Supporting Information

Entry	Nucleophile (2 eq.)	Solvent	Ratio **8** / **9**(**10**)*
1	EtMgI	THF or Et_2O	1.0 / 26.4
2	EtMgBr	THF or Et_2O	1.0 / 1.2
3	EtLi	Et_2O	1.0 / 0.0
4	EtMgCl	Et_2O	1.0 / 0.0

Table 1. Screening of nucleophiles in the ring opening of epoxide **6**.

* Ratio **8** : **9**(**10**) determined by LC-MS analysis of crude reaction mixtures.

Entry	Pd-salt (mol. eq.)	Solvent mixture	Oxidant (mol. eq.)	Temp. / Time	Yield*
1	$PdCl_2$ (0.1)	DMF/H_2O (8/1)	O_2/CuCl (2)	r.t. / 24 h	61%
2	$PdCl_2$ (0.1)	DMF/H_2O (8/1)	air/CuCl (1)	r.t.-30°C / 24 h	59%
3	$PdCl_2$ (0.1)	THF/H_2O (8/1)	O_2/CuCl (1)	r.t. / 48 h	57%
4	$PdCl_2$ (0.1)	MeOH/H_2O (8/1)	O_2/CuCl (1)	r.t.-40°C / 3 d	22%
5	$PdCl_2$ (0.1)	Acetone/H_2O (8/1)	O_2/CuCl (1)	r.t.-40°C / 3 d	27%
6	$PdCl_2$ (0.1)	Dioxane/H_2O (8/1)	O_2/CuCl (0.2)	r.t.-80°C / 21 d	16%
7	$PdCl_2$ (0.1)	THF/H_2O (8/1)	O_2/$Cu(OAc)_2$ (2)	r.t. / 14 d	32%
8	$PdCl_2$ (0.1)	THF/H_2O (8/1)	O_2/CuCl (0.2)	r.t. / 24 h	66%
9	$PdCl_2$ (0.1)	THF/H_2O (8/1)	air/CuCl (0.2)	r.t. / 24 h	44%
10	$PdCl_2(PhCN)_2$ (0.1)	THF/H_2O (8/1)	air/CuCl (0.2)	r.t.-30°C / 5 d	54%
11	$PdCl_2(PPh_3)_2$ (0.1)	THF/H_2O (8/1)	air/CuCl (0.2)	r.t. / 21 d	0%
12	$PdCl_2$(sparteine) (0.05)	THF/H_2O (8/1)	O_2 (balloon)	r.t.-60°C / 6 d	0%
13	$Pd(OAc)_2$ (0.1)	THF/H_2O (8/1)	O_2/CuCl (0.2)	r.t. / 21 d	42%
14	$Pd(OCOCF_3)_2$ (0.1)	THF/H_2O (8/1)	O_2/CuCl (0.2)	r.t.-reflux / 7 d	39%
15	10% Pd/C (0.1)	THF/H_2O (8/1)	O_2/CuCl (0.2)	reflux / 7 d	21%
16	$PdCl_2$ (0.2)	DMA/H_2O (8/1)	O_2 (balloon)	r.t. / 48 h	73%
17	$PdCl_2$ (0.2)	NMP/H_2O (8/1)	O_2 (balloon)	r.t. / 24 h	85%
18	$PdCl_2$ (0.15)	DMF/H_2O (8/1)	O_2 (balloon)	reflux / 7 d	40%
19	$Pd(OAc)_2$ (0.05)	Dioxane/H_2O (8/1)	$K_2S_2O_8$ (2)	r.t. / 3 h	17%
20	$Pd(OAc)_2$ (0.05)	THF/H_2O (8/1)	$K_2S_2O_8$ (2)	reflux / 24 h	29%

Table 2. Reaction screening of Wacker-Tsuji oxidation of alkenylazide **12** to azidoketone **4**.

* Isolated yield of **4** after FLC purification.

Entry	$LiAlH_4$ (mol. eq.)	Me_3Al (mol. eq.)	Solvent	Order of sequential addition of reagents	Ratio **1** / **2** (*d.e. %*)
1	7	7	THF	$LiAlH_4$ → **13** → Me_3Al	1 / 4 (60)
2	7	7	THF	$LiAlH_4$ → Me_3Al → **13**	-
3	7	7	THF	**13** → Me_3Al → $LiAlH_4$	1 / 40 (95)
4	2	2	THF	**13** → Me_3Al → $LiAlH_4$	1 / 1.5 (20)
5	2	7	THF	**13** → Me_3Al → $LiAlH_4$	1 / 2 (33)
6	25	None	THF	$LiAlH_4$ → **13**	6 / 1 (71)
7	25	None	Et_2O	$LiAlH_4$ → **13**	1.3 / 1 (13)

Table 3. Reaction screening of diastereoselective reduction of cyclic imine **13**.

* Ratio **1** / **2** determined by ^1H NMR of crude reaction mixtures.