Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2015

Supporting Information.

Polyphosphazenes for the Stille reaction: A new type of recyclable stannyl reagents.

Sheila Martínez-Arranz, David Presa Soto, Gabino A. Carriedo,* Alejandro Presa Soto,* Ana C. Albéniz.*

1- Additional Stille-coupling experiments and data

2- NMR spectra of polyphosphazenes.

3- NMR spectra of cross-coupling products.

1- Additional Stille-coupling experiments.

Table S1. Stille coupling of C_6H_5I and **3** with different catalysts and reaction conditions.[a]

Entry	[Pd]	Solvent	Time (h)	Conversion /Yield (%)[b]
1	$[Pd(PPh_3)_4]$	Toluene	5	62/47
			18	71/50
2	$[PdCl_2dppf]$[c]	Toluene	5	32/21
			18	43/27
3	$[PdCl_2\{P(o\text{-}Me\text{-}C_6H_4)_3\}_2]$[d]	Toluene	5	23/23
			18	33/23
4[e]	$[Pd(PPh_3)_4]$	DMA	5	95/68
			18	95/68
5[e]	$[Pd(PPh_3)_4]$	CD_3CN	5	31/25
			18	33/27

a) The reactions were carried out at 100 ˚C unless otherwise noted. The molar ratio of reagents used was **3**:C_6H_5I:[Pd]=25:20:1. b) Conversions and crude yields were determined by integration of ^1H NMR signals. c) Catalyst prepared as reported before: T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsa. *J. Am. Chem. Soc.* 1984, **106**, 158. d) Catalyst prepared as reported before: J. Chatt, F. G. Mann, *J. Chem. Soc.* 1939, 1622. e) Reaction temperature 90 ˚C.

Table S2. Stille reactions using polymers **3** or **6** as reagents.[a]

Entry	R^1X	**PP** (**PP**:R^1X)[b]	Time (h)	Conv. (%)[c]	R^1-An (%)[c]	R^1- R^1 (%)[c]	R^1-H (%)[c]
1	PhI	**3** (1.25:1)	18	87	68	12	7
2	$p\text{-}CHOC_6H_4I$	**3** (1.25:1)	18	100	93	7	
3[d,e]	C_6F_5I	**3** (1.25:1)	5	50	40	-	10
4[d]	$p\text{-}F_3CC_6H_4I$	**3** (1.25:1)	5	87	75	9	4
5[d]	$p\text{-}MeOC_6H_4I$	**3** (1.25:1)	5	86	86	-	-
6[f]	$CH_2{=}CHCH_2Cl$	**3** (1.1:1)	5	100	100	-	-
7	PhI	**6** (2:1)	48	87	68	19	-
8	$p\text{-}F_3CC_6H_4I$	**6** (2:1)	44	100	91	5	4
9[f]	$CH_2{=}CHCH_2Cl$	**6** (2:1)	5	100	100	-	-

a) The reactions were carried out in DMA at 90 ˚C, using $[Pd(PPh_3)_4]$ as catalyst (5% mol Pd) unless otherwise noted. b) Molar ratio. c) Conversions and crude mol-based yields were determined by integration of ^1H or ^{19}F NMR signals. The experiments where the spectra showed some signal overlap for the reaction mixtures (entries 1, 5 and 7) were repeated using an internal standard (1,3,5-$(CF_3)C_6H_3$) and led to similar yield values (75%, 87% and 72% for entries 1, 5, and 7 respectively).d) $[PdBrPf(AsPh_3)_2]$ was used as catalyst. e) Dioxane as solvent and 100 ˚C. The yield did not improve upon increasing the reaction time. f) The reaction was carried out in THF at 50 ˚C, using $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ as catalyst (1% mol Pd) and benzoquinone (1% mol).

Table S3. Recycling experiments for the Stille coupling of C_6H_5I and polymer **3**.[a]

Cycle	Conv. (%)[b]	Recovered PP-SnBu$_2$X (yield %)	R^1-R^2 (crude yield, %)[b]	R^1- H[b]	R^1- R^1 [b]	R^1-R^2 (isolated yield, %)
1	76	71	64	5	7	41
2	64	74	40	12	12	35
3	66	82	45	10	11	31
4[d]	81	87	55	14	12	40
5	100	91	50	34	16	37
6	100	92	66	28	6	37
7[e]	84	91	79	3	2	63
8[e]	64	90	47	8	9	43
9[f]	70	98	54	9	7	48

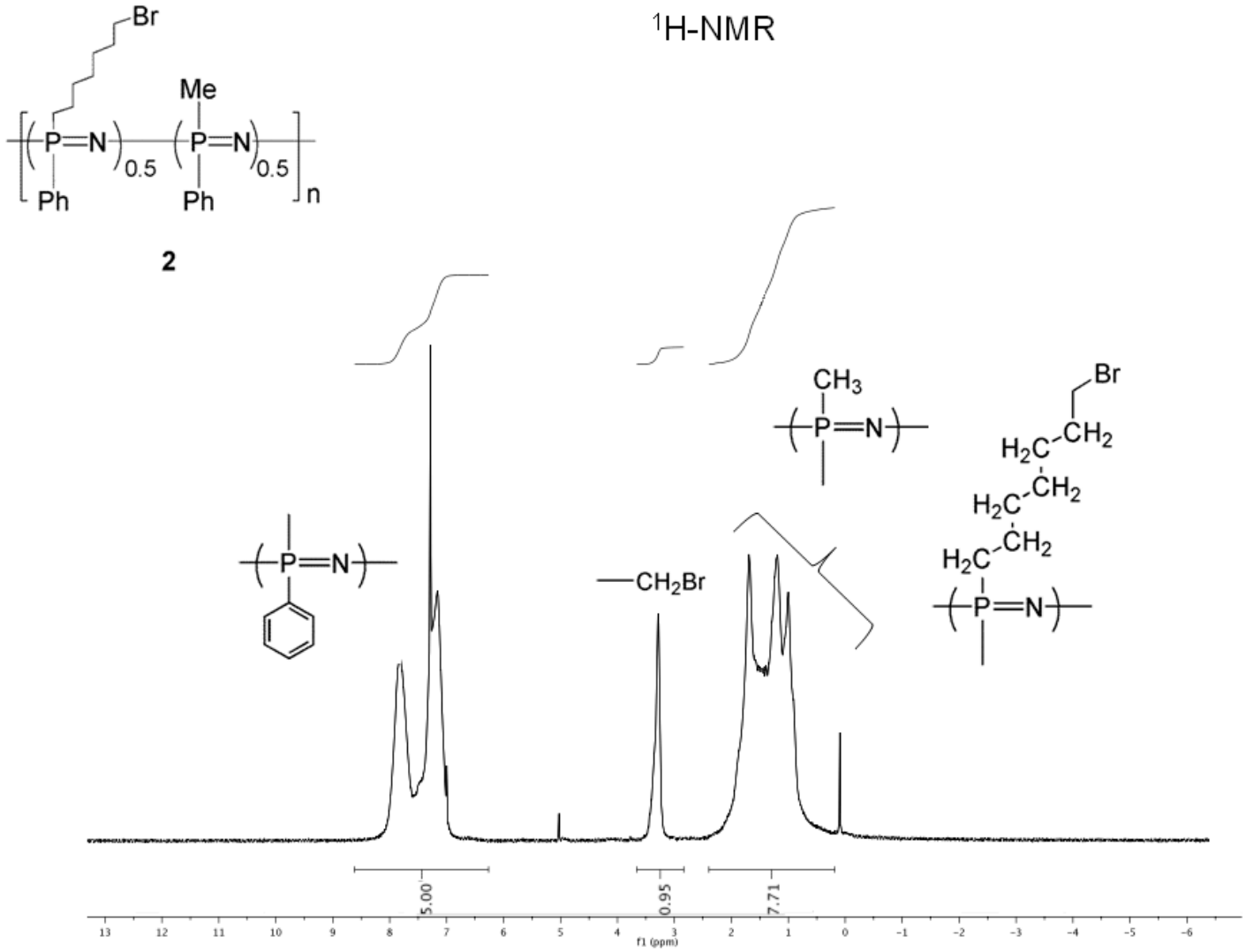
a) The reactions were carried out in DMA at 90 ˚C for 24 h using [Pd(PPh_3)$_4$] as catalyst. The molar ratio of reagents used was **3**:C_6H_5I:[Pd]=25:20:1. b) Conversions and mol-based crude yields were determined by integration of ^{1}H NMR signals. c) Determined by ICP-MS on samples of the coupling product obtained by evaporation of the solvents and filtration through silica (see Experimental part). d) The molar ratio of reagents was changed to **3**:C_6H_5I:[Pd]=40:20:1. e) No catalyst added. f) The amount of catalyst used is 0.5% mol.

Table S4. Recycling experiments for the Stille coupling of p-$CF_3C_6H_4I$ and polymer **6**.[a]

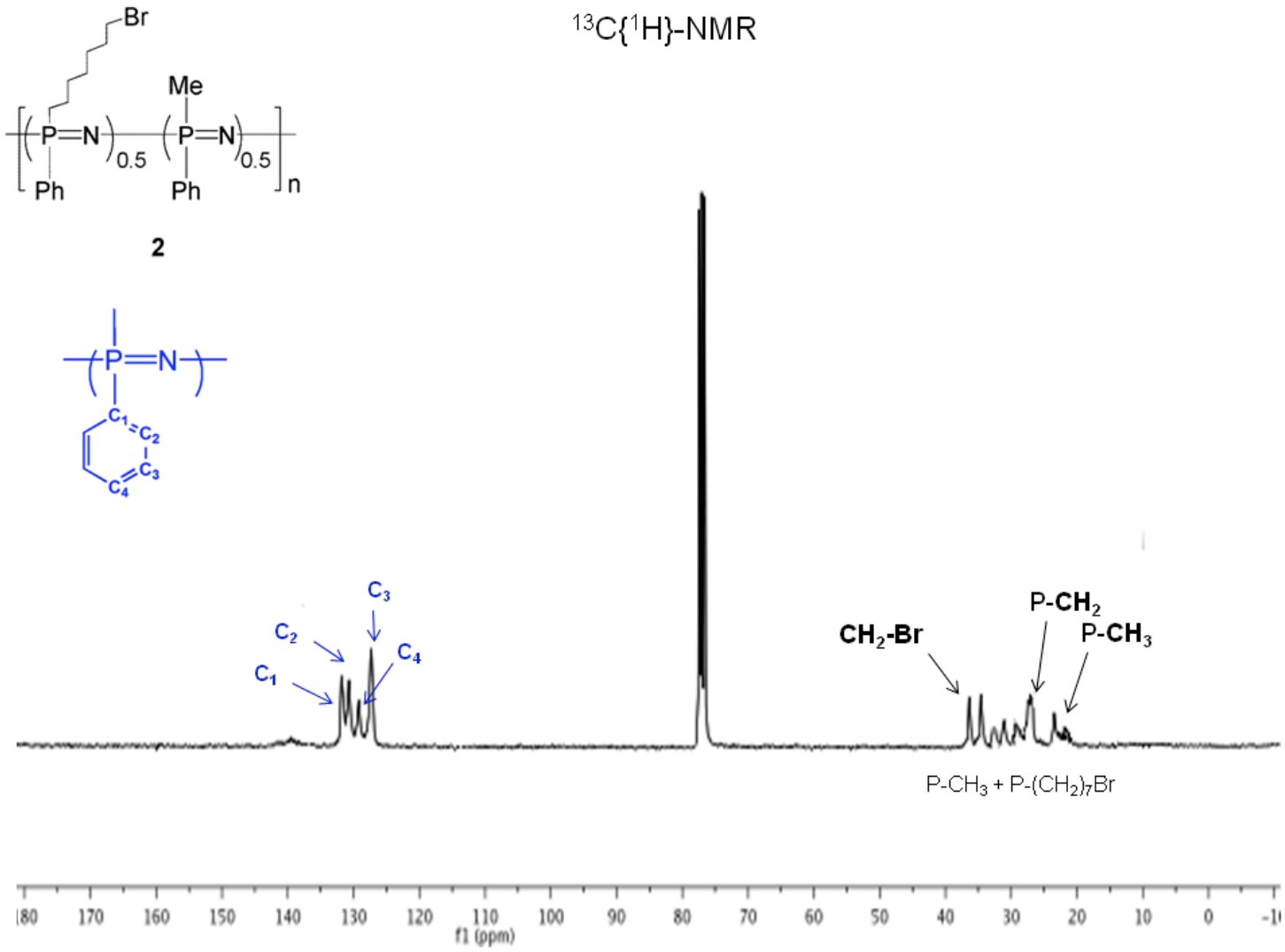
Cycle	R^1-R^2 Conversion (crude yield %)[b]		Recovered PP-SnBu$_2$X (Yield %)	R^1- H[b]	R^1- R^1 [b]	R^1-R^2 (Isolated yield, %)	Sn in R^1-R^2 % weight[c]
	24 h	≥ 48 h					
1	100(81)	-	78	10	9	69	0.0002
2	100(82)	-	82	9	9	65	0.00061
3	100(77)	-	94	9	14	60	0.00024
4	77(58)	80(60)	92	5/6	14/14	42	0.00067
5	32(17)	48(22)[d]	89	-/-	15/26	-	0.0089
6	30(25)	64(40)[e]	88	-/7	5/17	-	0.0066
7	35(18)	43(19)[e]	86	-/-	17/24	-	0.0219

a) The reactions were carried out in DMA at 90˚ C using [Pd(PPh_3)$_4$] as catalyst. The molar ratio of reagents used was **6**:p-$CF_3C_6H_4I$:[Pd]=40:20:1. b) Conversions and mol-based crude yields were determined by integration of ^{19}F NMR signals. c) Determined by ICP-MS on samples of the coupling product obtained by evaporation of the solvents and filtration through silica (see Experimental part). d) Reaction time 4 days. e) Reaction time 3 days.

