

Literature Presentation

John H. Tipping

1/08/10

Pd-Catalyzed Synthesis of Allylic Silanes from Allylic Ethers

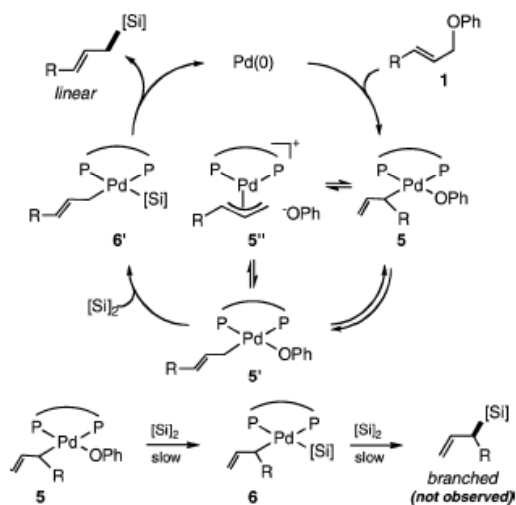
Table 2. Pd-Catalyzed Silylation Reactions with Hexamethyldisilane^a

entry	substrate	product ^b	yield (%) ^c
1			91
	1a	3a ; <i>t.b</i> = 25:1; <i>E:Z</i> = 10:1	
2 ^d			83
	1b	3a ; <i>t.b</i> = 25:1; <i>E:Z</i> = 3:1	
3 ^d			90
	1c	3b ; <i>t.b</i> = 25:1; <i>E:Z</i> = 9:1	
4 ^d			86
	1d	3c ; <i>t.b</i> = 25:1; <i>E:Z</i> = >25:1	
5 ^e			85
	1e	3d ; <i>t.b</i> = 25:1; <i>E:Z</i> = 3:1	

Table 3. Pd-Catalyzed Silylations with Disilane **2b**^a

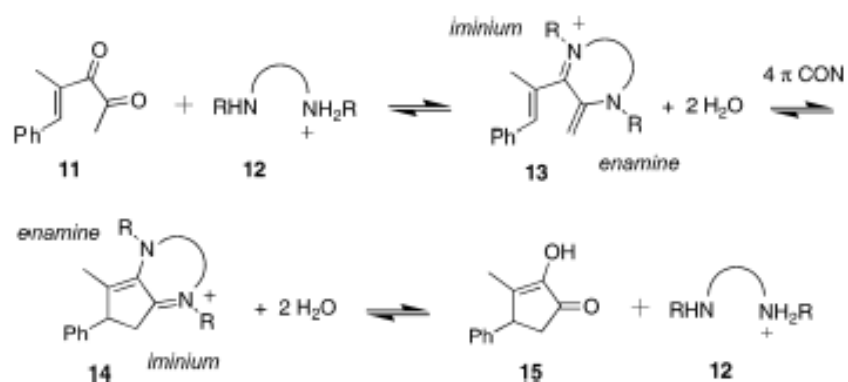
entry	substrate	product ^b	yield (%) ^c
1			91
	1a	3e ; <i>t.b</i> = 25:1; <i>E:Z</i> = >25:1	
2			83
	1b	3e ; <i>t.b</i> = 25:1; <i>E:Z</i> = 3:1	
3			93
	1f	3f ; <i>t.b</i> = 25:1; <i>E:Z</i> = >25:1	
4			94
	1g	3g ; <i>t.b</i> = 25:1; <i>E:Z</i> = >25:1	
5			91
	1c	3h ; <i>t.b</i> = 25:1; <i>E:Z</i> = 24:1	
6			87
	1d	3i ; <i>t.b</i> = 25:1; <i>E:Z</i> = >25:1	
7			95
	1h	3j ; <i>t.b</i> = 25:1; <i>E:Z</i> = >25:1	
8 ^d			73
	1i	3k	

