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Supplementary Materials

Tetraalkynylstannanes in the Stille cross coupling reaction: a new effective approach to arylalkynes

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Supplementary Table 1. The results of the optimization experiments

$$\begin{pmatrix} \mathsf{R} - \mathsf{C} \equiv \mathsf{C} \end{pmatrix}_{4}^{\mathrm{Sn}} & \mathsf{Pd} \text{ catalyst, amine} \\ \mathbf{1} & \mathsf{argon, solvent} \\ \mathbf{4} & \mathsf{Ar-Hal} & \mathsf{Hal} = \mathsf{I} \text{ or } \mathsf{Br} \\ \mathbf{3} & \mathsf{R} & \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{Ar} + \mathsf{Sn}\mathsf{Hal}_{4} \\ \mathbf{4} & \mathsf{and} / \mathsf{or} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathbf{5} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathsf{R} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathsf{R} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathsf{R} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} & \mathsf{R} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} \\ \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} \\ \mathsf{R} - \mathsf{R} \mathsf{R} - \mathsf{R} - \mathsf{R} - \mathsf{R} \\ \mathsf{R} - \mathsf{R}$$

Unless otherwise stated, the reaction conditions were as follows: tetraalkynylstannane **1** (0.038 mmol), aryl halide **3** (0.153 mmol), a catalyst (5 mol % with respect to aryl halide **3**), an amine (0.153 mmol) and the corresponding solvent (2 mL). The yields were determined by GCMS, except for the values marked with stars(*) which are isolated yields

No	Acetylene 1	Aryl Halide 3	Solvent	Catalyst (and amine, if any)	Temp. °C	Time, h	Yield of 4 , %	Yield of diacetylene by- product 5 , %
1	(DhC=C) Sp 1a	4-NO ₂ C ₆ H ₄ -I 3d	dioxane	$Pd(PPh_3)_2Cl_2$	80	2,5	0	4
1		4-NO ₂ C ₆ H ₄ -I 3d	dioxane	$Pd(PPh_3)_2Cl_2$	80	4,5	0	4
2	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	PhMe	$Pd(PPh_3)_2Cl_2$	80-100	3,5	0	8,7
3	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	PhMe	$Pd(PPh_3)_2Cl_2 + PPh_3$	80	2,5	0	10
1	(Ph(=C), Sn 1a)	4-NO-C.H. 1 3d	DhMo	Dd(DDb.).Cl. Ft.N	80	3	13	9,5
- T	(1 IIC=C)4511 1a	4-110206114-1 Ju	I IIIvic	1 u(1 1 113)2012, Bu31	80	12	14	9
					80	3	68	2
5	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	Pure Et ₃ N	Pd(PhCN) ₂ Cl ₂	80	5	76	2,5
					80	12	83	2,6
6	(Dh(-C), Sn 1a)	4 NO.C.H. 12d	Duro Et. N	Dd(DDh.).Cl.	80		97	3
0		4-NO2C6114-1 3u	Fulle Etgin	Fu(FFII3J2CI2	80	2,5	95,5	4,5
7	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	Pure Et ₃ N	$Pd(PPh_3)_2Cl_2 + PPh_3$	80	3,5	2	2
					80	0,25	0	0
					80	0,5	4	0
					80	1	17	0
8	(PhC≡C)₄Sn 1a	4-MeC ₆ H ₄ -I 3b	Pure Et ₃ N	$Pd(PPh_3)_2Cl_2$	80	2	31	0
					80	3,5	34	1,9
					80	5	41	1,7
					80	11	45	1,5

		N			80	2	0	0
9	(PhC≡C)₄Sn 1a	3e	Pure Et ₃ N	$Pd(PPh_3)_2Cl_2$	80	6,5	8	3,5
					80	1	62	9
10	$(\mathbf{D} \mathbf{h} \mathbf{C} - \mathbf{C}) \in 1$		$DhM_{2} \to N(1,1)$	$\begin{array}{c c} \text{Me-Et}_{3}\text{N} (1:1) & \text{Pd}(\text{PPh}_{3})_{2}\text{Cl}_{2} & \begin{array}{c} 8 \\ 8 \\ 8 \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\$	80	2	76	9
10	$(PIIC=CJ_4SII Ia$	4-NU ₂ U ₆ н ₄ -1 30	PIME-EL ₃ N $(1:1)$	$Pu(PPII_3)_2 CI_2$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	9		
					80	6	79	9
					75	2	70	3,5
					75	3	81	4,5
11	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	Pure Et ₃ N	$Pd(PPh_3)_2Cl_2$	75	5	87	4
					75	8	89	4
					75	16	95	4
					75	3	0	3
12	(Dh(-C)) So 10	4 NO C H 1 2 d	Duro Et NU	Dd(DDh) Cl	75	5	4	5
12		4-NO2C6H4-1 3U	Pule El2NH	Fu(FFII3J2CI2	75	9	42	6,5
					75	16	34	6,5
					75	1	0	5
12	(Ph(=C), Sn 1a)	4-NO.C.H. 1 3d	PhMe, DABCO	Dd(DDh.).Cl.	75	2	17	8,5
15	(1 IIC=C)4511 1a	4-100206114-1 Ju	(0,018г)	1 u(1 1 113J2C12	75	3	23	8,5
					75	9,3	20	7
					75	1	50	9,5
					75	2	52	9,5
14	(Ph(=C), Sn 1 a)	4-NO ₂ C, H, _I 3d	PhMe, DABCO	Pd(PPh_)_Cl	75	3	55	9,5
17	(1110–0)4511 1a	H -110206114-1 Ju	(0,15г)	1 u(1 1 113)2C12	75	5	52	10
					75	9,5	53	9,5
					75	16	55	9,5
					80	0,5	49	3,4
15	(PhC=C), Sn 1 a	4-NO ₂ C2H2-1 3d	Duro EtaN	Pd(PPh_)_Cl_	80	1	84	1,7
15	(1 IIC=C)4511 1a	4-100206114-1 Ju	I UIE Etgin	1 u(1 1 113)2C12	80	2	91	5,2
					80	3	93	6,6
				Dd(DDh.).Cl	80	0,5	81	9
16	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	THF	DARCO	80	1	87	8
		I Ia 4-NO ₂ C ₆ H ₄ -I 3u Pure F n 1a 4-NO ₂ C ₆ H ₄ -I 3d Pure E n 1a 4-NO ₂ C ₆ H ₄ -I 3d PhMe, D n 1a 4-NO ₂ C ₆ H ₄ -I 3d PhMe, D n 1a 4-NO ₂ C ₆ H ₄ -I 3d PhMe, D n 1a 4-NO ₂ C ₆ H ₄ -I 3d PhMe, D n 1a 4-NO ₂ C ₆ H ₄ -I 3d PhMe, D n 1a 4-NO ₂ C ₆ H ₄ -I 3d Pure I n 1a 4-NO ₂ C ₆ H ₄ -I 3d Pure I			80	2	85	9

