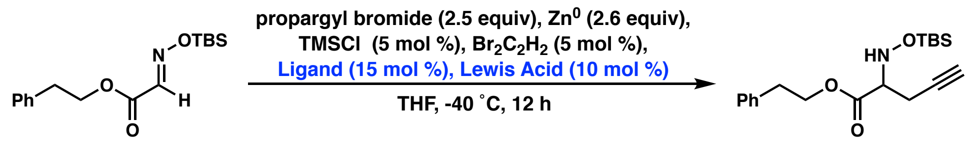
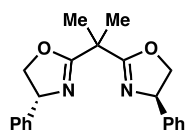
Appendix 2

Additional Tables Relevant to Chapter 2

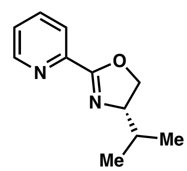
Table 2.2. *Effects of Lewis Acids in conjunction with different ligands on the propargylation.*



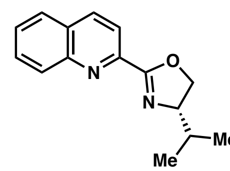
	PhBox (L19)				^{i}PrPyOx (L20)				^{i}PrQuinox (L21)			
Metal	Entry	Conv. (%)	Yield (%)	ee (%)	Entry	Conv (%)	Yield (%)	ee (%)	Entry	Conv (%)	Yield (%)	ee (%)
$Yb(OTf)_3$	1	72	64	0	8	59	53	0	15	51	29	2
$In(OTf)_3$	2	47	47	0	9	53	33	0	16	89	6	1
$Sc(OTf)_3$	3	74	71	0	10	69	33	0	17	56	37	3
$Cu(OTf)_2$	4	73	72	0	11	84	16	2	18	53	33	1
$MgBr_2$	5	77	77	0	12	71	45	0	19	55	36	1
$NiCl_2$•dme	6	50	49	0	13	44	22	0	20	65	9	2
$(CuOTf)_2$•PhMe	7	74	18	0	14	62	34	0	21	46	46	1



A: PhBox (**L19**)

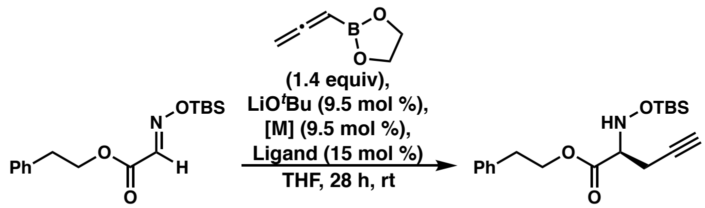


B: ^{i}PrPyOx (**L20**)

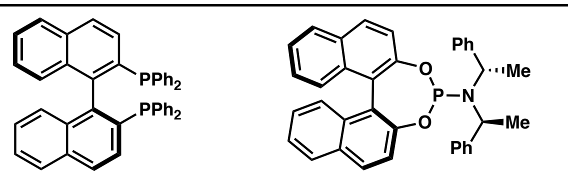


C: ^{i}PrQuinox (**L21**)

Table 2.4. *Survey of copper sources for the asymmetric propargylation.*



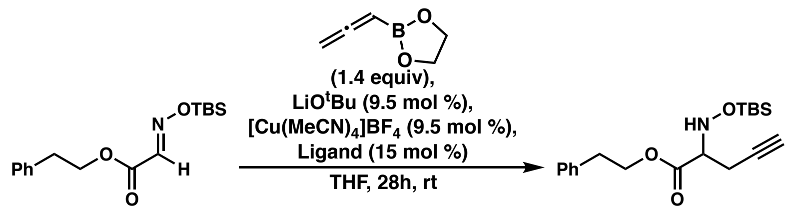
Entry	[M]	Ligand	Conversion (%)	Yield (%)	ee (%)
1	$(CuOTf)_2$•PhMe	A	23	6	70
2	$(CuOTf)_2$•PhMe	B	65	40	34
3	CuBr•DMS	A	35	9	0
4	CuBr•DMS	B	50	11	28
5	$[Cu(MeCN)_4]BF_4$	A	41	12	72
6	$[Cu(MeCN)_4]BF_4$	B	80	51	30
7	$[Cu(MeCN)_4]PF_6$	A	43	7	65
8	$[Cu(MeCN)_4]PF_6$	B	66	39	30
9	$[Cu(MeCN)_4]ClO_4$	A	47	11	70
10	$[Cu(MeCN)_4]ClO_4$	B	89	47	30
11	$Cu(acac)_2$	A	51	28	66
12	$Cu(acac)_2$	B	92	47	31
13	CuI	A	48	6	0
14	CuI	B	76	15	29
15	$Cu(OTf)_2$	A	16	0	–
16	$Cu(OTf)_2$	B	31	0	–
17	$Cu(OAc)_2$	A	29	1	–
18	$Cu(OAc)_2$	B	41	4	30
19	Cu(^{i}butyrate)$_2$	A	36	trace	–
20	Cu(ibutyrate)$_2$	B	45	4	28
21	Cu(2-pyrazinecarboxylate)	A	35	4	71
22	Cu(2-pyrazinecarboxylate)	B	70	36	34



