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Supporting Information

Nickel-Catalyzed Cross-Coupling of Arylchlorides and Aryl Grignard Reagents

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Contents:

General considerations

Materials and methods

Reactions were carried out with standard Schlenk technique under an atmosphere of dry nitrogen. Palladium(II) diacetate and nickel(II) diacetylacetonate were gifts from Degussa-Hüls AG. Phosphines, phosphites and arsines were either obtained from the former Hoechst AG, purchased from Aldrich or Strem, or prepared by literature methods: P(*o*-tol)$_3$,[1] P[*o*-(CF$_3$)C$_6$H$_5$]$_3$,[2] As(*o*-tol)$_3$,[3] P[*o*-(HO)C$_6$H$_5$]$_3$,[4] P[N(*i*Pr)$_2$]$_3$,[5] P(carbazolyl)$_3$ (for analytical

data *vide infra*).[6] Other chemicals were purchased from Fluka and Aldrich and used as received. $Pd_2(dba)_3$ was prepared according to a literature procedure.[7]

Except for work-up of reaction mixtures, catalysis was carried out under an atmosphere of dry nitrogen. THF was dried and deoxygenated according to a literature procedure.[8] All other reagents have not been dried or deoxygenated prior to use. The preparation of the imidazolium salts does not require inert atmosphere or dry solvents.

Physical and analytical methods

NMR spectra (^1H, ^{13}C, ^{31}P) were recorded on a Jeol JMX-GX 400 or a Bruker DPX 400 instrument and are referenced to residual protons in the solvent (^1H), the solvent carbon-13 signal (^{13}C) or 85% H_3PO_4 as an external standard (^{31}P). $^{19}F\{^1H\}$-NMR spectra were recorded on a Bruker DPX 400 and are referenced to trifluoromethylbenzene ($C_6H_5CF_3$) as the external standard. NMR multiplicities are abbreviated as s = singulet, d = doublet, t = triplet, sept = septet, br = broad signal. Coupling constants *J* are given in Hz. GC-MS spectra were measured on a Hewlett Packard gas chromatograph GC 5890 A equipped with a mass selective detector MS 5970 B. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Catalysis yields were generally determined by gas chromatography and the products were identified by comparison to authentic samples: 2-fluorobiphenyl,[9] 2-phenylpyridin,[10] 4-trifluoromethylbipyridin,[11] 4-methylbiphenyl,[12] 4-methoxybiphenyl,[13] 2-methylbiphenyl,[14] 2,6-dimethylbiphenyl,[15] 2,4,6-trimethylbiphenyl,[16,17] 4-methoxy-4'-trifluoromethylbiphenyl,[18] 4-methoxy-4'-methylbiphenyl,[19] 4-methoxy-2'-methylbiphenyl,[18,19] 4-methoxy-2',4',6'-trimethylbiphenyl,[16,20] 2-(2',4',6'-trimethylphenyl)pyridine,[10] 4-trifluoromethyl-2',4',6'-trimethylbiphenyl,[20] 2,4,4',6-tetramethylbiphenyl,[21] 2,2',4,6-tetramethylbiphenyl,[17] 2,2',4,6,6'-pentamethylbiphenyl,[22] 2,2',4,4',6,6'-hexamethylbiphenyl.[22,23,24]

Preparation of imidazolium chlorides [25,26]

10 mmol of paraformaldehyde are dissolved in 10 mL of toluene. 10 mmol of the amine are added as a liquid dropwise or as a solid in small portions. The mixture is stirred and heated until clarification of the solution and subsequently cooled to 0 °C by means of an ice bath. After addition of further 10 mmol of amine, an approximately 3 M aqueous solution of 10 mmol of HCl is added slow enough not to raise the temperature. After removal of the ice bath, 10 mmol of glyoxal (40% in water) are added dropwise. The reaction is stirred at 40 °C

for 15 h. After addition of a saturated aqueous solution of $NaHCO_3$, the aqueous phase is extracted 3 times with 2 mL of Et_2O. The water is removed *in vacuo* and the remaining solids are extracted 3 times with 5 mL of CH_2Cl_2. Yield: 50 - 80%.

Preparation of 1,3-bis(arene)imidazolium chlorides without *para*-substitution

10 mmol of 1,4-bis(arene)diazabutadiene and 10 mmol of paraformaldehyde are dissolved in 20 mL of toluene. The mixture is stirred and heated until clarification of the solution and subsequently cooled to ambient temperature. A solution of 10 mmol of HCl (4 M in dioxane) is added dropwise over a period of 1 h. The resulting mixture is stirred for an additional 8 h. A white precipitate forms which is filtered and washed twice with 2 mL of cold THF. Yield: 10 - 20%.

The shorter reaction time as compared to the literature procedure[27] led to better yields in our hands. Related approaches to this type of imidazolium salts have been described.[28,29]

Preparation of imidazolium salts with non-coordinating anions

The same procedure as with the chloride salts is used. Instead of aqueous HCl one uses $H[BF_4]$ or $H[PF_6]$ in water in the same concentration. Work-up is achieved either by filtration of the solid product *via* a Büchner funnel or by phase separation in the case of a liquid product. Yield: 60 - 95%.

Preparation of 1,3-bis(arene)imidazolium salts without *para*-substitution with non-coordinating anions

The same procedure as with the chloride salts is used but toluene is replaced by THF. Furthermore, instead of HCl in dioxane one uses $H[BF_4]$ or $H[PF_6]$ in diethylether. Yield: 20 - 40%.

1,3-bis(2,6-di-*iso*-propylphenyl)imidazolium chloride **2a**:

^{1}H (400 MHz, CD_2Cl_2, 22 °C, TMS): *d* [ppm] = 11.08 (s, 1 H, NCHN), 7.77 (s, 2 H, NCHCHN), 7.62 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, 4-H_{aryl}), 7.40 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, 3,5-H_{aryl}), 2.42 (2 sept, $^3J_{HH}$ = 7.0 Hz., 4 H, CH_{iPr}), 1.28 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, H_3C_{iPr}), 1.26 (d,

$^{3}J_{HH}$ = 7.0 Hz, 12 H, H_3C_{iPr}). $^{13}C\{^{1}H\}$ (100 MHz, CD_2Cl_2, 22 °C, TMS): *d* [ppm] = 145.5 (NCHN), 141.0 (2 C, Aryl), 132.3 (4 C, Aryl), 130.4 (2 C, Aryl), 125.9 (4 C, Aryl), 125.0 (2 C, NCHCHN), 29.5 (4 C, CH_{iPr}), 24.8 (4 C, H_3C_{iPr}), 23.7 (4 C, H_3C_{iPr}). $C_{27}H_{37}N_2Cl$ (425.06): calcd C 76.29, H 8.77, N 6.59; found C 76.44, H 8.71, N 6.50. Yield: 27%.

