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Citation:

2-Furyl Phosphines as Ligands for Transition-Metal-Mediated Organic Synthesis
Neil G. Andersen and Brian A. Keay
pp 997 – 1030.

Charts:

Chart 1. The Tolman Cone Angle

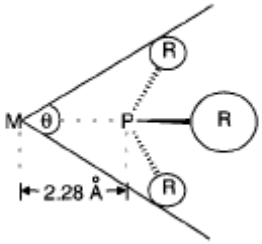


Chart 2. Equations Describing Complexation of TFP with Pd(dba)$_2$

$$Pd(dba)_2 + 2TFP \longrightarrow Pd(dba)(TFP)_2 + dba \quad (1)$$

$$Pd(dba)(TFP)_2 + S \rightleftharpoons SPd(TFP)_2 + dba$$

$$K_1 = \frac{[SPd(TFP)_2][dba]}{[Pd(dba)(TFP)_2]} \quad (2)$$

$$Pd(dba)(TFP)_2 + TFP \rightleftharpoons SPd(TFP)_3 + dba$$

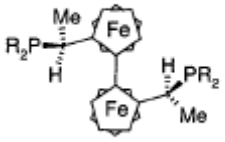
$$K_0 = \frac{[SPd(TFP)_3][dba]}{[Pd(dba)(TFP)_2][TFP]} \quad (3)$$

$$SPd(TFP)_3 \rightleftharpoons SPd(TFP)_2 + TFP$$

$$K_2 = \frac{[SPd(TFP)_2][TFP]}{[SPd(TFP)_3]} = K_1/K_0 \quad (4)$$

$$SPd(TFP)_2 + ArX \longrightarrow ArPdX(TFP)_2 + S \quad k \quad (5)$$

Chart 3. Selected Trans-Chelating Chiral Diphosphine Ligands (TRAPs)



(*S*,*S*)-(*R*,*R*)-TRAP

389a, R=Ph
389b, R=2-furyl
389c, R=(*p*-$CF_3C_6H_4$)
389d, R=Et
389e, R=*n*-Bu

Tables:

Table 1. Tolman Cone Angle (θ^c) for a Variety of Phosphines and Phosphinites[3]

ligand	cone angle (θ^c)	ligand	cone angle (θ^c)
PH_3	87°	$P(p\text{-Tol})_3$	145°
$P(OMe)_3$	107°	$P(m\text{-Tol})_3$	165°
PMe_3	118°	PCy_3	170°
$P(OPh)_3$	128°	$P(O\text{-}t\text{-Bu})_3$	172°
PEt_3	132°	$P(t\text{-Bu})_3$	182°
TFP	133°	$P(C_6F_5)_3$	184°
$P(CF_3)_3$	137°	$P(o\text{-Tol})_3$	194°
PPh_3	145°	P(mesityl)$_3$	212°

Table 2. Electronic Parameter ν for a Variety of Phosphines and Phosphinites[8]

ligand	ν (cm^{-1})	ligand	ν (cm^{-1})
PF_3	2110.8	$P(p\text{-Tol})_3$	2066.7
$P(C_6F_5)_3$	2090.9	$P(o\text{-Tol})_3$	2066.6
$P(OPh)_3$	2085.3	PMe_3	2064.1
PH_3	2083.2	PEt_3	2061.7
$P(OMe)_3$	2079.5	PBu_3	2060.3
PPh_3	2068.9	PCy_3	2056.4
$P(m\text{-Tol})_3$	2067.2	$P(t\text{-Bu})_3$	2056.1

Table 3. $^{31}P-^{77}Se$ Coupling Constants for Various Phosphine Selenides ($R_3P{=}Se$)[9]

PR_3	^1J (Hz)	PR_3	^1J (Hz)
$P(p\text{-}MeOC_6H_4)_3$	708	PPh_2(2-furyl)	754
$PPh_2(o\text{-Tol})$	730	P(2-thienyl)$_3$	757
PPh_3	732	$PPh_2(m\text{-}CF_3C_6H_4)$	766
PPh_2(2-thienyl)	743	PPh(2-furyl)$_2$	774
PPh(2-thienyl)$_2$	752	P(2-furyl)$_3$	793

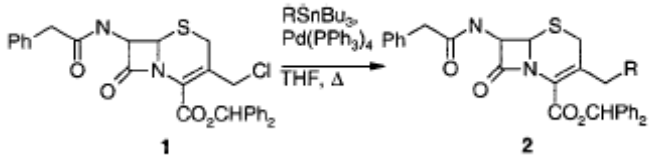
Table 4. Relative Rates of Stille Coupling between Iodobenzene and Vinyltributyltin with Various $Pd_2(dba)_3$/Ligand Catalysts at 50 °C in THF[10]

	ligand[a]	cone angle	relative rate[b]	inhibition factor[c]	yield (%)[d]
1	PPh_3	145°	1	19	15.2
2	$(p\text{-Tol})_3P$	145°	<0.07	>100	<2
3	$(o\text{-Tol})_3P$	194°	35.2	3.4	19
4	TFP	133°	105	3.7	>95
5	$P(C_6F_5)_3$	184°	e	- -	13.2
6	Ph_3As	142°	1100	1.3	>95

[a] Pd:L ratio = 1:4. [b] For PPh_3, $k = 4.6 \times 10^{-5}$ min^{-1}. [c] Ratio of PdL_2 catalyst rate to PdL_4 catalyst rate. [d] HPLC yield after 72 h. [e] Catalyst decomposition was instantaneous (<2 min).

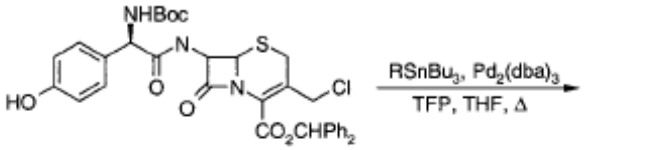
Schemes:

Scheme 1



1 2

Scheme 2



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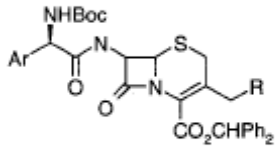
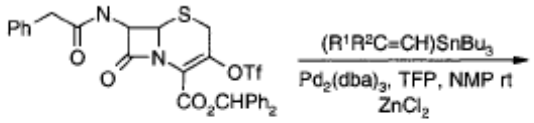


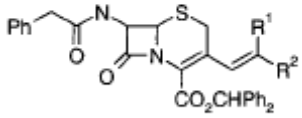
4-8

R	Time (h)	Yield (%)	Product
vinyl	3	82	**4**
Z-propenyl	16	78	**5**
2-methylpropenyl	72	60	**6**
1,2,2-trifluorovinyl	72	65	**7**
1-ethoxyvinyl	2	71	**8**

Scheme 3

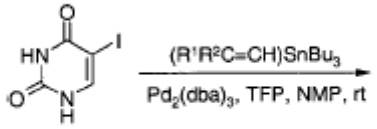


9



10 R^1=R^2=H, 79%
11 R^1=Me, R^2=H, 90%
12 R^1=R^2=Me, 66%

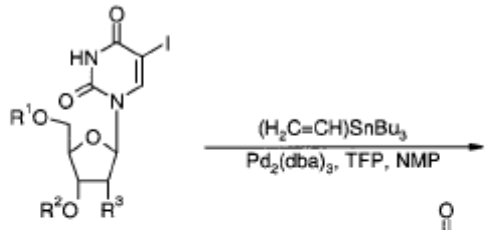
Scheme 4



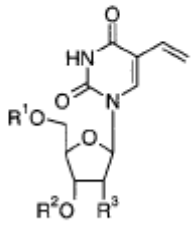
13

14 R^1=R^2=H, 89%
15 R^1=Ph, R^2=H, 92%
16 R^1=H, R^2=Me, 70%

Scheme 5

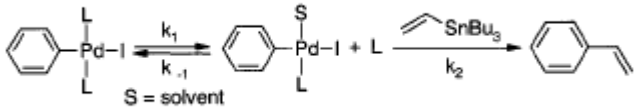


17 R^1=R^2=(*p*-Tol)CO, R^3=H
18 R^1=R^2=(*p*-Tol)CO, R^3=OCO(*p*-Tol)
19 R^1=TBS, R^2=R^3=H



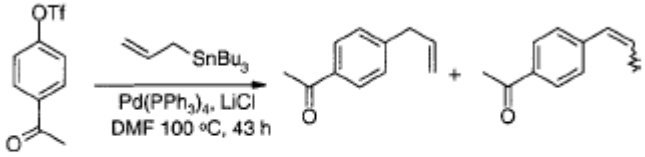
20 R^1=R^2=(*p*-Tol)CO, R^3=H, 76%
21 R^1=R^2=(*p*-Tol)CO, R^3=OCO(*p*-Tol), 98%
22 R^1=TBS, R^2=R^3=H, 91%

Scheme 6



23 **24** Product

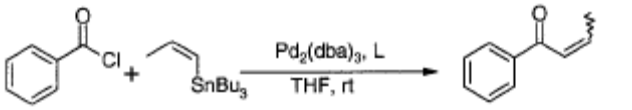
Scheme 7



25 **26** 18% **27** 54%

Catalyst	% Yield 26	% Yield 27
$Pd(PPh_3)_4$	18	54
Pd_2dba_3 + 8TFP	78.5	0

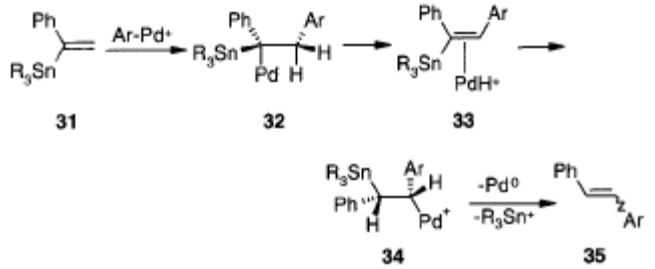
Scheme 8



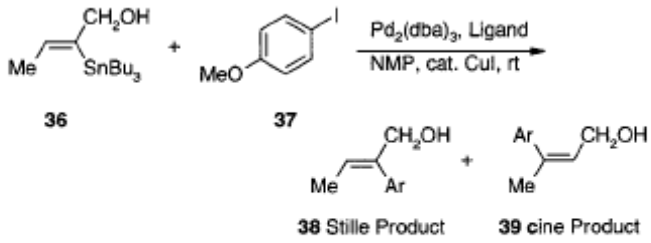
L=PPh_3, 71% stereospecificity
L=TFP, 97% stereospecificity

