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.-C Tertiary A

Chenglong Zhao,[†] Xiao Jia,[†] Xuan Wang, and Hegui Gong*

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Supporting Information



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1. _ , D C ,

 $\underbrace{t}_{t} \underbrace{t}_{t} \underbrace{t}_{t}$ _I . I_ . . . ff . _____ _ · t t · , W 11_1, , t_tt t .F. t_ , t , t. 1 t Llt I 1 1 2 _t _t ,._(, ₩t_l t .7 I 💌 1 1 t $\begin{array}{c} 1 \\ \hline \\ - \\ \end{array} \begin{array}{c} F' \\ t \end{array}$ ĩt 0 ٠t t t t, t, , 2 | , К ___ 1 t. __ **I-9-BB** 2 |-] 🔽 JI 1-/. Jt J. It.t L. t II t I. t l_tt / t t t l t _t . t .^{3,4}

🗇 , t t / t t t <u>t</u> t / t $\begin{array}{cccc} \mathbf{t} & \mathbf{l} & \overrightarrow{\mathbf{t}} & \mathbf{t} & \mathbf{t} & \mathbf{t} \\ \mathbf{t} & \mathbf{l} & \mathbf{t} & \mathbf{l} & \mathbf{t} & \mathbf{t} \\ \end{array}$ _t] • . . . t $(F = 1),^{13-16}, J = (C^{-3}), C^{-2}, C^{$ ff t I t (F t ., **⊥**t . ^w. _ t . . t . . t t. 🎵 t l t 🤨 _t t, , t 1 t . t [∿]″ t t_t_t_!__,~~. -1L. 1. ∠t l^wt ...t l ffi $\underbrace{t}_{16} \int_{-\infty}^{W} t f t \cdot \underbrace{t}_{-16} \int_{-\infty}^{\infty} t f \cdot \underbrace{t}_{-16} \int_{-\infty}^{\infty} t f \cdot \underbrace{t}_{-16} \int_{-\infty}^{\infty} t \cdot \underbrace{t}_{-16$ 111.. -





Figure 1. -t l = t - t - l + l = t

______ t___t___,¹⁹⁻²¹_____t___t___t___t___t___t___t___t 3)___ - - - − t; I I C1 (1]] I ffi lt t _____ 1 t, ~ 1 _____t _t _ t t 1 _t1 ª _ l_t - 1-1 t. .²⁴ A _____ It, ___ t. ۱ffi t Itt 11 $\begin{array}{c} \underline{1} \\ \underline{25,26} \\ \underline{1} \\ \underline{1}$ _t t ... t t 1 1 .1_. $t \cdot t - 1$ -t - t→_t t、^wt ⊥↓__↓↓

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t t <u>B</u> -- t .^{27,28} It <u>J</u> 1 t t . . _t_t__ . fi t t t . . _ . _ 1 t - 1 α- I t t . F _II, t t J 1, t ·t _ · _ Π 1 L_ttt.t Ť

2. E A D D C

2.1	. с	Tert	iary A	, A
A,	• •	t t.	JI	, J I , J .
	t	t, t 📕	−B B. (1a) ^w t	1.7 -3-
,	_ ، ا	V/	t I	t ,
B	2 0 /	_ 1.5	$\neg \neg Cl_2$ (_	$1).^{29}$ t

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

	→Br 1a	+ Ph (1.7 equiv	OH Ni(ac ligano MgCl N Boc ₂ Zn (3 solve	ac) ₂ (10%) d (12%) ₂ (100%) O (200%) 00%) nt, temp, 12 h	→	0 2a	`Ph
t	I	I	t	(%) Et	(%)	°C	l. (%)
1	3a	HF		0	150	25	16
2	3b	HF		0	150	25	7
3	4a	HF		0	150	25	24
4	4a	DI FO		0	150	25	25
5	4a	DJ		0	150	25	34
6	4a	DJ PO /DJ	E = 8:2	0	150	25	44
7	4a	DI TO /DI	E = 2:8	0	150	25	36
8	4a	DI TO /DI	E = 2:8	150	150	25	47
9	4b	DI TO /DI	E = 2:8	150	150	25	19
10	4c	DI TO /DI	E = 2:8	150	150	25	46
11	5a	DI TO /DI	E = 2:8	150	150	25	<10
12	6a	DI TO /DI	E = 2:8	150	150	25	<10
13	4a	DI TO /DI	E = 2:8	150	100	25	39
14	4b	DI TO /DI	E = 2:8	150	100	25	65
15	4b	DI TO /DI	E = 2:8	85	100	25	79
16	4b	DMSO/DM	E = 2:8	85	100	30	82
17	4a	DI TO /DI	E = 2:8	85	100	30	39
%),	_t C	$t : B_{2}(10 \%),$	B. (0.3	I, 100 2. Ⅰ%), B	۱%), ₂0(2	(1 00	.70 1 %),