Scheme 4

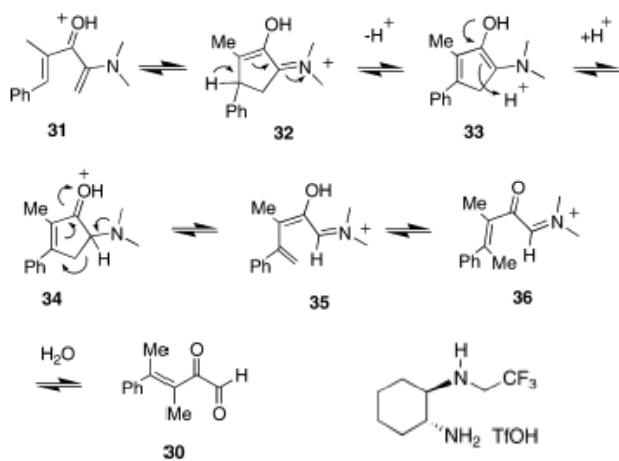


Enamine-Iminium Ion Nazarov Cyclization of α -Ketoenones

Scheme 3

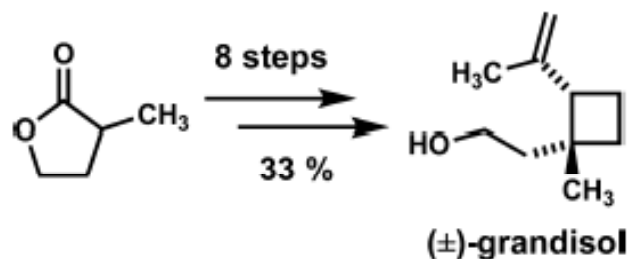


Scheme 5

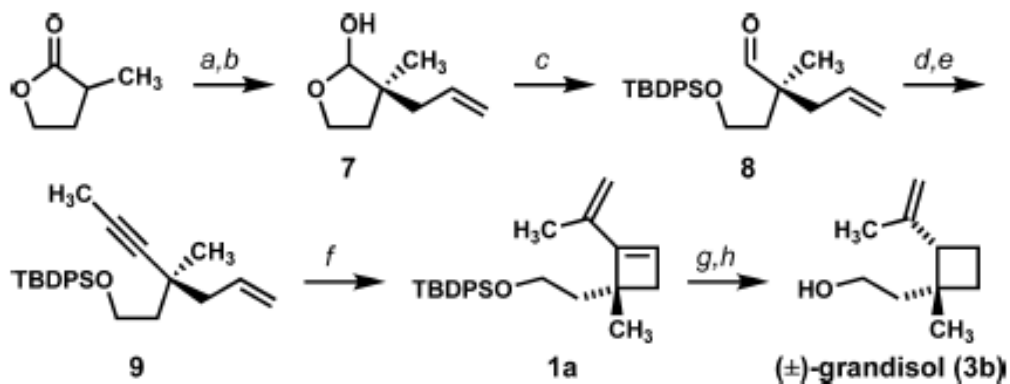


entry	diketone	cyclopentenone	yield	er ^a	rxn time
1			60(63)% ^b	97/3	7.5 d
2			66(73)%	>99/1	7.5 d
3			49% ^c	>99/1	6.5 d
4			65%	>99/1	7.5 d
5			62%	>99/1 ^d	7.5 d
6			11%	90/10	5.5 d
7			20%	91/9	6 d
8			24%	81/19 ^d	5 d

An Efficient Synthesis of (±)-Grandisol Featuring 1,5-Enyne Metathesis



SCHEME 3. Synthesis of (±)-Grandisol^a



^aReagents and conditions: (a) (i) LDA, (ii) allyl bromide, THF, $-78\text{ }^{\circ}\text{C}$, 91%; (b) DIBAL-H, PhCH_3 , $-78\text{ }^{\circ}\text{C}$, 95%; (c) TBDPSCl, imidazole, DMF, $60\text{ }^{\circ}\text{C}$, 92%; (d) $\text{CH}_3\text{COC}(\text{N}_2)\text{PO}(\text{OCH}_3)_2$, K_2CO_3 , CH_3OH , 87%; (e) (i) LDA, (ii) CH_3OTf , THF, $-78\text{ }^{\circ}\text{C}$, 91%; (f) 10 (20 mol%), CH_2Cl_2 , microwave, $75\text{ }^{\circ}\text{C}$, 83%; (g) Raney Ni, $i\text{PrOH}$, hexanes, 63%; (h) see ref 12.

SCHEME 2. Challenges Associated with Selective Semihydrogenation of 1

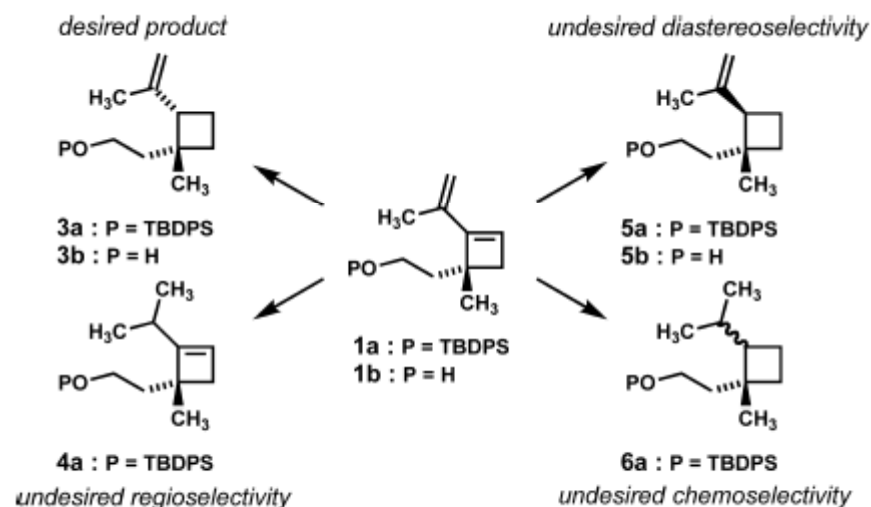


TABLE 1. Results of Representative Regioselective Semihydrogenations of 1a after 10 Minutes of Reaction Time

catalyst ^c	solvent	temp	1a ^a	3a	4a ^b	6a
Pd/C	THF	25 °C	15%	31%	10%	44%
Pd/C	THF	0 °C	14%	35%	11%	40%
Pd/C	PhCH ₃	25 °C	42%	19%	10%	29%
Pd/C	EtOH	25 °C	0%	35%	12%	53%
Pd/C	hexane	25 °C	0%	43%	12%	45%
Pd/CaCO ₃	EtOH	25 °C	0%	43%	5%	52%
Raney Ni ^d	ⁱ PrOH	25 °C	0%	70%	8%	22%

^aPercentages based on relative NMR integrations of distinctive peaks and scaled to 100%. ^bProduct 5a was formed in < 5% yield in each run. ^c5 mol %. ^dPerformed in the absence of a hydrogen atmosphere.