28 **29** **30**

Scheme 9

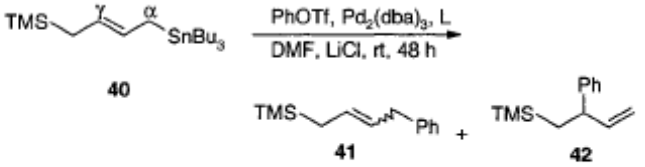


Scheme 10



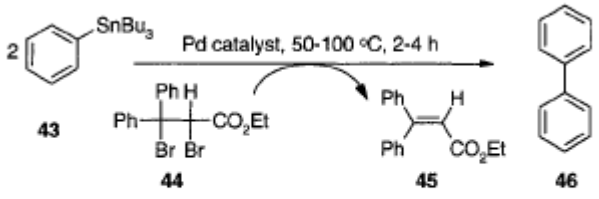
Ligand	Time (h)	Conversion (%)	Stille:cine
TFP	90	30	4 : 1
Ph_3As	160	>90	2 : 1

Scheme 11



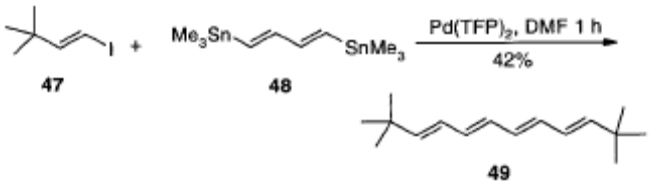
Ligand (L)	Yield (%)	41 (% E isomer)	α : γ
PPh_3	66	15	61 : 39
TFP	83	57	83 : 17
Ph_3As	87	84	91 : 9

Scheme 12



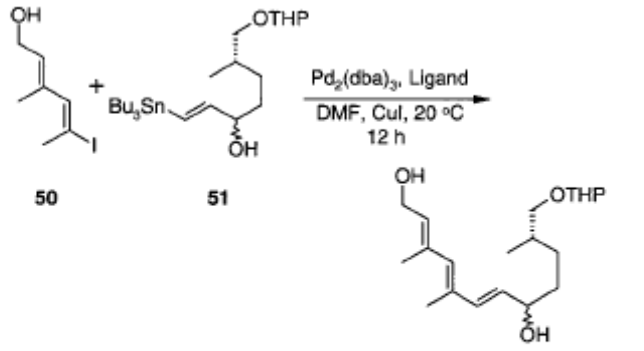
Catalyst	Yield (%)
$PdCl_2(MeCN)_2$/TFP	64
$PdCl_2(MeCN)_2/PPh_3$/CuI	54
$PdCl_2(MeCN)_2$/dppp	83

Scheme 13



47 48 49

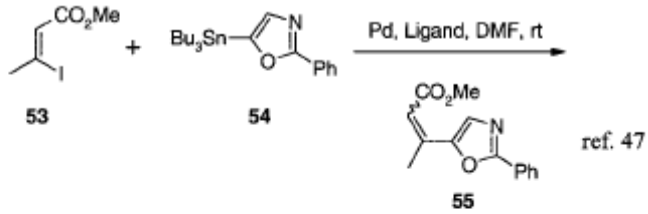
Scheme 14



50 51 52

Ligand	Yield (%)
PPh_3	34
TFP	26
$AsPh_3$	44

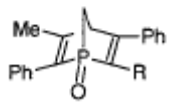
Scheme 15



53 54 55 ref. 47

Catalyst	Yield (%)	*Z* : *E*
$PdCl_2(MeCN)_2$	50	20 : 1
$Pd_2(dba)_3$/TFP	70	10 : 1

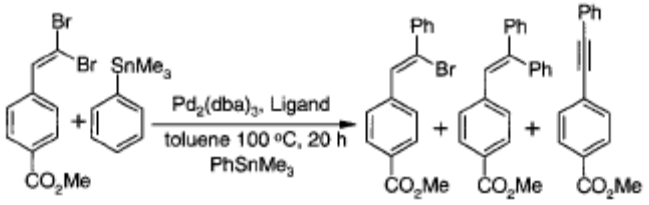
56 **57** R=alkynyl, vinyl, aryl



ref. 48

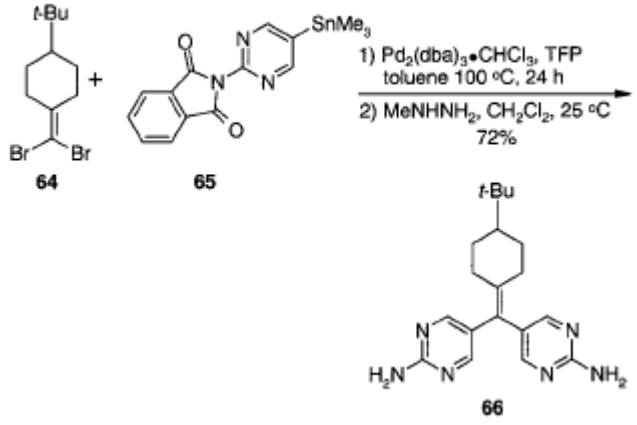
58

Scheme 16

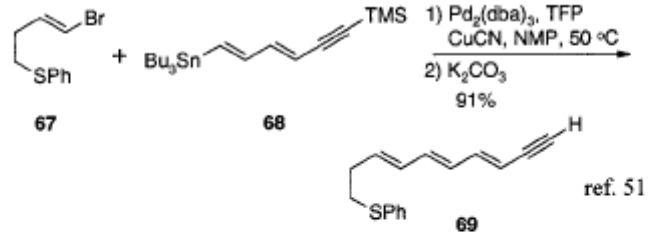


		Yield (%)		
Ligand	**Conv. (%)**	**61**	**62**	**63**
PPh_3	23	4	1	18
TFP	100	92	8	0
$AsPh_3$	69	37	32	0

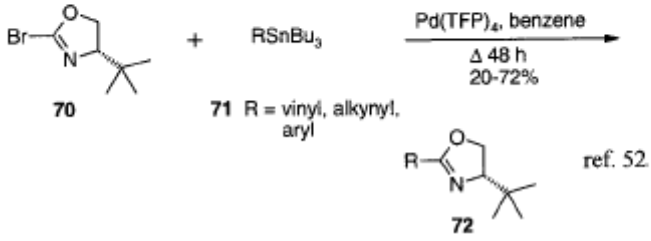
Scheme 17



Scheme 18

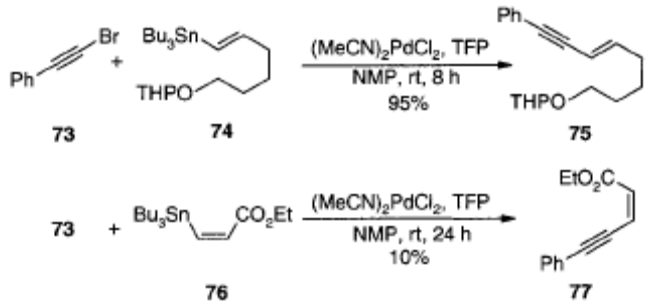


ref. 51

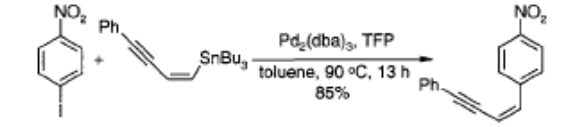


ref. 52

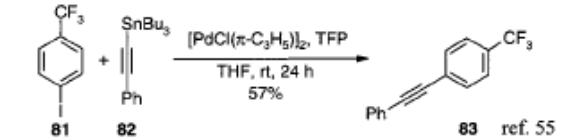
Scheme 19


Br
Ph
Bu3Sn
THPO
(MeCN)2PdCl2, TFP
NMP, rt, 8 h
95%
Ph
THPO
73
74
75
73
Bu3Sn
CO2Et
(MeCN)2PdCl2, TFP
NMP, rt, 24 h
10%
EtO2C
Ph
76
77