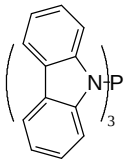
1,3-bis(2,6-di-*iso*-propylphenyl)imidazolium trifluoroborate **2b**:

^{1}H (400 MHz, [D_6]DMSO, 22 °C, TMS): *d* [ppm] = 10.15 (s, 1 H, NCHN), 8.55 (s (br), 2 H, NCHCHN), 7.68 (t, $^{3}J_{HH}$ = 7.7 Hz, 2 H, 4-H_{aryl}), 7.52 (d, $^{3}J_{HH}$ = 7.7 Hz, 4 H, 3,5-H_{aryl}), 2.34 (sept, $^{3}J_{HH}$ = 7.0 Hz, 2 H, CH_{iPr}), 2.34 (sept, $^{3}J_{HH}$ = 6.6 Hz, 2 H, CH_{iPr}), 1.25 (d, $^{3}J_{HH}$ = 6.6 Hz, 12 H, H_3C_{iPr}), 1.15 (d, $^{3}J_{HH}$ = 7.0 Hz, 12 H, H_3C_{iPr}). $^{13}C\{^{1}H\}$ (100 MHz, [D_6]DMSO, 22 °C, TMS): *d* [ppm] = 144.8 (NCHN), 139.3 (2 C, Aryl), 131.9 (4 C, Aryl), 130.0 (2 C, Aryl), 126.2 (4 C, Aryl), 124.6 (2 C, NCHCHN), 28.6 (4 C, CH_{iPr}), 24.1 (4 C, H_3C_{iPr}), 23.1 (4 C, H_3C_{iPr}). $C_{27}H_{37}N_2BF_4$ (476.41): calcd C 68.07, H 7.83, N 5.88; found C 68.33, H 8.09, N 6.00. Yield: 38%.

Analytical data for 1,3-bis(2-mesityl)imidazolium salts **1**.[29]

1,3-bis(2-mesityl)imidazolium chloride: ^{1}H (200 MHz, $CDCl_3$, 22 °C, TMS): *d* [ppm] = 10.52 (s, 1 H, NCHN), 7.63 (s, 2 H, NCHCHN), 6.88 (s, 4 H, Ar), 2.22 (s, 6 H, 4-CH_3), 2.05 (s, 12 H, 2,6-CH_3).

N,N',N''- Tris(carbazolyl)phosphine



Carbazole is deprotonated by butyllithium in THF at –78 °C. Subsequent addition of PCl_3 in THF, warming to ambient temperature and stirring affords the white product after crystallization.

^{1}H (400 MHz, $CDCl_3$, 22 °C, TMS): *d* [ppm] = 8.06 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, 6 H), 7.25 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, 6 H), 7.18 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, 6 H), 7.12 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, 6 H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$, 22 °C, TMS): *d* [ppm] = 141.8 (6 C, J_{PC} = 9.7 Hz), 126.5 (6 C, J_{PC} = 1.9 Hz), 121.9 (6 C), 120.3 (6 C), 113.1 (6 C, J_{PC} = 13.6 Hz). ^{31}P (162 MHz, $CDCl_3$, 22 °C): *d* [ppm] = 76.2. $C_{36}H_{24}N_3P$ (529.57): calcd C 81.65, H 4.57, N 7.93; found C 81.60, H 4.37, N 7.88.

General procedure for the *Grignard* cross-coupling

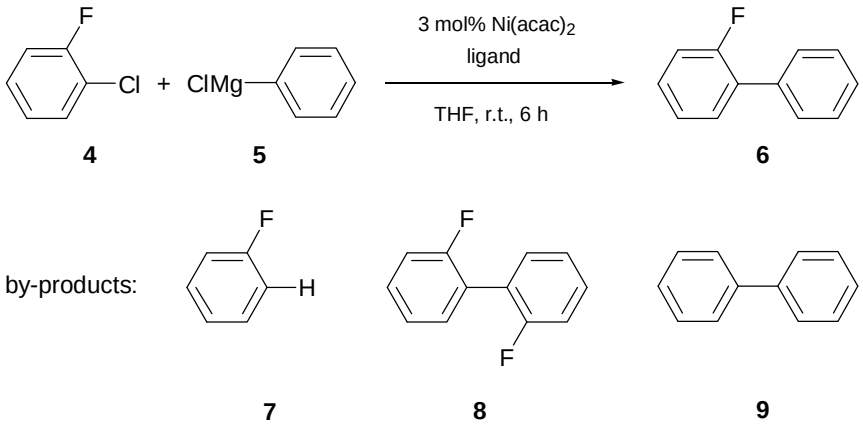
A Schlenk tube is charged with $Ni(acac)_2$ (7.7 mg, 0.03 mmol), ligand **1**, **2**, or **3** (0.03 mmol) and the chloroarene (1 mmol) under an atmosphere of dry nitrogen. After addition of 1 mL of THF and the internal standard diethyleneglycol-di-*n*-butylether (50 mg) the mixture is stirred for 5 min until the catalytic reaction is started by dropwise addition of the *Grignard* reagent (1.5 mmol, ~ 1 M in THF) *via* syringe at ambient temperature.[30] After the reaction time the solution is quenched by addition of 1 mL of methanol turning yellow or red after some minutes. An aliquot is examined by GC/MS or the product is isolated by column chromatography.

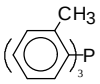
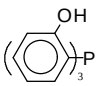
Results of the ligand screening

Reaction conditions: 400 μmol of phenylmagnesium chloride in diethylether (3 M, 0.133 mL) are added to 267 μmol of 1-chloro-2-fluorobenzene (1 M, 267 mL),[31] 8 μmol of the metal precursor and the appropriate amount of ligand in 0.7 mL of THF under an atmosphere of dry nitrogen. The mixture turns dark and the reaction is allowed to stir for 6 h until it is quenched by the addition of 0.5 mL of methanol. The yellow solution is transferred to an NMR tube and a $^{19}F\{^{1}H\}$-NMR is recorded.