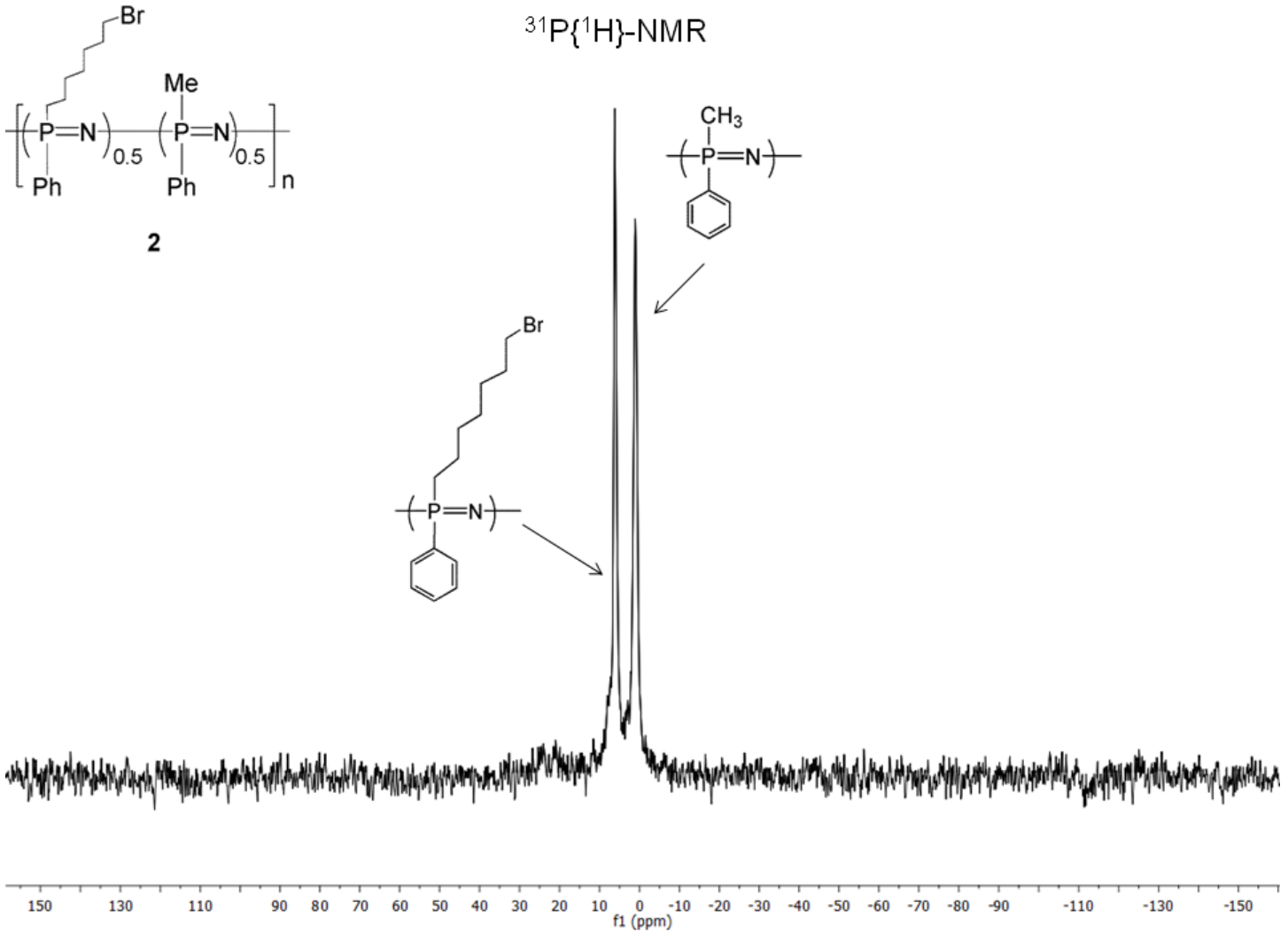
2- NMR spectra of polyphosphazenes.



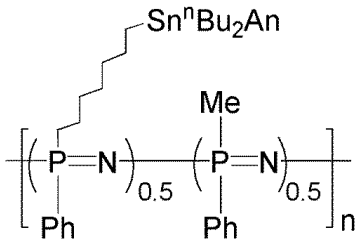
2- NMR spectra of polyphosphazenes.



2- NMR spectra of polyphosphazenes.

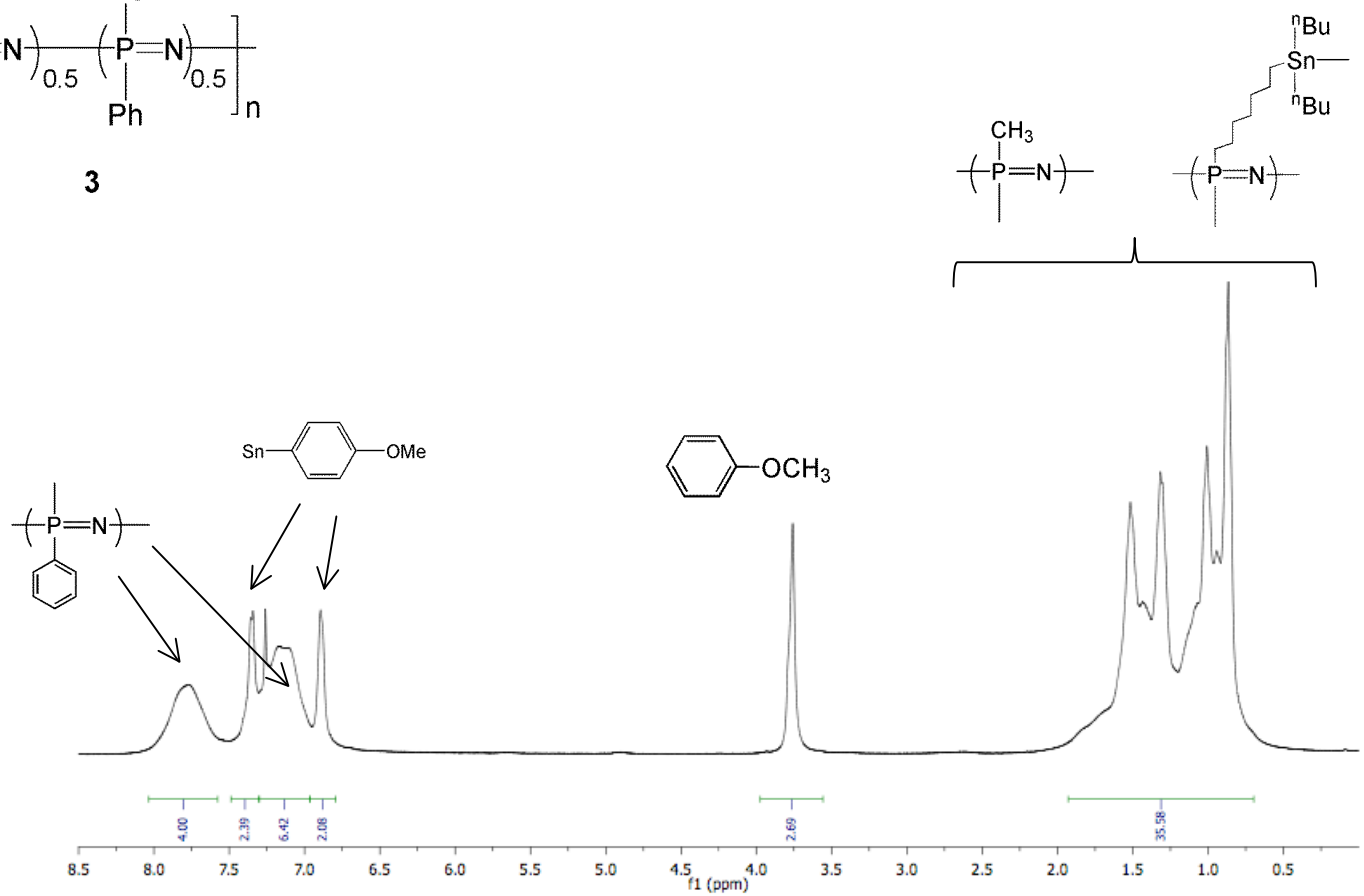


2- NMR spectra of polyphosphazenes.

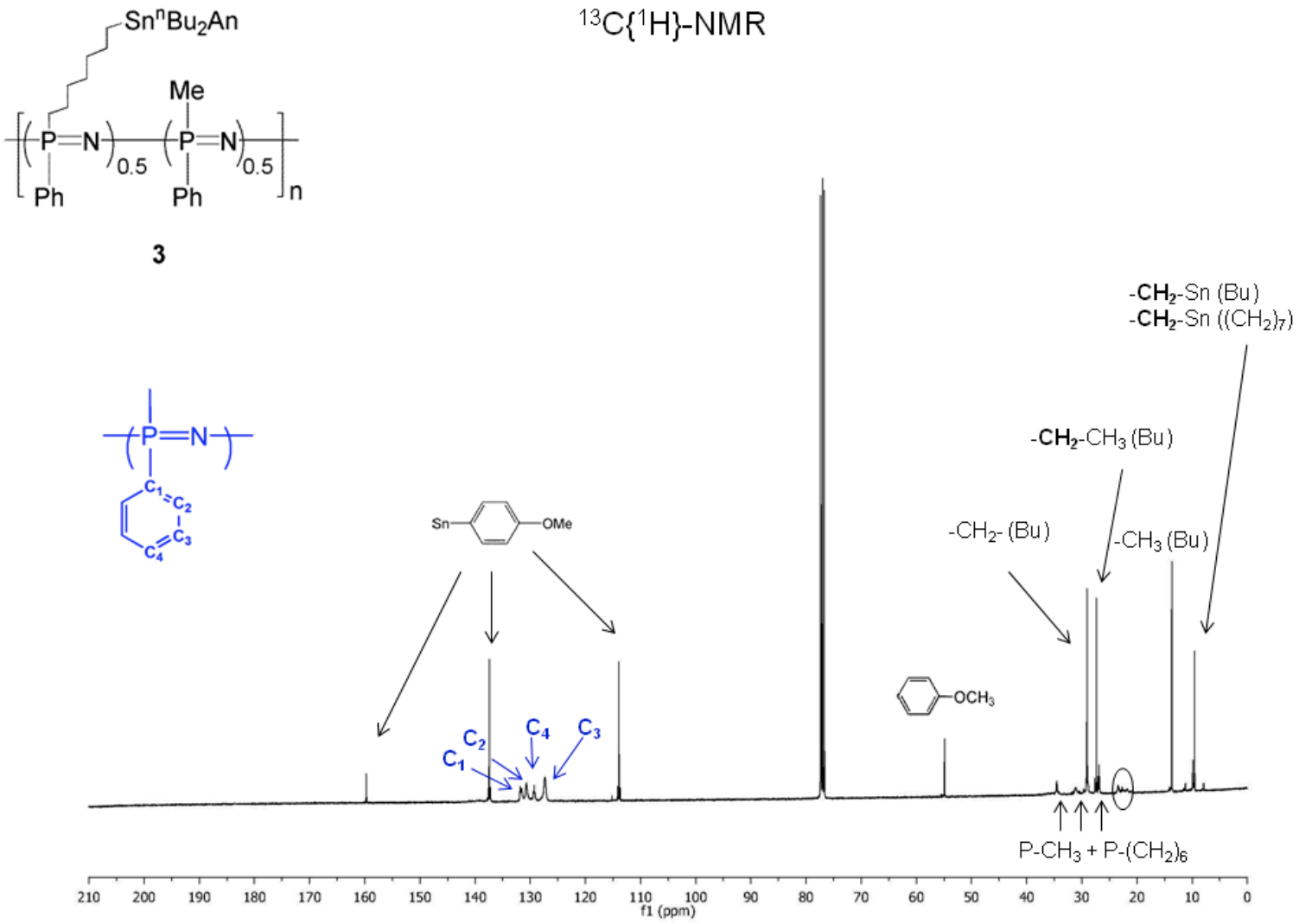


3

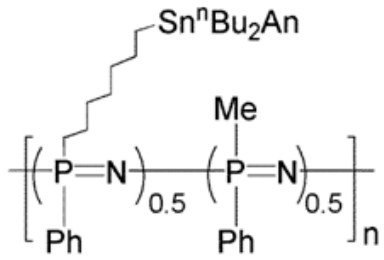
^{1}H-NMR



2- NMR spectra of polyphosphazenes.

