

Synthesis, Characterization and Evaluation of Bulky *Bis*(Pyrazolyl) Palladium Complexes in Suzuki-Miyaura Cross-Coupling Reactions

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Electronic Supplementary information

Table SI-0: Effect of reducing reaction time and temperature on optimized conditions for Suzuki cross-coupling reaction.

Entry	Cat.	Temp. (°C)	Time	Conv. (%)	TON	TOF (hr ⁻¹)	Selectivity (%)
1	5	140	3	85	257	64	>99
2	6	140	3	62	189	47	>99
3	7	140	3	86	260	65	>99
4	8	140	3	65	198	49	>99
5	5	130	4	73	221	55	>99
6	6	130	4	50	152	38	>99
7	7	130	4	76	229	57	>99
8	8	130	4	55	167	42	>99

Reactions carried out in toluene (4.2 mL) with 5 mmol of bromobenzene, 8 mmol of phenyl boronic acid, 10 mmol of KOH and Pd catalyst loading = 0.33 mol % at various reaction time and temperature. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimate; **5** (± 0.5920), **6** (± 0.6141), **7** (± 0.4341), **8** (± 0.5391).

Table SI-1: Effect of reaction time on Suzuki cross coupling reactions.

Entry	Cat.	Time (h)	Conv. (%)	TON	TOF (hr ⁻¹)	Selectivity (%)
1	5	4	49	742	185	>99
2	6	4	26	395	99	>99
3	7	4	41	614	154	>99
4	8	4	21	314	78	>99
5	5	8	46	695	87	>99
6	6	8	32	479	60	>99
7	7	8	40	605	76	>99
8	8	8	20	305	38	>99
9	5	12	47	708	59	>99
10	6	12	30	456	38	>99
11	7	12	40	606	50	>99
12	8	12	26	398	33	>99
13	5	16	45	678	43	>99
14	6	16	26	372	23	>99
15	7	16	37	420	26	>99
16	8	16	24	366	23	>99
17	5	20	45	676	34	>99
18	6	20	31	463	23	>99
19	7	20	36	547	27	>99
20	8	20	18	273	14	>99

Reactions carried out in toluene (5 mL) with 5 mmol of bromobenzene, 8 mmol of phenyl boronic acid, 10 mmol of Na₂CO₃ and 3.3×10⁻³ mmol Pd catalyst (loading = 0.066 mol%) at 80 °C and 600 rpm varying reaction time. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimates; **5** (± 0.4141), **6** (0.5211), **7** (± 0.5314), **8** (± 0.4413).

Table SI-2: Effect of Temperature for Suzuki cross-coupling reaction.

Entry	Cat.	Temp. (°C)	Conv. (%)	TON	TOF (hr ⁻¹)	Selectivity (%)
1	5	100	30	455	114	>99
2	6	100	22	334	83	>99
3	7	100	24	364	91	>99
4	8	100	33	501	125	>99
5	5	120	36	540	135	>99
6	6	120	25	379	95	>99
7	7	120	28	429	107	>99
8	8	120	38	576	144	>99
9	5	140	51	767	192	>99
10	6	140	33	415	124	>99
11	7	140	56	851	213	>99
12	8	140	42	632	158	>99
13	5	160	33	499	125	>99
14	6	160	18	278	69	>99
15	7	160	26	401	100	>99
16	8	160	26	386	97	>99

Reactions carried out in toluene (4.27 mL) with 5 mmol of bromobenzene, 8 mmol of phenyl boronic acid, 10 mmol of Na₂CO₃ and 3.3×10⁻³ mmol Pd catalyst (loading= 0.066 mol%) at various temperatures and 600 rpm for 4 h. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimates; **5** (± 0.4241), **6** (± 0.3901), **7** (± 0.5322), **8** (± 0.3414).

Table SI-3: Effect of base for Suzuki cross-coupling.

Entry	Cat.	Base	Conv. (%)	TON	TOF (hr ⁻¹)	Selectivity (%)
1	5	Na ₂ CO ₃	51	767	192	>99
2	6	Na ₂ CO ₃	33	415	124	>99
3	7	Na ₂ CO ₃	56	851	213	>99
4	8	Na ₂ CO ₃	42	632	158	>99
5	5	K ₂ CO ₃	79	1196	299	>99
6	6	K ₂ CO ₃	56	849	212	>99
7	7	K ₂ CO ₃	62	944	236	>99
8	8	K ₂ CO ₃	59	888	222	>99
9	5	KOH	82	1239	310	>99
10	6	KOH	67	1014	253	>99
11	7	KOH	90	1359	340	>99
12	8	KOH	62	946	237	>99
13	5	Et ₃ N	26	401	100	>99
14	6	Et ₃ N	22	327	82	>99
15	7	Et ₃ N	25	372	93	>99
16	8	Et ₃ N	8	123	31	>99