					80	4	83	10
					80	2	36	8,5
				ן אמטר מ	80	3	42	9
17	(PhC≡C)₄Sn 1a	2-NO ₂ C ₆ H ₄ -I 3k	Pure Et ₃ N	Pa(PPn ₃ J ₂ Cl ₂	80	4	42	9
					80	6	39	8,6
					80	7	40,5	8
18	(PhC≡C)₄Sn 1a	2-IC ₆ H ₄ COOH 31	Pure Et ₃ N	$Pd(PPh_3)_2Cl_2$	80	4	63	40
				Dd(DDh) Cl		0,5	0	0
19	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	THF	$Pu(PPII_3J_2U_2)$	80	2	0	0
				2-methymmuazole		5	0	0
						0,5	0	5,5
				Dd(DDh) Cl		2	4,5	9
20	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	THF	Pu(PPII3J2CI2	80	3	3	4
				isophorone utalilite		5	6,5	8
						7	8,5	8,5
						0,5	0	8,2
				Dd(DDh) Cl		2	11	17
21	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	THF	$Fu(PPII_3J_2UI_2)$ Ft_N	80	3	8	17,5
				E131N		5	20	22
						7	16,5	19
						0,5	67	6
				Dd(DDh) Cl		1	65	4
22	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	dioxane		100	2	75,5	6
				DADCO		3	75	5
						5	73	5
						0,5	0	0
22	(Ph(=C), Sn 1a)	4-NO-C.H. 1 3d	diovano	$Pd(PPh_3)_2Cl_2$	100	1	0,02	5,5
23		4-NO ₂ C ₆ 114-1 Ju	uloxalle	2-methylimidazole	100	2	0	-
						5	0	-
				Dd(DDh) Cl		1	8	3
24	(PhC≡C)₄Sn 1a	\equiv C) ₄ Sn 1a 4-NO ₂ C ₆ H ₄ -I 3d	dioxane	$Pd(PPh_3)_2Cl_2$	100	2	27	4
24				isophorone diamine		3	38	4

						5	63	4,5
						7	75	5
						8	81	5
						9	86	5
						1	18	4
25	(DhC-C) Cr 1a		diawana	$Pd(PPh_3)_2Cl_2$	100	2	44	6
25	$(PIIC=CJ_4SII \mathbf{1a})$	$4 - NO_2 C_6 H_4 - I 30$	uloxalle	Et ₃ N	100	3	42	7
						5	42	7
				Dd(DDh) Cl		0,5	87	8
26	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	PhMe		100	1	86	9
				DADLU		2	87	8
						1	10,5	7
						2	22	6,5
27	(DhC-C) Sp 1a	4 NO C U L 2 d	DhMo	$Pd(PPh_3)_2Cl_2$	100	3	36	7
27		4-NO ₂ C ₆ Π ₄ -1 3u	PIIMe	Isophorone diamine	100	5	39	6
						7	54	7
						9	50	6
						1	23	14
						2	22	11
20	(Dh(-C) Sn 1)	4 NO C H 12d	DhMo	$Pd(PPh_3)_2Cl_2$	100	3	18	12
20		4-NO ₂ C ₆ 114-1 Ju	FIIME	Et ₃ N	100	5	27	14
						7	28	15
						9	24	14
						1	17	8
						2	26,5	8
20	(Dh(-C) Sn 1)	4 NO C H 12d	DhMo	$Pd(PPh_3)_2Cl_2$	100	3	44	9
29		4-NO ₂ C ₆ 114-1 Ju	FIIME	Et ₂ NH	100	5	50	10
						7	55	10
						9	53	9
				Dd(DDb) ርነ		2	63	2
30	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	dioxane	N mothylmorpholing	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1,8		
30				in-methymnol phonne		5	66	2

				Pd(PPh_)_Cl_		2	0	1
31	(PhC≡C) ₄ Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	dioxane	pyridine	100	3	0	1.3
				FU -		0,5	78	5
						2	78	7
32	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	dioxane	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	8			
				DABCO		5	71	9,5
						7	73	9
						0,5	47	2
						1	70	3
22	(Dh(-C) Sn 1a)	4 NO C H I 2d	diovana	$Pd(PPh_3)_2Cl_2$	100	2	79	2
55	$(FIIC=C)_4$ SII Ia	4-110206114-1 3u	uloxalle	Et ₂ NH	100	3	84	2
						5	82	2
						7	79	3
						0,5	33,5	2
						1	54	4
34	(PhC=C), Sp 12	4-NO-C.H. I 3d	diovano	$Pd(PPh_3)_2Cl_2$	100	2	52	3
54	(1 IIC=C)4511 1a	4-110206114-1 3u	uloxalle	morpholine	100	3	56	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
						5	57	4
						7	69	5
						0,5	87	4
25	(PhC=C). Sn 1 2		FtOAc	$Pd(PPh_3)_2Cl_2$	80	1	88	4
55	(1 IIC=C)4511 1a	4-110206114-1 Ju	LUAL	DABCO	00	2	88,6	4
						3	85	4
						1	7	0
						2	52	1
36	(PhC=C), Sp 12	4-NO-C.H. I 3d	FtOAc	$Pd(PPh_3)_2Cl_2$	80	3	72	1
30	(1 IIC=C)4511 1a	4-110206114-1 3u	LUAL	Et ₂ NH	00	5	81	1
						7	88	1
						9	91	1
				Pd(PPh.).Cl.		1	27	3
37	(PhC≡C)₄Sn 1a	a $4-NO_2C_6H_4-I$ 3d	EtOAc	Pd(PPh_3)_2Cl_2 Et_2NH100Pd(PPh_3)_2Cl_2 morpholine100Pd(PPh_3)_2Cl_2 DABCO80Pd(PPh_3)_2Cl_2 DABCO80Pd(PPh_3)_2Cl_2 Et_2NH80Pd(PPh_3)_2Cl_2 Et_2NH80	80	2	36	3
						3	25	2

						5	28	5
						0,5	40	4
20			$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4				
38	(PhC≡C) ₄ Sn 1a	4-NU₂C ₆ H₄−I 3α	EtUAc	Et3N	80	2	87	4
						3	86,5	5
						1	57	6
39	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	MeCN		85	2	51	6
				DABCO		5	63	6,5
				Dd(DDh) Cl		1	44	4
40	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	MeCN	N mothylmorpholino	85	2	58	4,5
				N-methymioi phomie		5	57	5
				Dd(DDh) Cl		1	58	13
41	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	MeCN	Fu(FH3J2CI2) Et.N	85	2	59	14
				E131N		5	68	13
				Pd(PPh_)_Cl		1	78	6
42 (F	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	MeCN	Ft _o NH	85	2	79,5	7
						5	89	6
				Pd(PPh_)_Cl		1	83	6
43	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc		125	2	87	5
				DIIDCO		5	89	10,5
44	(PhC=C), Sn 1a	4-NO ₂ C2H4-L 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	125	1	12,5	0
11	(1110–0)4511 Iu	1110206114 150	Duone	N-methylmorpholine	125	2	5	0
				Pd(PPh _a) _a Cl _a		1	90	1,5
45	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	BuOAc	Ft_2N	125	2	98	2
						5	98	2
				Pd(PPh ₂) ₂ Cl ₂		0,5	83	6
46	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	BuOAc	Et ₂ NH	125	1	98,3	1,7
						2	98	2
						1	0	0
47	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	Et ₂ O	Pd(PPh ₃) ₂ Cl ₂ DABCO	35	2	10	3
.,	(1 110-0)4011 14	$\mathbf{a} \qquad 4 \cdot \mathrm{NO}_2 \mathrm{C}_6 \mathrm{H}_4 - \mathrm{I} 3 \mathbf{d}$	Et ₂ U			3	47,5	5
						5	70,6	5,7