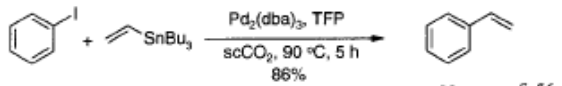
Scheme 20



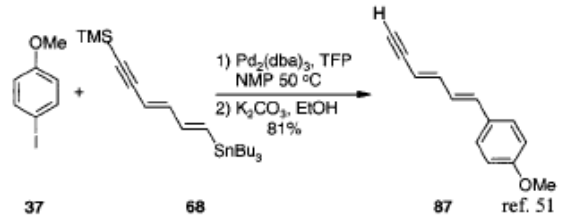
78 **79** **80** ref. 54



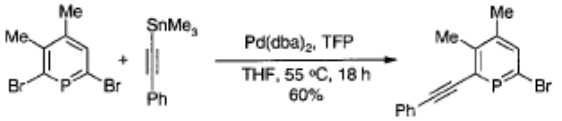
81 **82** **83** ref. 55



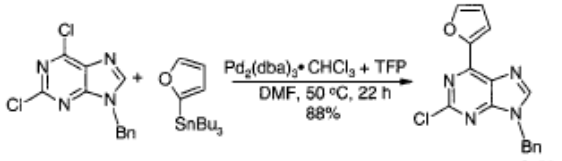
84 **85** **86** ref. 56



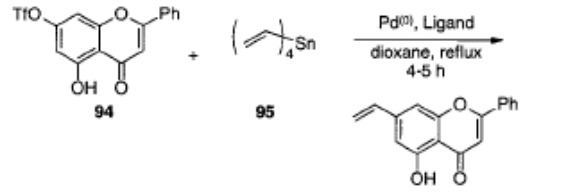
37 **68** **87** ref. 51



88 **89** **90** ref. 58

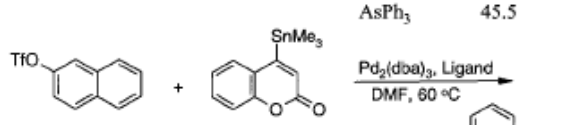


91 **92** **93** ref. 59

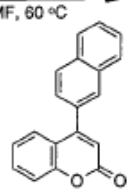


94 **95** **96** ref. 60

Ligand	Yield (%)
PPh_3	55
TFP	45
$AsPh_3$	45.5



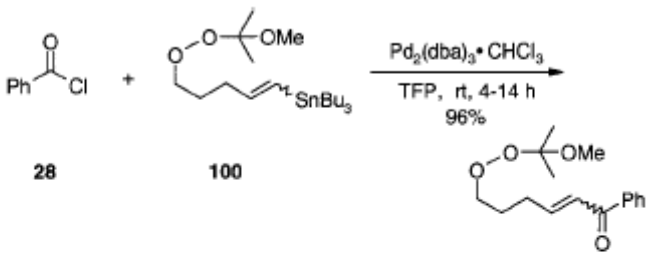
97 **98**



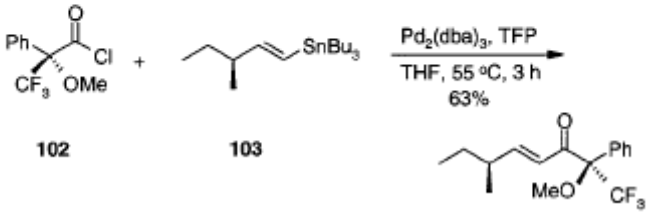
99 ref. 61

Ligand	Yield (%)
TFP	<10
$AsPh_3$	72

Scheme 21

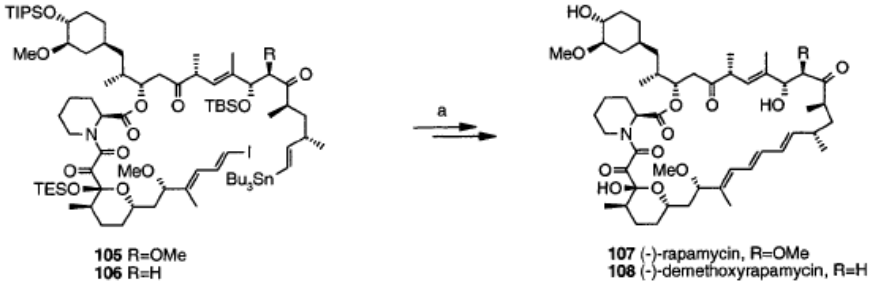


28 **100** **101** ref. 62



102 **103** **104** ref. 63

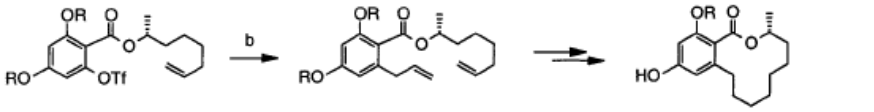
Scheme 22[a]



105 R=OMe
106 R=H

107 (-)-rapamycin, R=OMe
108 (-)-demethoxyrapamycin, R=H

ref. 64

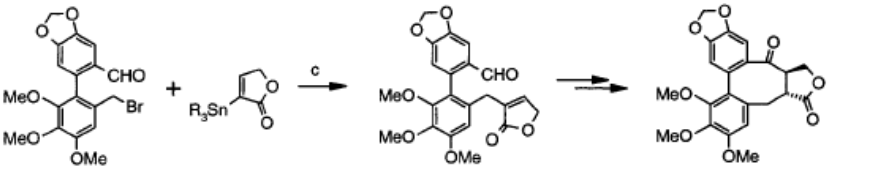


109 R=Me

110 R=Me

111 (+)-lasiodiplodin, R=Me
112 R=H

ref. 65



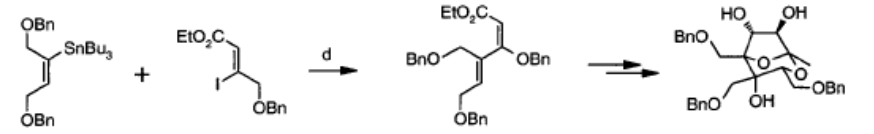
113

114 R=Bu

115

116 (+/-)-steganone

ref. 66



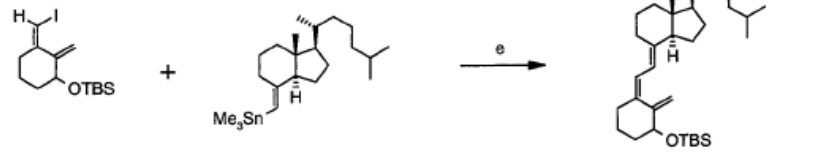
117

118

119

120

ref. 67



121

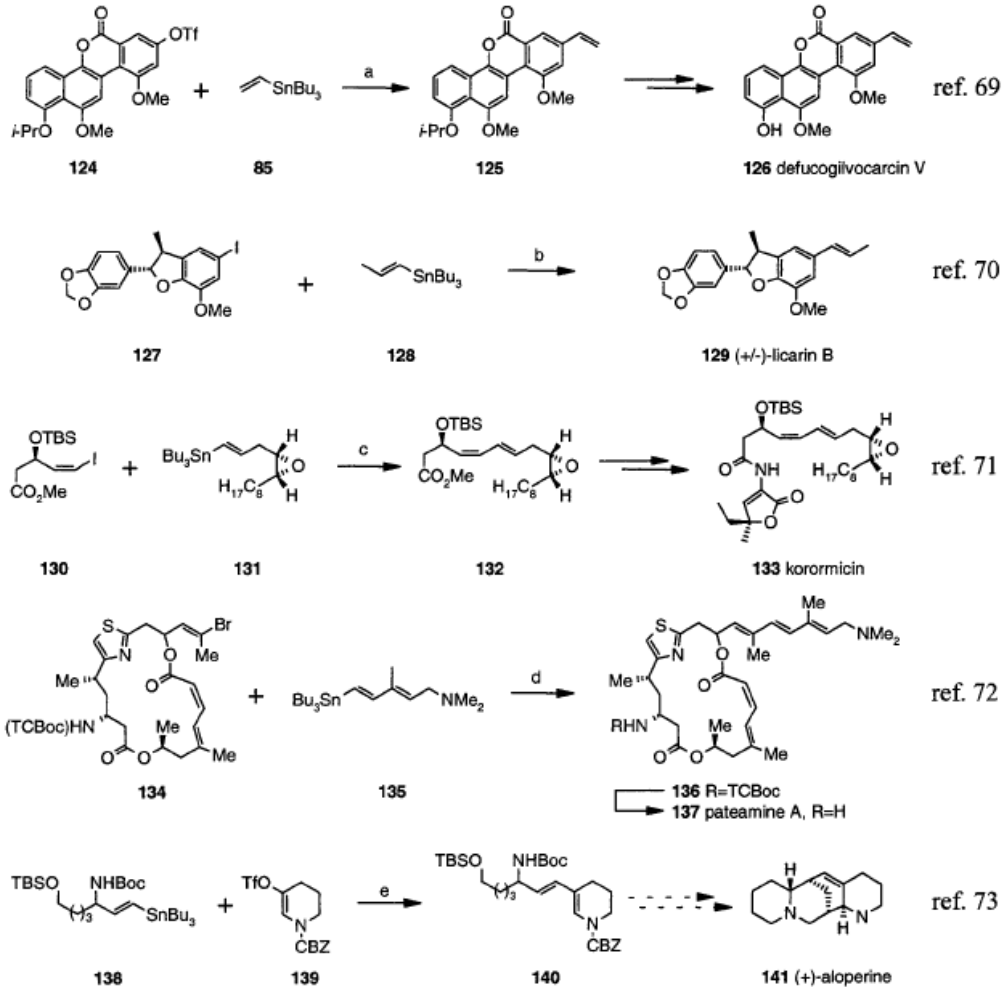
122

123

ref. 68

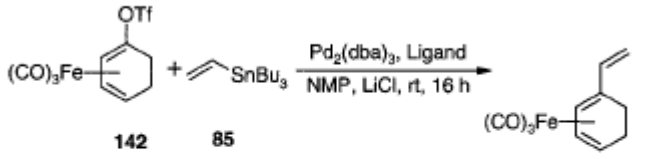
[a] Conditions: (a) $(TFP)_2PdCl_2$, *N,N*-diisopropylethylamine (DIPEA), DMF, THF, rt, 74% R = OMe; 65% R = H. (b) allyltributylstannane, LiCl, $Pd_2(dba)_3$, TFP, 1-methyl-2-pyrrolidinone (NMP), 40 °C, 93%. (c) $Pd_2(dba)_3$, TFP, *N,N*-dimethylacetamide (DMA), 80 °C, 83%. (d) $Pd_2(dba)_3$, TFP, $ZnCl_2$, DMF, 50 °C, 4.5 days, 86%. (e) $Pd_2(dba)_3$, TFP, CuI, DMF, 25 °C, 4 days, 33%.

Scheme 23[a]



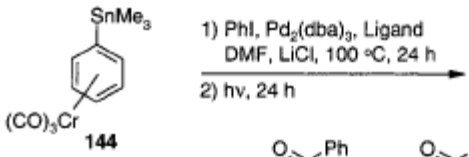
[a] Conditions: (a) $Pd_2(dba)_3$, TFP, NMP, rt, 5 h, 69%. (b) $Pd_2(dba)_3$, TFP, LiCl, DMF, 120−130 °C, 84−86%. (c) $Pd_2(dba)_3$·$CHCl_3$, TFP, NMP, rt, 6 days, 34%. (d) $Pd_2(dba)_3$, TFP, NMP, 25 °C, 27% (57% based on recovered starting material); TCBoc = 1,1-dimethyl-2,2,2-trichloroethoxycarbonyl. (e) $Pd_2(dba)_3$, TFP, LiCl, NMP, rt, 1.5 days, 93%.