Products and educts were identified by comparison with pure samples and literature data.[9] Product ratios were determined by comparison of integral values in the $^{19}F\{^{1}H\}$-NMR. It has to be stressed that the values obtained can differ from absolute values due to integration of proton decoupled signals. Nevertheless, relative ratios of different catalyst systems still allow comparisons in terms of activity and selectivity. This information proved more than satisfactory to judge on the efficiency of different metal/ligand combinations in the primary screen.

- $Pd_2(dba)_3$ and $Pd(OAc)_2$ did not show conversions of > 10% with or without any ligand.
- Results with $Ni(acac)_2$:



Ligand	Anion	Metal:Ligand	**6** [%]	**4** [%]	**7** [%]	**8** [%]
$P(Bu)_3$	–	1:1	10	89	1	0
	–	1:2	11	89	0	0
$P(iPr)_3$	–	1:1	9	91	0	0
	–	1:2	11	88	1	0
$P(tBu)_3$ **3**	–	1:1	76	23	1	0
	–	1:2	68	30	2	0
$P(Cy)_3$	–	1:1	47	50	2	1
	–	1:2	44	53	2	1
$P(Ph)_3$	–	1:1	39	57	2	2
	–	1:2	24	75	1	1
	–	1:1	10	89	1	0
	–	1:2	12	86	1	1
	–	1:1	3	97	0	0
	–	1:2	6	94	0	0
	–	1:1	52	44	3	1
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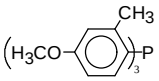
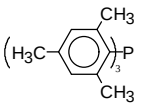
	–	1:1	30	69	1	0
	–	1:2	31	54	2	3
	–	1:1	23	77	0	0
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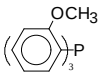	–	1:1	23	77	0	0
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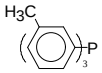	–	1:1	19	81	0	0
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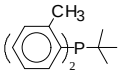	–	1:1	35	64	1	0
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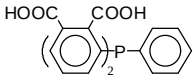	–	1:1	13	87	0	0
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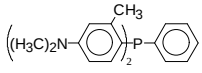	–	1:1	21	77	1	1
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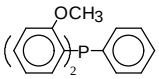
Ligand	Anion	Metal:Ligand	**6** [%]	**4** [%]	**7** [%]	**8** [%]
	–	1:1	15	85	0	0
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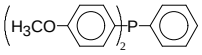	–	1:1	15	85	0	0
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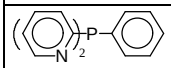	–	1:1	4	96	0	0
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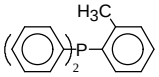	–	1:1	31	67	1	1
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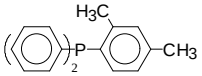	–	1:1	39	59	1	1
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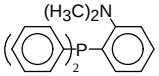	–	1:1	13	87	0	0
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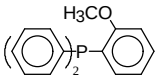	–	1:1	17	83	0	0
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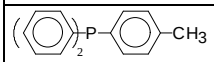	–	1:1	8	92	0	0
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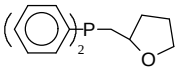	–	1:1	4	96	0	0
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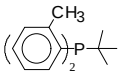	–	1:1	19	78	3	0
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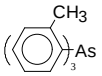	–	1:1	13	85	2	0
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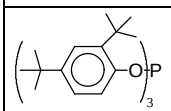	–	1:1	27	64	1	8
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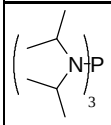
Ligand	Anion	Metal:Ligand	**6** [%]	**4** [%]	**7** [%]	**8** [%]
	–	1:1	39	58	3	0
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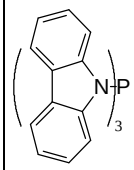	–	1:1	22	78	0	0
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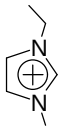	Br	1:1	3	97	0	0
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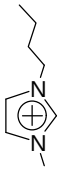
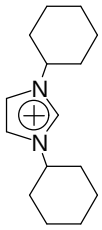
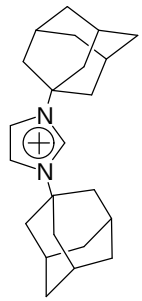
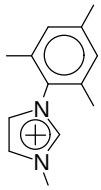
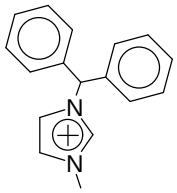
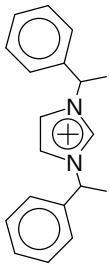
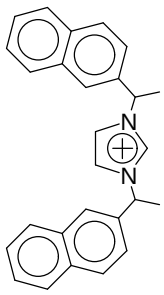
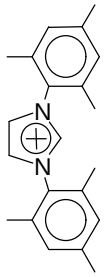
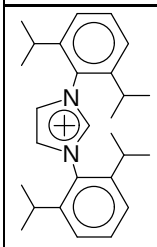
	PF_6	1:1	4	95	1	0
		1:2	3	97	0	0
	Br	1:1	5	95	0	0
		1:2	5	95	0	0
	PF_6	1:1	4	95	1	0
		1:2	7	93	0	0
	Cl	1:1	3	97	0	0
		1:2	3	97	0	0
	Cl	1:1	10	89	1	0
		1:2	14	83	1	2

Ligand	Anion	Metal:Ligand	**6** [%]	**4** [%]	**7** [%]	**8** [%]
	Cl	1:1	9	80	1	0
		1:2	12	76	1	1
	BF_4	1:1	10	88	2	0
		1:2	19	71	0	0
	Cl	1:1	10	89	1	0
		1:2	8	91	1	0
	Cl	1:1	7	93	0	0
		1:2	18	81	1	0
	BF_4	1:1	17	81	1	1
		1:2	12	87	1	0
	Cl	1:1	12	88	0	0
		1:2	28	70	1	1
	BF_4	1:1	17	83	0	0
		1:2	15	72	2	1
	Cl	1:1	20	78	2	0
		1:1	16	84	0	0
	BF_4	1:1	11	89	0	0
		1:2	22	76	1	1