						7	71,7	6
						1	0	0
48	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	Et_2O	Pu(PPII ₃ J ₂ CI ₂	35	3	0	0
				N-methymnorphonne		5	0	0
						1	0	0
49	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	Et_2O	$Pa(PPn_3)_2Cl_2$	35	3	0	0
				Et3N		5	0	3
						1	0	0
50	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	Et_2O	$Pa(PPn_3)_2Cl_2$	35	3	0	0
				El ₂ NH		5	0	0
						0,5	60	4
F 1	$(\mathbf{D}\mathbf{h}\mathbf{C}-\mathbf{C})$ $\mathbf{C}\mathbf{n}$ 1		DOA-	$Pd(PPh_3)_2Cl_2$	100	1	55	5
51	(PnC≡CJ ₄ Sn Ia	4-NU ₂ U ₆ H ₄ −I 3α	BUOAC	DABCO	100	2	68	5
						5	63	6
						0,5	71	2
						1	77	3
52	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pa(PPn_3)_2Cl_2$	100	2	76	2
		_ • -		Et ₃ N		5	85	2
						7	89	11
						0,5	13	1
53	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pa(PPn_3)_2Cl_2$	100	1	81	2
				El ₂ NH		2	98	2
						2	62	1
54	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pa(PPn_3)_2Cl_2$	100	3	58	1,5
				piperiaine		5	52	3
						2	14	2,5
55	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pd(PPn_3)_2Cl_2$	100	3	25	2
				PnCH ₂ NH ₂		5	41	3
F۲	$(\mathbf{D} \mathbf{h} \mathbf{C} - \mathbf{C}) \mathbf{C} \cdot \mathbf{A} =$			$Pd(PPh_3)_2Cl_2$	100	2	0	0
56	(Pnc≡cJ₄Sn Ia	4-NU2U6H4−I 30	BUUAC	H ₂ NCH ₂ CH ₂ NH ₂	100	3	0	0
F 7	$(\mathbf{D} \mathbf{h} \mathbf{C} - \mathbf{C}) \mathbf{C} \cdot \mathbf{A} =$			Pd(PPh ₃) ₂ Cl ₂	100	1	53	4
57	$(Pnl=lJ_4Sn \mathbf{1a})$	4-NU ₂ U ₆ H ₄ -I 30	BUOAC	Bu ₃ N	100	2	93	3

						3	97	3		
						0,5	41	2		
						2	55	3		
58	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	dioxane	Pu(PPII ₃ J ₂ Cl ₂	100	3	46	3		
				piperiume		The pro	The product of piperidine alkylation			
						was formed in up to 48,5% yield				
						0,5	6	6		
						2	32	8		
59	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	dioxane	$Pd(PPh_3)_2Cl_2$	100	3	33	7		
				PIICH ₂ INH ₂		5	56	7		
						The unic	lentified by-	product is formed		
						0,5	0	0		
						2	10	1,7		
60	60 (PhC≡C)₄Sn 1a	4 NO C II I 2 4	diovana	$Pd(PPh_3)_2Cl_2$	100	3	23	2		
60	$(PIIC=CJ_4SII \mathbf{Ia})$	4-NU ₂ U ₆ П ₄ -1 3U	uloxalle	(PhCH ₂) ₂ NH	100	5	26	2		
						Significa	ant amounts	of dibenzyl were		
							detect	0 1,7 2 2 its of dibenzyl were ected 2 2,4 2,4 2,4 2,4 2		
						1	72	2		
61	(Dh(-C) Sn 1a)	4 NO C H I 2d	diovana	$Pd(PPh_3)_2Cl_2$	100	2	86	2,4		
01		4-NO ₂ C ₆ Π ₄ -1 3u	uloxalle	Bu ₃ N	100	3	87	2,4		
						5	89	2		
						1	64	4		
62	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	PhMe	Pu(PPII3J2CI2	110	3	46,5	5		
				piperiume		5	49	6		
				Dd(DDh) Cl		1	3,4	10		
63	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	PhMe	$Pu(PPII_3)_2U_2$ (DbCH_)_NH	110	3	11	10,6		
						5	8	14		
						1	21	9		
64	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	PhMe	$Pu(PPII_3)_2U_2$	110	3	28	9,5		
				DU3IN		5	31	10		
65	$(Dh(-C)) \leq 12$		DhMo	$Pd(PPh_3)_2Cl_2$	110	1	16,6	11		
05	(FIIC=CJ45II Ia	4-NU2U6H4-1 3U	FIIMe	PhCH ₂ NH ₂	110	2	24	10,5		

						3	35	10
						5	43	11
						0,5	5	0,6
						1	43	1,6
						2	79	2
	$(Dh(-C)) \leq 1c$	2 NO C II I 21-	D ₁ OAa	$Pd(PPh_3)_2Cl_2$	100	3	74	2
66	$(PIIC=CJ_4SII Ia$	$2-NO_2C_6\Pi_4-I$ 3K	BUOAC	Et ₂ NH	100	5	77	2
						7	67,5	2
						9	81	2
						10	83	2
						0,5	0	0
						1	3	1
				$Pd(PPh_3)_2Cl_2$		2	19	3,7
67	(PhC≡C)₄Sn 1a	4-МеС ₆ Н ₄ –I 3b	BuOAc	Et ₂ NH	100	3	36	5,6
						5	47	5
						7	45	5,4
						9	54	7
						0,5	0	11,5
						1	0	100
68	(PhC≡C)₄Sn 1a	2-IC ₆ H ₄ COOH 31	BuOAc	$Fu(PPII_3J_2CI_2)$	100	2	0	100
				Et2MI		3	0	100
						5	0	100
						0,5	0	0
						1	0	6
				Dd(DDh) Cl		2	0	18
69	(PhC≡C)₄Sn 1a	4-MeC ₆ H ₄ -Br 3h	BuOAc	$Fu(FFII_3J_2UI_2)$	100	3	0	23
				$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				
						7	8	11
						Up to 57	% of uniden	tified side product
						1	0	0
70	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	BuOAc PdCl ₂ , Et ₂ NH	100	2	0	0
70						3	0	0