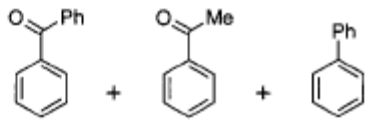
Scheme 24



Ligand	Yield (%)
PPh_3	38
TFP	50

Scheme 25

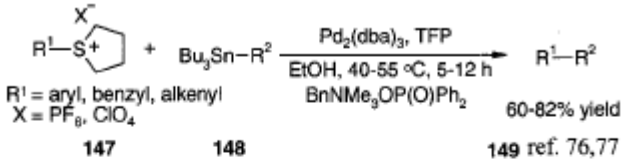




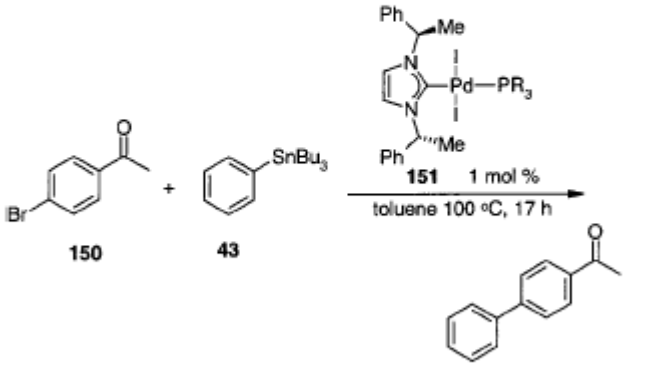
145 146 46

Ligand	Yield (%) 145	146	46
PPh_3	44	24	13
TFP	36	25	2

Scheme 26



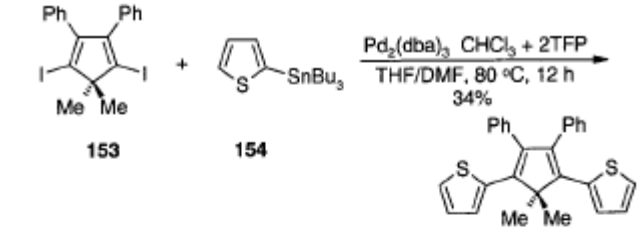
147 148 60-82% yield 149 ref. 76,77



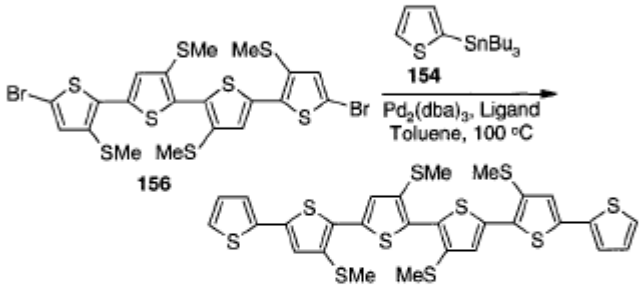
152 ref. 78

R = Ph, Yield = >99%
R = 2-furyl, Yield = 68%

Scheme 27

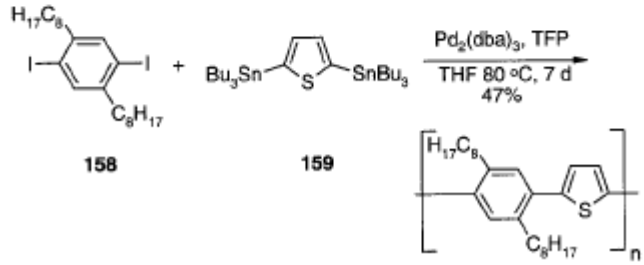


153 **154** **155** ref. 79



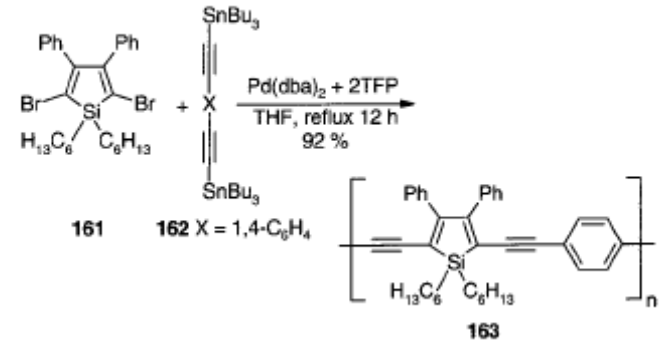
156 **157** ref. 80

Ligand	Yield (%)
PPh_3	65
TFP	80
$AsPh_3$	85



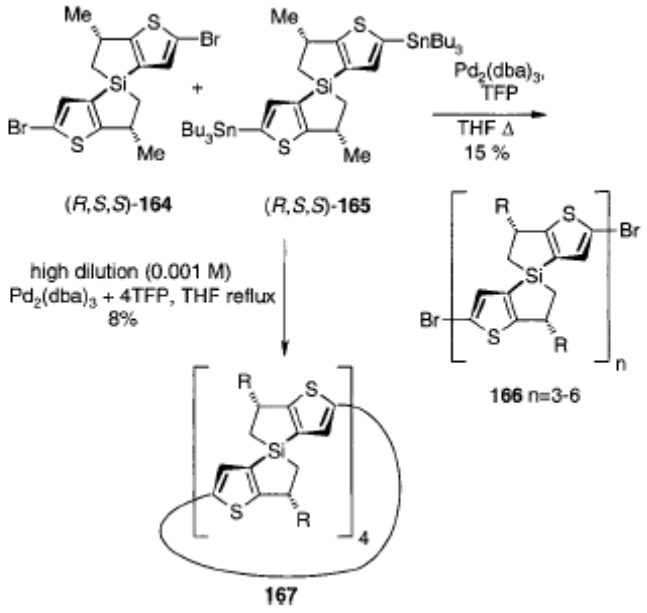
158 **159** **160** ref. 81

Scheme 28

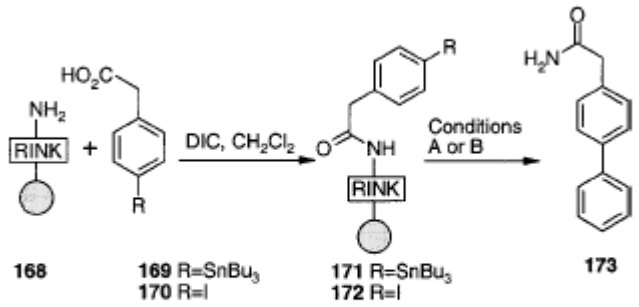


161 **162** X = 1,4-C_6H_4 **163**

Scheme 29

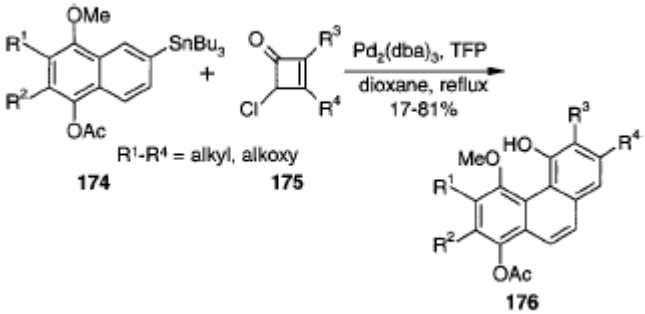


Scheme 30[a]

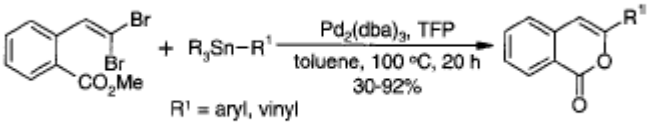


[a] Conditions A: (i) 3 equiv of iodobenzene (**84**), 10 mol % $Pd_2(dba)_3$, 10 mol % TFP, 2 equiv of LiCl, NMP, 25 °C, 12 h; (ii) 5% TFA−CH_2Cl_2, 15% yield (2 steps). Conditions B: (i) 3 equiv of trimethylphenyltin, 10 mol % $Pd_2(dba)_3$, 10 mol % TFP, 2 equiv of LiCl, NMP, 25 °C, 12 h; (ii) 5% TFA−CH_2Cl_2, 33% yield (2 steps).

