Ni-Catalyzed Reductive Coupling of Alkyl Acids with Unactivated *Tertiary* Alkyl and Glycosyl Halides

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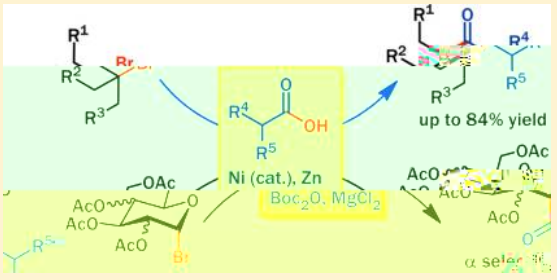
Supporting Information

ABSTRACT: tertiary % % % α- C- % % ffi (, 1) % % 2



1. INTRODUCTION

tertiary – [1,2] tertiary [3,4] ffi primary secondary secondary [5,6] % [7] % [8–11] tertiary – [7,12] tertiary % % -/% - -9- [3,4]

primary secondary ffi ([3])–([3]) ([3])–([2]) (1),[13–16] tertiary ffi % alkyl acids prove to be ineffective.[16] tertiary C- C- % % % [17,18] % % C-

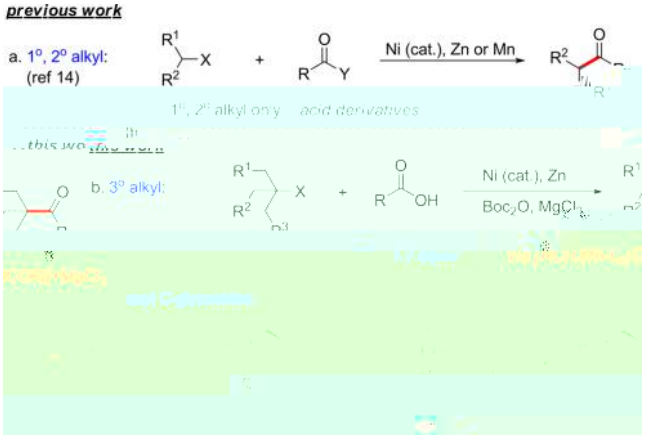


Figure 1. - -

[19–21] % C- 1 ([3]) ffi [22,23] % β-C- % 1- [24] 1- ffi C- [25,26] C- α- ffi – tertiary (1). % , this work

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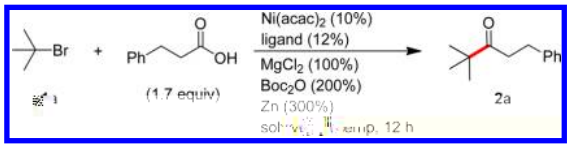
demonstrates the first construction of all carbon quaternary centers via the reductive coupling of unactivated tertiary alkyl halides with a second electrophile [27,28] fi C- α- 2 %.

2. RESULTS AND DISSCUSIONS

2.1. Coupling of *Tertiary* Alkyl Halides with Alkyl Acids.

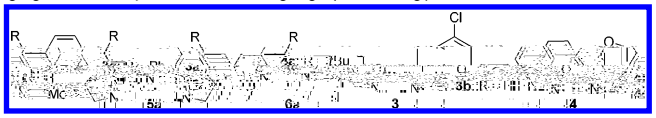
tertiary t (1a) 1.7 3- 2 / 1.5 2 (% 1).[29]

Table 1. Optimization for the Reaction of BuBr (1a) with 3-Phenylpropanoic Acid[a]



				i 2 (%)	(%) 2	°	(%)[b]
1	3a	H		0	150	25	16
2	3b	H		0	150	25	7
3	4a	H		0	150	25	24
4	4a			0	150	25	25
5	4a			0	150	25	34
6	4a	/	= 8:2	0	150	25	44
7	4a	/	= 2:8	0	150	25	36
8	4a	/	= 2:8	150	150	25	47
9	4b	/	= 2:8	150	150	25	19
10	4c	/	= 2:8	150	150	25	46
11	5a	/	= 2:8	150	150	25	<10
12	6a	/	= 2:8	150	150	25	<10
13	4a	/	= 2:8	150	100	25	39
14	4b	/	= 2:8	150	100	25	65
15	4b	/	= 2:8	85	100	25	79
16	4b	DMSO/DME	= 2:8	85	100	30	82
17	4a	/	= 2:8	85	100	30	39

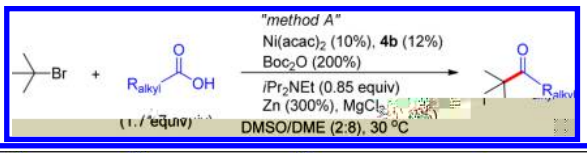
[a] : t (0.3 , 100 %), (170 %), ( )2 (10 %), (12 %), 2 (200 %), (300 %), 2 (100 %), (1). [b] (%).