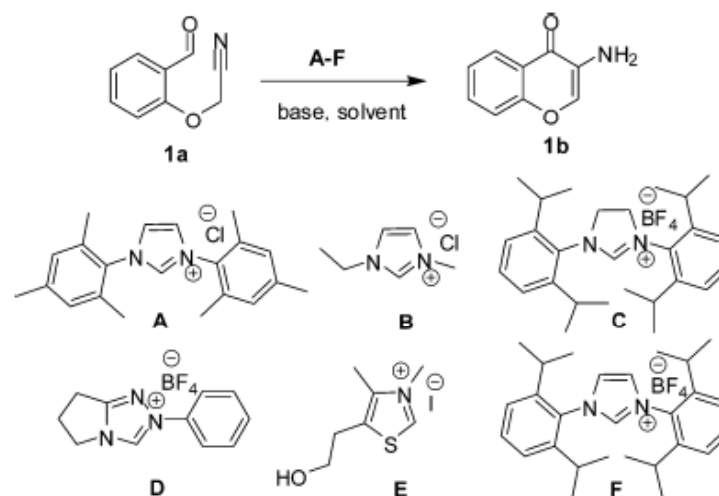
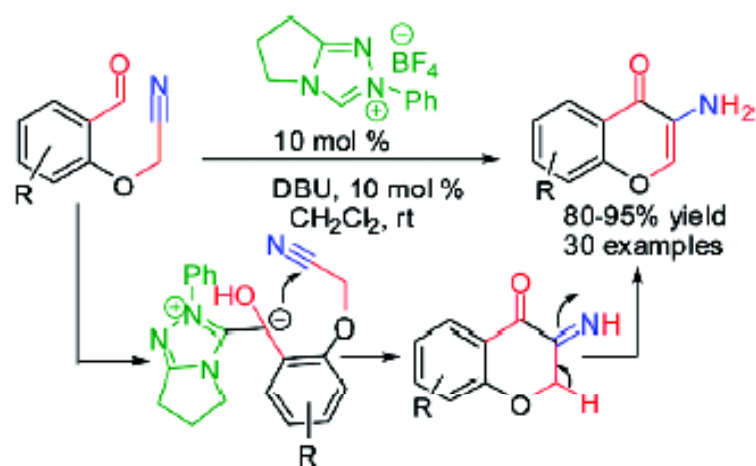
Literature Presentation

Chunli Cao

1/08/10

N-Heterocyclic Carbene-Catalyzed Intramolecular Aldehyde–Nitrile Cross Coupling: An Easy Access to 3-Aminochromones[†]

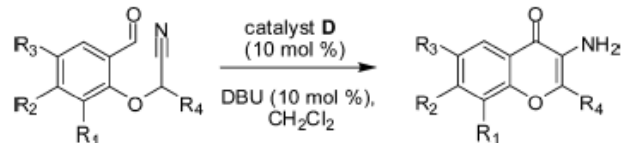
Table 1. Optimization of Intramolecular Aldehyde–Nitrile Cross Coupling



entry ^a	catalyst (equiv)	base ^b	solvent (0.1 M)	yield ^c (%)
1	A (0.10)	DBU	CH ₂ Cl ₂	53
2	B (0.10)	DBU	CH ₂ Cl ₂	trace
3	C (0.10)	DBU	CH ₂ Cl ₂	65
4	D (0.10)	DBU	CH₂Cl₂	83
5	E (0.10)	DBU	CH ₂ Cl ₂	77
6	F (0.10)	DBU	CH ₂ Cl ₂	67
7	D (0.15)	DBU	CH₂Cl₂	84
8	D (0.05)	DBU	CH ₂ Cl ₂	70
9	D (0.10)	DBU	THF	59
10	D (0.10)	DBU	CH ₃ CN	63
11	D (0.10)	DBU	Toluene	54
12	D (0.10)	DBU	DMF	72
13	D (0.10)	DBACO	CH ₂ Cl ₂	43
14	D (0.10)	Cs ₂ CO ₃ ^d	CH ₂ Cl ₂	69
15	D (0.10)	LiHMDS	CH ₂ Cl ₂	53

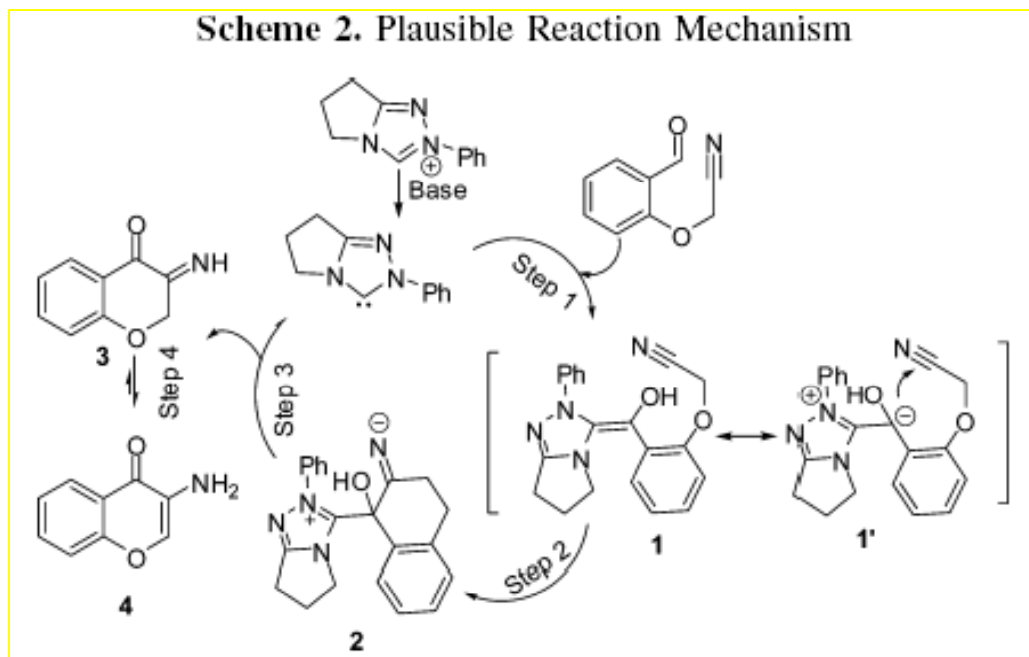
^a Unless otherwise specified, all of the reactions were carried out with freshly distilled dry solvents at room temperature for 24 h. ^b Equal mol % with respect to catalyst. ^c Isolated yields. ^d 3 equiv of base was used with respect to catalyst.