Reactions carried out in toluene (4.27 mL) with 5 mmol of bromobenzene, 8 mmol of phenyl boronic acid, 10 mmol of base and 3.3×10^{-3} mmol Pd catalyst (loading= 0.066 mol%) at 140°C and 600 rpm for 4 h. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion . Average error estimates; **5** (± 0.5120), **6** (± 0.6230), **7** (± 0.4374), **8** (± 0.3491).

Table SI-4: Effect of catalyst loading for Suzuki cross-coupling reaction.

Entry	Cat.	Loading (mol%)	Conv. (%)	TON	TOF (hr ⁻¹)	Selectivity (%)
1	5	0.066	82	1239	310	>99
2	6	0.066	67	1014	253	>99
3	7	0.066	90	1359	340	>99
4	8	0.066	62	946	237	>99
5	5	0.165	91	549	137	>99
6	6	0.165	72	434	108	>99
7	7	0.165	91	554	138	>99
8	8	0.165	74	447	112	>99
9	5	0.33	98	298	74	>99
10	6	0.33	87	263	66	>99
11	7	0.33	98	297	74	>99
12	8	0.33	81	245	61	>99

Reactions carried out in toluene (4.27 mL) with 1 eq. of bromobenzene, 1.6 eq of phenyl boronic acid, 2 eq. of KOH and varying Pd catalyst loading and 600 rpm at 140 °C for 4h. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimates: **5** (± 0.5132), **6** (± 0.6111), **7** (± 0.4989), **8** (± 0.6410).

Figure SI-5: Representative Gas chromatogram before Suzuki-Miyaura cross-coupling reaction.

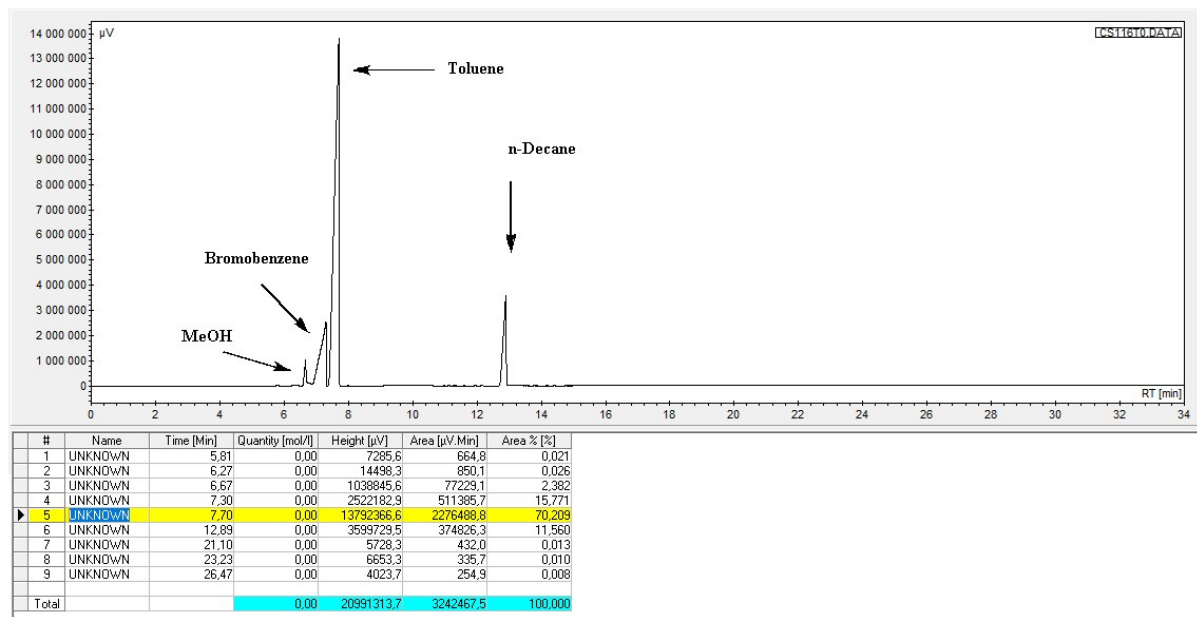


Figure SI-6: Representative Gas chromatogram after Suzuki-Miyaura cross-coupling reaction.