						5	10,5	0
						7	13	0
						0,5	_	_
						1	61	0
						2	$\begin{array}{c ccccc} 10,5 & 0 \\ 13 & 0 \\ \hline - & - \\ 61 & 0 \\ 65 & 0 \\ 72 & 0 \\ 66 & 0 \\ 77 & 0 \\ 74 & 0 \\ 53 & 4 \\ 57 & 4 \\ 56,5 & 4,5 \\ 62 & 4 \\ 53,5 & 5 \\ 53,5 & 5 \\ 53,5 & 5 \\ 38 & 0 \\ 46 & 0 \\ 49 & 0 \\ 55 & 0 \\ 60 & 0 \\ 59,5 & 0 \\ 60 & 0 \\ 59,5 & 0 \\ 0 & 1,5 \\ 0,5 & 6 \\ 4,5 & 7 \\ 7 & 10,5 \\ 11 & 9 \\ 11 & 8 \\ 15 & 9,5 \\ 12 & 6,5 \\ 0 & 0 \\$	
71	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$\begin{array}{ c c c c c } PdCl_2, Et_3N & 100 & \hline 0,5 & - & - \\ \hline 1 & 61 & 0 \\ \hline 2 & 65 & 0 \\ \hline 3 & 72 & 0 \\ \hline 5 & 66 & 0 \\ \hline 7 & 77 & 0 \\ \hline 9 & 74 & 0 \\ \hline 9 & 53,5 & 4.5 \\ \hline 4 & 62 & 4 \\ \hline 7 & 53,5 & 5 \\ \hline 9 & 55 & 0 \\ \hline 7 & 60 & 0 \\ \hline 9 & 59,5 & 0 \\ \hline \end{array}$				
						5	66	0
						7	77	0
						9	74	0
						1	53	4
						2	57	4
70	$(Dh(-C)) \leq 1c$	4 NO C U L 2 4	DuOA a	PdCl ₂	100	3	56,5	4,5
12		4-NO ₂ C ₆ Π ₄ -I 3u	DUUAC	DABCO	100	4	62	4
						7	53,5	5
						9	53,5	5
						1	38	0
					$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0		
72	(Dh(-C) Sn 1a)	4 NO C II 1 2 4	BuOAc	PdCl ₂ Bu ₃ N		3	49	0
75		4-1102C6114-1 3u	DUOAC			5	55	0
						7	60	0
						9	59,5	0
						1	0	1,5
71	(PhC=C), Sp 1 a	$A_{-}M_{0}OC_{+}H_{-}Br$ 3i	BuOAc	$Pd(PPh_3)_2Cl_2$	100	2	0,5	6
74	(1 IIC=C)45II 1a	4-MCOC6114-DI 31	DUOAC	Et ₂ NH	100	3	4,5	7
						5	7	10,5
						1	11	9
75	(PhC=C), Sp 1 a	$A_{-}M_{0}OC_{+}H_{-}Br$ 3i	BuOAc	$Pd(PPh_3)_2Cl_2$	100	2	11	8
75	(1110–0)4511 1a	4-MCOC6114-DI 31	DUOAC	DABCO	100	3	15	9,5
						5	12	6,5
				Pd(PhCN) _a Cl _a		0,5	0	0
76	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	BuOAc	$Pd(PhCN)_2Cl_2$ EtaNH	100	1	0	0
70 (FIIC=CJ ₄ 5)		- 2 - 0 - 7		Et2IVII		3	0	0

						5	7	0
						1	14	0
77	$(Dh(-C)) \leq 1c$	4 NO C II I 2 4	DuOA a	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0,3			
//	$(PIIC=CJ_4SII \mathbf{1a})$	4-NU ₂ U ₆ П ₄ -I 3U	DUUAC	Et ₃ N	100	3	72	0
						5	71	1
						1	22	1,7
70	$(\mathbf{D}\mathbf{h}\mathbf{C}-\mathbf{C})$ $\mathbf{C}_{\mathbf{r}}1_{\mathbf{r}}$		DOA -	Pd(PhCN) ₂ Cl ₂	100	3	43,5	1,8
78	$(PnC=CJ_4Sn \mathbf{1a})$	4-NU ₂ U ₆ H ₄ -1 30	BUOAC	Bu ₃ N	100	5	50	1,5
						7	48,5	3
						1	56	4
79	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pa(PnLNJ_2LI_2)$	100	3	50,5	3,4
				DABCO		5	51	4
	(D, OCH, C-C)					1	9	0
80	$(tBuOCH_2C\equiv C)_4Sn$	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pa(PPn_3)_2Cl_2$	100	2	32,5	0
	1e			Et ₂ NH		3	26,5	0
						1	73,6	5
01	$(tBuOCH_2C\equiv C)_4Sn$		DOA -	$Pd(PPh_3)_2Cl_2$	100	2	72	5,5
81	1e	$4 - NO_2 C_6 H_4 - I 30$	BUOAC	DABCO	100	3	69	5
						5	65	5,5
						0,5	0	0
						1	0	0
02	$(C \cup C = C) \subseteq 1_{\mathbf{z}}$		DOA -	$Pd(PPh_3)_2Cl_2$	100	3	11,6	0
82	$(C_8H_{17}C=C_4SH \mathbf{1g})$	4-NU ₂ U ₆ H ₄ -1 30	BUOAC	Et ₂ NH	100	5	30	0,8
						7	50	1
						9	47	6
						1	35,6	6,6
02	$(C \cup C = C) C = 1_{C}$		Du O A a	$Pd(PPh_3)_2Cl_2$	100	3	45	5,5
83	$(L_8H_{17}L=L_4SH Ig$	4-NU ₂ U ₆ H ₄ -1 30	BUOAC	DABCO	100	5	52	7
						Another	by-product	was also detected
04	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	DuOAa 15 ml	$Pd(PPh_3)_2Cl_2$	100	F	60	n
84	0,25 mmol	1 mmol	DUUAC 15 IIL	Et ₂ NH 1eq, 103 μL	100	5	09	Δ
85	(PhC≡C) ₄ Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	100	6	97	1,2