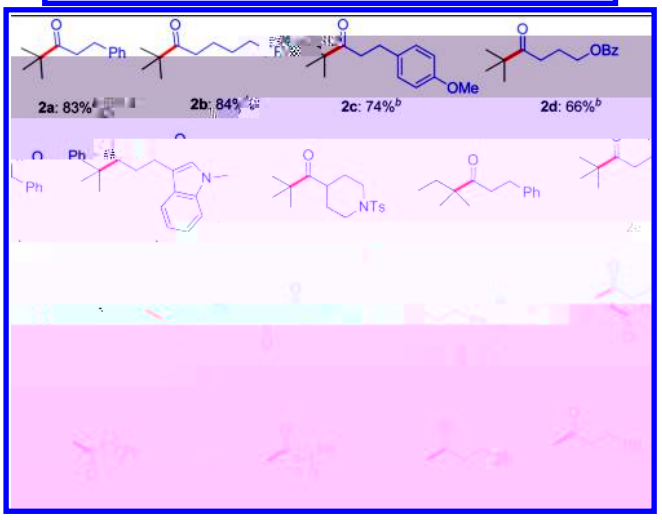


( )2 % 4a 2a 24% H , 3a 3b (% 1, 1–3). ff 4a , % (4–5). / 8/2 (/) % 2/8 (6 7), 1.5 i 2 47% (8). , ., 4b–c, 5a, 6a % (9–12). 2 1.5 1 4a (8, 13), % 65% 19% 4b (9, 14). i 2 1.5 0.85 79% (15). 25 30 °, 82% (16). (method A), 4a % ffi (17).

(method A, % 1, 16) % t - 2a–f, % 2g % tert- % 7–15 (% 2). %, 14 % trans- (trans-4- /) cis-% (cis-4-% /).[29]

Table 2. Coupling of Unactivated *e* -Alkyl Bromides with Acids[a]





[a] (*e h d A*): tert- (0.3 , 100 %), (170 %), ( )2 (10 %), 4b (12 %), 2 (100 %), i 2 (85 %), 2 (200 %), (300 %), / (0.2:0.8, / , 1). [b] % t-% (2). [c] [d]15 % ( )2 15 % 4b [e] 14 % - ff (= 19:1); 14 % - ff ( ).

2.2. Coupling of *Tertiary* Alkyl Halides with Aryl Acids.

method A (% 1, 16), % (1.7) (3-% -3- %)% 1b 11c, % % tert-% % % 3 (0.85 % 1b 11a 60% 11c (1). 1b 4-% -1- (16a)

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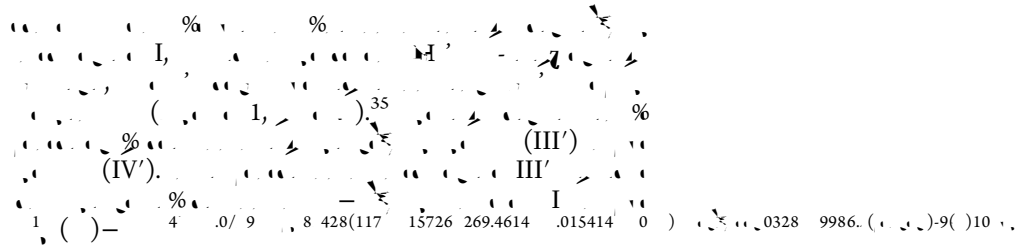
% 10%
1b
16a (2).
ffi
tertiary
secondary %
tertiary %

2.3. Coupling of ***Primary*** and ***Secondary***



(I-c) [illegible] 29,30 [illegible] 2+, [illegible] 2 I-
c [illegible] i [illegible] n- (0)
[illegible] 1 H [illegible] I-a/ [illegible] 2

(5) ( ) . Angew. Chem., Int. Ed. 2008, 47, 9334.
(%) H . J. Am. Chem. Soc. 2009, 131, 7532.
( ) . Nat. Chem. 2010,

Chem. 1981, 21, 451. (%) J. Organomet. Chem. 1993, 447, 131.

(33) ( ) (15).

(34) % : ( ) Angew. Chem., Int. Ed. 2007, 46, 8790. (%) J. Am. Chem. Soc. 2006, 128, 13175.

(35) ( ) J. Am. Chem. Soc. 2013, 135, 12004. (%) J. Am. Chem. Soc. 2013, 135, 16192. ( ) J. Am. Chem. Soc. 2014, 136, 48. ( ) Science 2014, 345, 433. ( ) Science 2014, 345, 437. ( ) J. Am. Chem. Soc. 2014, 136, 16588–16593.

(36) ( ) % J. Am. Chem. Soc. 2006, 128, 5360. (%) J. Am. Chem. Soc. 2005, 127, 510. ( ) Org. Lett. 2011, 13, 2138. ( ) Chem. Sci. 2013, 4, 4022. ( ) Science 2012, 338, 647.

(37) % I-a (I-a] % [1] [13] ( ).

(38) [2] J. Am. Chem. Soc. 2009, 131, 16656.

(39) ( )– % % Organometallics 2014, 33, 5874.

(40) [2] Angew. Chem., Int. Ed. 2014, 53, 4386.