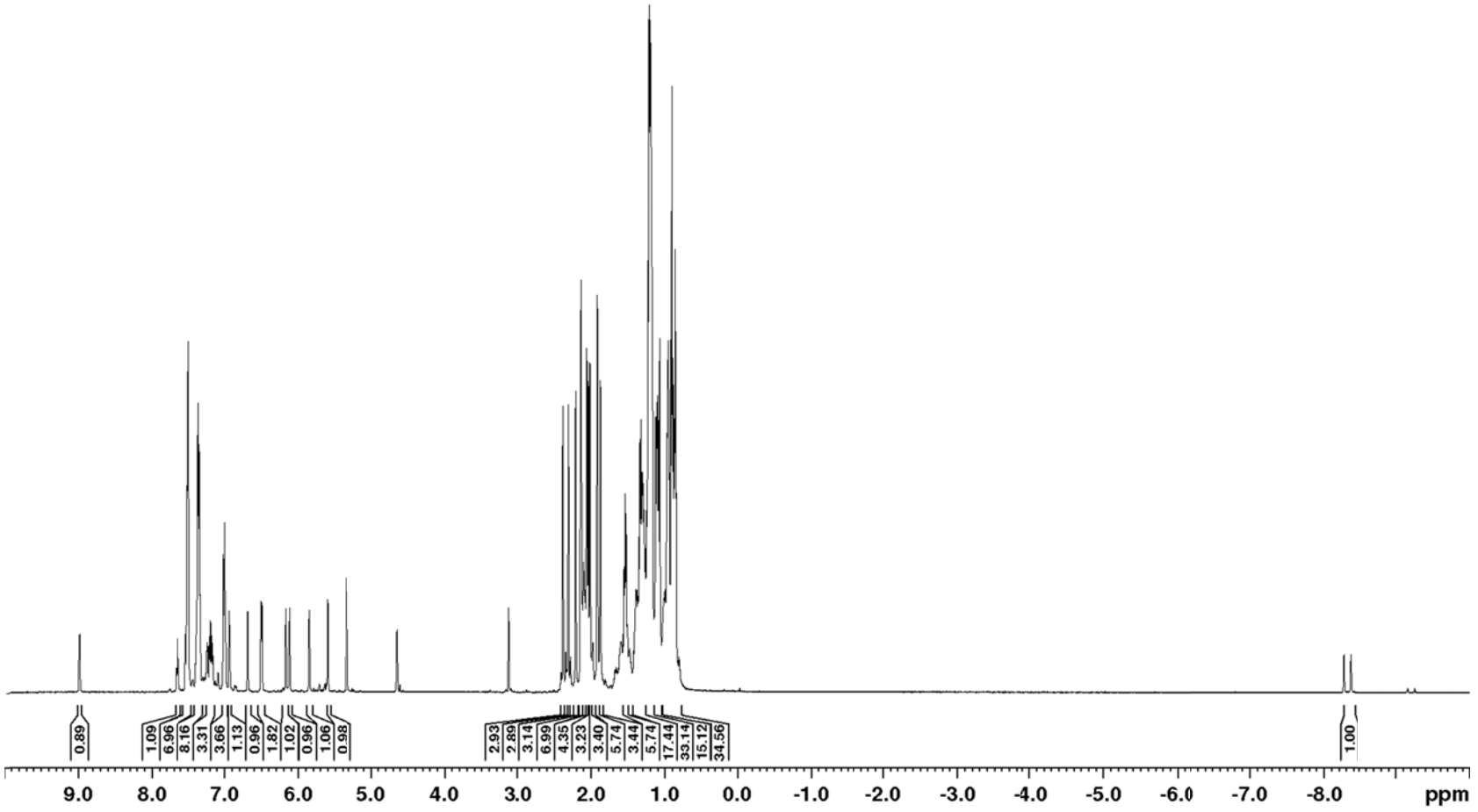


Figure S138 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): Competition experiment: b) Premixing of [**5b**]$^{+}$[BAr^{F}_{4}]$^{-}$ with *n*Bu_3SnH (**2a**) and subsequent addition of phenyl acetylene (**1a**)

10 References

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