	0,25 mmol	1 mmol	15 mL	Et ₂ NH 145eq, 12 mL			86.4*	
86	(PhC≡C)₄Sn 1a	2-Br-pyridine 3g	BuOAc	Pd(PPh ₃) ₂ Cl ₂ Et ₂ NH 38eq, 9 mL	100	5	14,6*	_
	0,57 mmol	2,28 mmol	1 mL					
87		4-BrC ₆ H ₄ I 3c 0,153 mmol	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₂ NH 57eq, 0,9 mL 10		1	81,8	0
	$(PIIC=CJ_4SII \mathbf{1a})$				100	2,5	84,4	2,4
	0,038 mmoi					4.5	90.5	3,3
	$(\mathbf{D}) (\mathbf{C} - \mathbf{C}) (\mathbf{C} - \mathbf{A})$	4 D C U L 2 -	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₂ NH 57eq, 0,9 mL Pd(PPh ₃) ₂ Cl ₂	100 100	1	80,0	16,4
88	$(PnC=CJ_4Sn \mathbf{Ia})$	$4-BrU_6H_4I 3C$				2,5	83,3	16,7
	0,076 mmol	0,153 mmoi				4.5	84,4	15,6
00	(PhC≡C)₄Sn 1a	2,6-Br ₂ -4-NO ₂ C ₆ H ₄ I	BuOAc			2 5	04.4	2.4
89	0,076 mmol	3j 0,153 mmol	0,1 mL	Et ₂ NH 57eq, 0,9 mL		2,5	04,4	۷,4
90	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	100	4.5	76,3* (52,8% after recrystallization)	
90	0,382 mmol	1,53 mmol	1 mL	Et ₃ N 42eq, 9 mL				
91	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	100	4.5	90.5	3,3
91	0,382 mmol	1,53 mmol	1 mL	Et ₃ N 42eq, 9 mL				
92	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	100	6	96.4	1,5
,,	0,038 mmol	0,153 mmol	0,1 mL	Et ₂ NH 57eq, 0,9 mL				
93	(PhC≡C) ₄ Sn 1a	2-Br-pyridine 3g	BuOAc 0.1 mL	$Pd(PPh_3)_2Cl_2$	100	6.5	72.5	12
,0	0,038 mmol	0,153 mmol		Et ₂ NH 57eq, 0,9 mL	100	0,0	, 2,0	14
94	(PhC≡C) ₄ Sn 1a	$4-NO_2C_6H_4-I$ 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	100	6	70.8*	-
<i>,</i> ,	0,382 mmol	1,53 mmol	0,5 mL	Et ₂ NH 23eq, 4 mL	100			
95	(PhC≡C) ₄ Sn 1a	$4-\mathrm{NO}_{2}\mathrm{C}_{6}\mathrm{H}_{4}-\mathrm{I}\mathbf{3d}$	DMF 2 mL	$Pd(PPh_3)_2Cl_2$	100	6	57.4*	_
	0,382 mmol	1,53 mmol		Et ₂ NH 12eq, 2 mL			- ,-	
96	(PhC≡C) ₄ Sn 1a	PhI 3a	BuOAc 0,5 mL	$Pd(PPh_3)_2Cl_2$	100	6	84,1*	
	0,420 mmol	1,53 mmol		Et ₂ NH 23eq 4 mL				
97	$(PhC \equiv C)_4 Sn \mathbf{1a}$	PhI 3a	DMF, 0,5 mL	$Pd(PPh_3)_2Cl_2$	100	6	88	12
,,	0,042 mmol	0,153 mmol		$Et_2NH 32eq, 0,5 mL$				
98	$(PhC \equiv C)_4 Sn \mathbf{1a}$	Phi 3a	DMF, 2 mL	$Pd(PPh_3)_2Cl_2$	100	3	69*	
	0,401 mmol	1,53 mmol		$Et_2NH IZeq, ZmL$				
99	$(Pn \cup \exists \cup J_4 Sn \mathbf{1a})$	Pni 3a	DMF, 2 mL	$\begin{bmatrix} Fu(FFII_3J_2CI_2) \\ Ft NH I I 2 2 q 2 mI \end{bmatrix} = 100$	100	100 6	68*	
100	$\frac{0,401 \text{ IIIII01}}{(\text{DbC}-\text{C}) \text{ Cr} 12}$			Dd(DDb) Cl	100	2	60	20
100	(Pnu=uj4Sn 1a	4-NU ₂ L ₆ H ₄ -I 3a	DMF, Z ML	$Pa(PPn_3J_2Cl_2)$	100	3	by	52

	0,401 mmol	1,53 mmol		Et ₂ NH 12eq, 2 mL			32*	
101	(PhC≡C)₄Sn 1a 0,401 mmol	4-MeC ₆ H ₄ –I 3b 1,53 mmol	DMF, 2 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₂ NH 12eq, 2 mL	100	6	84 32*	
102	(PhC≡C)₄Sn 1a	PhI 3a, 0,153 mmol	DMF, 0,5 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₃ N 23.4eq, 0,5 mL	100	2,5 3,5	86,6 83,5 84,1	1,8 6,8 9.1
103	(PhC≡C)₄Sn 1a 0,04 mmol	4-MeC ₆ H ₄ –I 3b 0,153 mmol	DMF, 0,5 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₃ N 23.4eq, 0,5 mL	100	2,5 3,5	94,5 92,7 95	2,4 3,7 4,4
104	(PhC≡C)₄Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ –I 3d 0,153 mmol	DMF 0,5 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₃ N 23.4eq, 0,5 mL	100	2,5 3,5 5	88,9 84,8 87	8,8 13,2 13
105	(PhC≡C)₄Sn 1a 0,42 mmol	4-MeC ₆ H ₄ -I 3b 1,53 mmol	DMF 2 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₃ N 9.4eq, 2 mL	100	2	40	30
106	(PhC≡C)₄Sn 1a 0,401 mmol	4-MeC ₆ H ₄ -I 3b 1,53 mmol	DMF 5 mL	Pd(PPh ₃) ₂ Cl ₂ Et ₃ N 23.4eq, 5 mL	100	5	40	20
107	(PhC≡C)₄Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ -I 3d 0,153 mmol	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ , Pr ₂ NH 42,9eq, 0,9 mL	100	0,5 1	90,5 99	1,2 1
108	(PhC≡C)₄Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ –I 3d 0,153 mmol	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 42,9eq, 0,9 mL +2 mg NaBH ₄	100	0,5	91,5	1,5
109	(PhC≡C)₄Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ –I 3d 0,153 mmol	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ i-Pr ₂ NH 41,9eq 0,9 mL	100	0,5 1 2	82,8 94,7 96,4	1,3 0,9 1
110	(PhC≡C)₄Sn 1a 0,04 mmol	4-BrC ₆ H₄I 3c 0,153 mmol	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ i-Pr ₂ NH 41,9eq 0,9 mL	100	0,5 1 2	2 53,3	0,9 1,9 2,6
111	(PhC≡C)₄Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ –I 3d 0,153 mmol	BuOAc 0,98 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:1 21 μL	100	1	99,5	0,5
112	(PhC≡C) ₄ Sn 1a	$4-NO_2C_6H_4-I \mathbf{3d}$	BuOAc 0,9 mL	Pd(PPh ₃) ₂ Cl ₂	100	1	99,2(0,8)	0,8