Table 2. Reaction Scope for 3-Aminochromone Derivatives



entry ^a	substrate	R ₁	R ₂	R ₃	R ₄	product	yield ^b (%)
1	1a	H	H	H	H	1b	83
2	2a	Me	H	H	H	2b	81
3	3a	^t Bu	H	^t Bu	H	3b	88
4	4a	H	H	-Ph-	H	4b	83
5	5a	H	H	Me	H	5b	85
6 ^c	6a	Allyl	H	H	H	6b	81
7	7a	OMe	H	H	H	7b	92
8	8a	H	OMe	H	H	8b	95
9	9a	H	H	OTBS	H	9b	91
10	10a	H	H	OMe	H	10b	89
11	11a	H	H	OH	H	11b	86
12	12a	H	H	Cl	H	12b	95
13	13a	Cl	H	Cl	H	13b	93
14	14a	H	H	Br	H	14b	86
15	15a	Br	H	Br	H	15b	91
16	16a	I	H	I	H	16b	82
17	17a	OMe	H	I	H	17b	89
18	18a	Br	H	Cl	H	18b	93
19	19a	OMe	H	NO ₂	H	19b	90
20	20a	H	H	NO ₂	H	20b	83
21	21a	F	H	H	H	21b	83
22	22a	H	F	H	H	22b	87
23	23a	F	H	F	H	23b	81
24	24a	H	H	OCF ₃	H	24b	88
25	25a	H	H	F	H	25b	85
26	26a	H	F	H	Me	26b	90
27	27a	F	H	H	Me	27b	81
28	28a	H	H	F	Me	28b	80
29	29a	OMe	H	H	Me	29b	83
30	30a	OMe	H	H	Ph	30b	85

Scheme 2. Plausible Reaction Mechanism



Concise Total Syntheses of the *Lycopodium* Alkaloids (±)-Nankakurines A and B via Luciduline

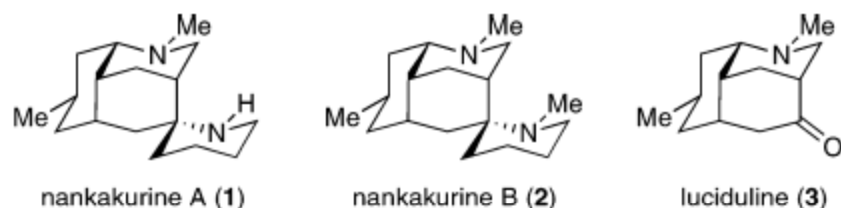
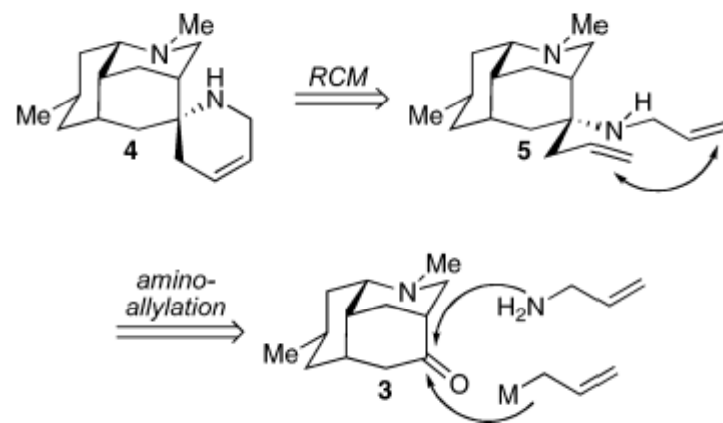
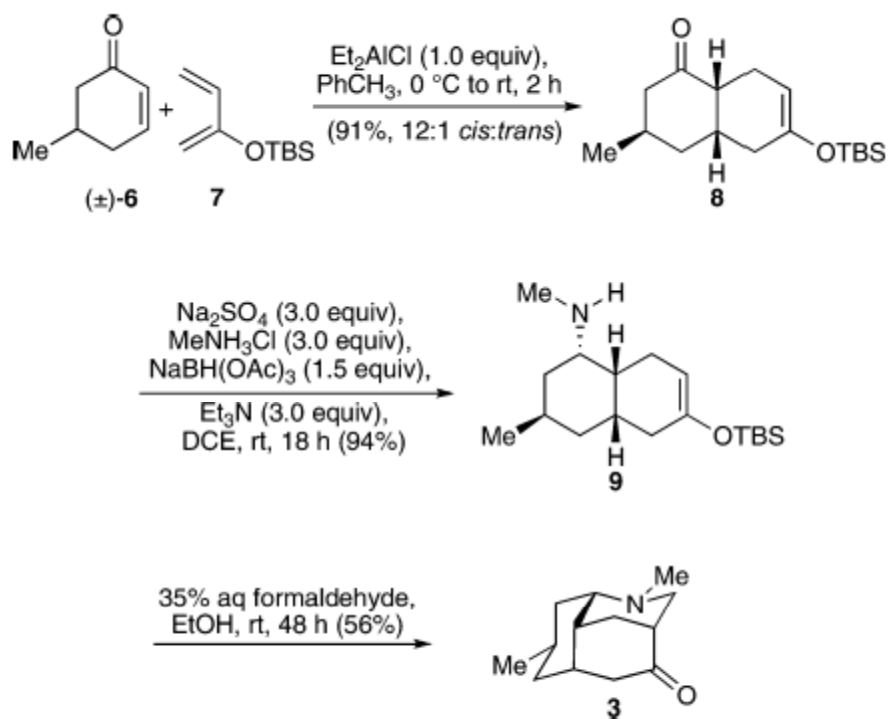