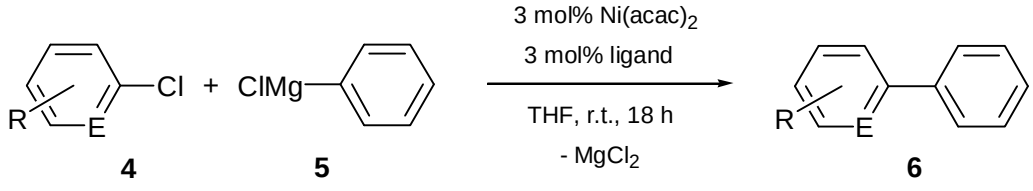
Ligand	Anion	Metal:Ligand	**6** [%]	**4** [%]	**7** [%]	**8** [%]
	I	1:1	49	51	0	0
		1:2	54	44	1	1
	I	1:1	4	95	0	1
		1:2	6	94	0	0
	Cl	1:1	21	75	2	2
		1:2	20	76	1	3
	BF_4	1:1	18	78	3	1
		1:2	21	77	2	0
	Cl	1:1	22	77	1	0
		1:2	30	66	1	3
	BF_4	1:1	28	68	3	1
		1:2	21	77	2	0
 **1**	Cl	1:1	65	32	2	1
		1:2	60	36	3	1
	BF_4	1:1	65	33	1	1
		1:2	69	30	1	0

Ligand	Anion	Metal:Ligand	**6** [%]	**4** [%]	**7** [%]	**8** [%]
 **2**	Cl	1:1	65	28	4	3
		1:2	71	25	2	2
	BF_4	1:1	75	23	1	1
		1:2	78	21	1	0
–	–	–	6	92	2	0

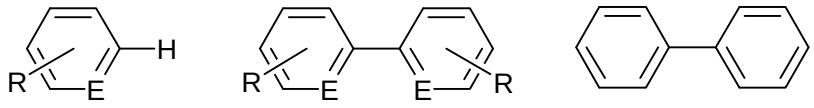
Any by-products not containing fluorine, e.g. biphenyl **9** formed by homocoupling of the *Grignard* reagent, cannot be detected by this assay.

Detailed results of the bulk reactions

Table 1. *Grignard* cross-coupling reaction with phenylmagnesium chloride.[a]



by-products:



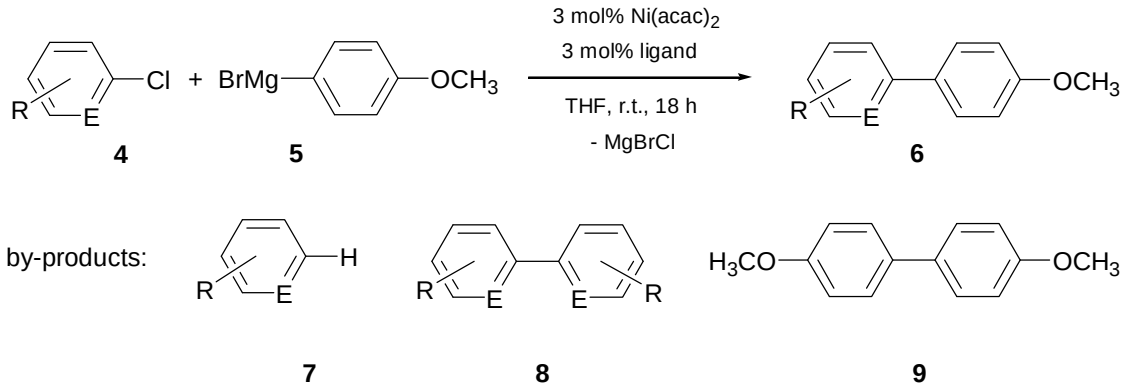
7 **8** **9**

R	E	IMes **1**[b]	IPr **2**[b]	P(*t*Bu)$_3$ **3**[b]
H	N	100/0/0/0/5	100/0/0/0/4	92/0/9/0/13
4-CF_3	C	90/8/2/0/8	96/4/0/0/4	47/53/0/0/11
4-CH_3		72/18/3/7/5	81/7/3/9/11	89/0/6/5/12
4-OCH_3		67/18/2/7/6	71/19/1/9/16	71/17/1/11/19
2-CH		70/17/8/5/10	73/9/10/8/15	72/0/16/12/17
2,6-CH_3		4/87/9/0/25	13/72/15/0/26	12/63/25/0/20
bromomesitylene		23/58/19/0/6	5/80/15/0/12	16/69/15/0/4

[a] 1.0 eq aryl halide, 1.5 eq phenyl *Grignard*, 3 mol% Ni(acac)$_2$, 3 mol% ligand, THF, r.t., t = 18 h.

[b] GC-yield using diethyleneglycol-di-*n*-butylether as the internal standard. Product distribution is given as **6**/**4**/**7**/**8**/**9**; amount of **8** was approximated by comparison of peak integrations.

Table 2. *Grignard* cross-coupling reaction with 4-anisylmagnesium bromide.[a]