	0.04 mmol	0.153 mmol		Pr₂NH 1:5 105 µL				
113	(PhC≡C) ₄ Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ –I 3d 0,153 mmol	BuOAc 0,79 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:10 210 μL	100	1	98,8(1,2)	1,2
114	(PhC≡C)₄Sn 1a 0,04 mmol	4-NO ₂ C ₆ H ₄ -I 3d 0,153 mmol	BuOAc 0,16 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:40 0,84 mL	100	1	98,9(1,1)	1,1
115	(PhC≡C)₄Sn 1a 0.04 mmol	4-NO ₂ C ₆ H ₄ –I 3d 0.153 mmol	Pure Pr ₂ NH 1 mL	Pd(PPh ₃) ₂ Cl ₂	100	1	98,3(1,6) 98,3(1,7)	1,6
116	(PhC≡C) ₄ Sn 1a 0,401 mmol	PhI 3a 1,53 mmol	BuOAc 3 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:10 2,1 mL	100	5	86,1*	_
						0,5	27,8	0,3
117	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ –I 3d 0,153 mmol	BuOAc 0,96 mL	Pd(PPh ₃) ₂ Cl ₂ Bu ₃ N 1:1, 36 μL	100	1	51,5	0,1
11/	0,04 mmol				100	2	63,6	1
						4	75,7	2
110	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	$NO_2C_6H_4$ -I 3d Pd(PPh_3)_2Cl_2 0,153 mmol BuOAc 0,82 mL Pd(PPh_3)_2 Ll_2	$Pd(PPh_3)_2Cl_2$	100	0,5	93,9	0,5
118	0,04 mmol	0,153 mmol		100	1	99,5	0,5	
110	(PhC≡C)₄Sn 1a	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	Pd(PPh ₃) ₂ Cl ₂	100	0,5	98,8	0,5
119	0,04 mmol	0,153 mmol	0,64 mL	Bu ₃ N 1:10 365 μL	100	1	99.5	0.5
						0.5	58.5	5
	(PhC=C) ₄ Sn 1a $4-NO_2C_6H_4-$ 0,04 mmol0,153 mm	4-NO ₂ C ₆ H ₄ -I 3d 0,153 mmol	BuOAc 0,1 mL	Pd(PPh ₃) ₂ Cl ₂ Bu ₃ N 1:25 0,91 mL	100	1	72.6	3.6
120						2	78.3	6.7
		-,				4	83,7	9,2
121	(PhC≡C)₄Sn 1a 0,42 mmol	PhI 3a 1,53 mmol	BuOAc 3 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:10 2,1 mL	100	4	78,1*	_
122	(PhC≡C)₄Sn 1a 0,42 mmol	4-MeC ₆ H ₄ –I 3b 1,53 mmol	BuOAc 3 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:10 2,1 mL	100	5	80,7*	-
123	(PhC≡C)₄Sn 1a 0,42 mmol	4-NO ₂ C ₆ H ₄ -I 3d 1,53 mmol	BuOAc 8,85 mL	Pd(PPh ₃) ₂ Cl ₂ TMEDA 1:5 1,15 mL	100	1,3	87,2*	_
124	(PhC≡C)₄Sn 1a 0,42 mmol	4-NO ₂ C ₆ H ₄ -I 3d 1,53 mmol	BuOAc 7,9 mL	Pd(PPh ₃) ₂ Cl ₂ Pr ₂ NH 1:10 2,1 mL	100	1,25	92.9*	_
125	(PhC≡C)₄Sn 1a 0,287 mmol	PhI 3a 1,043 mmol	BuOAc 6 mL	Pd(PPh ₃) ₂ Cl ₂ TMEDA 1:5 782 μL	100	5	68.4*	_

126	(PhC≡C)₄Sn 1a	4-BrC ₆ H ₄ I 3c	BuOAc	$Pd(PPh_3)_2Cl_2$	100	5	80*	_
120	0,287 mmol	1,043 mmol	6 mL	TMEDA 1:5 782 μL	100	5	00	
107	(PhC≡C)₄Sn 1a	4-BrC ₆ H ₄ I 3c	PuOAc 6 ml	$Pd(PPh_3)_2Cl_2$	100	ц	80*	-
127	0,287 mmol	1,043 mmol	BuOAc, 6 mL BuOAc, 6 mL BuOAc BuOAc	Pr ₂ NH 1:10 1,43 mL	100 100 100 100	5	00	
170	(PhC≡C)₄Sn 1a	$4-BrC_6H_4C(0)Me$		$Pd(PPh_3)_2Cl_2$		Ę	65*	
120	0,287 mmol	3o 1,043 mmol		TMEDA 1:5 782 μL		5	03.	-
120	(PhC≡C)₄Sn 1a	2-IC ₆ H ₄ COOEt 3m		$Pd(PPh_3)_2Cl_2$		Г	Q1*	
129	0,287 mmol	1,043 mmol		TMEDA 1:10		5	01	-
120	(PhC≡C)₄Sn 1a	2-NO ₂ C ₆ H ₄ -I 3k		$Pd(PPh_3)_2Cl_2$		25	97.0*	
130	0,287 mmol	1,043 mmol		Pr ₂ NH 1:10		5.5	07.9	-
101	(t-BuOCH ₂ C≡C) ₄ Sn	4-NO ₂ C ₆ H ₄ -I 3d	BuOAc	$Pd(PPh_3)_2Cl_2$	100	55	19.6*	
151	1e		DUUAL	Pr ₂ NH 1:10	100	5.5	40,0	-
		Br						
132	(PhC≡C)₄Sn 1a		BuOAc	$Pd(PPh_3)_2Cl_2$	100	F	Traces	
	0,287 mmol	1,04		Pr ₂ NH 1:10		5	by GC-MS	-
		3 mmol						

2. Synthesis of starting tetraalkynylstannanes 1

Synthesis of tetra(phenylethynyl)tin 1a



A three-necked, round-bottomed flask equipped with a dropping funnel, a reflux condenser, with argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with anhydrous $ZnCl_2$ (2.50 g, 0.018 mol), dry Et_2NH (2.7 g, 0.036 mol) and dry toluene (15 mL). The reaction mixture was heated up to the moment when all the $ZnCl_2$ will react to give a complex compound with Et_2NH (~ 50 °C, 0.25 h). The reaction was carried out under argon. The mixture was allowed to cool to the ambient temperature, and phenylacetylene (1.73 g, 0.017 mol) was added. Then, a solution of 1.67 g (0.0064 mol) of $SnCl_4$ in PhMe (10 mL) was added slowly, dropwise under vigorous stirring. The mixture was stirred for 20 min, then the upper layer was separated and the lower layer was extracted with PhMe. The combined toluene extracts were passed through a column of silanized silica and evaporated in vacuo. The residue was recrystallized from heptane to give a white solid of **1a**. Tetra(phenylethynyl)tin **1a** is a colorless crystalline solid, mp 174 °C, yield was 1,84 g (83%).

IR spectrum, v, cm⁻¹: 2152 (C≡C). ¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.59–7.61 (8H, m), 7.32–7.40 (12H, m). ¹³C NMR (100 MHz, CDCl₃): δ 132.47, 129.37, 128.38, 122.18, 109.78, 85.45. ¹¹⁹Sn NMR (149 MHz, CDCl₃): δ -332.29.

Synthesis of tetra(4-methylphenylethynyl)tin 1b



Tetra(4-methylphenylethynyl)tin **1b** was prepared according to a similar procedure as for **1a**, using 0,017 mol (1,97 g) of 4-(methylphenyl)acetylene, $SnCl_4$ (0,0064 mol, 1,67 g), anhydrous zinc chloride (2.5 g, 0,018 mol), dry diethylamine (2.7 g, 0,036 mol) and dry toluene (15 mL). The yield was 1,73 g (70%), mp 202-203 °C.

IR spectrum, v, cm⁻¹: 2150 (C \equiv C).

¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.49 (2H, m), 7.12 – 7.15 (2H, m), 2.37 (3H, s).

¹³C NMR (100 MHz, CDCl₃): δ 139.60, 132.41, 129.16, 119.22, 109.93, 84.85.

¹¹⁹Sn NMR (149 MHz, CDCl₃), δ, ppm: -322.29.

MS (*m/z*, EI, 70 eV): 579 [M]⁺ (9), 460 (27), 350 (89), 230 (100), 120 (40), 115 (51).

Synthesis of tetra(4-chlorophenylethynyl)tin 1c



Tetra(4-chlorophenylethynyl)tin **1c** was prepared according to a similar procedure as for **1a**, using 0,017 mol of 4-(chlorophenyl)acetylene, $SnCl_4$ (0,0064 mol, 1,67 g), anhydrous zinc chloride (2.5 g, 0,018 mol), diethylamine (2.7 g, 0,036 mol) and toluene (15 mL). The yield was 2,0 g (72%), mp 161 °C.