Figure 1. *Lycopodium* alkaloids nankakurines A and B and their structural relationship to luciduline.

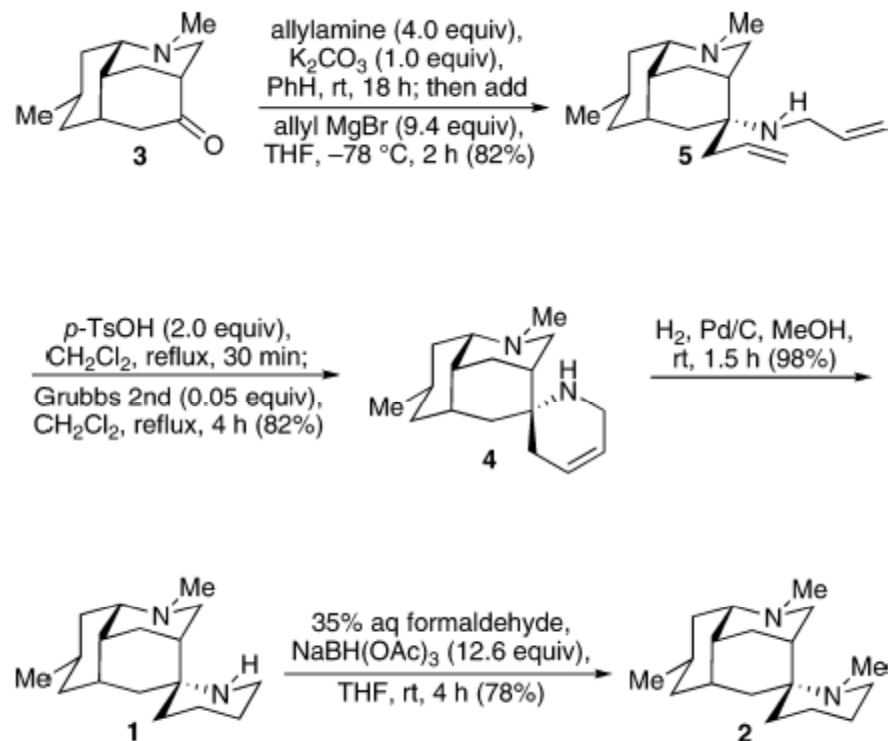
Scheme 1. Selected Bond Formations toward the Nankakurines



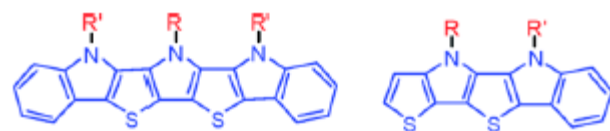
Scheme 2. Three-Step Total Synthesis of Luciduline