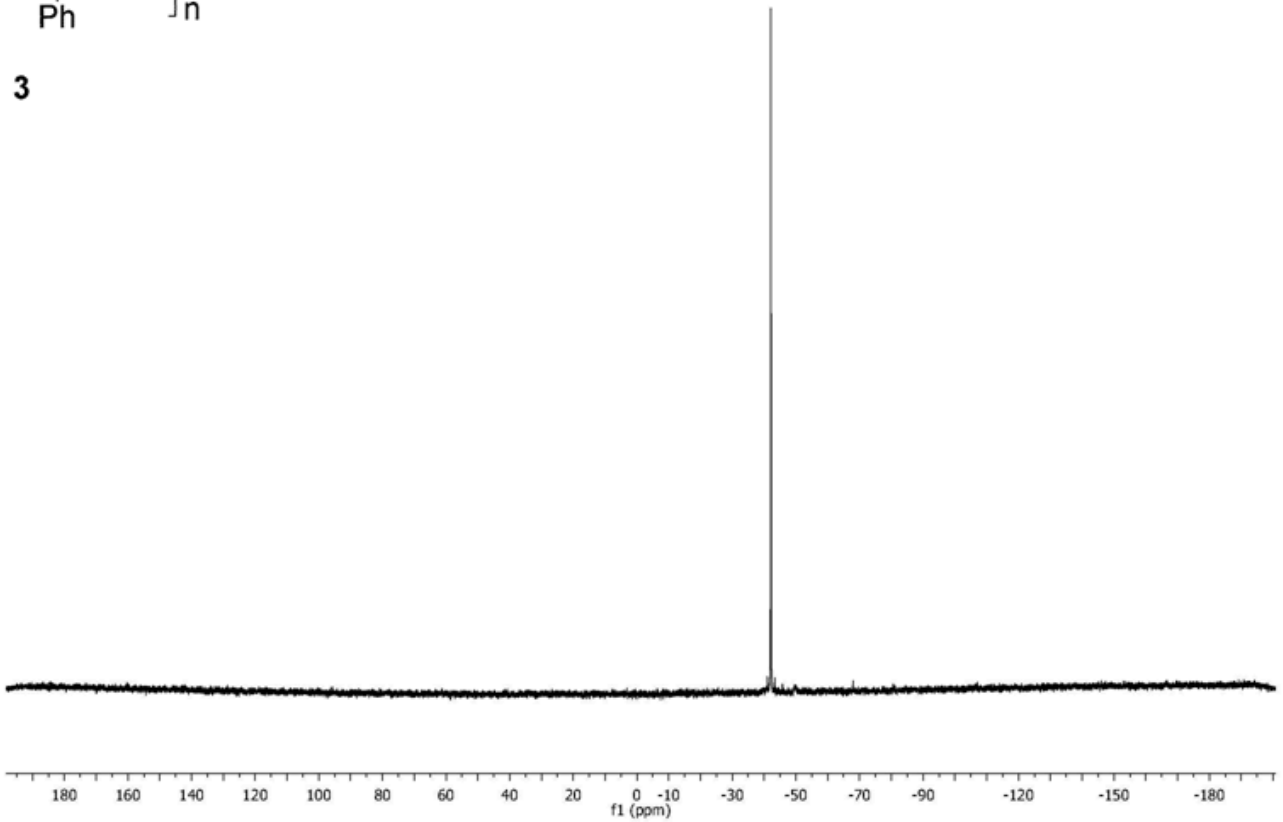


2- NMR spectra of polyphosphazenes.

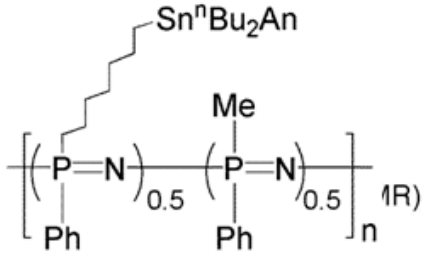


3

^{119}Sn{^{1}H}-NMR

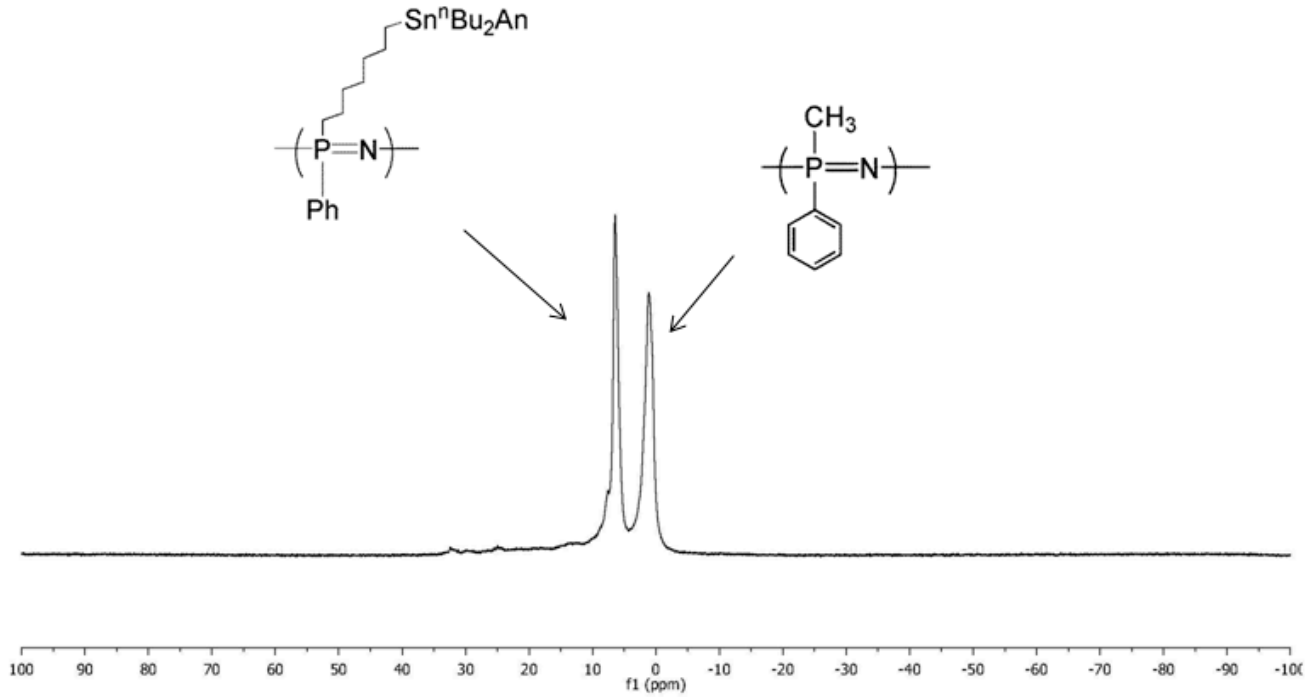


2- NMR spectra of polyphosphazenes.