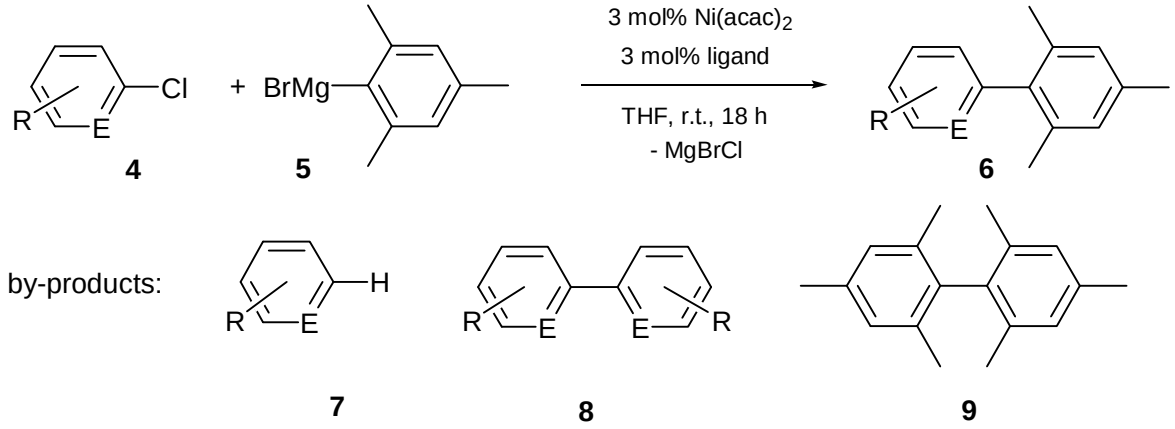


R	E	IMes **1**[b]	IPr **2**[b]	P(*t*Bu)$_3$ **3**[b]
H	N	100/0/0/0/2	100/0/0/0/1	100/0/0/0/10
4-CF_3	C	100/0/0/0/4	100/0/0/0/8	38/20/0/42/0
H		95/3/2/0/8	93/3/3/1/16	100/0/0/0/5
4-CH_3		85/13/2/0/14	88/5/4/3/15	87/10/0/3/9
2-CH_3		77/19/2/2/18	77/20/0/3/10	77/18/3/2/18
2,6-CH_3		8/90/2/0/33	5/94/1/0/30	28/67/5/0/25
bromomesitylene		16/79/5/0/22	0/71/29/0/21	16/70/14/0/12

[a] 1.0 eq aryl halide, 1.5 eq anisyl *Grignard*, 3 mol% Ni(acac)$_2$, 3 mol% ligand, THF, r.t., *t* = 18 h.

[b] GC-yield using diethyleneglycol-di-*n*-butylether as internal standard. Product distribution is given as **6**/**4**/**7**/**8**/**9**; amounts of **8** and **9** were approximated by comparison of peak integrations.

Table 3. *Grignard* cross-coupling reaction with mesitylmagnesium bromide.[a]