Scheme 3. Syntheses of Nankakurines A and B

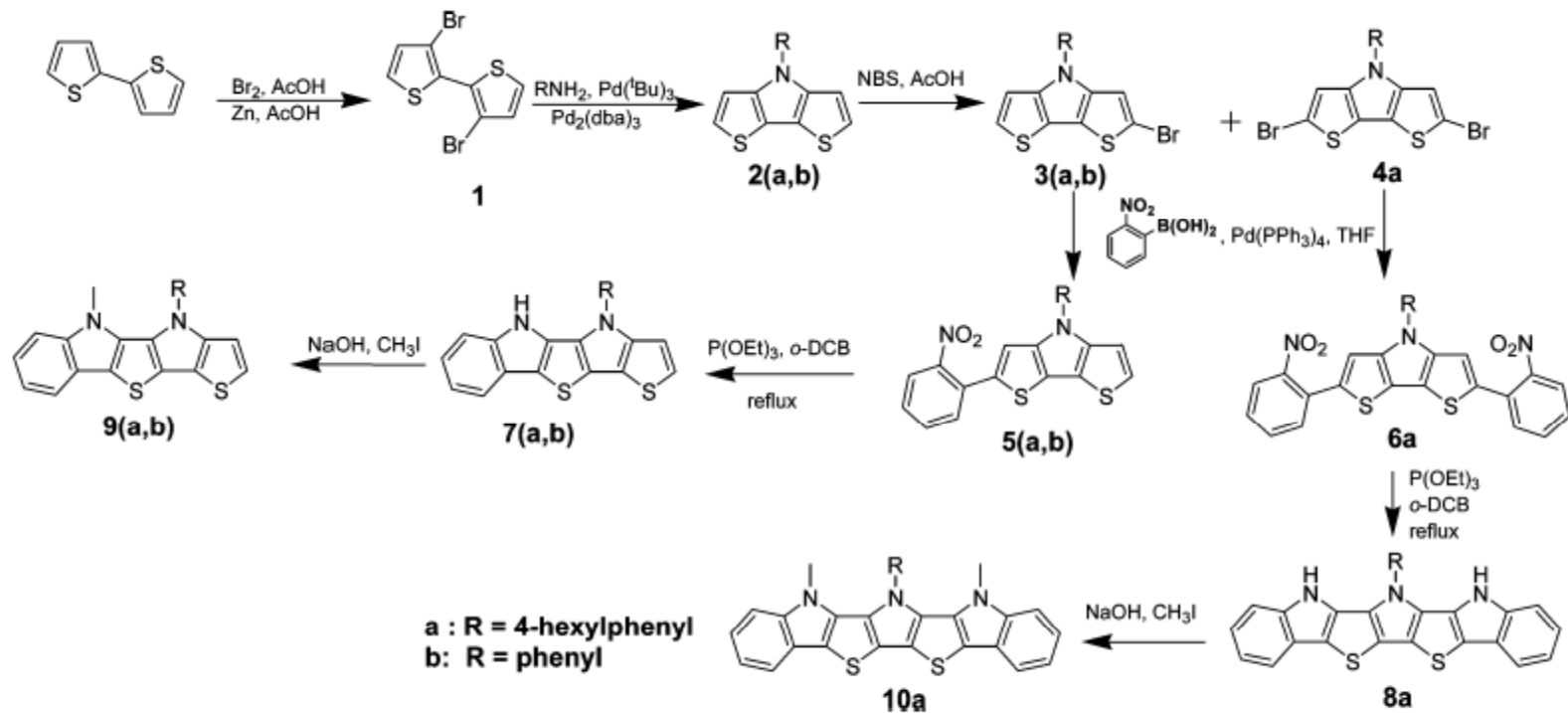


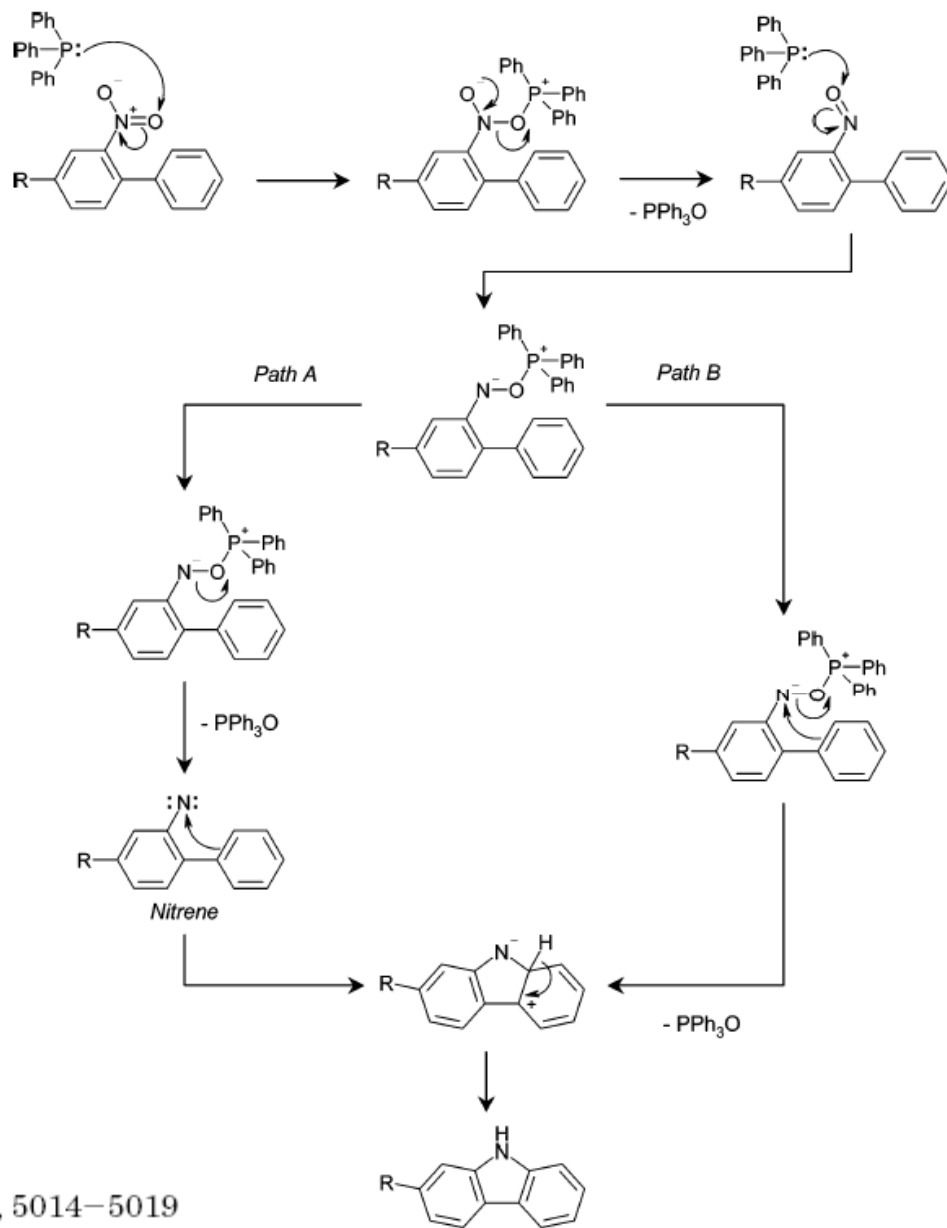
Synthesis and Characterization of Unsymmetric Indolodithienopyrrole and Extended Diindolodithienopyrrole



