Iron-Catalyzed Direct Arylation through an Aryl Radical Transfer Pathway

Frédéric Vallée, James J. Mousseau, and André B Charrette
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Mathieu Candy

Famous RCC Séminaire STeRéO

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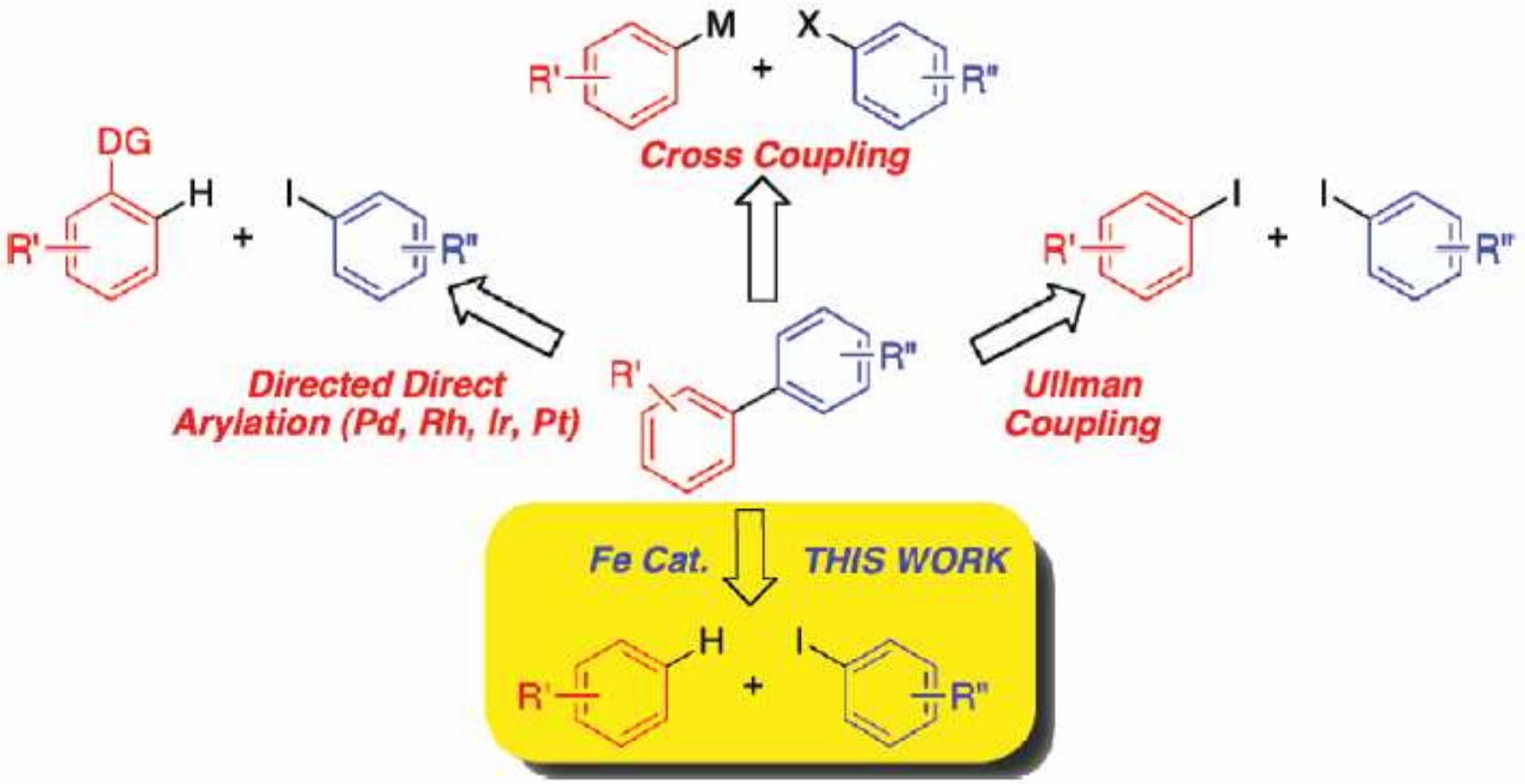
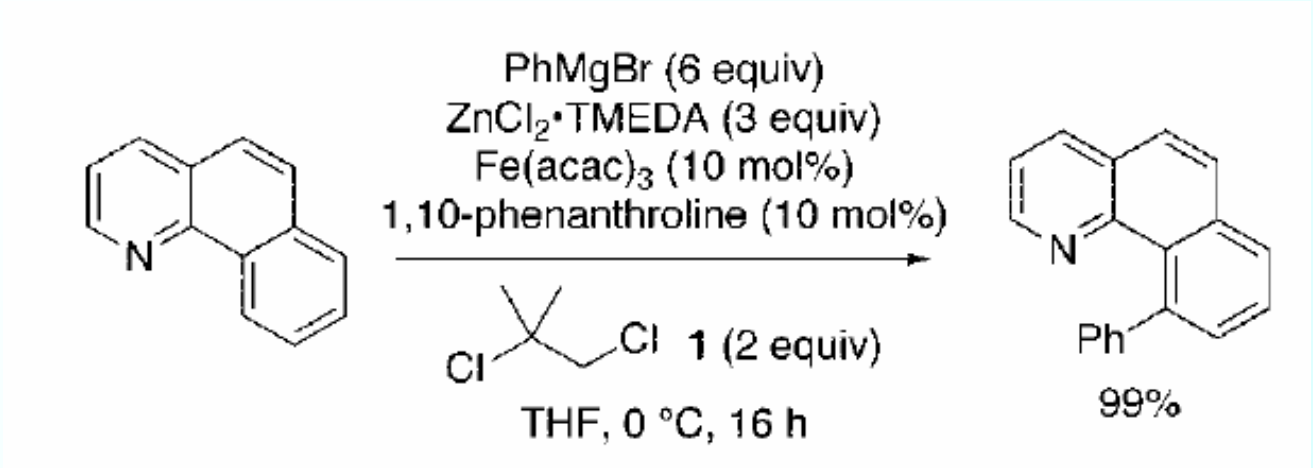
Introduction

