

Supplementary Material

Alcohols in Direct Carbon-carbon and Carbon-heteroatom Bond-forming Reactions: Recent Advances

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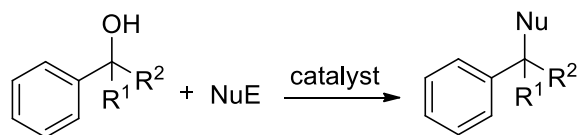
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Dedicated to Prof. Kenneth Laali on the occasion of his 65th birthday

Table of Contents

Table 22. Nucleophilic substitution of alcohols	S2
References	S11

Table 22. Nucleophilic substitution of alcohols.

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
1	C-C	R ¹ = H, R ² = Ph		[NMP] ⁺ HSO ₄ ⁻	90	1
2		R ¹ = H, R ² = Ph		PTS or TfOH	84	2
3		R ¹ = H, R ² = Me		PWA	84	3
4		R ¹ = H, R ² = Me		/EMITf	81	4
5		R ¹ = H, R ² = Ph		Fe(HSO ₄) ₃	80	5
6		R ¹ = H, R ² = Ph	1-methyl-1 <i>H</i> -indole, 1,3-dibenzoylmethane, 1,3,5-trimethoxybenzene,	DBSA	82-89	6
7		R ¹ = H, R ² = Ph		[BsOdP][OTf]	91	7
8		R ¹ = H, R ² = CH=CHPh	1 <i>H</i> -indole, 4-nitroaniline, 1,3,5-trimethoxybenzene, acetylacetone	PTS or	74-86	8
9		R ¹ = H = R ² = CPh	ethanol, phenylmethanol, prop-2-en-1-ol	PTS	74-80	9
10		R ¹ = Et, R ² = CPh		PTSA	78	10
11		R ¹ = H, R ² = CPh		C ₆ F ₅ B(OH) ₂	41	11
12		R ¹ = R ² = Ph		C ₆ F ₅ B(OH) ₂	99	12
13		R ¹ = H, R ² = CPh	1 <i>H</i> -indole, naphthalen-2-ol, cyclohexane-1,3-dione	Amberlite IR-120H resin	87-90	13

Table 22. (Continued)

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
14	C-C	R ¹ = H, R ² = CH=CHPh		TfOH	87	14
15		R ¹ = H, R ² = CH=CHPh	TMSCN	Sn or Ti-Monts	98 or 94	15
16		R ¹ = H, R ² = CH=CHPh		H ₂ SO ₄	87	16
17		R ¹ = H, R ² = CCPh		PTSA	54	17
18		R ¹ = H, R ² = CCPh	Phenol, anisole, <i>o</i> -cresol, 2-naphthol, 1 <i>H</i> -indole	PMA-SiO ₂	90-96	18
19		R ¹ = H, R ² = Me		TfOH-SiO ₂	90	19
20		R ¹ = H, R ² = Me		HClO ₄	88	20
21		R ¹ = H, R ² = Ph	Phenol, mesitylene, 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, naphthalen-2-ol, 1 <i>H</i> -indole, 2-methylfuran, benzo[b]thiophene	NaHSO ₄ /SiO ₂	59-98	21
22		R ¹ = H, R ² = CCPh		PTS	73	22
23		R ¹ = H, R ² = Ph		PMA	90	23
24		R ¹ = H, R ² = CH=CHPh		Calix	0-100	24
25		R ¹ = H, R ² = Ph		TfOH/HC(OMe) ₃	60	25
26		R ¹ = H, R ² = Ph		HBF ₄ •OEt ₂	67	26
27		1-(naphthalen-2-yl)ethanol	2-methoxynaphthalene, anisole, methylfuran, 3,4-dihydronaphthalen-1-yl acetate, styrene	La(OTf) ₃	74-96	27
28		R ¹ = H, R ² = CH=CHPh		InCl ₃	69	28

Table 22. (Continued)