IR spectrum, v, cm⁻¹: 2154 (C \equiv C).

¹H NMR (400 MHz, CDCl₃): *δ* 7.50 – 7.53 (2H, m), 7.31 – 7.34 (2H, m).

¹³C NMR (100 MHz, CDCl₃): δ 135.75, 133.80, 133.71, 128.86, 120.41, 108.80, 86.00.

MS (*m/z*, EI, 70 eV): 658 [M]⁺ (7), 390 (71), 270 (100), 200 (49), 155 (60), 136 (41), 120(19).

Synthesis of tetra(4-nitrophenylethynyl)tin 1d



A three-necked, round-bottomed flask equipped with a dropping funnel, a reflux condenser, with argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with anhydrous ZnCl_2 (0.66 g, 0.00484 mol), Et_2NH (1 mL, 0.00963 mol) and dry toluene (8 mL). The reaction was carried out under argon. The reaction mixture was heated up to the moment when all the ZnCl_2 will react to give a complex compound with Et_2NH (~ 50 °C, 0.25 h). The mixture was allowed to cool to the ambient temperature, and 4-nitrophenylacetylene (0.00448 mol) was added. Then, SnCl_4 (0.2 mL) was added dropwise under vigorous stirring. The mixture was stirred for 2 h, then the upper layer was separated and the lower layer was extracted with PhMe. The combined toluene extracts were passed through a column of silanized silica and evaporated *in vacuo*. The residue was recrystallized from heptane to give a white solid of **1d**. The product was purified by recrystallization from toluene. Light yellow crystal. mp 150 °C (toluene).

IR spectrum, v, cm⁻¹: 2162.2 (C≡C). ¹H NMR (400 MHz, CDCl₃): δ 8.22 – 8.25 (8H, m), 7.74 – 7.76 (8H, m). ¹³C NMR (100 MHz, CDCl₃): δ 148.11, 133.36, 128.04, 123.80, 108.06, 89.30. ¹¹⁹Sn NMR (149 MHz, CDCl₃): δ -336.76.

Synthesis of tetra(tert-buthoxypropynyl)tin 1e



A three-necked, round-bottomed flask equipped with a dropping funnel, a reflux condenser, with argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with anhydrous $ZnCl_2$ (0.66 g, 0.00484 mol), Et_2NH (1 mL, 0.00963 mol) and dry toluene (5 mL). The reaction was carried out under argon. The reaction mixture was heated up to the moment when all the $ZnCl_2$ will react to give a complex compound with Et_2NH (~ 50 °C, 0.25 h). The mixture was allowed to cool to the ambient temperature, and *t*-buthoxypropyne (0,38 g, 0.003 mol) was added. Then, $SnCl_4$ (0.196 g, 0.00075 mol) was added dropwise under vigorous stirring. The mixture was stirred for 1 h, then the upper layer was separated and the lower layer was extracted with PhMe. The combined toluene extracts were passed through a column of silanized silica and evaporated *in vacuo*. The residue was recrystallized from heptane to give a white solid of **1e**. The yield was 55%. Colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 4.06 (2H, s), 1.20 (9H, s).

¹³C NMR (100 MHz, CDCl₃): *δ* 110.61, 75.62, 68.43, 38.93, 9.44.

¹¹⁹Sn NMR (149 MHz, CDCl₃): δ -344.22 – (-343.64) (m).

IR (CCl₄): 2175 (C≡C)



Tetra(hexyn-1-yl)tin **1f** was prepared according to a similar procedure as for **1a**, using 0,017 mol (1.39 g) of 1-hexyne, $SnCl_4$ (0,0064 mol, 1,67 g), anhydrous zinc chloride (2.5 g, 0,018 mol), dry diethylamine (2.7 g, 0,036 mol) and dry hexane (20 mL). The yield was 1.26 g (67%). Colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 2.20 (2H, t), 1.32 – 1.52 (4H, m), 0.86 (3H, t).

 ^{13}C NMR (100 MHz, CDCl₃): δ 111.40, 75.88, 30.23, 21.69, 19.55, 13.36.

¹¹⁹Sn NMR (149 MHz, CDCl₃): δ -51.51 (m).

IR (CCl₄): 2165 (C≡C).

MS (*m*/*z*, EI, 70 eV): 444 [M⁺] (10), 363 (100), 282 (22), 201 (20), 120 (10).

Synthesis of tetra(decyn-1-yl)tin 1g



A three-necked, round-bottomed flask equipped with a dropping funnel, a reflux condenser, with argon gas inlet tube and a magnetic stirrer was flushed with argon and charged with anhydrous ZnCl_2 (0.54 g, 0.004 mol), Et₂NH (0.8 mL, 0.008 mol) and dry toluene (5 mL). The reaction was carried out under argon. The reaction mixture was heated up to the moment when all the ZnCl₂ will react to give a complex compound with Et₂NH (~ 50 °C, 0.25 h). The mixture was allowed to cool to the ambient temperature, and decyne-1 (0,4 mL) was added. Then, SnCl₄ (0.1 mL) was added dropwise under vigorous stirring. The mixture was extracted with PhMe. The combined toluene extracts were passed through a column of silanized silica and evaporated *in vacuo*. The residue was recrystallized from heptane to give **1g** (yield 51%) as colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 2.18 – 2.24 (2H, m), 1.47 – 1.54 (2H, m), 1.25 – 1.40 (10H, m), 0.84 – 0.87 (3H, m).

¹³C NMR (100 MHz, CDCl₃): δ 111.71, 76.13, 31.90, 29.23, 29.14, 28.90, 28.41, 22.73, 20.14, 14.13.

¹¹⁹Sn NMR (149 MHz, CDCl₃): δ -345.47 (m).

IR (CCl₄): 2164 (C≡C).

The selected spectra of tetraalkynylstannaes 1

IR spectrum (KBr) of tetra(phenylethynyl)tin **1a**



¹H NMR spectrum (300 MHz, CDCl₃) of tetra(phenylethynyl)tin 1a



¹³C NMR spectrum (50 MHz, CDCl₃) of tetra(phenylethynyl)tin **1a**



 119 Sn NMR spectrum (149 MHz, CDCl₃) of tetra(phenylethynyl)tin **1a**



IR spectrum (KBr) of tetra(4-nitrophenylethynyl)tin **1d**



¹H NMR spectrum (400 MHz, CDCl₃) of tetra(4-nitrophenylethynyl)tin 1d



¹³C NMR spectrum (100 MHz, CDCl₃) of tetra(4-nitrophenylethynyl)tin **1d**



 119 Sn NMR spectrum (149 MHz, CDCl₃) of tetra(4-nitrophenylethynyl)tin **1d**





IR spectrum (KBr) of tetra(*tert*-buthoxypropynyl)tin **1e**

240.23 %Transn 1031.92 482 04 30 Wavenue mber (cm-1)