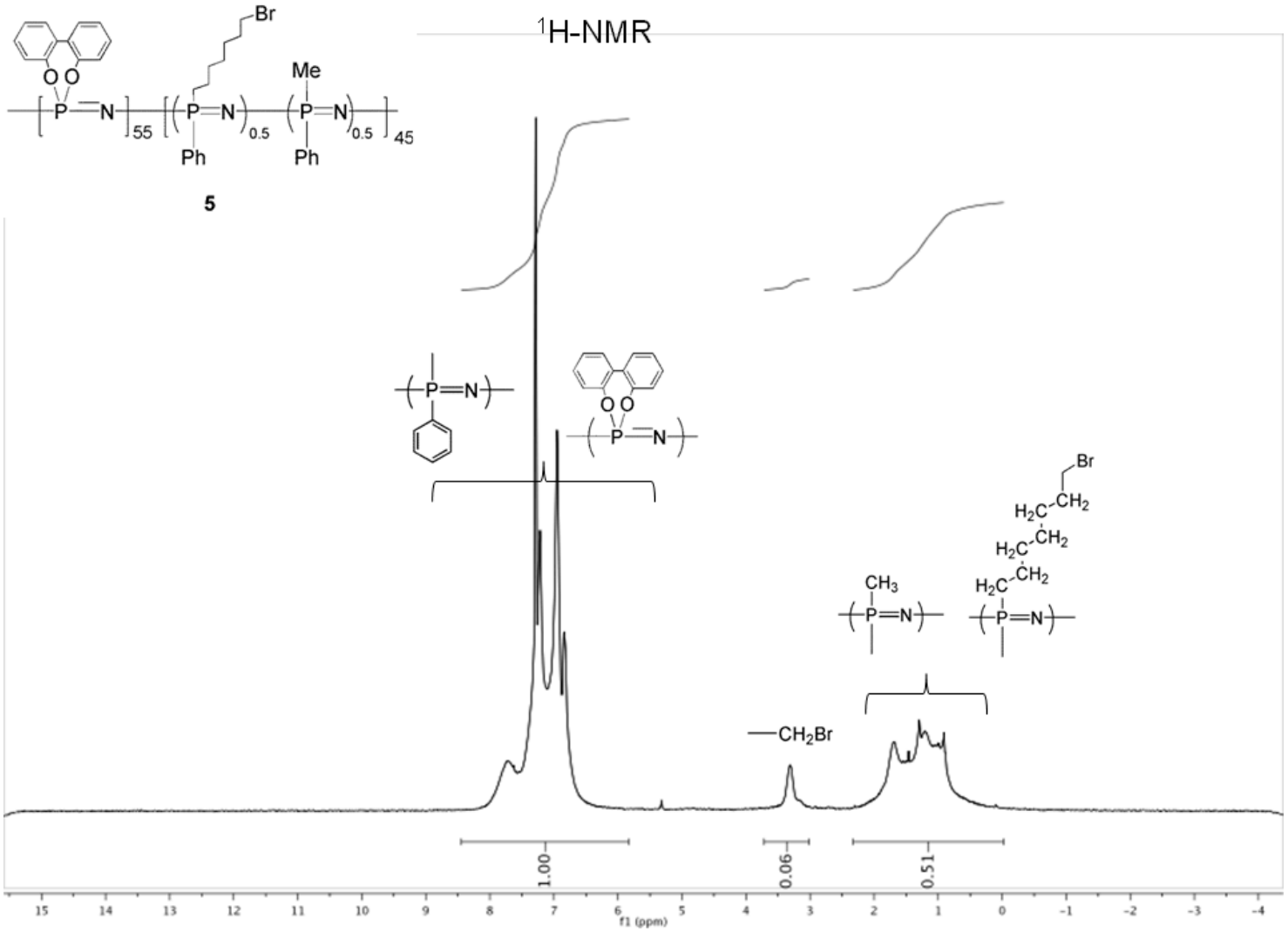


3

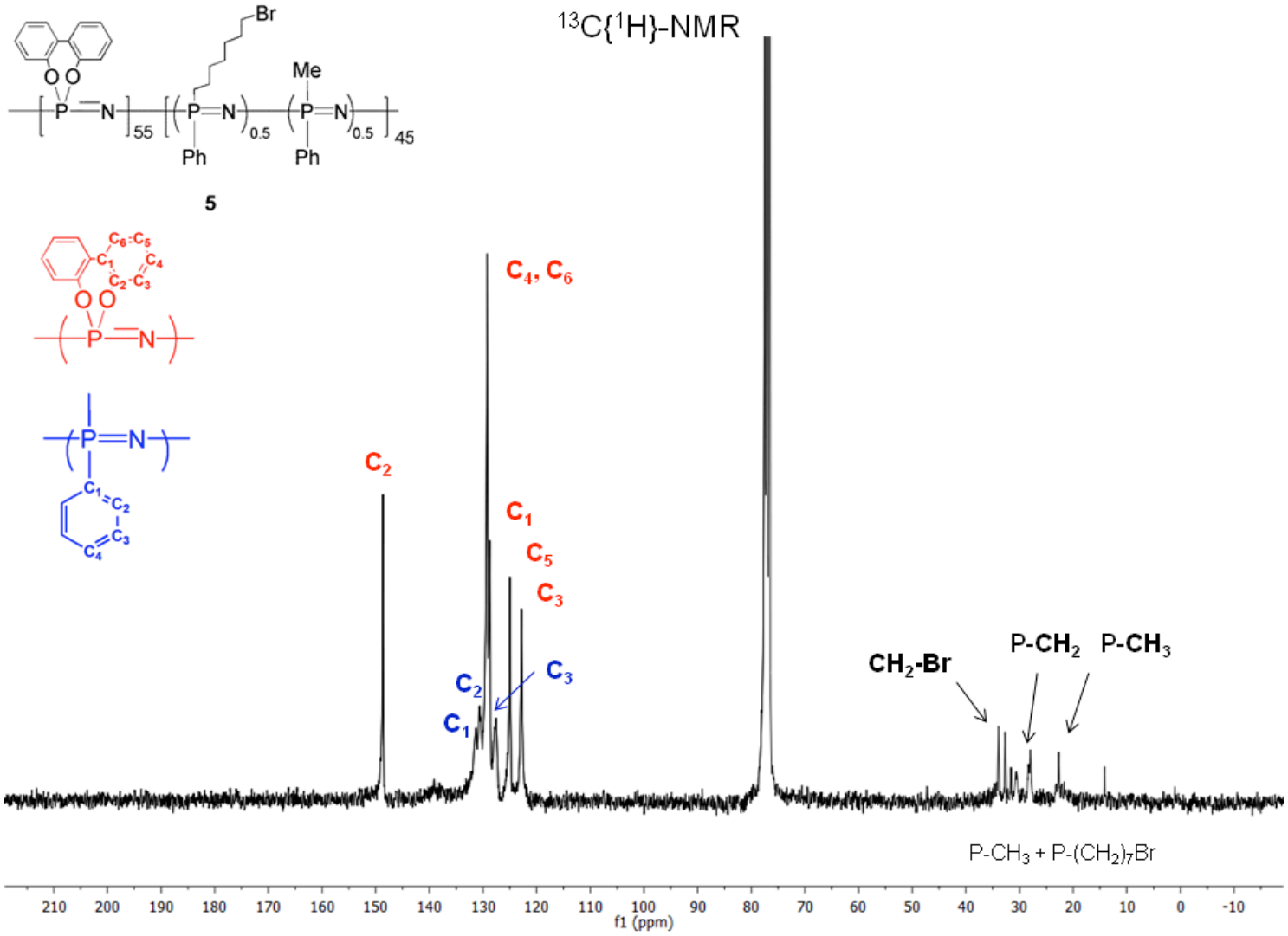
$^{31}P\{^1H\}$-NMR



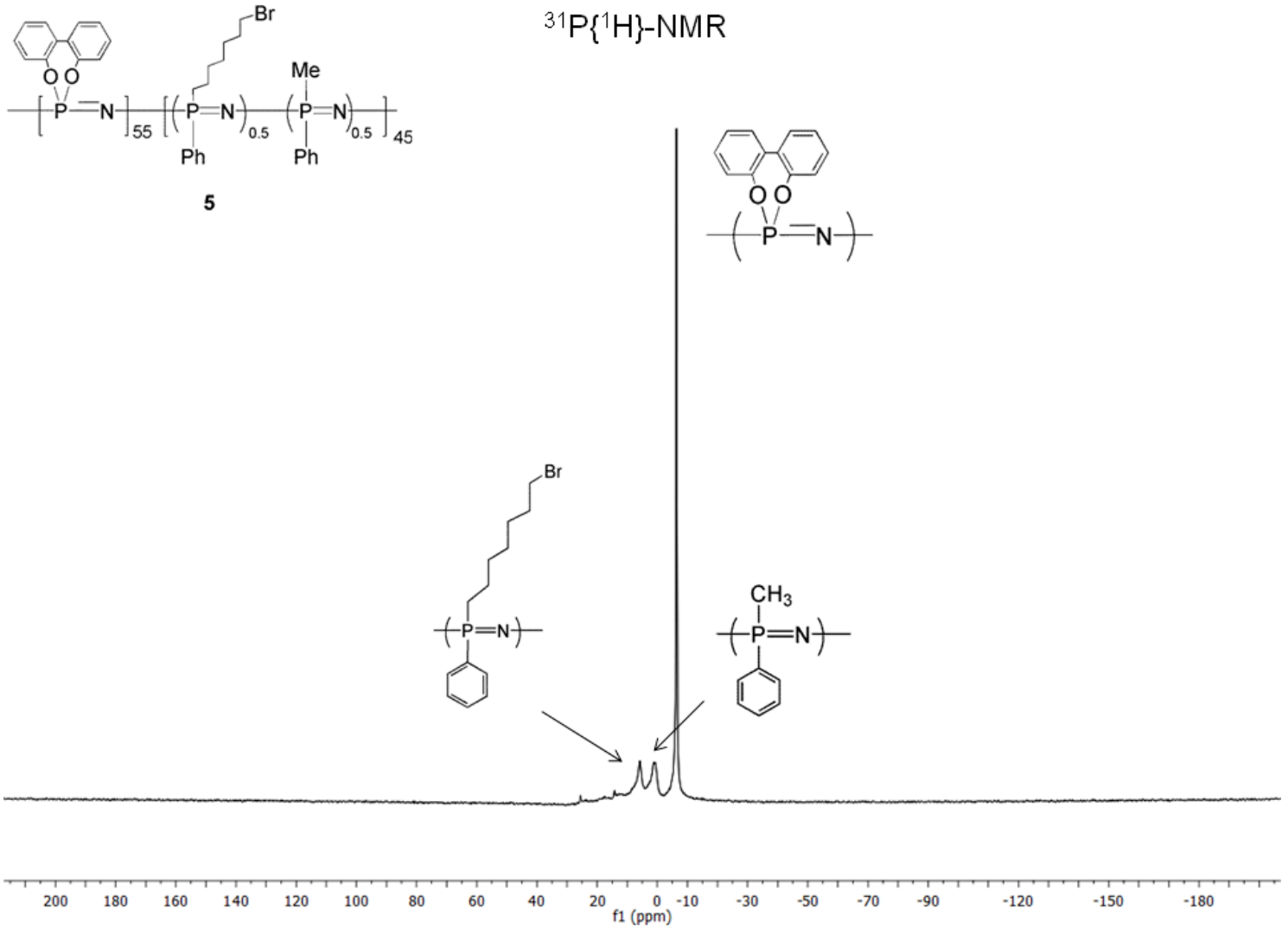
2- NMR spectra of polyphosphazenes.



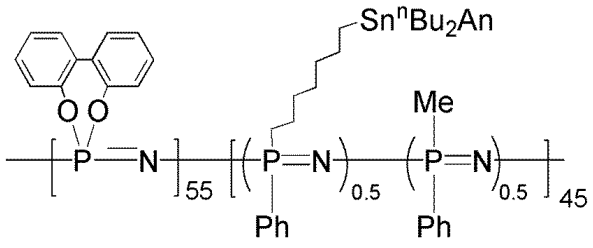
2- NMR spectra of polyphosphazenes.



2- NMR spectra of polyphosphazenes.

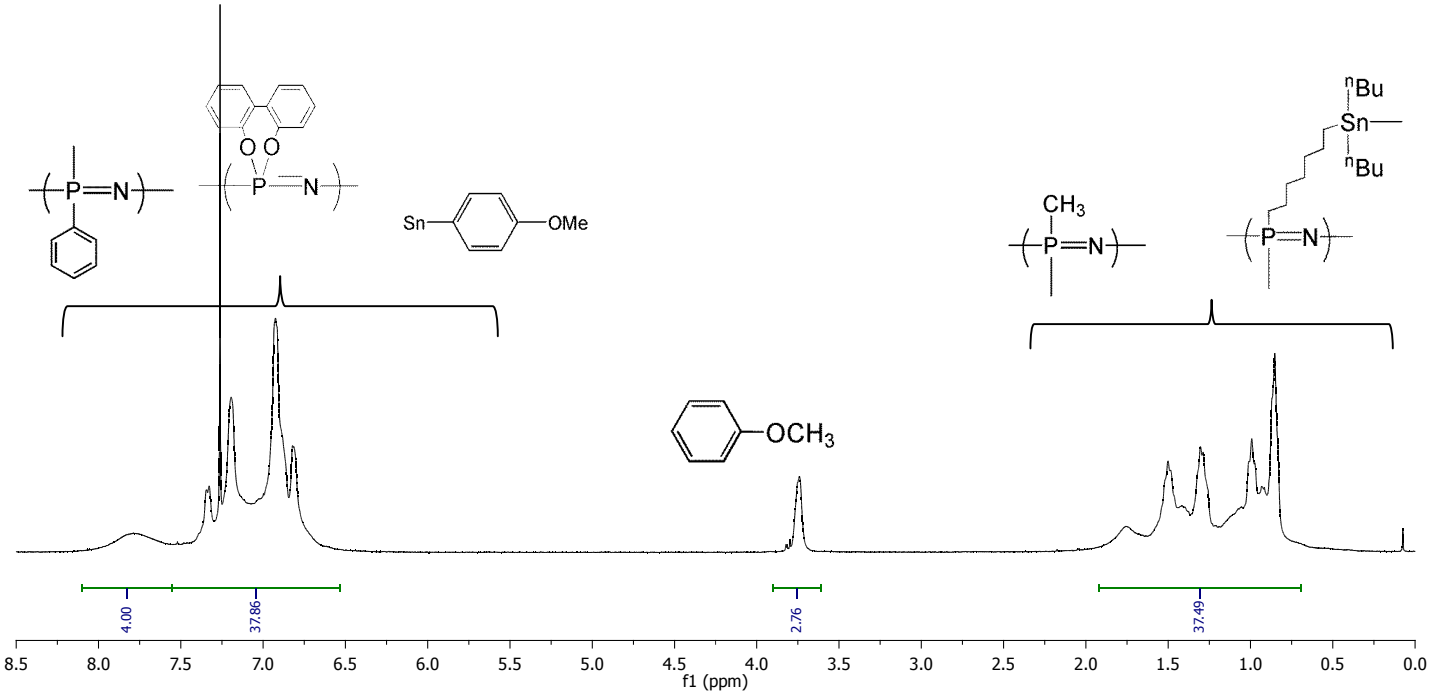


2- NMR spectra of polyphosphazenes.

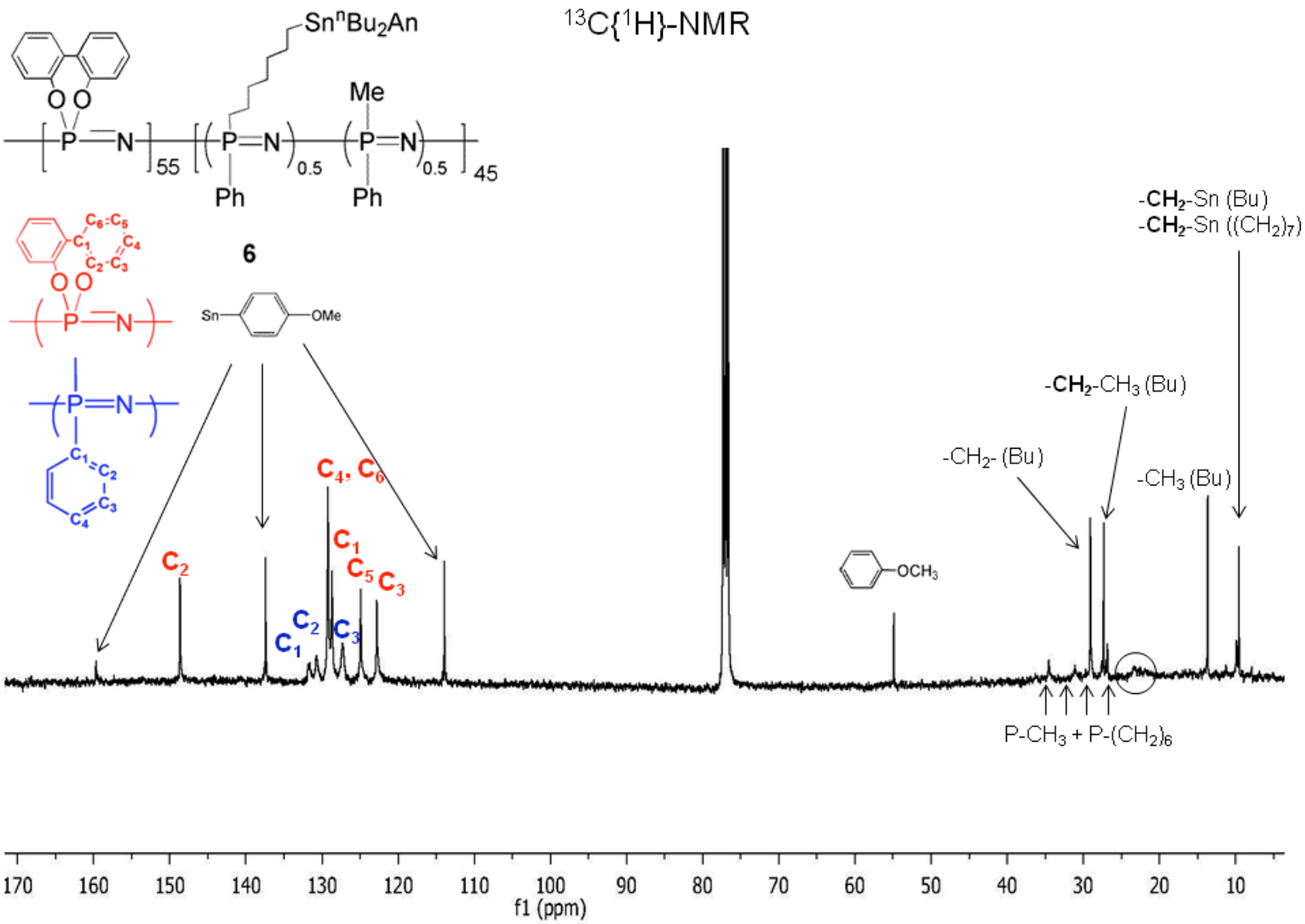


6

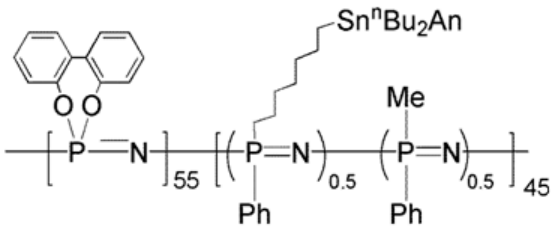
^{1}H-NMR



2- NMR spectra of polyphosphazenes.

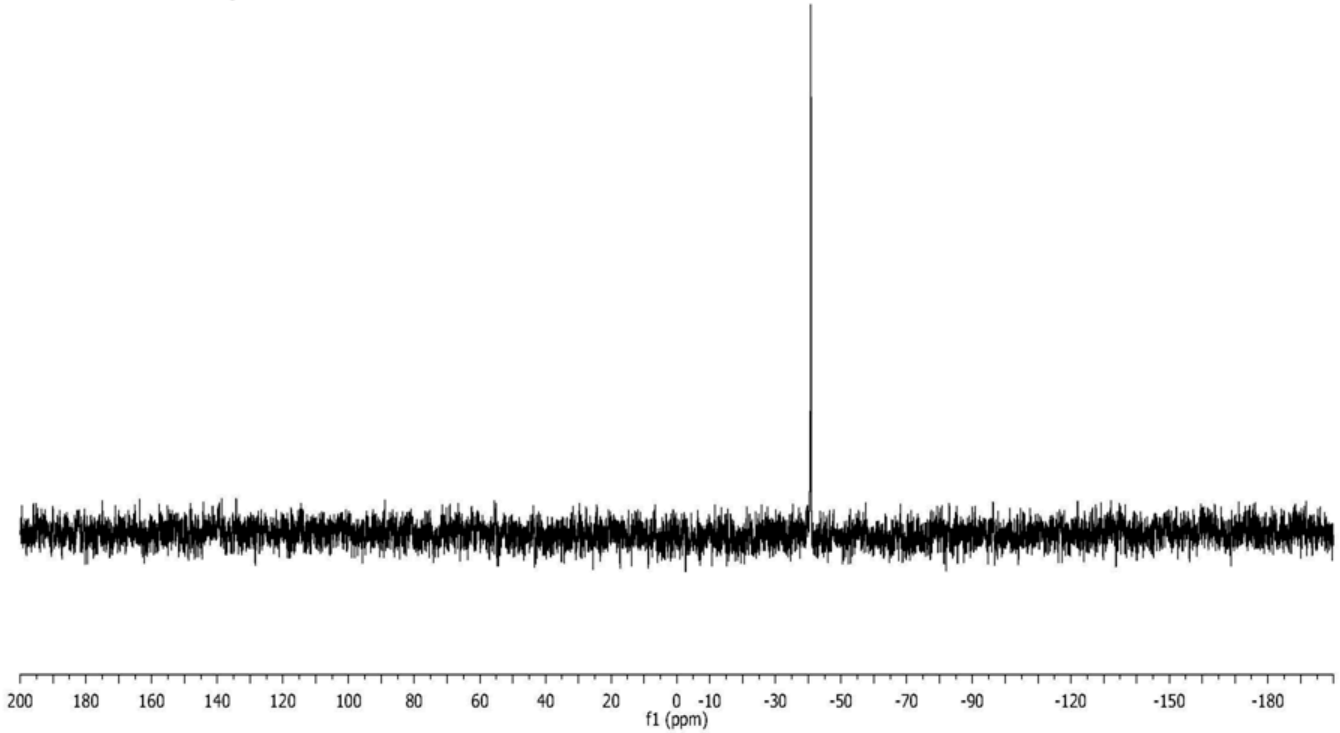


2- NMR spectra of polyphosphazenes.