Scheme 31

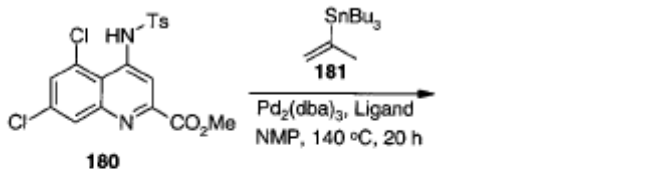


Scheme 32

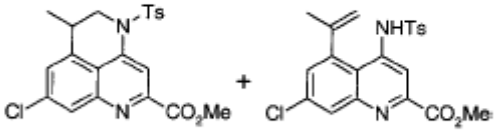


177 178 179

Scheme 33



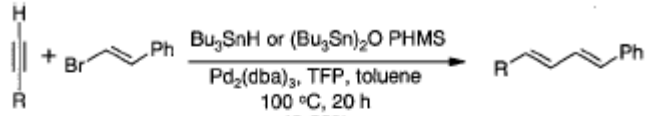
180



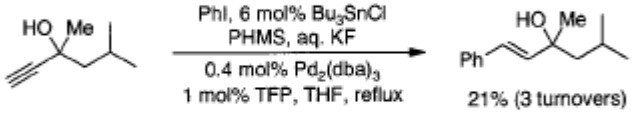
182 183

	Yield (%)	
Ligand	**182**	**183**
PPh_3	18	0
TFP	38	15

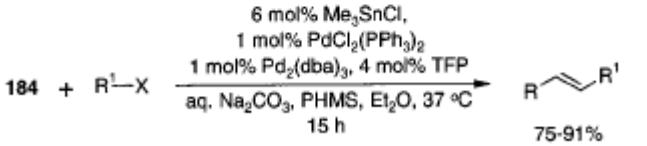
Scheme 34



184 185 186
ref. 91

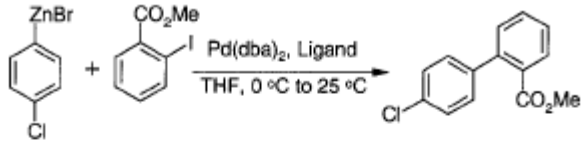


187 188
ref. 93



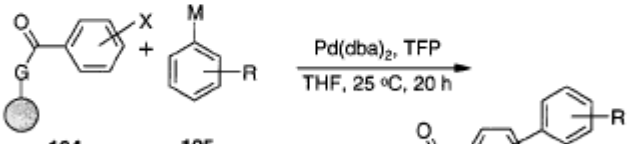
189 R1=aryl, vinyl 190
ref. 94

Scheme 35



191 **192** **193** ref. 96

Ligand	Time (h)	Yield (%)
PPh_3	4.0	79
TFP	1.5	83



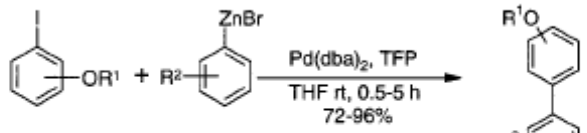
194 G=NH, O; X=I, Br

195 M=ZnBr, CH_2ZnBr; R=Cl, OMe, OTf, CF_3, CN

196 ref. 97

R=Cl, OMe, OTf, CF_3, CN

Scheme 36

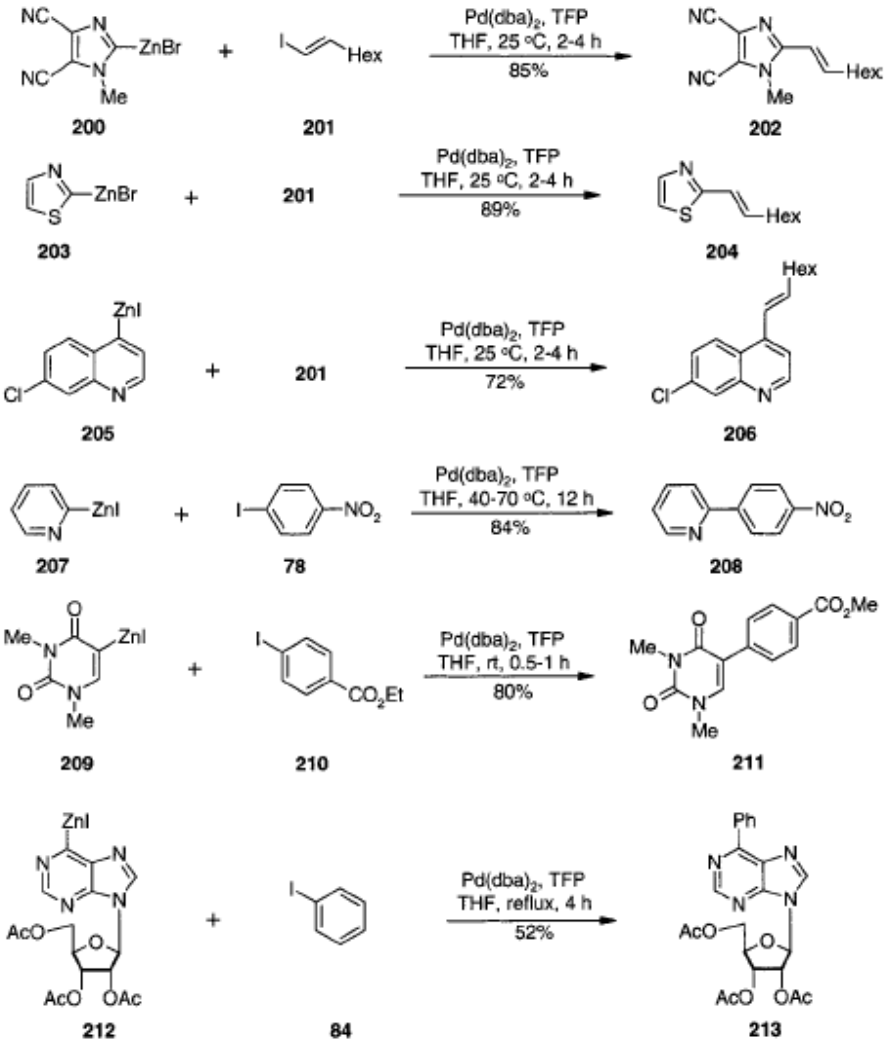


197 **198**

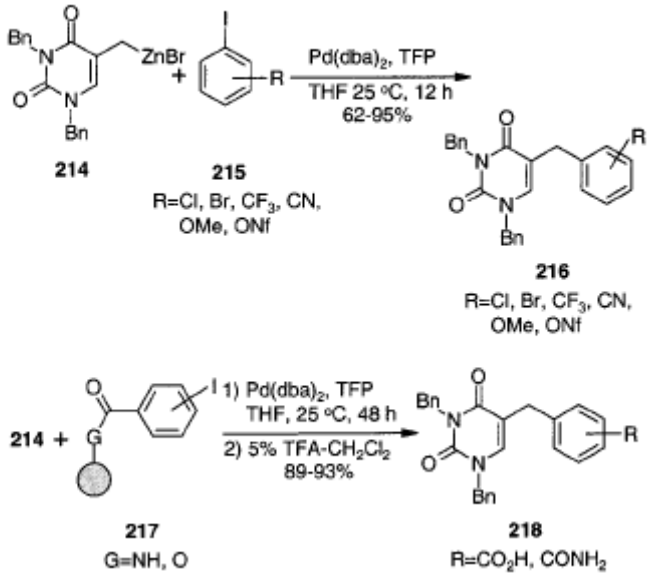
R^1=Tf, Nf
R^2=OTIPS, OMe, OTf, CF_3, CN, Cl

199

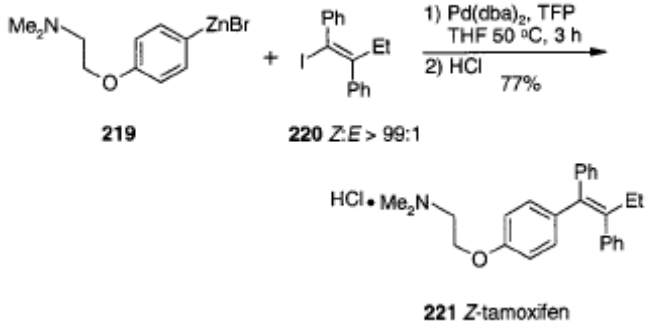
Scheme 37


Pd(dba)2, TFP
THF, 25 °C, 2-4 h
85%
200
201
202
Pd(dba)2, TFP
THF, 25 °C, 2-4 h
89%
203
201
204
Pd(dba)2, TFP
THF, 25 °C, 2-4 h
72%
205
201
206
Pd(dba)2, TFP
THF, 40-70 °C, 12 h
84%
207
78
208
Pd(dba)2, TFP
THF, rt, 0.5-1 h
80%
209
210
211
Pd(dba)2, TFP
THF, reflux, 4 h
52%
212
84
213

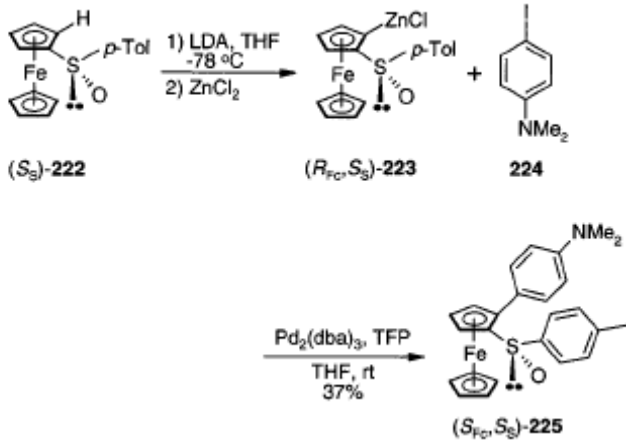
Scheme 38



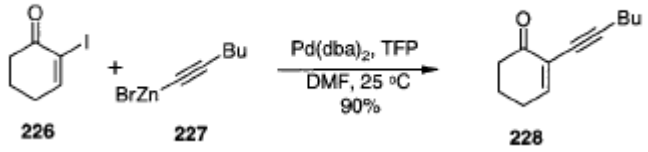
Scheme 39



Scheme 40

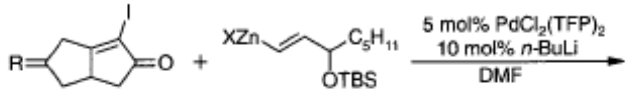


Scheme 41



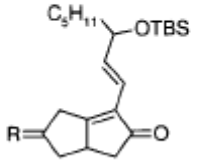
226 **227** **228**

Scheme 42



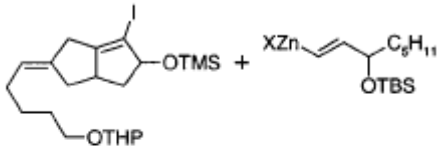
229 R=H_2
232 R=$CH(CH_2)_4OTBS$

230

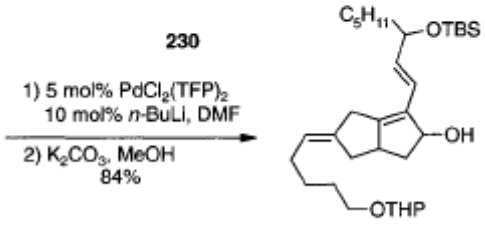


231 R=H_2, 72%
233 R=$CH(CH_2)_4OTBS$, <5%

Scheme 43

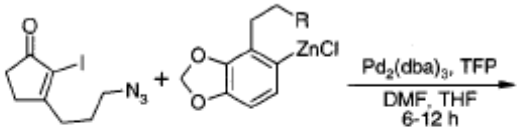


234 **230**

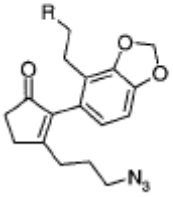


235

Scheme 44

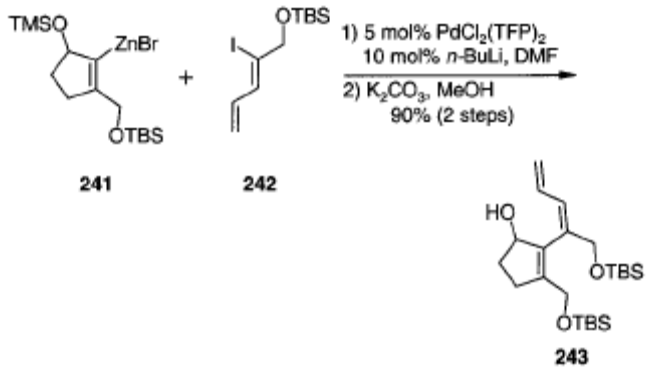


236 **237** R=OTBS
239 R=Cl



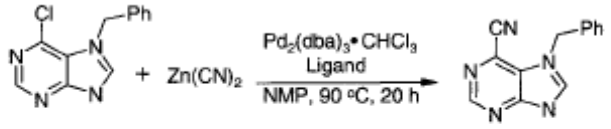
238 R=OTBS, 48%
240 R=Cl, 72%

Scheme 45



241 **242** **243**

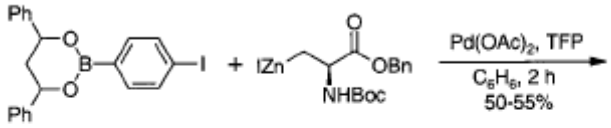
Scheme 46



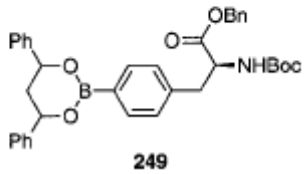
244 **245** **246**

Ligand	Yield (%)
PPh_3	52
TFP	75
$AsPh_3$	0

Scheme 47

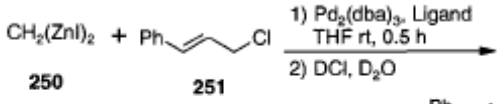


247 **248**

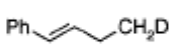


249

Scheme 48



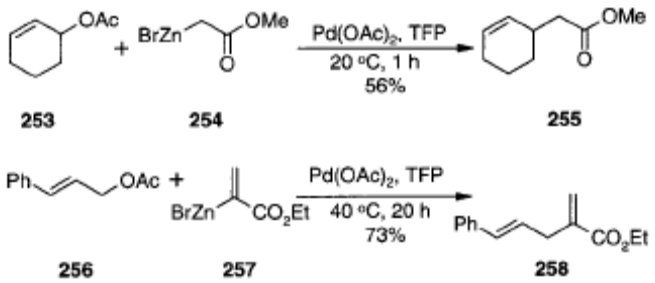
250 **251**



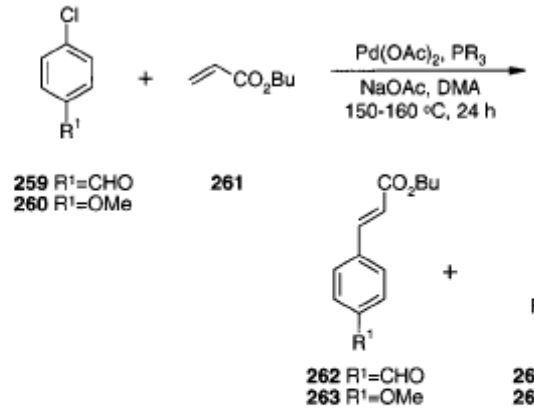
252

Ligand	Yield (%)
PPh_3	16
TFP	97

Scheme 49

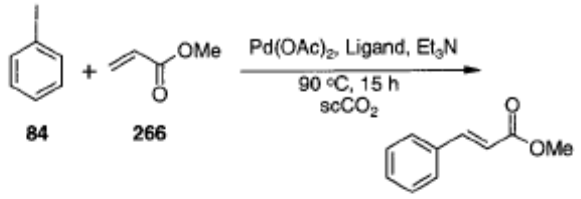


Scheme 50



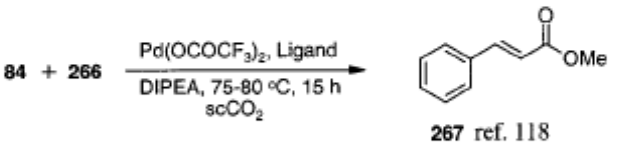
		Yield (%)			
R^1	**PR_3**	**262**	**263**	**264**	**265**
CHO	PPh_3	69		6.4	
CHO	TFP	64			4.1
OMe	PPh_3		41	6.4	
OMe	TFP		0		0

