Supporting Information

^BuOLi-Promoted Hydroboration of Esters and Epoxides

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1. General procedure for the hydroboration of lactones and epoxides.
1.1 Procedure for the lactones

In a nitrogen-filled glovebox, to a 10 mL Schlenk reaction tube equipped with a magnetic stirrer, 
$tBuOLi$ (8.0 mg, 5 mol%), THF (1.0 mL), HBpin (2.5 mmol) and the corresponding lactones (1 mmol) were added in sequence. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. Thereafter, the reaction mixture was cooled down to room temperature and NaOH/MeOH (2 mL, 10 % aq.) solution was added. The resulting mixture was stirred overnight for complete hydrolysis. Organic compounds were extracted from the mixture with CH$_2$Cl$_2$ (3 x 12 mL). The organic fraction was dried over Na$_2$SO$_4$ and all volatiles were removed using rotary evaporator. The crude mixture was monitored by $^1$H NMR analysis using biphenyl or hexamethylbenzene as internal standard. The crude mixture was purified by flash column chromatography using PE/EtOAc (2/1) as the eluent to give the corresponding products.

1.2 Procedure for the epoxides

In a nitrogen-filled glovebox, to a 10 mL Schlenk reaction tube equipped with a magnetic stirrer, 
$tBuOLi$ (4.0 mg, 5 mol%), THF (1.0 mL), HBpin (2.5 mmol) and the corresponding epoxides (1 mmol) were added in sequence. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. Thereafter, the reaction mixture was cooled down to room temperature and
NaOH/MeOH (2 mL, 10 % aq.) solution was added. The resulting mixture was stirred overnight for complete hydrolysis. Organic compounds were extracted from the mixture with CH$_2$Cl$_2$ (3 x 12 mL). The organic fraction was dried over Na$_2$SO$_4$ and all volatiles were removed using rotary evaporator. The crude mixture was monitored by $^1$H NMR analysis using hexamethylbenzene as internal standard. The crude mixture was purified by flash column chromatography using PE/EtOAc (3/1) as the eluent to give the corresponding products.

2. $^t$BuOLi-catalyzed decomposition of HBpin by $^{11}$B NMR spectroscopy.

A stock solution of HBpin (262.4 mg, 2.05 mmol), dimethyl sulfide (9 µL, 0.12 mmol) and $^t$BuOLi (9.6 mg, 0.12 mmol) in C$_6$D$_6$ (0.5 ml) were prepared under N$_2$. The reaction was heated to 100 °C for 30 minutes with stirring. Then $^{11}$B NMR spectrum was recorded.

![Figure S1: $^{11}$B-NMR spectrum of $^t$BuOLi+HBpin+SMe$_2$ at 100 °C (160M, C$_6$D$_6$).](image)
3. ^{1}BuOLi-catalyzed decomposition of Catecholborane by $^{11}$B NMR spectroscopy.

A stock solution of Catecholborane (246 mg, 2.05 mmol), dimethyl sulfide (9 µL, 0.12 mmol) and ^{1}BuOLi (16.8 mg, 0.21 mmol) in C$_6$D$_6$ (0.5 ml) were prepared under N$_2$. The reaction was heated to 100 ºC for 30 minutes with stirring. Then $^{11}$B NMR spectrum was recorded.

![Figure S2: $^{11}$B-NMR spectrum of $^{1}$BuOLi+ Catecholborane +SMe$_2$ at 100 ºC (400M, C$_6$D$_6$).](image)

4. ^{1}BuOLi-catalyzed decomposition of HBdan by $^{11}$B NMR spectroscopy.

A stock solution of HBdan (344.4 mg, 2.05 mmol), dimethyl sulfide (9 µL, 0.12 mmol) and ^{1}BuOLi (9.6 mg, 0.12 mmol) in C$_6$D$_6$ (0.5 ml) were prepared under N$_2$. The reaction was heated to 100 ºC for 30 minutes with stirring. Then $^{11}$B NMR spectrum was recorded.
Figure S3. $^{11}$B-NMR spectrum of $^t$BuOLi+HBdan+SM$_2$ at 100 °C (400M, C$_6$D$_6$).

5. $^t$BuOLi-catalyzed decomposition of 9-BBN by $^{11}$B NMR spectroscopy.

A stock solution of 9-BBN (250.1 mg, 2.05 mmol), dimethyl sulfide (9 µL, 0.12 mmol) and $^t$BuOLi (9.6 mg, 0.12 mmol) in C$_6$D$_6$ (0.5 ml) were prepared under N$_2$. The reaction was heated to 100 °C for 30 minutes with stirring. Then $^{11}$B NMR spectrum was recorded.
Figure S4: $^{11}\text{B}$-NMR spectrum of $^3\text{BuOLi}+9\text{-BBN}+\text{SMe}_2$ at 100 °C (400M, C$_6$D$_6$).
6. Copies of $^1$H and $^{13}$C NMR Spectra

$^1$H NMR (500 MHz, CDCl$_3$) of compound 2a

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2a

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$^1$H NMR (500 MHz, CDCl$_3$) of compound 2b

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2b
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2c

$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$) of compound 2c
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2d

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2d
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2e

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2e
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2f

$^{13}$C\{$^1$H\} NMR (125 MHz, CDCl$_3$) of compound 2f
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2g

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2g
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2h

$^{13}$C{H} NMR (125 MHz, CDCl$_3$) of compound 2h
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2i

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2i
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2j

$^{13}$C\{$^1$H\} NMR (125 MHz, CDCl$_3$) of compound 2j
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2k

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) of compound 2k
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2l

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2l
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2m

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2m
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2n

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2n
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2o

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2o
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2p

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2p
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2q

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2q
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2r

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2r
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2s

$^{13}$C\{$^1$H\} NMR (125 MHz, CDCl$_3$) of compound 2s
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2t

$^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2t
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2u

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2u
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2v

$^{13}$C\{\textsuperscript{1}H\} NMR (125 MHz, CDCl$_3$) of compound 2v
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2w

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2w
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2x

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2x
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2y

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2y
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2z

$^{13}$C-$^1$H NMR (125 MHz, CDCl$_3$) of compound 2z
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2za

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$) of compound 2za
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zb

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zb
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zc

$^{13}$C\{\textsuperscript{1}H\} NMR (125 MHz, CDCl$_3$) of compound 2zc
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zd

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zd
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2ze

$^{13}$C-$^1$H NMR (125 MHz, CDCl$_3$) of compound 2ze
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zf

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zf
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zg

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zg
\(^1\)H NMR (500 MHz, CDCl\(_3\)) of compound 2zh

\(^{13}\)C\(^{\{1\}H\}\) NMR (125 MHz, CDCl\(_3\)) of compound 2zh
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zi

$^{13}$C-$^1$H NMR (125 MHz, CDCl$_3$) of compound 2zi
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zj

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zj
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zk

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zk
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zl

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$) of compound 2zl
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zm

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) of compound 2zm
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zn

$^{13}$C{${^1}$H} NMR (125 MHz, CDCl$_3$) of compound 2zn
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zo

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$) of compound 2zo
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zo-1

$^{13}$C{$^1$}H NMR (125 MHz, CDCl$_3$) of compound 2zo-1
$^1$H NMR (500 MHz, CDCl$_3$) of compound 1zp

$^{13}$C{${}^1$H} NMR (125 MHz, CDCl$_3$) of compound 1zp
$^1$H NMR (500 MHz, CDCl$_3$) of compound 2zp

$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$) of compound 2zp