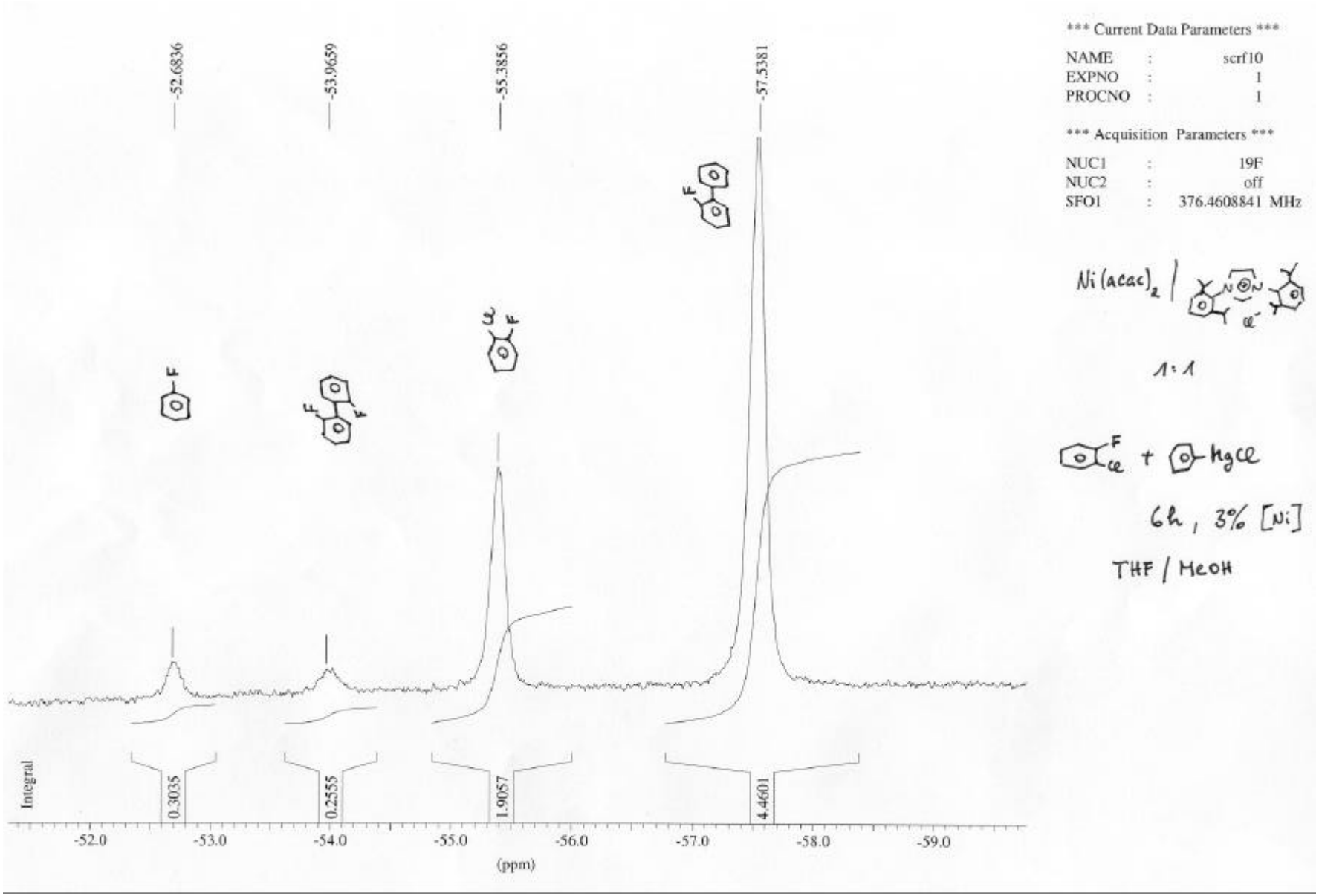


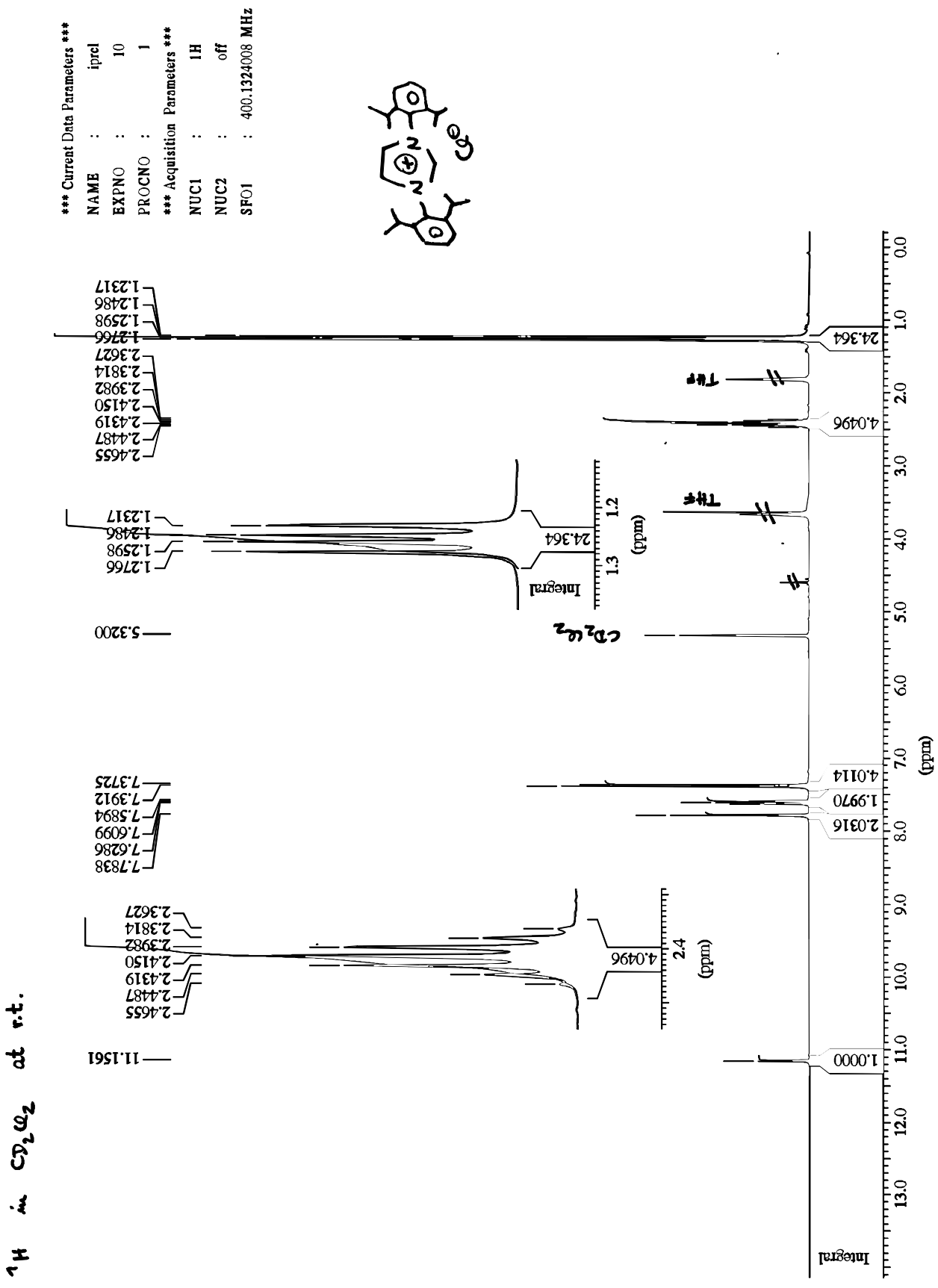
R/E	IMes **1**[b]	IPr **2**[b]	P(*t*Bu)$_3$ **3**[b]
H/N	100/0/0/0/0	100/0/0/0/1	94/6/0/0/5
4-CF_3/C	78/21/0/1/1	91/8/0/1/1	52/45/0/3/9
H/C	99/0/1/0/2	100/0/0/0/2	99/0/1/0/8
4-CH_3/C	96/3/1/0/3	95/5/0/0/4	100/0/0/0/5
4-OCH_3/C	98/0/0/1/2	98/0/0/0/5	87/4/0/6/14
2-CH_3/C	78/15/2/5/12	77/23/0/0/5	75/22/1/2/9
2,6-CH_3/C	3/95/2/0/5	2/97/1/0/5	5/91/4/0/39
bromomesitylene[c]	13/83/4/-/3	28/77/5/-/1	20/78/2/-/4

[a] 1.0 eq aryl halide, 1.5 eq mesityl *Grignard*, 3 mol% Ni(acac)$_2$, 3 mol% ligand, THF, r.t., *t* = 18 h.