Scheme 51



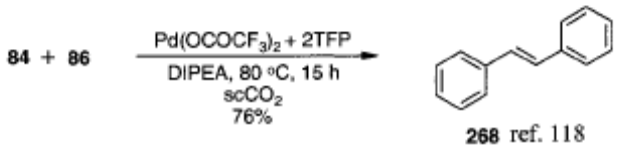
84 **266** **267** ref. 56

Ligand	Conversion (%)	TOF (h^{-1})
P(*o*-Tol)$_3$	35	1
TFP	>95	2.7



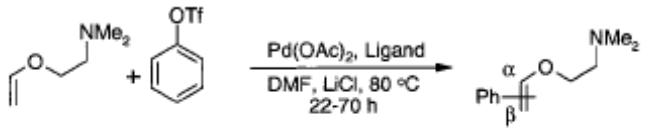
267 ref. 118

Ligand	Conversion (%)
PPh_3	71
TFP	>95



268 ref. 118

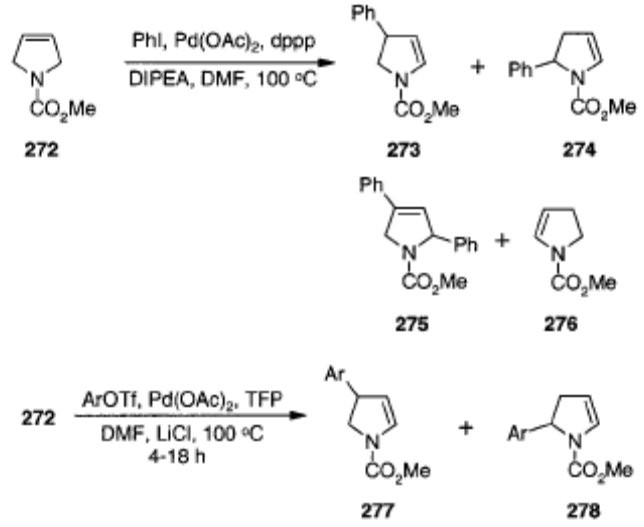
Scheme 52



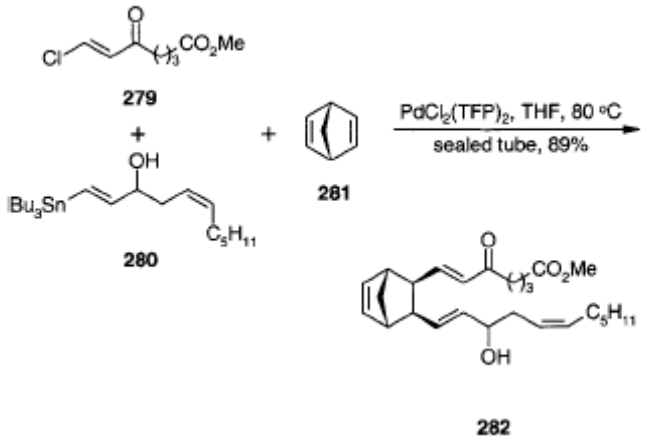
269 **270** **271**

Ligand	Yield (%)	*E*/*Z*	α : β
PPh_3	99	63/37	93 : 7
TFP	100	41/59	93 : 7
$AsPh_3$	8	23/77	94 : 6

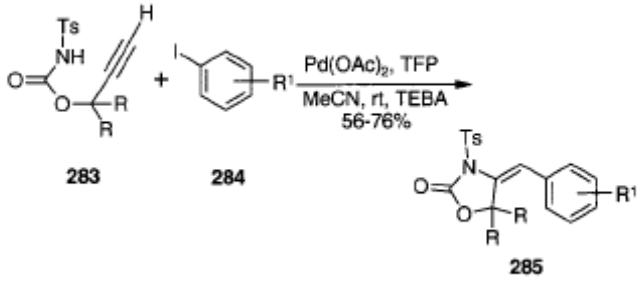
Scheme 53



Scheme 54

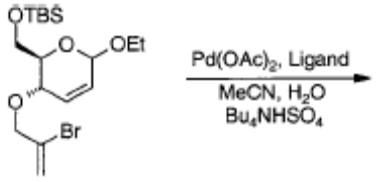


Scheme 55[a]

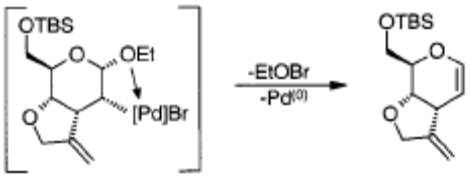


[a] TEBA = benzyltriethylammonium chloride.

Scheme 56



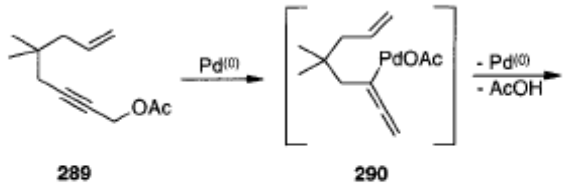
286



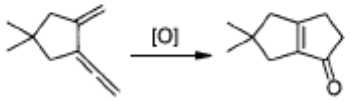
287 **288**

Ligand	Time (h)	Yield (%)
PPh_3	10	72
TFP	4	77
dppp	24	10

Scheme 57

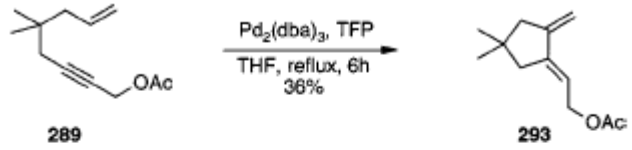


289 **290**

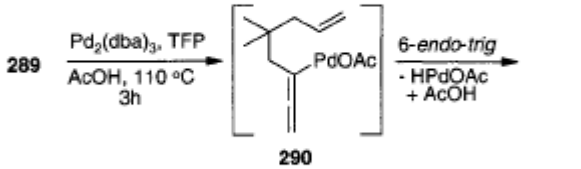


291 **292**

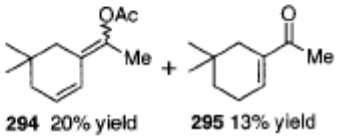
Scheme 58



289 **293**

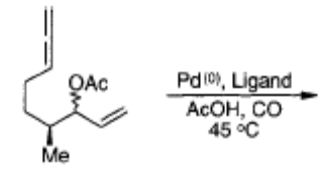


290

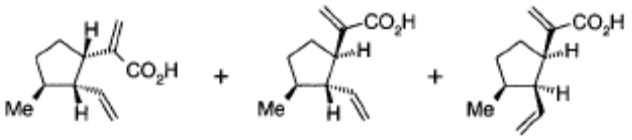


294 20% yield **295** 13% yield

Scheme 59



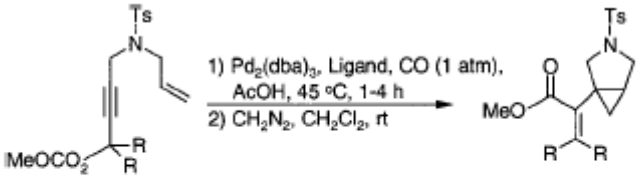
296



297 **298** **299**

		Ratio (%)		
Ligand	**Yield (%)**	**297**	**298**	**299**
PPh_3	19	71	19	10
TFP	61	61	30	9

Scheme 60

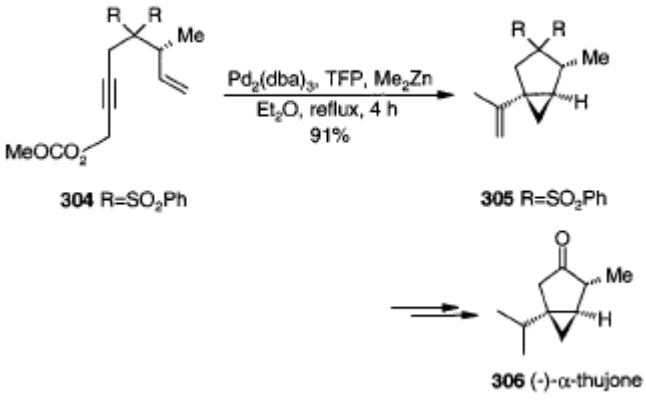


300 R=H
301 R=Me

302 R=H
303 R=Me

R	**Ligand**	**Yield (%)**
H	PPh_3	10
H	TFP	93
Me	PPh_3	65
Me	TFP	93

Scheme 61

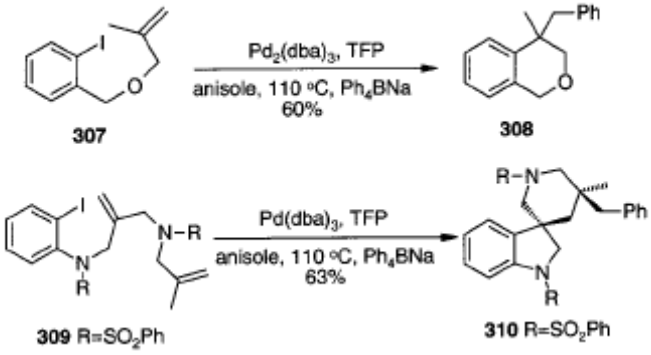


304 R=SO_2Ph

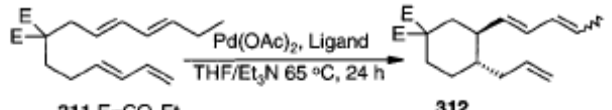
305 R=SO_2Ph

306 (-)-α-thujone

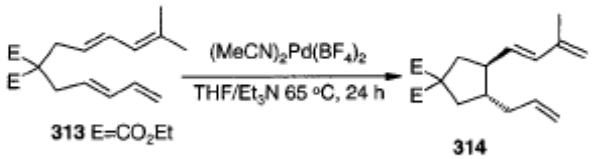
Scheme 62



Scheme 63

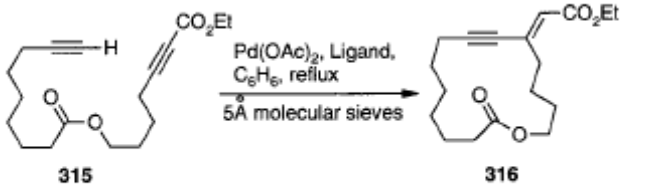


Ligand	Conversion (%)
PPh_3	100
TFP	100



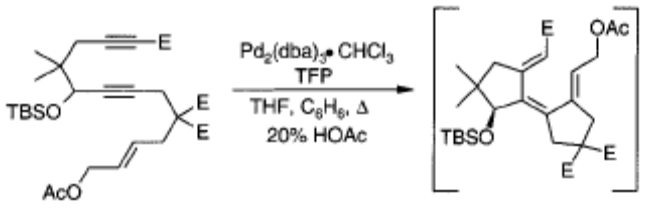
Ligand	Conversion (%)
PPh_3	>95
TFP	40
$AsPh_3$	40