((CH₃)₃COCH₂C=C)₄Sn

¹H NMR spectrum (400 MHz, CDCl₃) of tetra(*tert*-buthoxypropynyl)tin **1e**



¹³C NMR spectrum (100 MHz, CDCl₃) of tetra(*tert*-buthoxypropynyl)tin **1e**



¹¹⁹Sn NMR spectrum (149 MHz, CDCl₃) of tetra(*tert*-buthoxypropynyl)tin **1e**

((CH₃)₃COCH₂C=C)₄Sn



IR spectrum (KBr) of tetra(decyn-1-yl)tin **1g**



 ^1H NMR spectrum (400 MHz, CDCl_3) of tetra(decyn-1-yl)tin 1g



¹³C NMR spectrum (100 MHz, CDCl₃) of tetra(decyn-1-yl)tin **1g**



 119 Sn NMR spectrum (149 MHz, CDCl₃) of tetra(decyn-1-yl)tin ${\bf 1g}$

(C8H17C=C)4Sn



Spectra of acetylenes 4



IR spectrum (KBr) of tolane (diphenyl acetylene) (4aa)

¹H NMR spectrum (400 MHz, CDCl₃) of tolane (diphenyl acetylene) (4aa)



¹³C NMR spectrum (100 MHz, CDCl₃) of tolane (diphenyl acetylene) (**4aa**)



Mass-spectrum (EI, 70 eV) of tolane (diphenyl acetylene) (4aa)





IR spectrum (KBr) of 4-methyltolane (1-methyl-4-(phenylethynyl)benzene) (4ab)

¹H NMR spectrum (400 MHz, CDCl₃) of 4-methyltolane (4ab)



¹³C NMR spectrum (100 MHz, CDCl₃) of 4-methyltolane (**4ab**)



Mass-spectrum (EI, 70 eV) of 4-methyltolane (4ab)



1.15 1.10 Br 1.05 1.00 0.95 -2214.55 MMM 0.90 -2854.99 1649.34 1660.91 0.85 -1909.76 1178.65 -2924.44 0.80 -910.51 470.69 -1113.06 3441.43 028.18 1579.89 0.75 0.70 1441 0.65 0.65 0.60 -3049.83 Lunsur 1.55 σ -1599.18 1392.77 0.50 0.45 0.40 -511.2 1477.65 0.35 0.30 -1006.96 ---1068.69 0.25 -686.74 0.20 0.15 0.10 0.05 2200 2000 1800 Wavenumber (cm-1) 3400 1400 1200 400 3200 3000 2800 2600 2400 1600 1000 800 600

IR spectrum (KBr) of 4-bromotolane (4ac)





¹³C NMR spectrum (100 MHz, CDCl₃) of 4-bromotolane (4ac)



Mass-spectrum (EI, 70 eV) of 4-bromotolane (4ac)



Mass-spectrum (EI, 70 eV) of 4-nitrotolane (4ad)





IR spectrum (KBr) of 4-nitrotolane (4ad)

¹H NMR spectrum (400 MHz, CDCl₃) of 4-nitrotolane (4ad)





IR spectrum (KBr) of 2-bromo-4-nitrotolane (2-bromo-4-nitro-1-(phenyl-ethynyl)benzene) (**4af**)



¹H NMR spectrum (400 MHz, CDCl₃) of 2-bromo-4-nitrotolane (**4af**)



¹³C NMR spectrum (100 MHz, CDCl₃) of 2-bromo-4-nitrotolane (**4af**)



Mass-spectrum (EI, 70 eV) of 2-bromo-4-nitrotolane (4af)



Mass-spectrum (EI, 70 eV) of 2-nitrotolane (4ak)



¹H NMR spectrum (400 MHz, CDCl₃) of 2-nitrotolane (**4ak**)



¹³C NMR spectrum (100 MHz, CDCl₃) of 2-nitrotolane (4ak)



Mass-spectrum (EI, 70 eV) of ethyl 2-(phenylethynyl)benzoate (4am)



IR spectrum (KBr) of ethyl 2-(phenylethynyl)benzoate (4am)



¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 2-(phenylethynyl)benzoate (4am)



¹³C NMR spectrum (100 MHz, CDCl₃) of ethyl 2-(phenylethynyl)benzoate (4am)



IR spectrum (KBr) of 4-(phenylethynyl)benzaldehyde (4an)



¹H NMR spectrum (400 MHz, CDCl₃) of 4-(phenylethynyl)benzaldehyde (**4an**)



¹³C NMR spectrum (100 MHz, CDCl₃) of 4-(phenylethynyl)benzaldehyde (**4an**)



Mass-spectrum (EI, 70 eV) of 4-(phenylethynyl)benzaldehyde (4an)



Mass-spectrum (EI, 70 eV) of 1-[4-(phenylethynyl)phenyl]ethanone (4ao)



IR spectrum (KBr) of 1-[4-(phenylethynyl)phenyl]ethanone (4ao)



 $^1\mathrm{H}$ NMR spectrum (400 MHz, CDCl_3) of 1-[4-(phenylethynyl)phenyl]ethanone (4ao)



¹³C NMR spectrum (100 MHz, CDCl₃) of 1-[4-(phenylethynyl)phenyl]ethanone (**4ao**)





IR spectrum (KBr) of 1-methyl-4-[(4-nitrophenyl)ethynyl]benzene (4bd)

 $^1{\rm H}$ NMR spectrum (400 MHz, CDCl_3) of 1-methyl-4-[(4-nitrophenyl)ethynyl]benzene (**4bd**)



 ^{13}C NMR spectrum (100 MHz, CDCl₃) of 1-methyl-4-[(4-nitrophenyl)ethynyl]benzene (**4bd**)



Mass-spectrum (EI, 70 eV) of 1-methyl-4-[(4-nitrophenyl)ethynyl]benzene (**4bd**)





IR spectrum (KBr) of 1-chloro-4-[(4-nitrophenyl)ethynyl]benzene (4cd)

¹H NMR spectrum (400 nitrophenyl)ethynyl]benzene (**4cd**)







Mass-spectrum (EI, 70 eV) of 1-chloro-4-[(4-nitrophenyl)ethynyl]benzene (4cd)



IR spectrum (KBr) of *tert*-Butyl 3-(4-nitrophenyl)prop-2-ynyl ether (**4ed**)



¹H NMR spectrum (400 MHz, CDCl₃) of *tert*-Butyl 3-(4-nitrophenyl)prop-2-ynyl ether (**4ed**)



¹³C NMR spectrum (100 MHz, CDCl₃) of *tert*-butyl 3-(4-nitrophenyl)prop-2-ynyl ether (**4ed**)



Mass-spectrum (EI, 70 eV) of *tert*-butyl 3-(4-nitrophenyl)prop-2-ynyl ether (**4ed**)



Mass-spectrum (EI, 70 eV) of 1-hex-1-ynyl-4-nitrobenzene (4fd)





IR spectrum (KBr) of 1-hex-1-ynyl-4-nitrobenzene (4fd)

¹H NMR spectrum (400 MHz, CDCl₃) of 1-hex-1-ynyl-4-nitrobenzene (**4fd**)



¹³C NMR spectrum (100 MHz, CDCl₃) of 1-hex-1-ynyl-4-nitrobenzene (**4fd**)