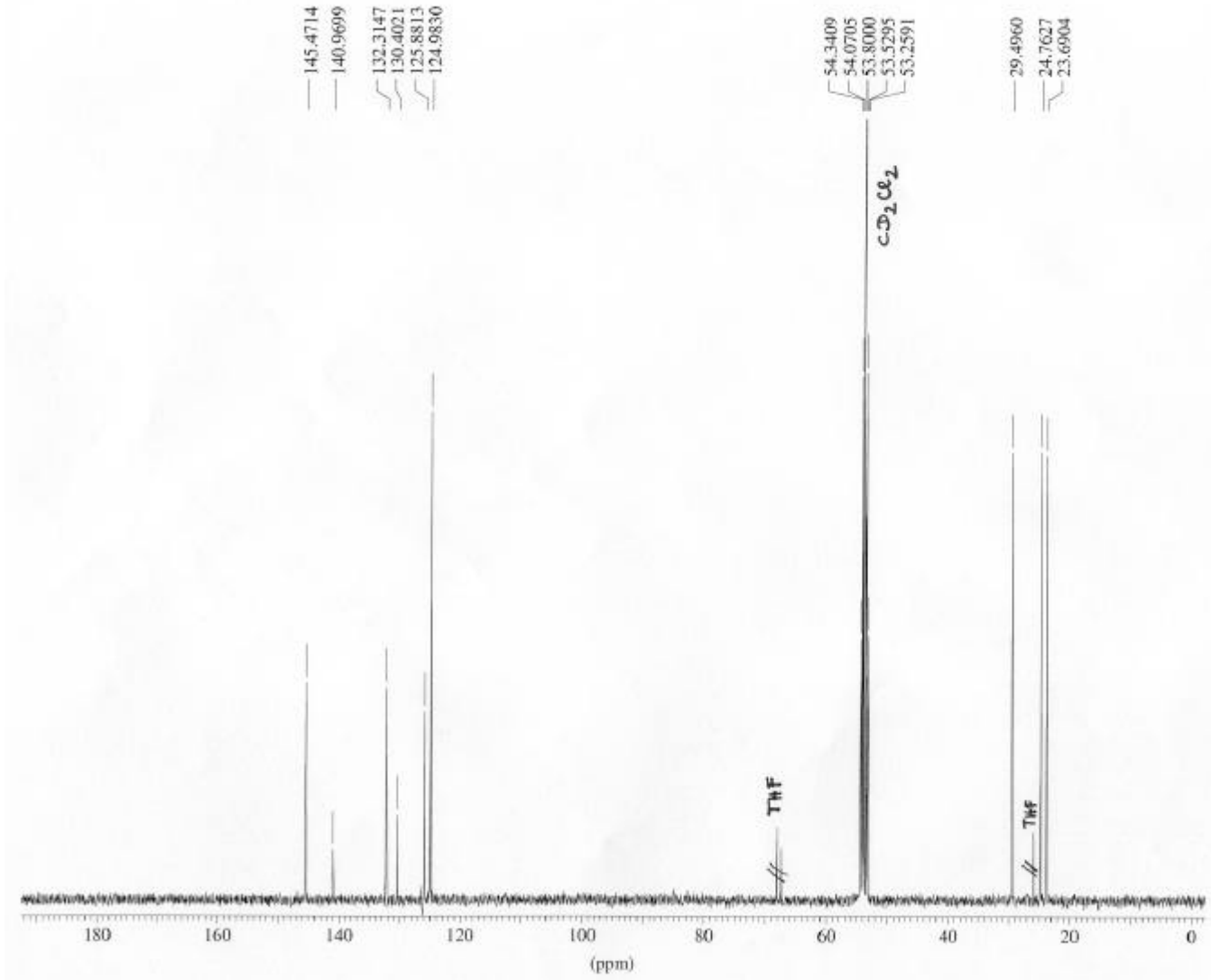
[b] GC-yield using diethyleneglycol-di-*n*-butylether as internal standard. Product distribution is given as **6**/**4**/**7**/**8**/**9**; amounts of **9** were approximated by comparison of peak integrations.

[c] **8** and **9** are identical and thus their yield cannot be determined independently. Therefore, the sum of the amounts is given as **9** only.


-52.6836
-53.9659
-55.3856
-57.5381
Integral
0.3035
0.2555
1.9057
4.4601
-52.0
-53.0
-54.0
-55.0
-56.0
-57.0
-58.0
-59.0
(ppm)
*** Current Data Parameters ***
NAME : scrf10
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
NUC1 : 19F
NUC2 : off
SFO1 : 376.4608841 MHz
Ni(acac)2 /
1:1
+ HgCl
6h, 3% [Ni]
THF / MeOH


*** Current Data Parameters ***
NAME : iprel
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
NUC1 : 1H
NUC2 : off
SFO1 : 400.1324008 MHz
1H in CD2Cl2 at r.t.
CD2Cl2
THF
Integral
(ppm)

$^{13}C\{^1H\}$ in CD_2Cl_2 at r.t.