Scheme 64

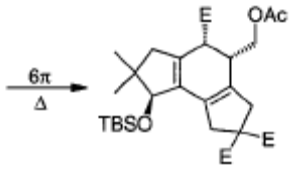


Ligand	Yield (%)
PPh_3	55
TFP	7.2

Scheme 65

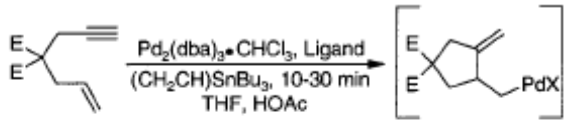


317 E=CO_2Me **318** E=CO_2Me

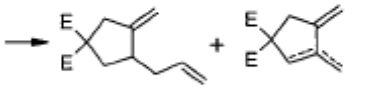


319 E=CO_2Me

Scheme 66



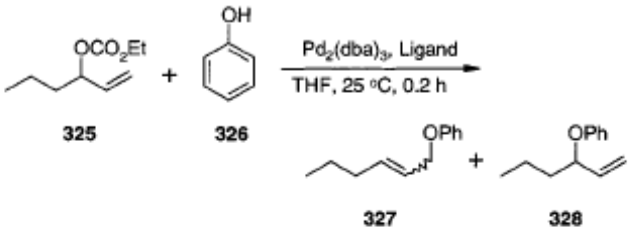
320 E=CO_2Bn **321** E=CO_2Bn



322 E=CO_2Bn **323/324** E=CO_2Bn

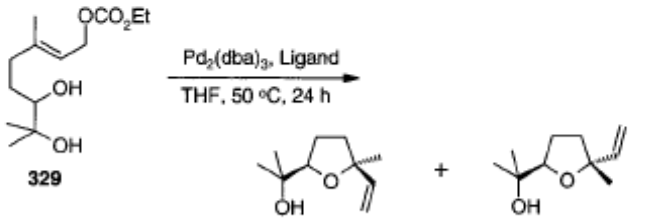
	Yield (%)	
Ligand	**322**	**323/324**
PPh_3	28	30
TFP	trace	69
none	45	0

Scheme 67



325 326 327 328

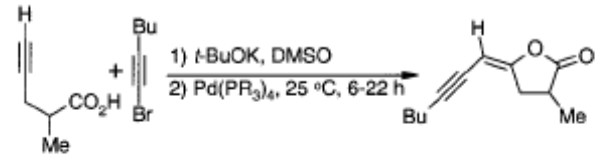
Ligand	Conversion (%)	327: 328
PPh_3	100	49 : 51
TFP	100	63 : 37



329 330 331

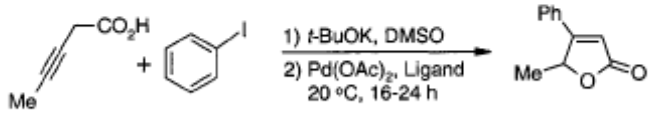
Ligand	Yield (%)	330 : 331
PPh_3	70	81 : 19
TFP	65	82 : 18

Scheme 68



332 333 334

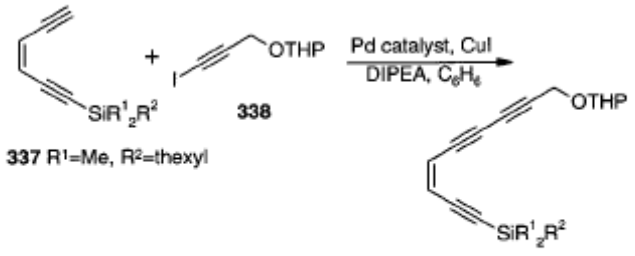
Ligand	Yield (%)
$P(o\text{-Tol})_3$	42
TFP	90



335 84 336

Ligand	Yield (%)
TFP	65
$AsPh_3$	46

Scheme 69

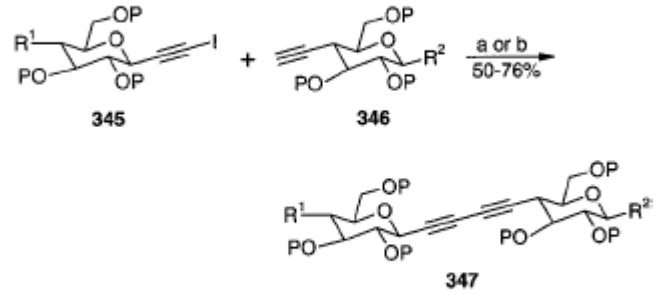


Catalyst	Yield (%)
$(MeCN)_2PdCl_2$	20
$Pd_2(dba)_3$/TFP	77

Scheme 70

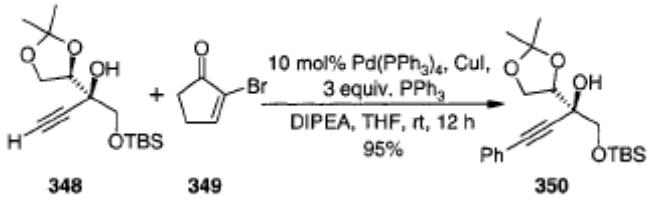
		Ratio (%)		
Ligand	Yield (%)	342	343	344
PPh_3	98	63	21	14
TFP	88	65	19	4

Scheme 71[a]

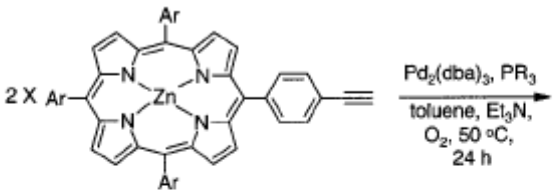


[a] Conditions: (a) $PdCl_2(PhCN)_2$, TFP, DIPEA, DMSO, 50 °C. (b) $Pd_2(dba)_3$, TFP, CuI, DMSO, rt.

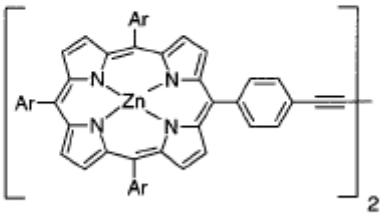
Scheme 72



Scheme 73



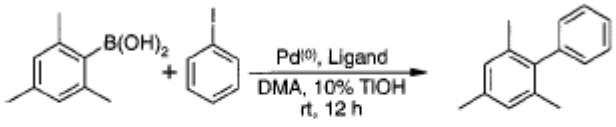
351 Ar=mesityl



352

PR_3	Yield (%)	HMWM : 352
PPh_3	37	0.94 : 1
TFP	67	0.30 : 1

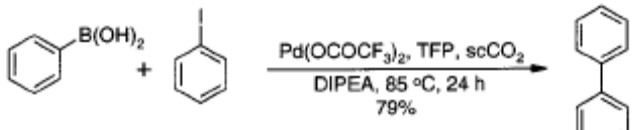
Scheme 74



353 **84** **354**

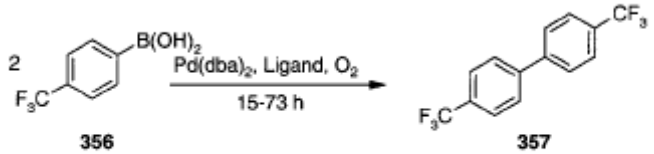
Ligand	Yield (%)
PPh_3	97
TFP	85
$AsPh_3$	51

Scheme 75



355 **84** **46**

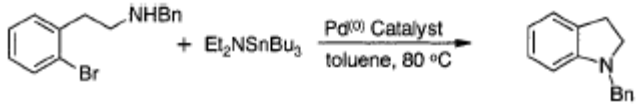
Scheme 76



356 **357**

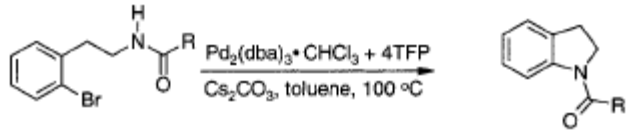
Ligand	Yield (%)	Time (h)
PPh_3	40	73
TFP	93	15

Scheme 77



358 **359** **360**

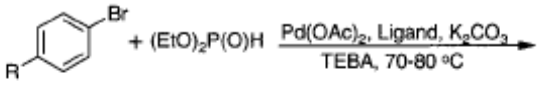
Catalyst	Yield (%)
$Pd(PPh_3)_4$	75
$Pd_2(dba)_3$/TFP	67



361 R=Me
362 R=*t*-Bu

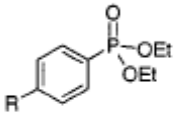
363 R=Me, 99%
364 R=*t*-Bu, 87%

Scheme 78[a]



365 R=H
366 R=OMe

367

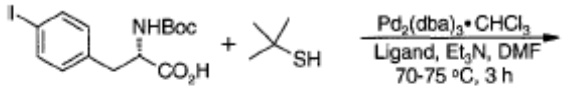


368 R=H
369 R=OMe

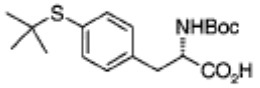
R	Ligand	Time (h)	Yield (%)
H	PPh_3	40	100
H	TFP	19	100
OMe	PPh_3	46	98
OMe	TFP	20	98

[a] TEBA = benzyltriethylammonium chloride.