 $(300 \ 1\%), \ TOL_2 (100 \ 1\%), \ I \ t (1 \ L). \ GC \ L$

t . _ t_ . _. (_ . _t .).

t



t . _t_l t, l _ . 4a _ t $(--)_{2}$ t 2a 24% L t t _ -11 . t 4a_t I_., D. 🐨 M_I, tI tt / t _ D = 0 (t 4-5). J = t - D = 0/D = 0_ 9-12). - t - Cl_2 1 ____ 4a



Table 2. Coupling of Unactivated-Alkyl Bromides withAcids



A): - B. (0.3 C t (I, 100 I %), t $(170 | \%), (-)_{2} (10 | \%), 4b (12 | \%), 1 - Cl_{2} (100 | \%), B_{2} O (200 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (300 | \%), (30$. (170 **I**%), _ DI (0.2:0.8, /, 1 L). I Lt. I _t. t _t t t_{2} t_{1} t_{2} t_{1} t_{2} t_{2} t_{2} t_{1} t_{2} t_{2 FA. I l_{t} . 1. 15 1% $(--)_{2}$ 15 1 I_t. 14^W GC-J 15 В -4b ₩ % . ff. t. t. ...t ١v _____ t = (1 = 19:1);t ~14[™]_.t. t l<u>t</u> t. 1 . t<u>l</u> -,t I → _t ._.ff_t __ ().

2.2. C Tertiary A . – А , J t (1 1, t 16), ~ 2) $t_{0} t_{1} (3-t_{1} - 3-t_{1} - t_{1} - t_{1})$ (1.7)1b . . 2 t 11c, 2 ._t . . . ; t _ / _ W ft t.t. , L . · _t., , t 2 _ t _, ... ^w, νt. t .,, - tl ≉ _t _ / t I . A . t ۱_ -3- , 1. _ (0.85) t -____ t 1b ___ t W 11a 60% Ι., 1 11c 1).I _ t , _ _t t.tt.(_ا (16a) ^w t t ____1b ___ 4-__ -1-t I . .

Table 5. Examples of -Acyl Glycosides Using Methods B and C1







」 | __ 」[₩]t _t l_tt.tH' __t I, -_t_ * _ _ | t, ΥF, Κ _<u>_</u>___. 11.2 ⊐l, L^{, w}t t $(\mathbf{III}') \mathbf{t}$._t t $\sum_{i=1}^{n} \frac{t_{i}}{t_{i}} = \frac{t_{i}}{t_{i}}$ $\int_{1}^{1} C(\mathbf{0}) - \int_{1}^{111} (\mathbf{0}C(\mathbf{0}) - \mathbf{0}) \int_{1}^{111} \mathbf{0}C(\mathbf{0}) d\mathbf{0}$ 2.5.2. Radical Process. [₩]___, fi, t, , t l**ª_**t / l ~47-D [₩] t 3- H - /H (3), W = t(t = 1) H - /H (3), W = t(_-**48-D** [₩]t _ 1:1 . _t / 1 _ _ (4).



2.5.3. Radical Chain versus Double Oxidative Addition



Article

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(I-c) t $t = t^{29,39} \text{ wr} t$ -t $T = C I_2 t I_2$ $\mathbf{c} = \begin{bmatrix} \mathbf{c} & \mathbf{c} \\ \mathbf{c} & \mathbf{c} \end{bmatrix} = \begin{bmatrix} \mathbf{c} & \mathbf{c} \\ \mathbf{c} \end{bmatrix} = \begin{bmatrix} \mathbf{c} & \mathbf{c} \\ \mathbf{c} \end{bmatrix} = \begin{bmatrix} \mathbf{c} \\ \mathbf{$ (F 2).^{37,40} It $\exists t t _ I-a t$ $I \longrightarrow t F$, 5), $t \longrightarrow t t I_{-}$, t t I, $t \longrightarrow t - 1-a/\mathbb{P}Cl_2$. H^{VV} , $t \longrightarrow I$

∠t_ t.

 $(--)_2$ = 2.5% t 15%, t _t = 49/50 I B.



t _t (49/50) Figure 3. D _t_l tl _ _____I . E__, _t ____. 4 . t. .

, $\| \mathbf{t} \mathbf{t} \|_{\mathbf{L}} = \mathbf{t} = \mathbf{t} \mathbf{t} \mathbf{t} \mathbf{t} \mathbf{t} \mathbf{t}$

3. Ç C 7

t t, _t l_l _ l _ -t - $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0$. t**^**

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