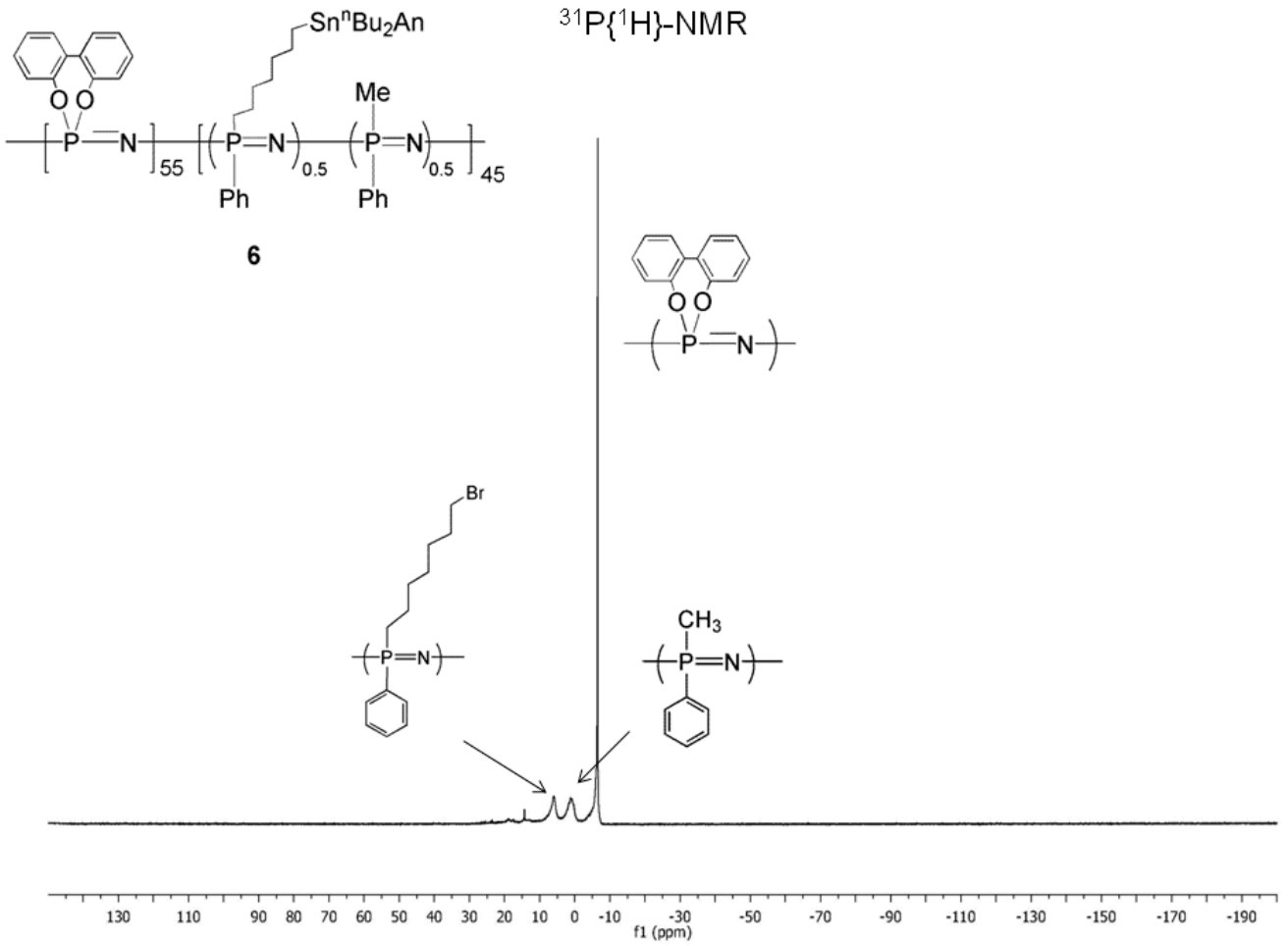


6

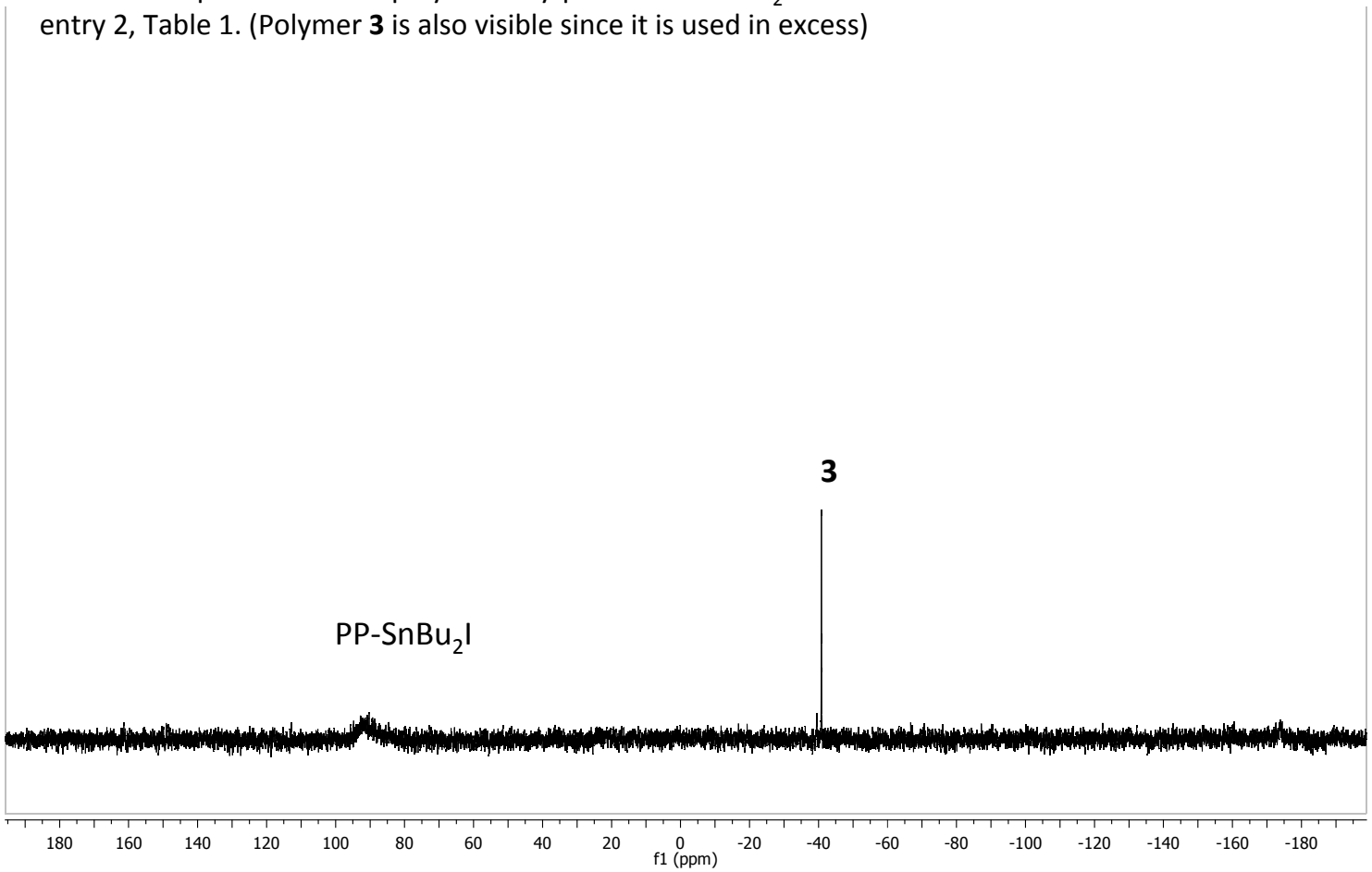
^{119}Sn{^{1}H}-NMR



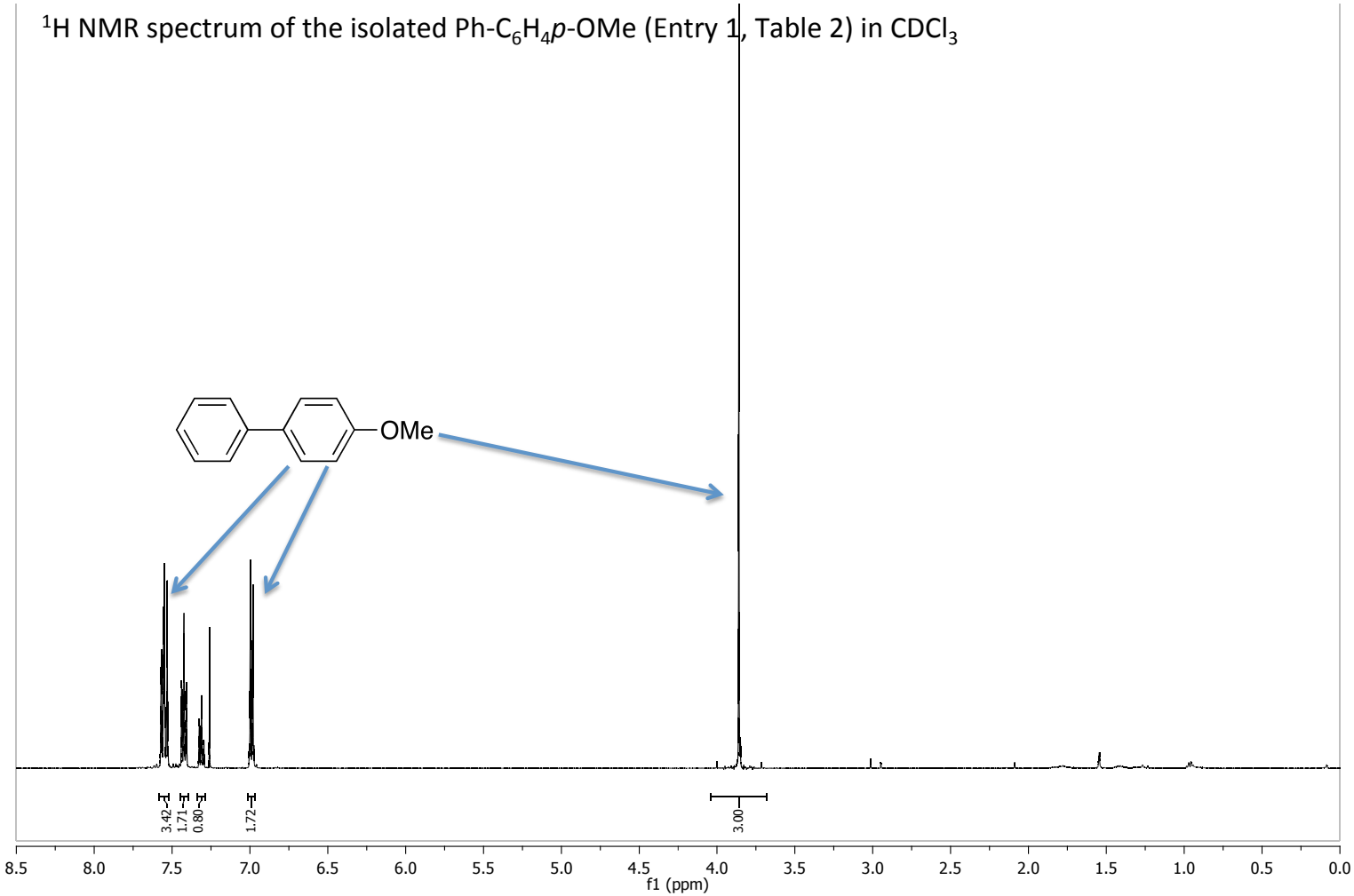
2- NMR spectra of polyphosphazenes.



^{119}Sn NMR spectrum of the polymeric by-product PP-$SnBu_2I$ derived from **3** after the Stille reaction in entry 2, Table 1. (Polymer **3** is also visible since it is used in excess)

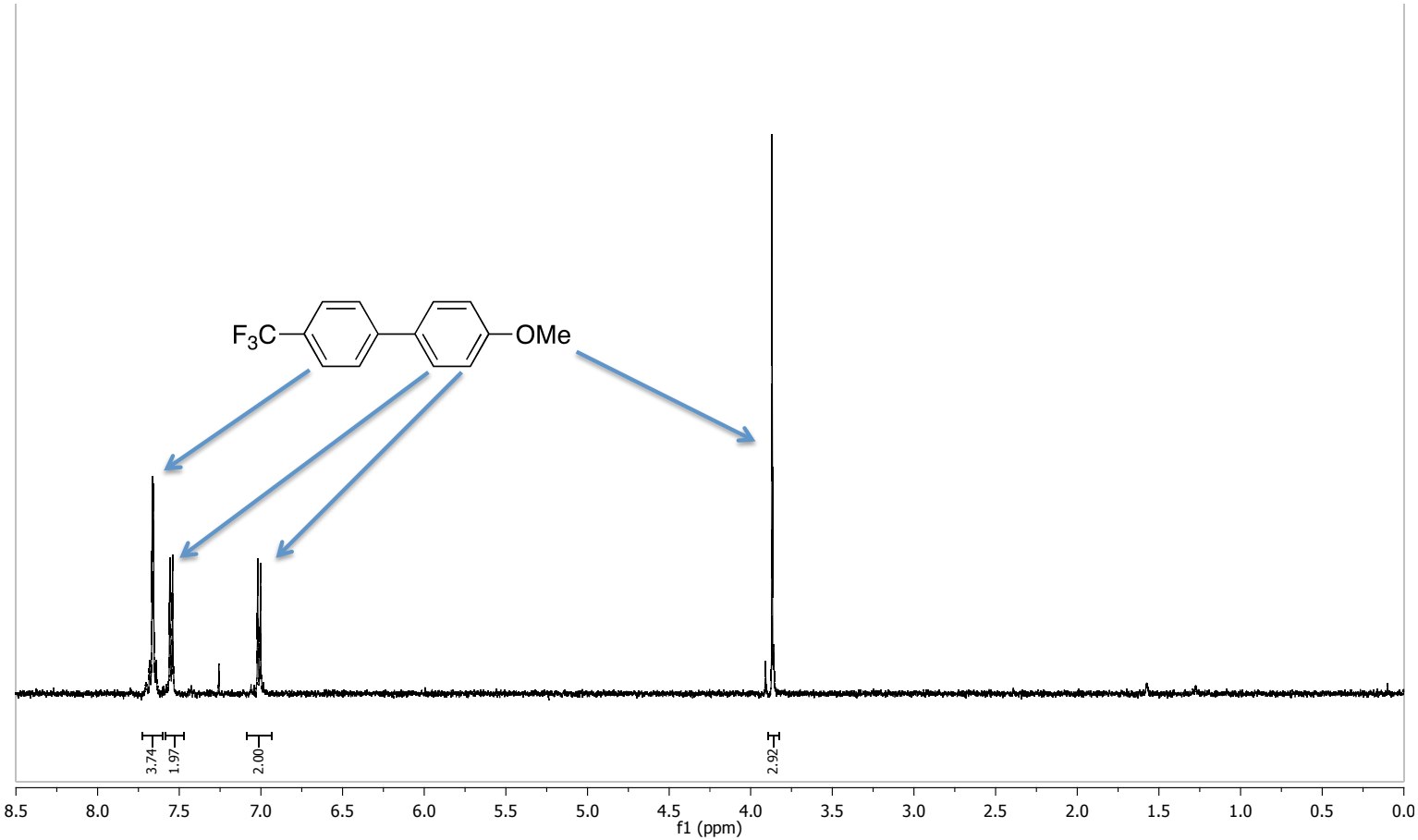


3- NMR spectra of cross-coupling products.