R = phenyl, 4-hexylphenyl
R' = H, CH₃

Scheme 1. Synthesis of Unsymmetrical and Extended Heteroacene





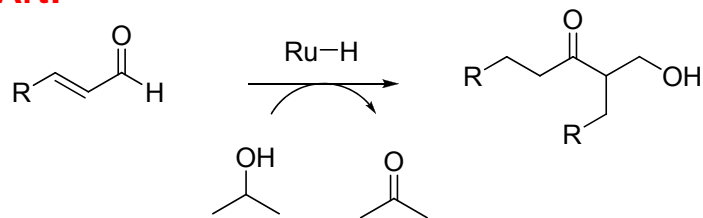
Literature Presentation

Kevin Olivier

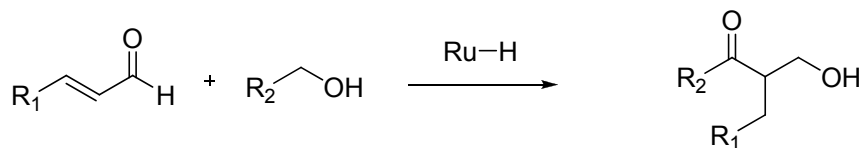
1/08/10

Synthesis of 2-Hydroxymethyl Ketones by Ruthenium Hydride-Catalyzed Cross-Coupling Reaction of α,β -Unsaturated Aldehydes with Primary Alcohols

Prior Art:



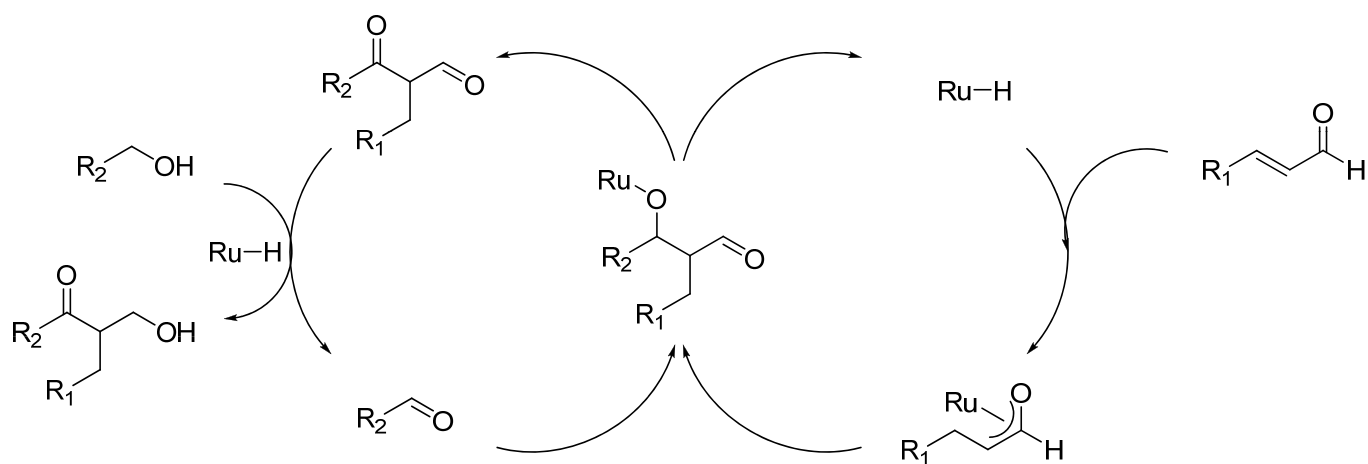
This Work:



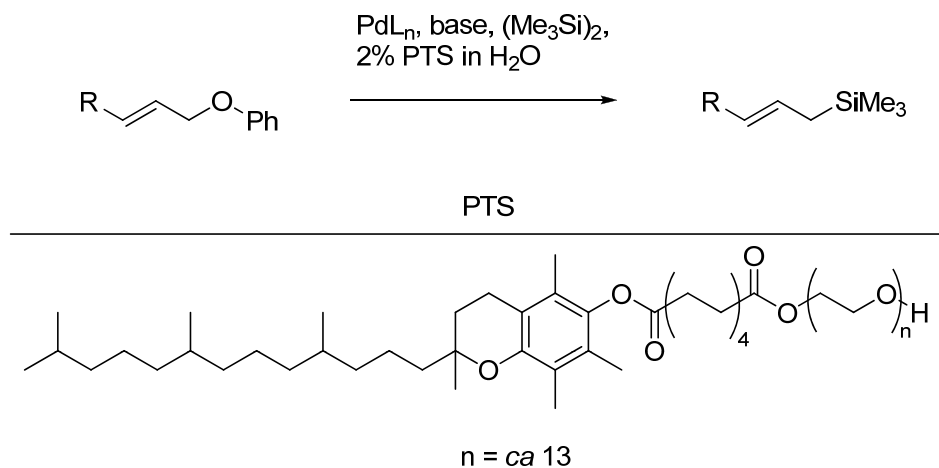
entry	R_1	R_2	yield (%)
1	<i>n</i> -propyl	Ph	72
2	<i>n</i> -propyl	<i>o</i> -MeO-Ph	53
3	<i>n</i> -propyl	<i>p</i> -Cl-Ph	74
4	<i>n</i> -propyl	2-furyl	66
5	2-furyl	Ph	60
6	Ph	<i>p</i> -Cl-Ph	69