A: (*S*)-BINAP (L23) **B: (*S,S*)-BINOL-P-N(CH(Me)Ph)$_2$ (L25)**

Table 2.5. *Standout ligands for [Cu(MeCN)$_4$]BF$_4$-catalyzed propargylation.*

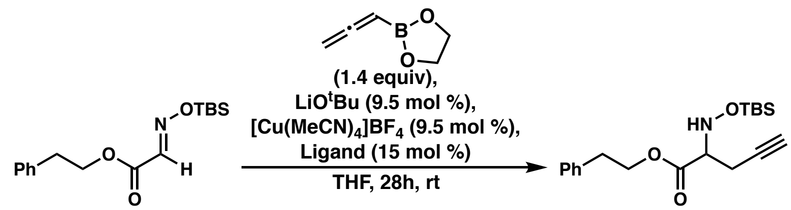
a) *BINAP ligands*



Ligand	Conversion (%)	Yield (%)	ee (%)
(*S*)-BINAP	36	12	65
(*S*)-T-BINAP	33	7	72
(*R*)-DM-BINAP	45	8	76
(*R*)-H8-BINAP	20	7	63
(*R*)-SDP	29	6	12
(*S*,*S*,*S*)-Ph-SKP	95	72	0
(*S*)-QUINAP	85	72	30
(*S*)-BINAPINE	25	trace	–

Table 2.5. *Standout ligands for $[Cu(MeCN)_4]BF_4$-catalyzed propargylation.*

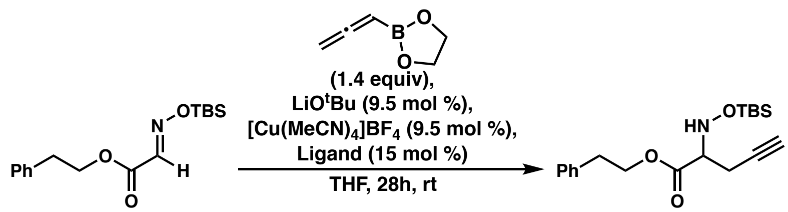
b) *Phosphoramidite ligands*



Ligand	Conversion (%)	Yield (%)	ee (%)
(*S*)-BINOL-P-NMe_2	88	60	24
(*S*)-H8-BINOL-P-NMe_2	77	46	24
(*R*)-SIPHOS	100	69	14
[3,3'-bis'PPh_2]-(*R*)-BINOL-P-NMe_2	38	9	7
(*R,R*)-TADDOl-P-NMe_2	97	70	34
(*S*)-BINOL-P-morpholine	60	9	31
(*S*)-BINOL-P-NMeBn	75	45	20
(*R*)-BINOL-P-NBn_2	76	41	2
(*R,R*)-Ph-TADDOL-P-NMe_2	100	45	32
(*R,R*)-Ph-TADDOL-P-NEt_2	90	43	32
(*R,R*)-Np-TADDOL-P-NEt_2	73	16	8
(*R,R*)-Ph-TADDOL-P-NBn_2	82	40	26
(*R,R*)-Ph-TADDOL-P-NMePh	75	22	32
(*R,R*)-Ph-TADDOL-P-pyrollidine	84	34	32
(*R,R*)-Ph-TADDOL-P-piperidine	91	46	20
(*R,R*)-Ph-TADDOL-P-morpholine	90	43	16
(*R,R,S,S*)-Ph-TADDOL-P-N*CH(CH_3)Ph)$_2$	52	15	9
(*R,R,R,R*)-Ph-TADDOL-P-N*CH(CH_3)Ph)$_2$	46	15	6
(*S*)-BINOL-P-(*R*)-NHCH(Me)Ph	58	26	19
(*S,S*)-BINOL-P-NBn(CH(Me)Np)	76	49	24
(*R,S*)-BINOL-P-NBn(CH(Me)Np)	87	56	10
(*S,S,S*)-BINOL-P-N[CH(Me)Ph]$_2$	78	54	30
(*S,R.R*)-BINOL-P-N[CH(Me)Ph]$_2$	48	8	16
[3,3'-bis-F]-(*R,R,R*)-BINOL-P-N[CH(Me)Ph]$_2$	69	25	41
(*R,R,R*)-BINOL-P-N(CH(Me)Ph)(CH(Me)Np)	59	36	30
(*R,R,R*)-BINOL-P-N(CH(Me)Np)$_2$	77	38	50
(*R,R,R*)-BINOL-P-Ph2pyrrolidine	98	84	15
(*R,R,R*)-BINOL-P-Np2pyrrolidine	61	32	16
(*S,Sa*)-BOGERPhos	82	73	31

Table 2.5. *Standout ligands for [Cu(MeCN)$_4$]BF$_4$-catalyzed propargylation.*

c) *Biaryl bisphosphine ligands*



Ligand	Conversion(%)	Yield (%)	ee (%)
(*R*)-SEGPHOS	39	10	54
(*R*)-DM-SEGPHOS	34	4	48
(*R*)-DTBM-SEGPHOS	28	2	54
(*R*)-DiFluoroPhos	32	11	80
(*R*)-SynPhos	50	9	34
SolPhos	61	45	4
(*S*)-Xyl-MeOBIPHEP	31	2	68
(*S*)-3,5-^{t}Bu-MeOBIPHEP	35	1	48
(*S*)-3,5-^{t}Bu-4-MeO-MeOBIPHEP	26	trace	--
(*S*)-3,5-^{i}Pr-4-Me$_2$N-MeOBIPHEP	20	trace	--
(*S*)-C3-TunePhos	25	3	45
(*R*)-P-Phos	34	12	80
(*R*)-BTFM-GarPhos	60	24	82