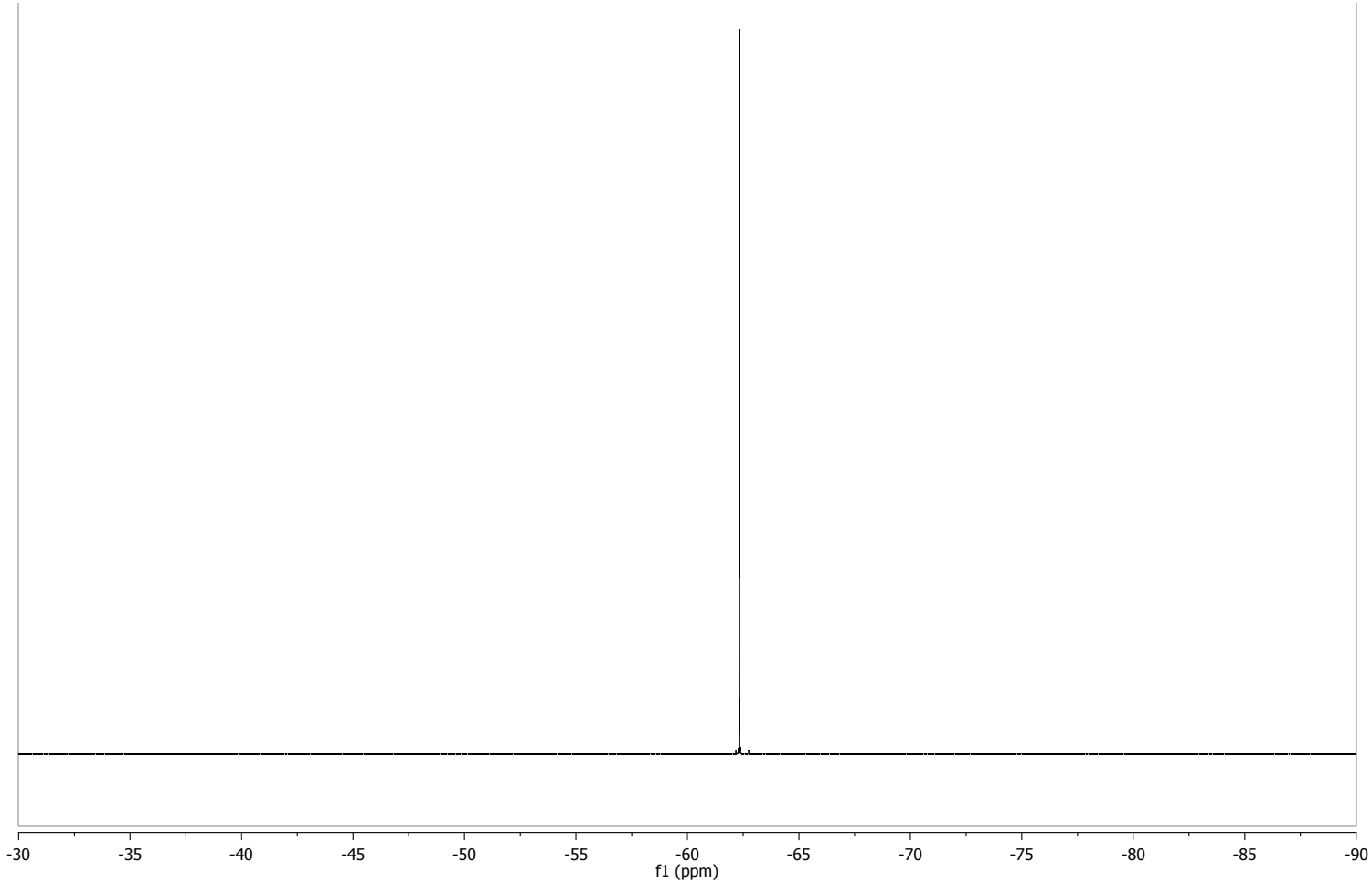
3- NMR spectra of cross-coupling products.

^{1}H NMR spectrum of the isolated *p*-$CF_3C_6H_4$-C_6H_4*p*-OMe (Entry 1, Table 3) in $CDCl_3$



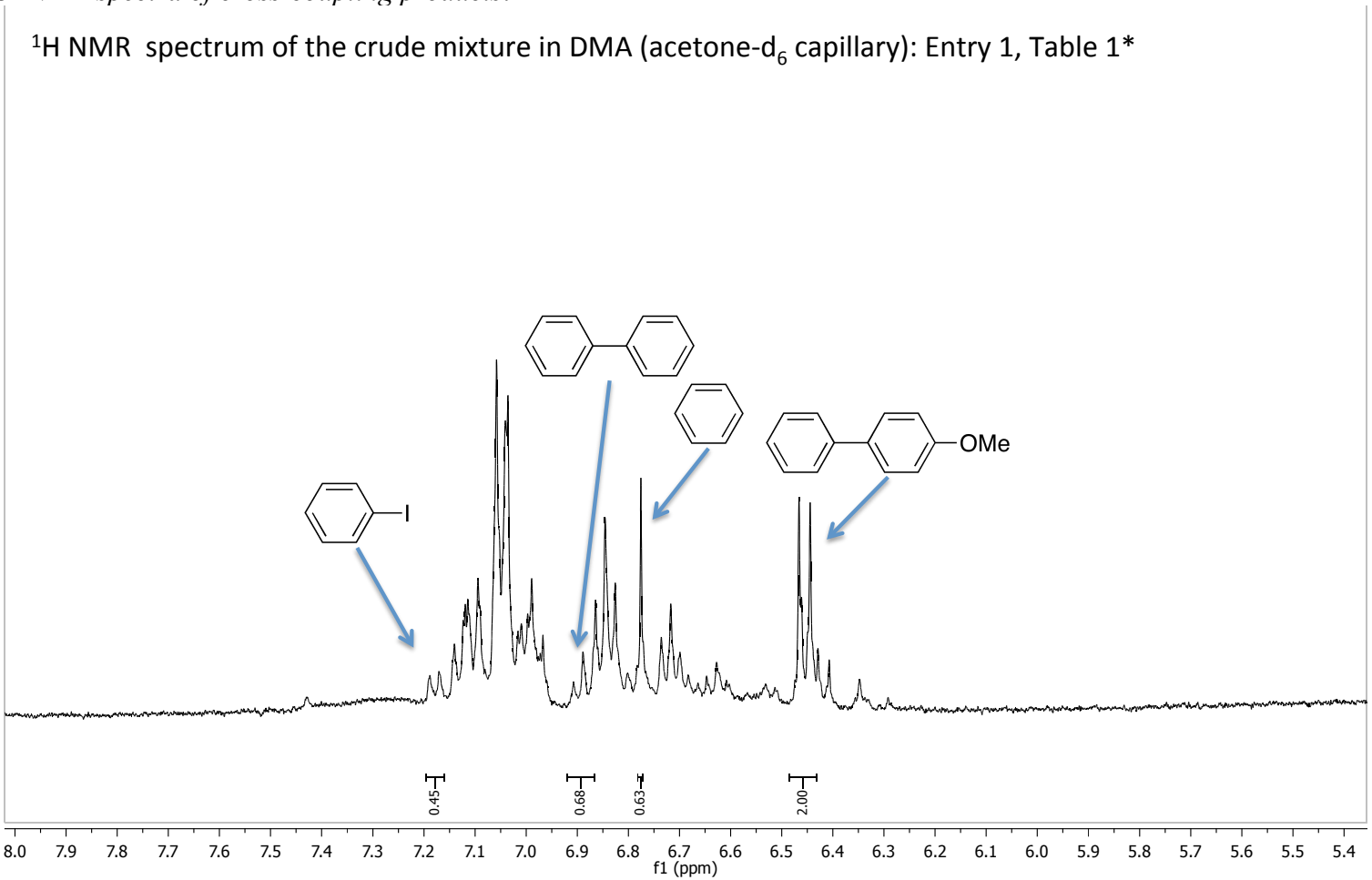
3- NMR spectra of cross-coupling products.

^{19}F NMR spectrum of the isolated *p*-$CF_3C_6H_4$-C_6H_4*p*-OMe (Entry 1, Table 3) in $CDCl_3$



3- NMR spectra of cross-coupling products.

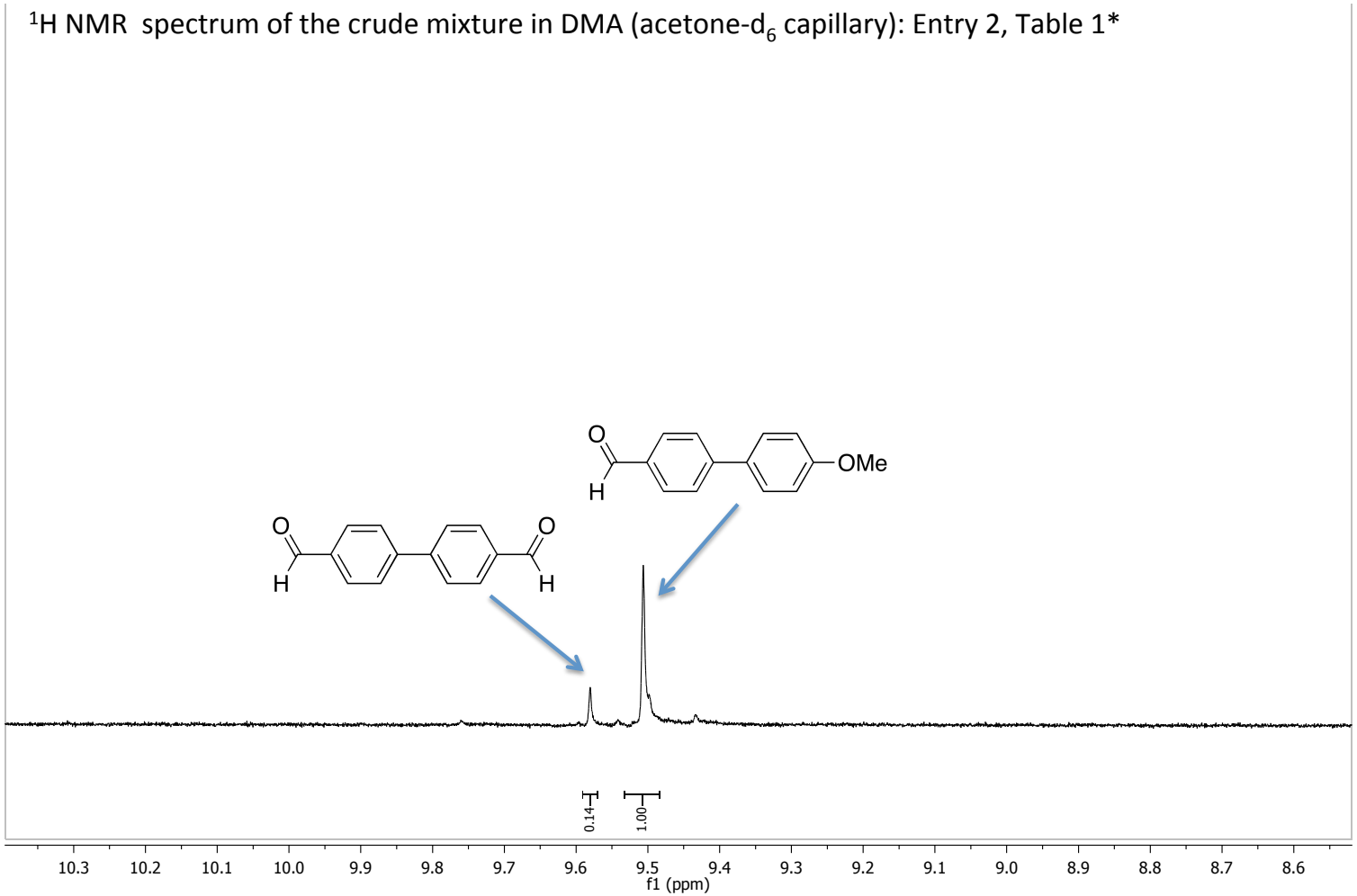
^{1}H NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 1, Table 1*



* Only the signals used for quantification are labeled

3- NMR spectra of cross-coupling products.