Scheme 79



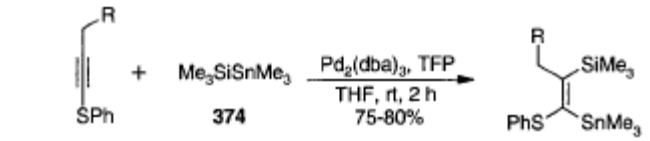
370 **371**



372

Ligand	Yield (%)
PPh_3	26
TFP	trace
dppf	99

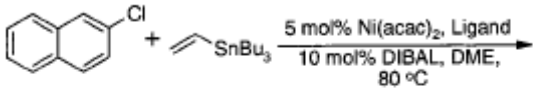
Scheme 80



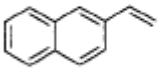
373 R=OH, OMe, OTHP, $(CH_2)_2OH$, *n*-Pr, CO_2Ar

375

Scheme 81



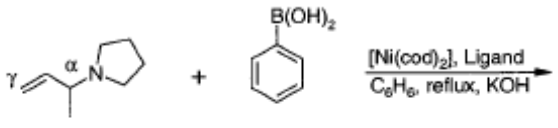
376 **85**



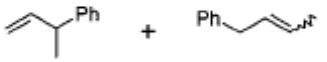
377

Ligand	Yield (%)
PPh_3	86
TFP	64

Scheme 82



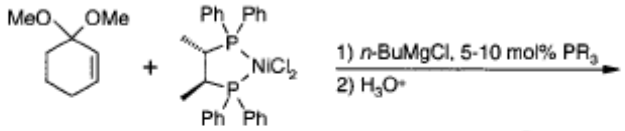
378 **355**



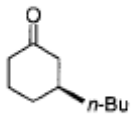
379 **380**

Ligand	Yield (%)	α : γ
PPh_3	72	1.6 : 1
TFP	54	1.6 : 1

Scheme 83



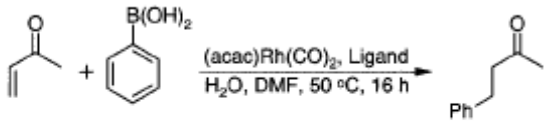
381 **382** 5 mol%



383

PR_3	Conversion (%)	ee (%)
PPh_3	61	82
TFP	60	40

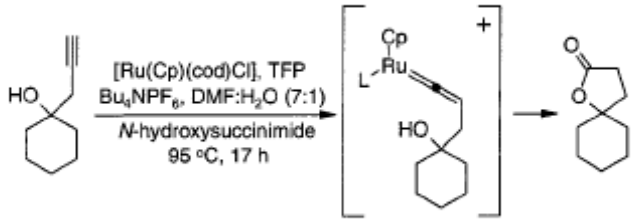
Scheme 84



384 355 385

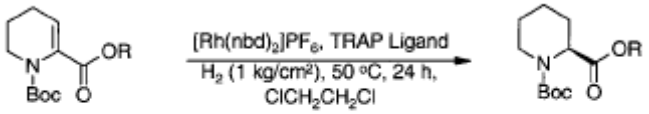
Ligand	Yield (%)
PPh_3	83
TFP	94

Scheme 85



386 387 388

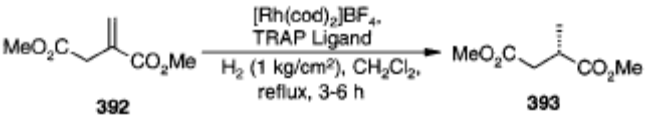
Scheme 86



390 R=i-Bu 391

TRAP Ligand	Conv. (%)	ee (%)	Config.
(*S*,*S*)-(*R*,*R*)-PhTRAP (**389a**)	100	90	*S*
(*S*,*S*)-(*R*,*R*)-FurTRAP (**389b**)	100	35	*S*

Scheme 87



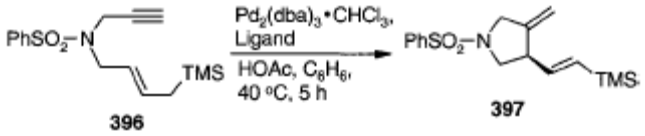
392 393

TRAP Ligand	Conv. (%)	ee (%)	Config.
(*R*,*R*)-(*S*,*S*)-EtTRAP (**389d**)	100	96	*S*
(*R*,*R*)-(*S*,*S*)-PhTRAP (**389a**)	100	26	*R*
(*R*,*R*)-(*S*,*S*)-FurTRAP (**389b**)	100	7	*R*

394 395

TRAP Ligand	Conv. (%)	ee (%)	Config.
(*R*,*R*)-(*S*,*S*)-BuTRAP (**389d**)	98	71	*S*
(*R*,*R*)-(*S*,*S*)-PhTRAP (**389a**)	trace	--	--
(*R*,*R*)-(*S*,*S*)-FurTRAP (**389b**)	13	6	*R*

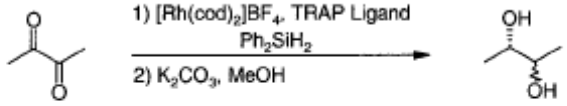
Scheme 88



396 397

TRAP Ligand	Yield (%)	ee (%)
(*S*,*S*)-(*R*,*R*)-**389c**	72	48
(*S*,*S*)-(*R*,*R*)-PhTRAP (**389a**)	77	36
(*S*,*S*)-(*R*,*R*)-FurTRAP (**389b**)	76	4

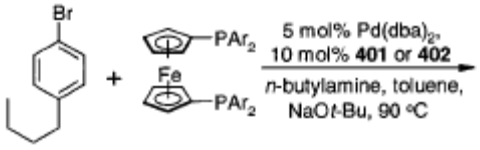
Scheme 89



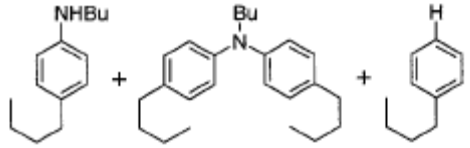
398 399

TRAP Ligand	*dl*:*meso*	ee (%)
(*R*,*R*)-(*S*,S)-FurTRAP (**389b**)	86:14	91
(*R*,*R*)-(*S*,*S*)-PhTRAP (**389a**)	49:51	29

Scheme 90



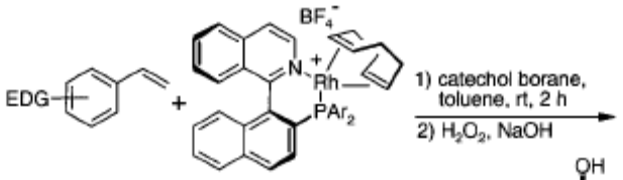
400 **401** Ar=Ph (dppf)
402 Ar=Fu (dfpf)
Fu=2-furyl



403 404 405

Ligand	Yield (%) 403	404	405
401, dppf	52	21.6	4.4
402, dfpf	40	2.9	16

Scheme 91

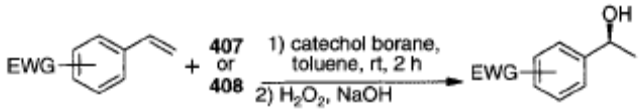


406 EDG=Me, OMe, OEt

407 Ar=Ph
408 Ar=Fu

409, 5 examples

Catalyst	Yield (%)	ee (%)
407	75-82	86-94
408	72-81	78-93

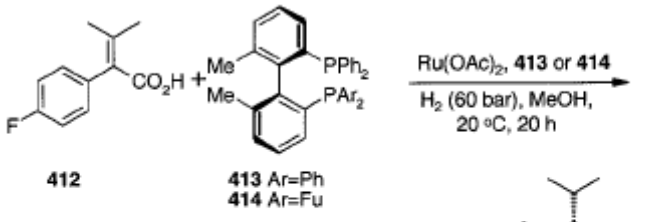


410 EWG=F, Cl, CF_3

411, 9 examples

Catalyst	Yield (%)	ee (%)
407	59-82	37-80
408	74-82	69-89

Scheme 92



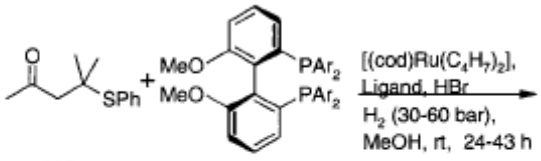
412

413 Ar=Ph
414 Ar=Fu

415

Catalyst	Conversion (%)	ee (%)
413	100	88
414	100	90

Scheme 93



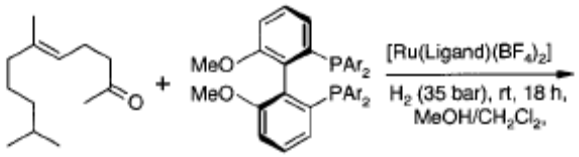
416

417 Ar=Ph
418 Ar=Fu

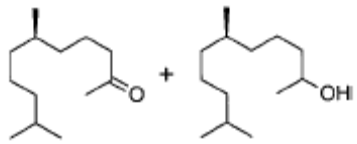
419

Ligand	Yield (%)	ee (%)
417	100	90
418	100	88

Scheme 94



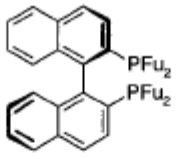
420 **417** Ar=Ph **418** Ar=Fu



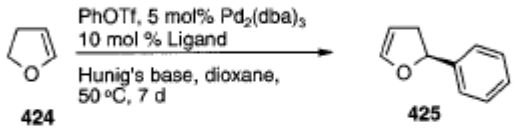
421 **422**

Ligand	421:422	ee of 421 (%)
417	97:3	77
418	98:2	91

Scheme 95

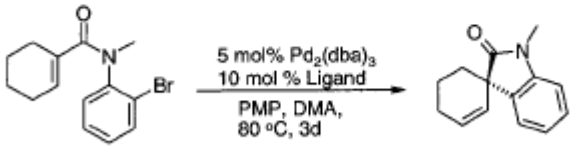


423 TetFuBINAP



424 **425**

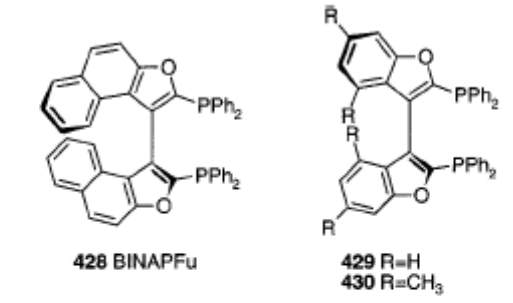
Ligand	Yield (%)	ee (%)
(*R*)-TetFuBINAP (**423**)	17	89
(*R*)-BINAP	53	66



426 **427**

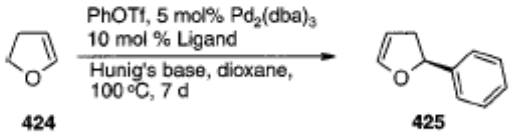
Ligand	Yield (%)	ee (%)
(*R*)-TetFuBINAP (**423**)	57	64
(*R*)-BINAP	61	18

Scheme 96



428 BINAPFu

429 R=H
430 R=CH_3



424 **425**

Ligand	Yield (%)	ee (%)
(*R*)-BINAPFu (**428**)	90	77
(*R*)-BINAP	73	41

DOI: 10.1021/cr000024o