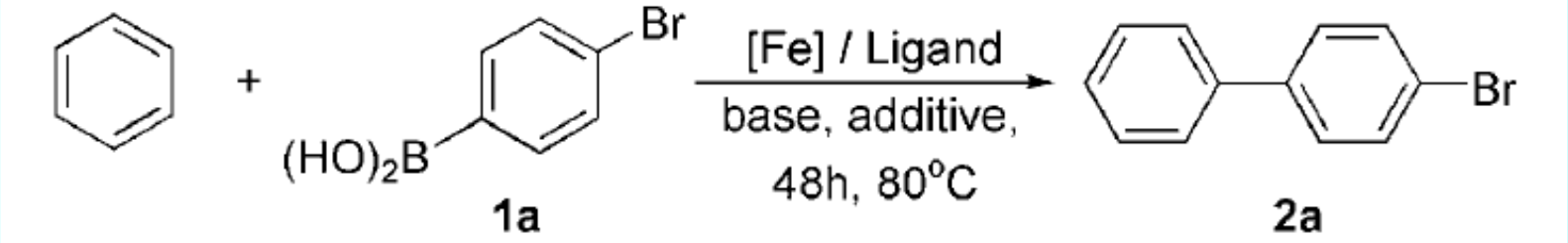


Previous on Iron Catalized C-H bond transformation

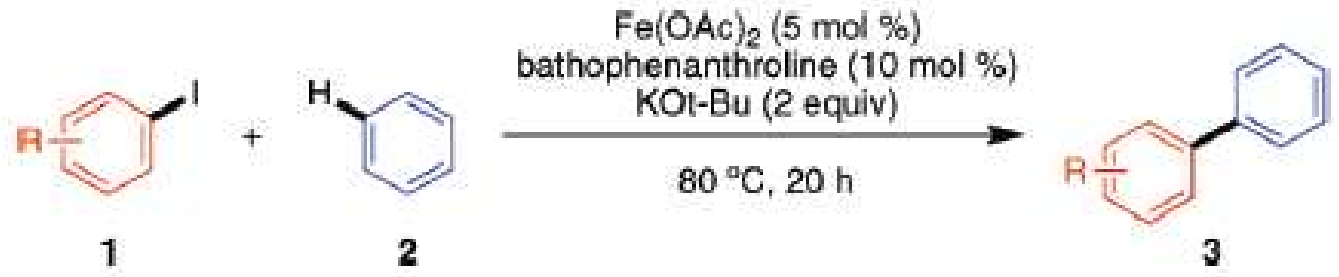
Nakamura *et al*. *JACS,* **2008**, 5858-5859