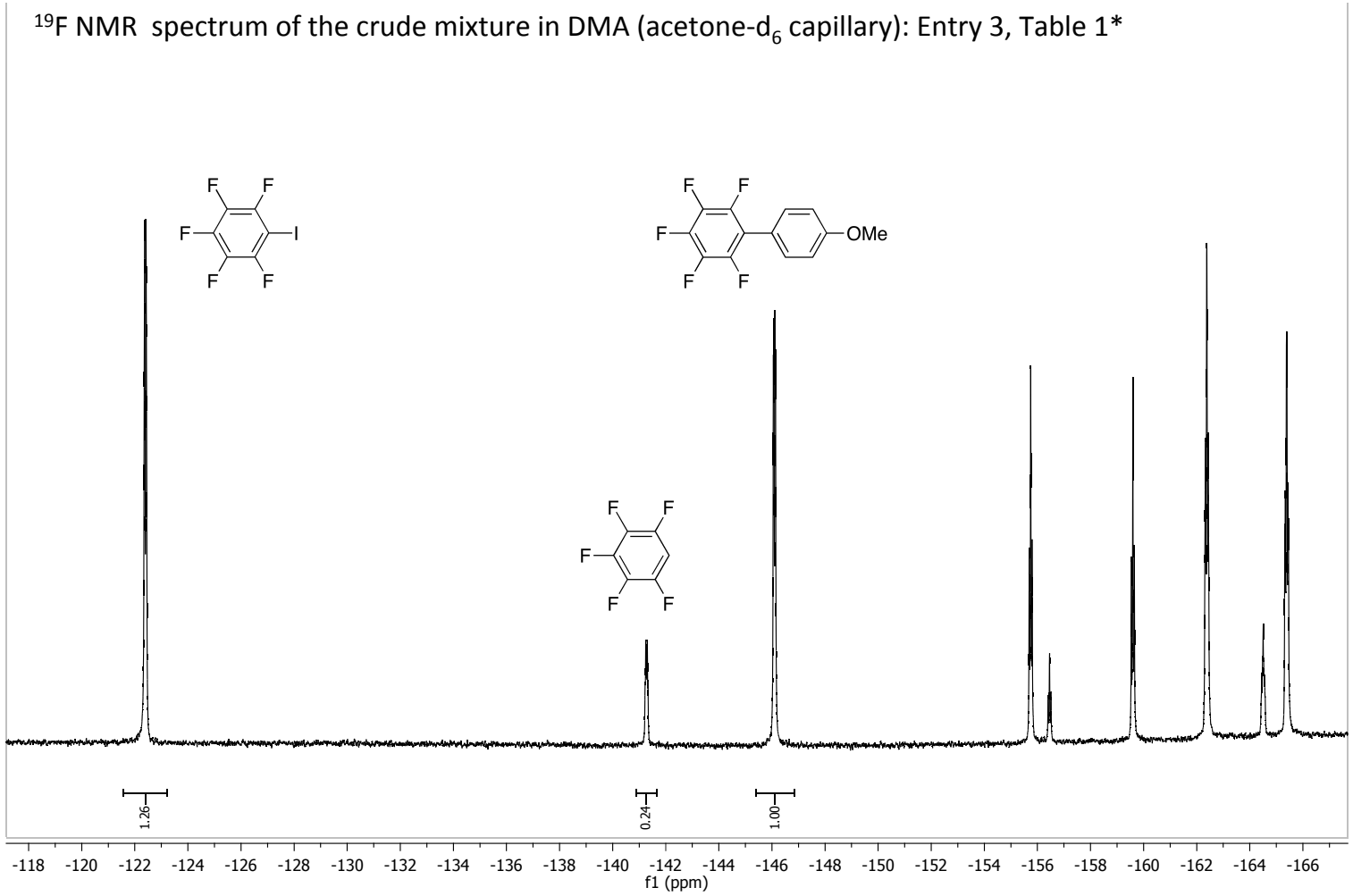
^{1}H NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 2, Table 1*



* Only the signals used for quantification are shown

3- NMR spectra of cross-coupling products.

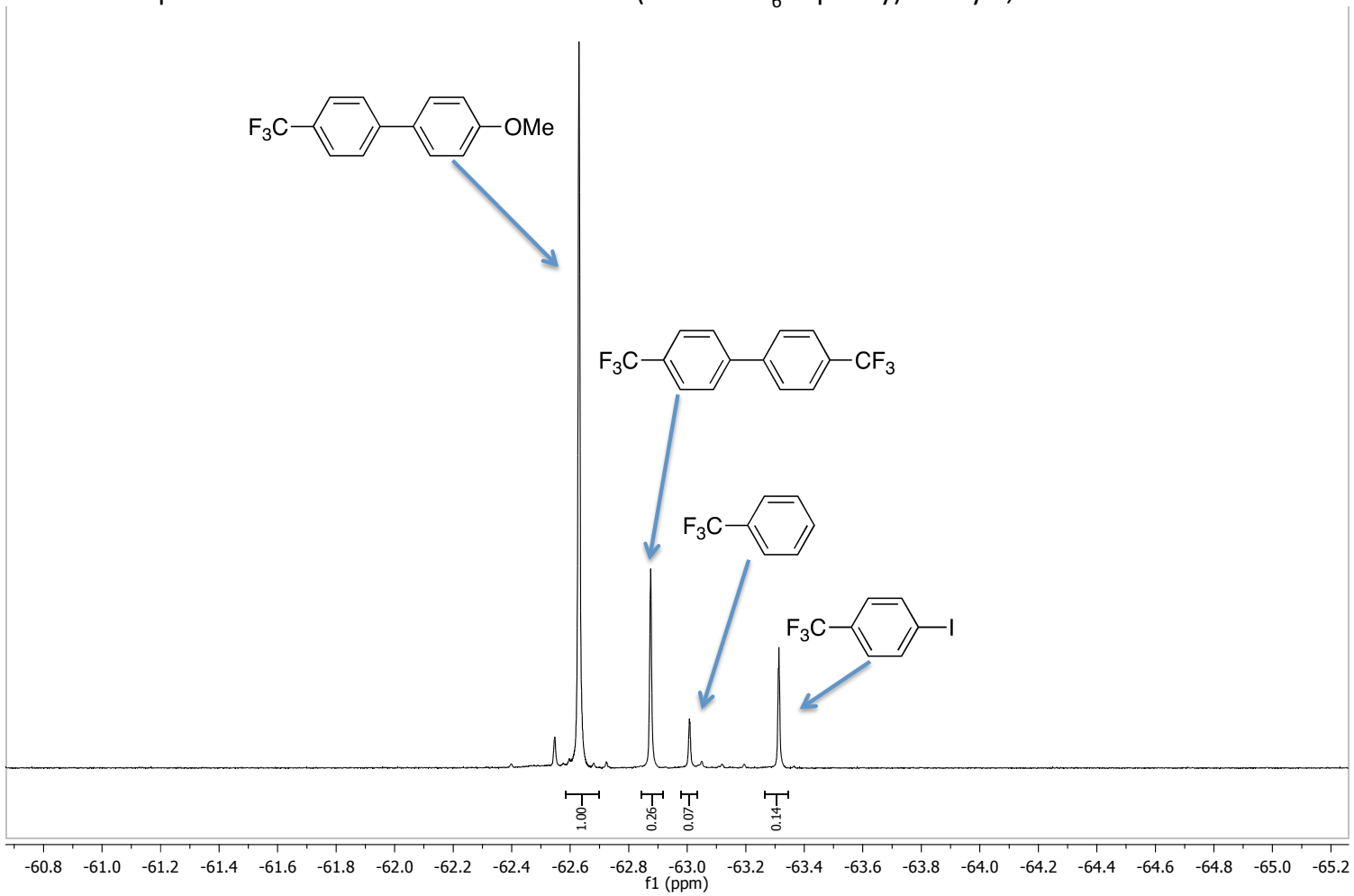
^{19}F NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 3, Table 1*



* Only the signals used for quantification are labeled

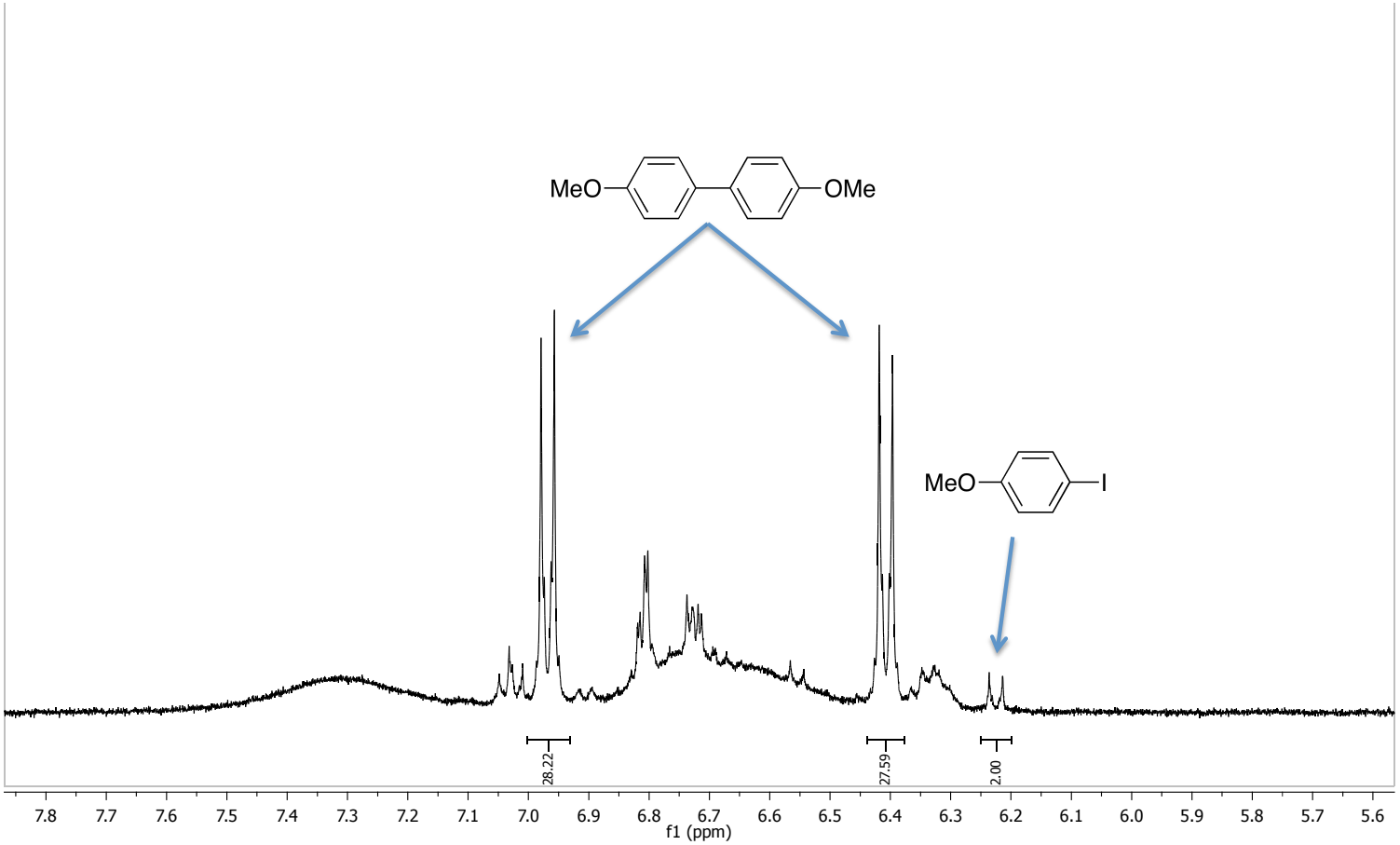
3- NMR spectra of cross-coupling products.

^{19}F NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 4, Table 1



3- NMR spectra of cross-coupling products.

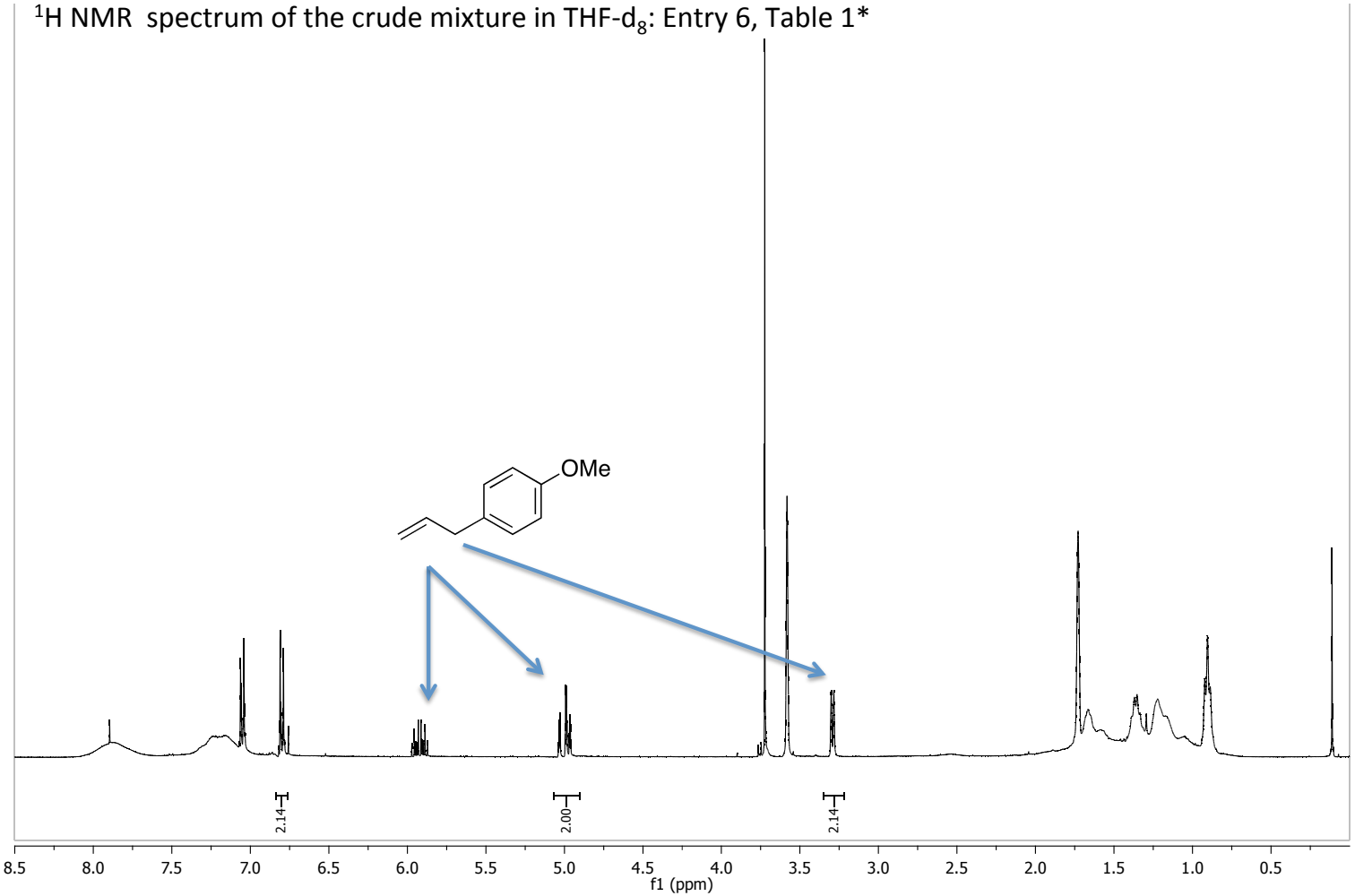
^{1}H NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 5, Table 1*



* Only the signals used for quantification are labeled

3- NMR spectra of cross-coupling products.