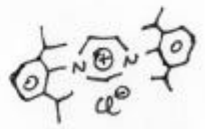


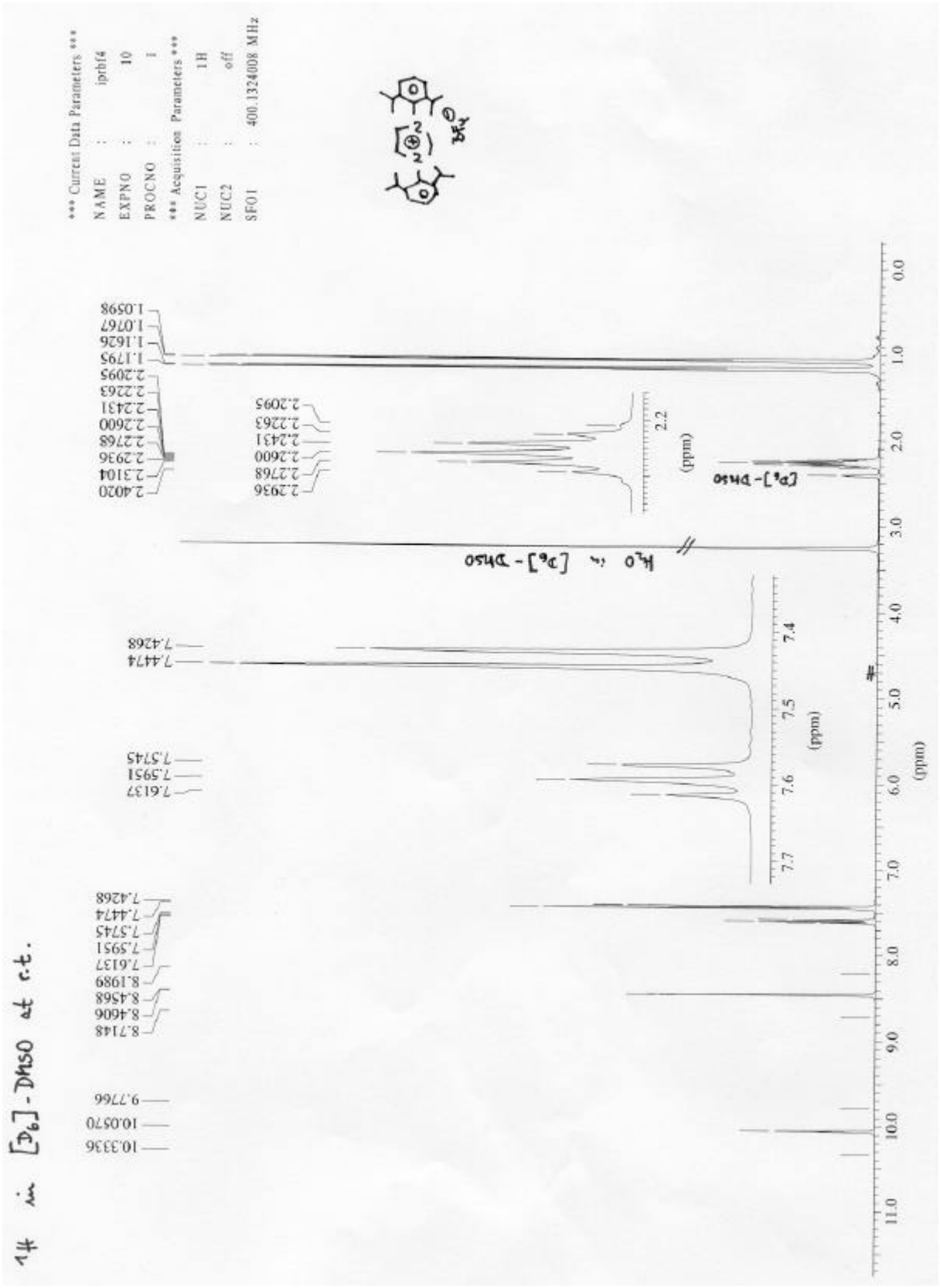
*** Current Data Parameters ***

NAME	:	iprcl
EXPNO	:	11
PROCNO	:	1

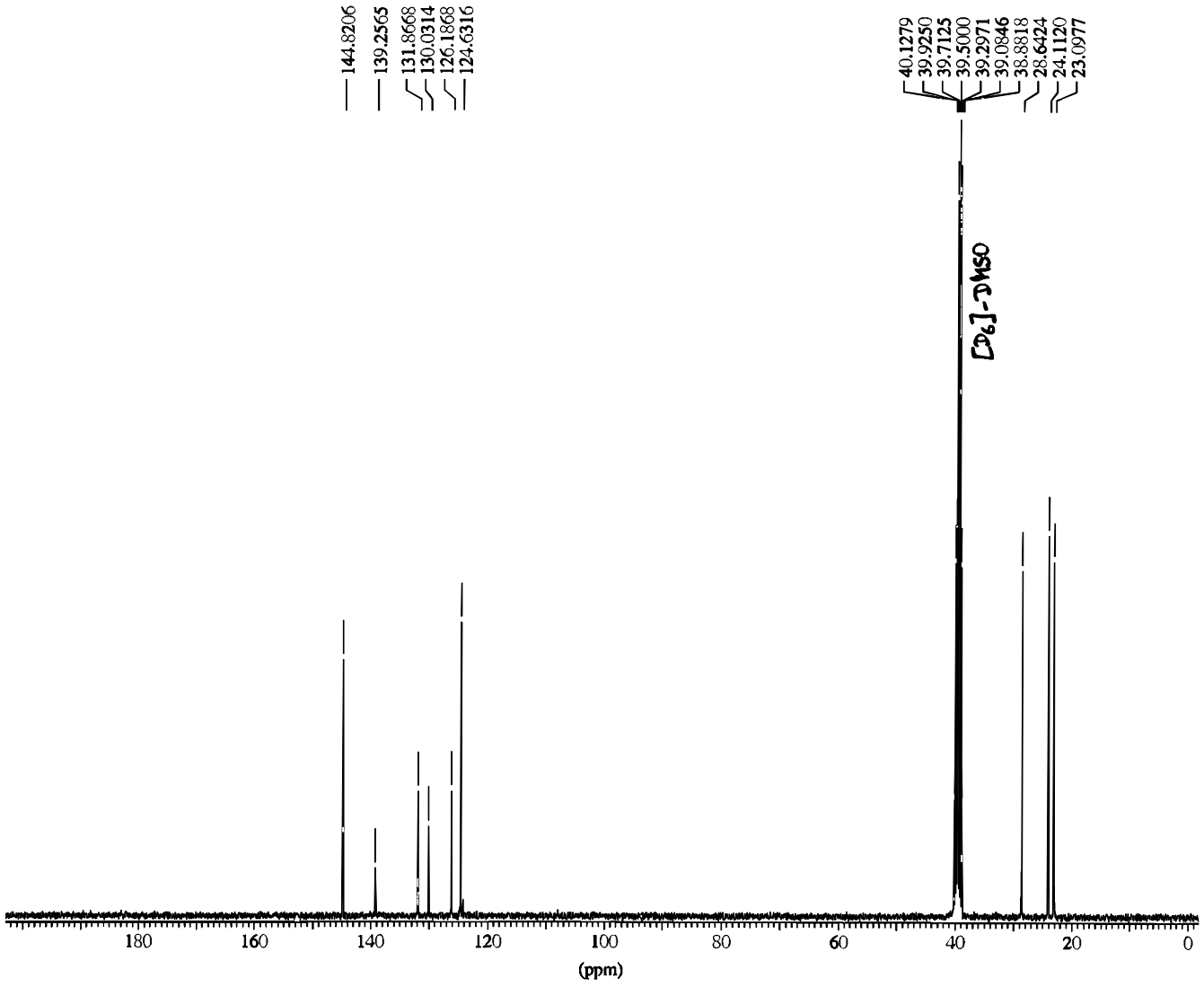
*** Acquisition Parameters ***

NUC1	:	13C
NUC2	:	1H
SFO1	:	100.6254358 MHz




1H in [D6]-DMSO at r.t.
*** Current Data Parameters ***
NAME : iprbf4
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
NUC1 : 1H
NUC2 : off
SFO1 : 400.1324008 MHz
10.3336
10.0570
9.7766
8.7148
8.4606
8.4568
8.1989
7.6137
7.5951
7.5745
7.4474
7.4268
2.4020
2.3104
2.2936
2.2768
2.2600
2.2431
2.2263
2.2095
1.1795
1.1626
1.0767
1.0598
H2O in [D6]-DMSO
[D6]-DMSO
(ppm)

$^{13}C\{^{1}H\}$ in [D6]-DMSO at r.t.

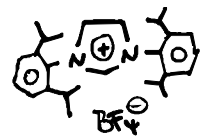


*** Current Data Parameters ***

NAME	:	iprbf4
EXPNO	:	11
PROCNO	:	1

*** Acquisition Parameters ***

NUC1	:	13C
NUC2	:	1H
SFO1	:	100.6254358 MHz



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30 The slow addition of the *Grignard* reagent allows the observation of color changes due to *in situ* complex formation and reduction of nickel(II). After full addition of the *Grignard* reagent the solution is dark.

31 1-Chloro-4-fluorobenzene rendered useless in this assay due to overlapping signals of product and educt.