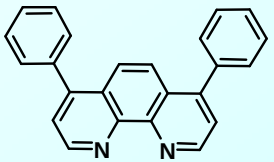


Xiao-Qi Yu *et al*. *ACIE,* **2008**, 8897-8900



Reaction and scope on Aryl iodides





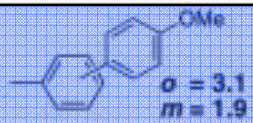
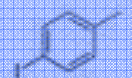
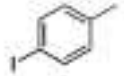
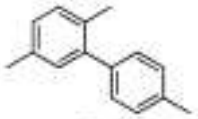
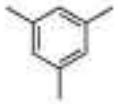
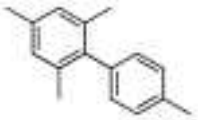
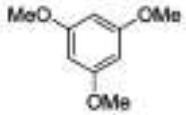
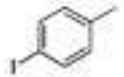
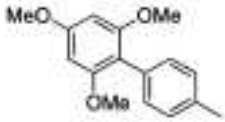
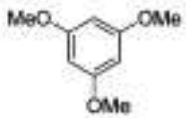
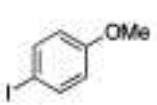
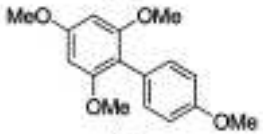
Bathophenanthroline

entry	aryl halide	product	yield (%)
1	1a	3a	89
2	1b	3b	60
3	1c	3c	86
4	1d		46
5[b]	1e	3d	80
6	1f	3e	93 (51)[c]
7	1g	3f	88
8			72

entry	aryl halide	product	yield (%)
9[d]	1h, 1i	3g, 3h	69
10	1j	3i	40
11	1k	3j	86
12	1l	3k	53
13	1m	3l	85
14	1n	3m	85
15	1o	3n	79

[a] Reaction conditions: **1** (1 equiv), benzene (100 equiv), $Fe(OAc)_2$ (5 mol %), bathophenanthroline (10 mol %), KO*t*-Bu (2 equiv), 80 °C, 20 h. [b] Reaction performed at 125 °C. [c] Reaction performed at rt for 60 h. [d] Reaction performed at 90 °C.

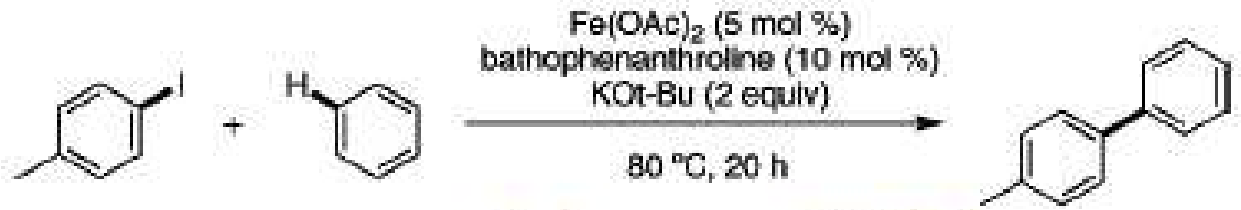
scope on Arene

entry	arene	aryl iodide	product	yield (%)
1	 **4a**	 **1f**	 **5a**	*o* = 3.1 *m* = 1.9 *p* = 1.0	50[b]
2	 **4b**	 **1c**	 **5b**	*o* = 1.0 *m* = 1.4 *p* = 2.0	28[b]
3	 **4c**	 **1c**	 **5c**		81
4	 **4d**	 **1c**	 **5d**		63
5	 **4e**	 **1c**	 **5e**		54
6	 **4f**	 **1f**	 **5f**		41

[a] Reaction conditions: **1** (1 equiv), arene (100 equiv), $Fe(OAc)_2$ (5 mol %), bathophenanthroline (10 mol %), KO*t*-Bu (2 equiv), 130 °C, 20 h. [b] Yield determined as a mixture of isomers.

Mechanistic studies

entry	catalyst	purity (%)	commercial source	yield(%)[b]
1	$Fe(OAc)_2$	99.995	Aldrich	98 (87)[c]
2	$Fe(OAc)_2$	97	Strem	91
3	Cu(OAc)	99	Strem	6
4	$Cu(OAc)_2$	97	Strem	9
5	$Fe(OAc)_2$ + Cu(OAc)	99.995 + 99	Aldrich Strem	57
6	$Fe(OAc)_2$ + $Cu(OAc)_2$	99.995 + 97	Aldrich Strem	48



No Scavenger = 91% (GC)
TEMPO = <1% (GC)
Galvinoxyl = <1% (GC)

entry	catalyst	ligand	KO*t*-Bu	yield (%)[b]
1	$Fe(OAc)_2$	10 mol %	2 equiv	91
2	none	10 mol %	2 equiv	0
3	AIBN	none	2 equiv	17
4	$Fe(OAc)_2$ + AIBN	10 mol %	none	0

Mechanistic studies