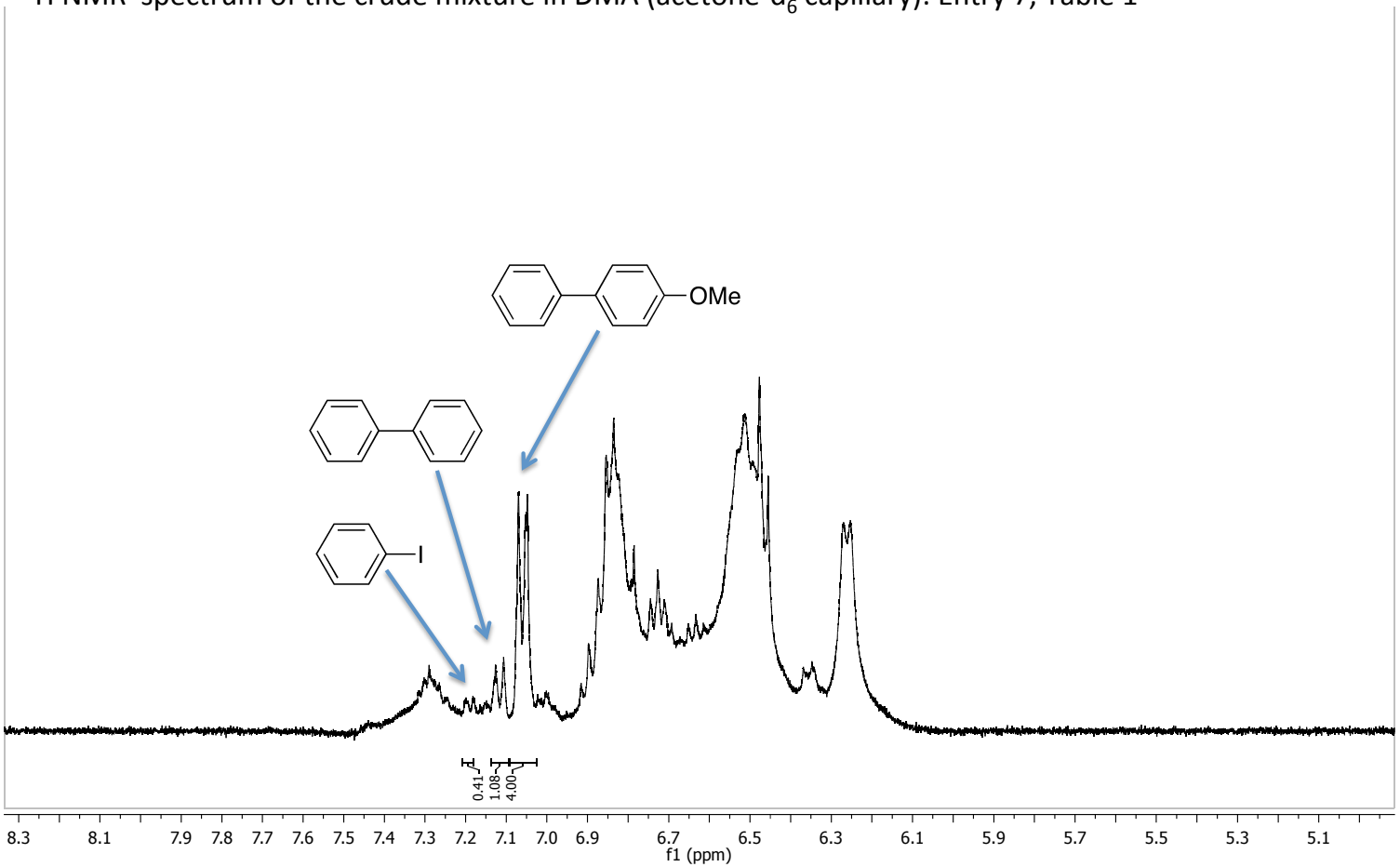
^{1}H NMR spectrum of the crude mixture in THF-d_8: Entry 6, Table 1*



* Only the signals used for quantification are labeled

3- NMR spectra of cross-coupling products.

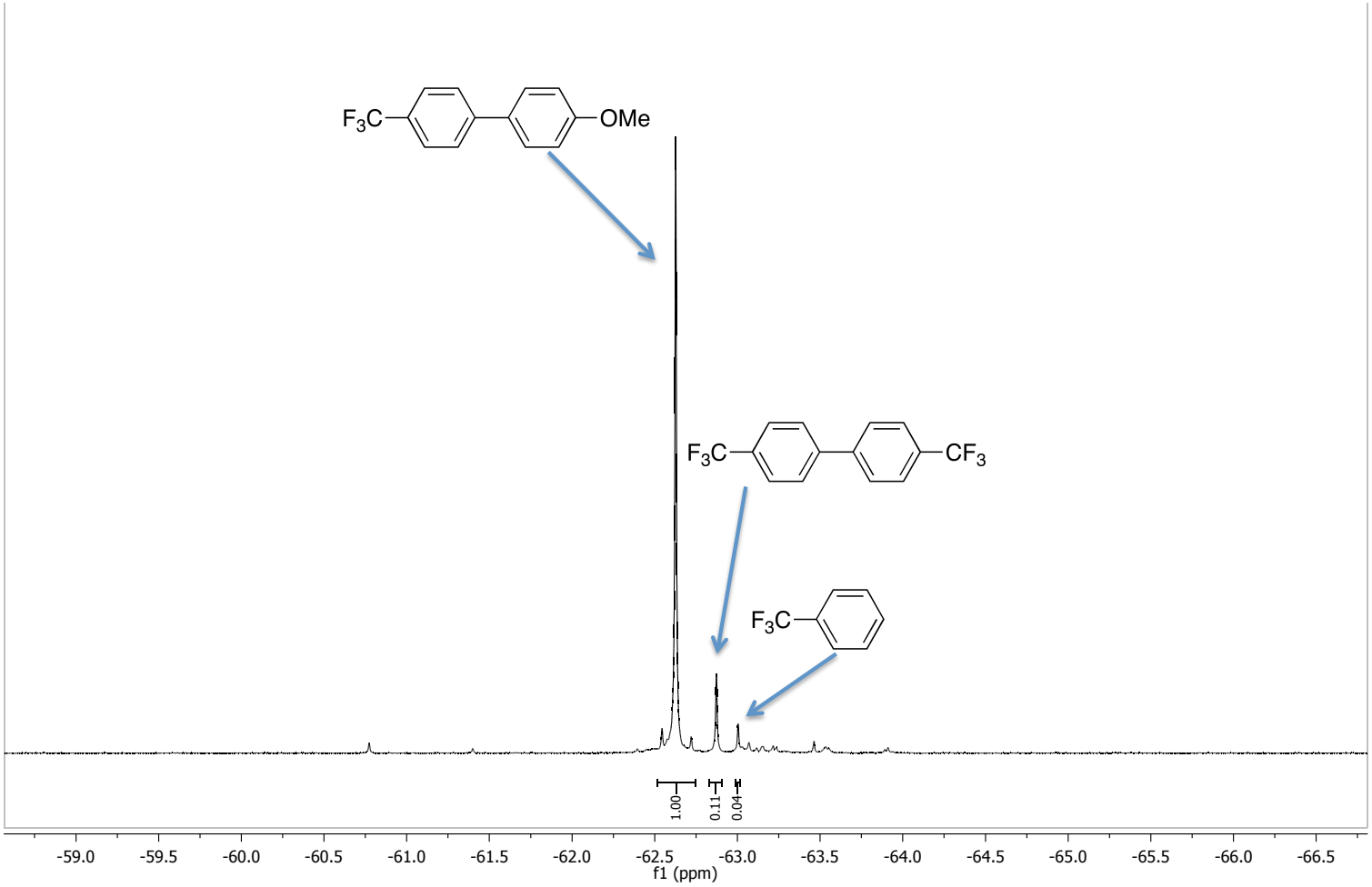
^{1}H NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 7, Table 1*



* Only the signals used for quantification are labeled

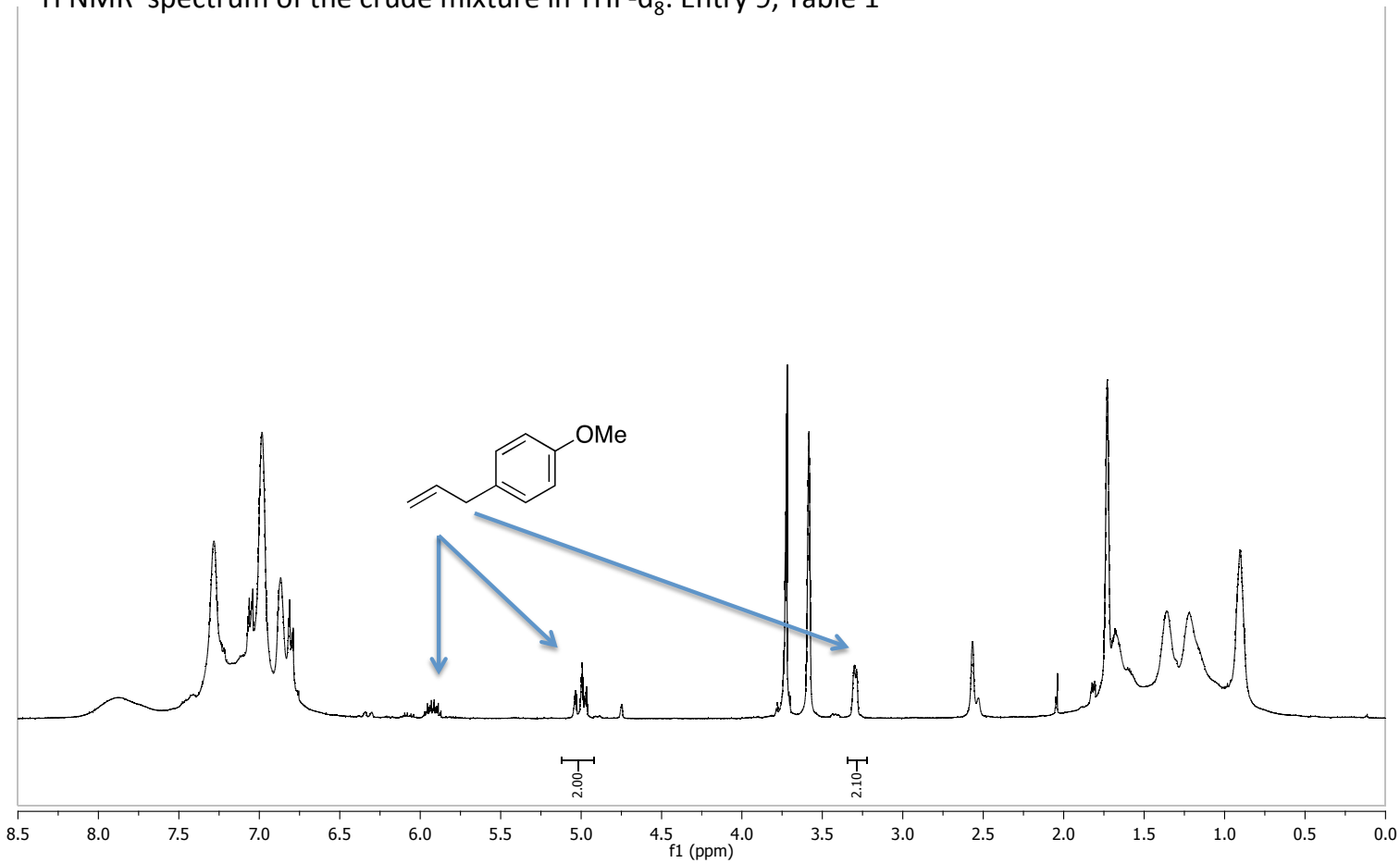
3- NMR spectra of cross-coupling products.

^{19}F NMR spectrum of the crude mixture in DMA (acetone-d_6 capillary): Entry 8, Table 1



3- NMR spectra of cross-coupling products.

^{1}H NMR spectrum of the crude mixture in THF-d_8: Entry 9, Table 1*



* Only the signals used for quantification are labeled