

Table S1. New methods of guanidine synthesis

Entry	Substrate	General conditions	Yields (%)	Ref.
1	R_2NH_2	<p>i) $\text{Br-CH}_2\text{-}$ 4-6 h ii) 2.5 eq. $R_2\text{-NH}_2$, 20 h 2:1 $\text{CH}_2\text{Cl}_2/\text{DMF}$, 50 °C</p>	42-99	6
2	HNRR'	<p>i) $\text{Br-CH}_2\text{-}$ 1.5 eq. $\text{CH}_2\text{Cl}_2/\text{DMF}$, 50 °C ii) 2.5 eq. HNRR', 1.5 eq. HgCl_2 Pr-OH, 90 °C, 20h</p>	51-82	6
3	$R\text{-NH}_2$	<p>i) $\text{Br-CH}_2\text{-}$ 1.7 eq. 12 h ii) 3 eq. $R\text{-NH}_2$, 24 h 2:1 $\text{CH}_2\text{Cl}_2/\text{DMF}$, 50 °C</p>	77-82	6
4	R_2R_3NH	<p>i) Tf-NH_2 (1.5 eq.), NaH (1.5 eq.) DMF (0.4 M), 80 °C ii) $R_2R_3\text{-NH}$ (2 eq.), EDCI (1.1 eq.), rt</p>	52-99	7
5	ArNH_2	<p>ArNH_2, 5 mol % AlClMe_2 toluene, 70-90 °C, 18h - 2d</p>	72-100	8
6		<p>3 mol % Sml_2 toluene, 60 °C, 6h</p>	86-97	9
7	ArNH_2	<p>amines, MeCN HgO, 4A Mol. sieves</p>	41-85	11

Table S1 (contd.). New methods of guanidine synthesis

Entry	Substrate	General conditions	Yields (%)	Ref.
8	R_2NH_2		71-95	12
9	R_1NH_2 or R_1R_2NH		21-97	13
10	R_1NH_2 or R_1R_2NH		52-98	14
11	$R-CH=CH_2$		48-86	15
12			63-83 77-90	16
13			64-87	17

Table S1 (contd.). New methods of guanidine synthesis

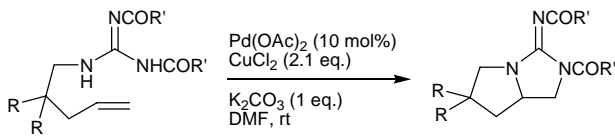
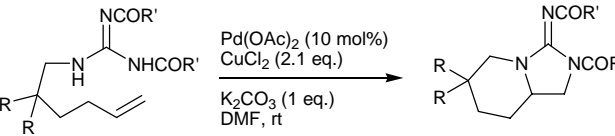
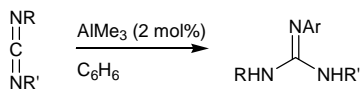
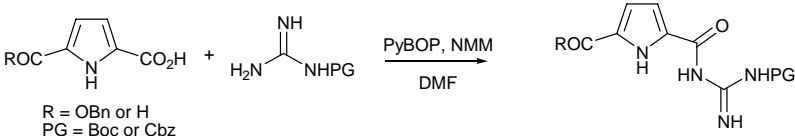
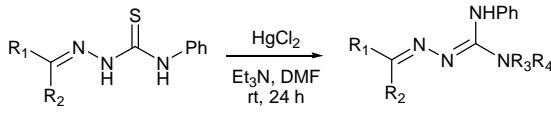
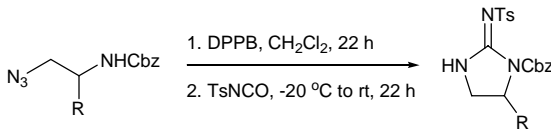
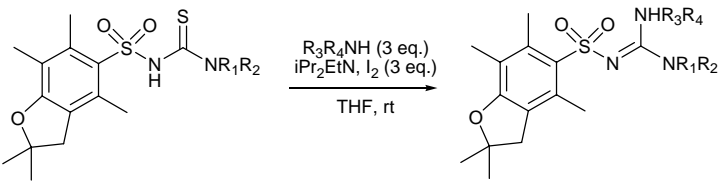
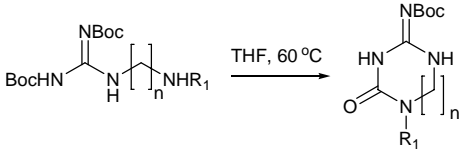
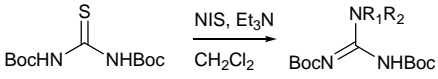
Entry	Substrate	General conditions	Yields (%)	Ref.
14		Pd(OAc) ₂ (10 mol%) CuCl ₂ (2.1 eq.) K ₂ CO ₃ (1 eq.) DMF, rt	70-99	18
15		Pd(OAc) ₂ (10 mol%) CuCl ₂ (2.1 eq.) K ₂ CO ₃ (1 eq.) DMF, rt	81-99	18
16	ArNH ₂		>99	19
17		PyBOP, NMM DMF	63, 93	20
18	R ₃ R ₄ NH		23-81	21
19		1. DPPB, CH ₂ Cl ₂ , 22 h 2. TsNCO, -20 °C to rt, 22 h	56, 71	22
20		R ₃ R ₄ NH (3 eq.) iPr ₂ EtN, I ₂ (3 eq.) THF, rt	54-94	23

Table S1 (contd.). New methods of guanidines synthesis

Entry	Substrate	General conditions	Yields (%)	Ref.
21			6-51	24
22	R ₁ NH ₂ or R ₁ R ₂ NH		15-85	25