Synthesis of 2-Hydroxymethyl Ketones by Ruthenium Hydride-Catalyzed Cross-Coupling Reaction of α,β -Unsaturated Aldehydes with Primary Alcohols

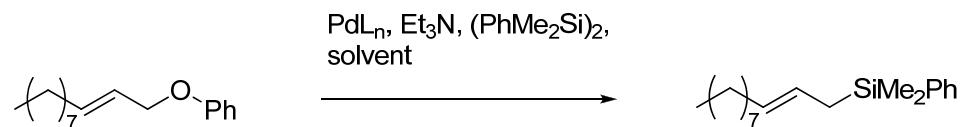
Proposed Mechanism:



Pd-Catalyzed Synthesis of Allylic Silanes from Allylic Ethers



entry	R	yield (%)	E:Z
1	Ph	91	10
2	<i>o</i> -MeO-Ph	86	> 25
3	<i>n</i> -octyl	85	3

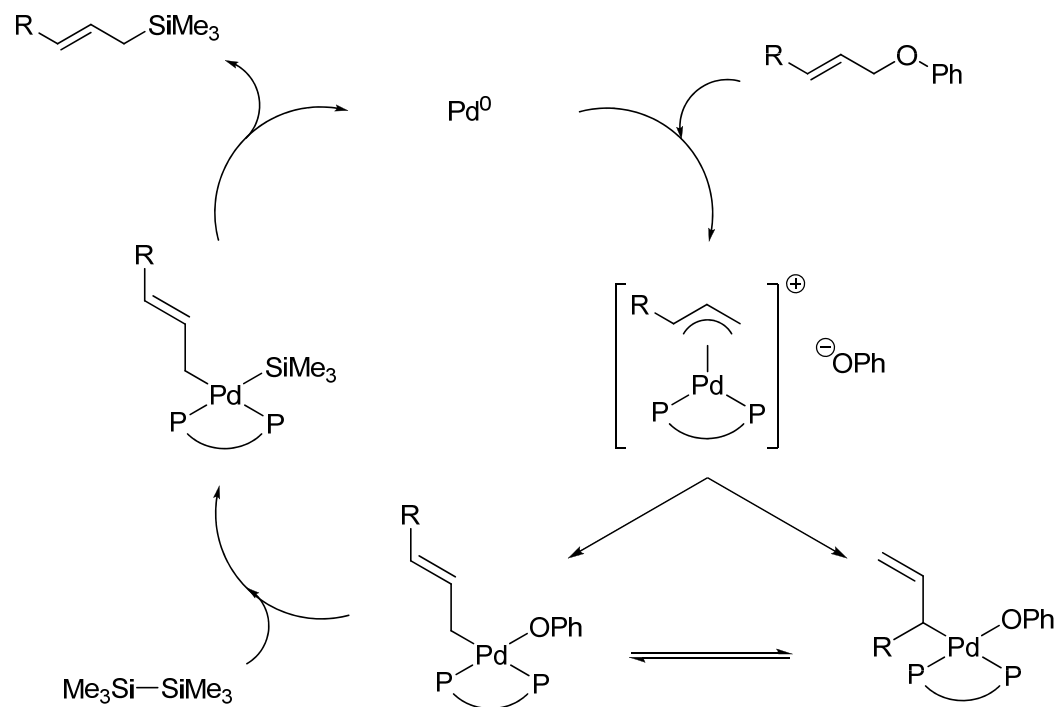


solvent = MeOH
solvent = PTS/H₂O

yield < 1%
yield = 89%

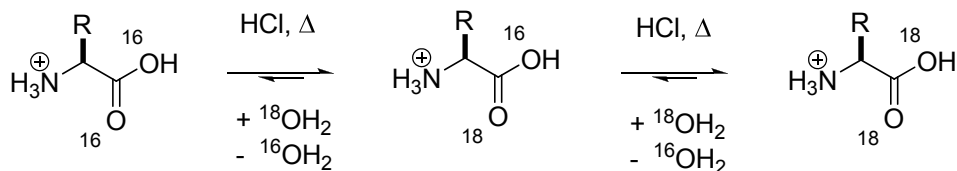
Pd-Catalyzed Synthesis of Allylic Silanes from Allylic Ethers

Proposed Mechanism:

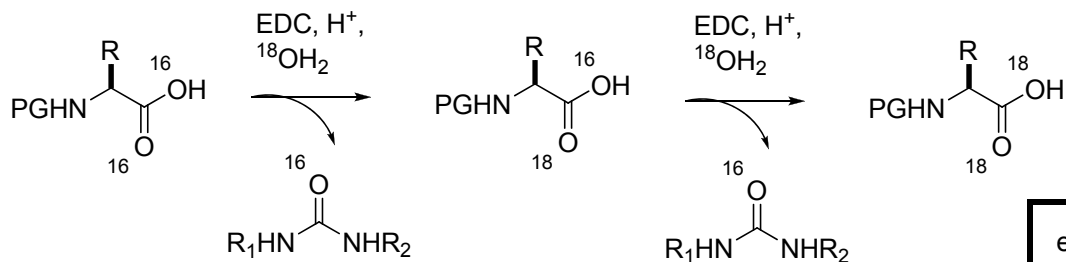


Multiple-Turnover Isotopic Labeling of Fmoc- and Boc-Protected Amino Acids with Oxygen Isotopes

Prior Art:



This Work:



entry	substrate	yield (%)	enrichment (%)
1	Fmoc-Glu(<i>t</i> Bu)-OH	94	93
2	Fmoc-Trp(Boc)-OH	88	92
3	Fmoc-Cys(Trt)-OH	95	95