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
29	C-C	R ¹ = H, R ² = CH=CHPh		AuCl ₃ /AgSbF ₆	91	29
30		R ¹ = H, R ² = Me		Hf(OTf) ₄	93	30
31		R ¹ = H, R ² = Ph		Cu(OTf) ₂	98	31
32		R ¹ = H, R ² = Ph	indole	Fe(ClO ₄) ₃ •xH ₂ O	92	32
33				Sn(NTf ₂) ₄	75	33
34		R ¹ = H, R ² = Me		FeCl ₃ •6H ₂ O	99	34
35		R ¹ = H, R ² = CCPh		[BMIM][PF ₆]/Bi(NO ₃) ₃ •5H ₂ O or [BMIM][PF ₆]/Sc(OTf) ₃ •5H ₂ O	91	35
36		R ¹ = H, R ² = Me		Bi(OTf) ₃	91	36
37		R ¹ = H, R ² = Ph	resorcinol, 1 <i>H</i> -indole, naphthalen-2-ol	NbCl ₅	86-92	37
38		R ¹ = H, R ² = Ph	1 <i>H</i> -indole	FeCl ₃	75	38
39		R ¹ = H, R ² = Ph		(CF ₃ CO) ₂ O/Pd(OAc) ₂ /PPh ₃	56	39
40		R ¹ = H, R ² = Me		[(C ₆ H ₆)(PCy ₃)(CO)RuH] ⁺ BF ₄ ⁻	94	40
41		R ¹ = H, R ² = Me		InCl ₃	51	41
42		R ¹ = H, R ² = CH=CHPh		Cu(BF ₄) ₂	86	42
43		R ¹ = H, R ² = Ph		TiCl ₄	96	43
44		R ¹ = R ² = Me		InCl ₃ /Me ₃ SiBr	75	44
45		R ¹ = H, R ² = CCH		FeCl ₃	70	45
46		R ¹ = H, R ² = CCH		BiCl ₃	89	46
47		R ¹ = H, R ² = CCPh		(dppm)ReOCl ₃ /NH ₄ PF ₆	79	47

Table 22. (Continued)

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
48	C-C	R ¹ = H, R ² = CCPh		NaAuCl ₄ •2H ₂ O	97	48
49		R ¹ = H, R ² = CCPh		Bi(OTf) ₃	93	49
50		R ¹ = H, R ² = CH=CH ₂		PdCl(COD)SnCl ₂	70	50
51		R ¹ = H, R ² = Me	1,3-dimethoxybenzene	Ca(NTf ₂) ₂ / Bu ₄ NPF ₆	85	51
52		R ¹ = R ² = H		Pt/θ-Al ₂ O ₃ -1.5 nm	87	52
53		Allyl alcohol		[(η ³ -allyl)Pd(cod)]BF ₄	80	53
54			CH ₃ CH ₂ OH	[RuCp(<i>o</i> -EtOdppe)](OTs)	86	54
55				[RuCp(<i>o</i> -EtOdppe)](OTs)	48	54
56				[RuCp(PPh ₃) ₂](OTs)	99	55
57				Pt(acac) ₂ /PPh ₃ /Ti(OPr ⁱ) ₄	64	56
58				Pt(cod)Cl ₂ /DPEphos	86	57
59		R ¹ = H, R ² = CCH		[Cp* ₂ RuCl(μ ₂ -SMe) ₂ RuCp*Cl]/NH ₄ BF ₄	68	58
60		R ¹ = H, R ² = CCPh		[Cp* ₂ RuCl(μ-SMe) ₂ Cp* ₂ Ru(OH ₂)]OTf	71	59
61		R ¹ = H, R ² = CCPh		[ReBr(CO) ₃ (thf)] ₂	37	60
62		R ¹ = H, R ² = CCPh		(dppm)Re(O)Cl ₃ /KPF ₆	81	61
63		R ¹ = H, R ² = CH=CHPh	≡-Ph	Cu(OTf) ₂	78	62
64		R ¹ = H, R ² = CH=CH ₂	<i>p</i> -xylene	Ag ₃ PW ₁₂ O ₄₀	84	63
65		R ¹ = H, R ² = CH=CHPh		SbCl ₃	67	64
66		R ¹ = Ph, R ² = CCPh		Yb(OTf) ₃	90	65

Table 22. (Continued)

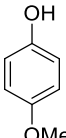
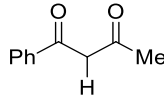
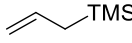

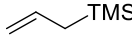
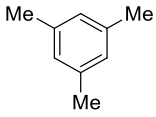
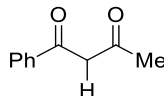
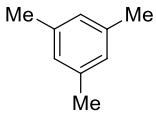
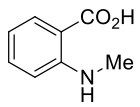

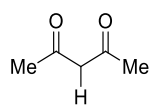
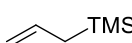
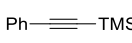
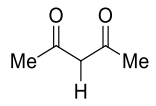
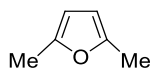
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
67	C-C	R ¹ = H, R ² = Me		Bi(OTf) ₃	58	66
68		R ¹ = H, R ² = Ph		[CHCl][ZnCl ₂] ₂	96	67
69		R ¹ = H, R ² = Ph		FeCl ₃ •6H ₂ O	98	68
70		R ¹ = H, R ² = Ph		Fe(OTf) ₃ /TfOH	77	69
71		R ¹ = H, R ² = CCPh		NaAuCl ₄ •2H ₂ O	97	70
72		R ¹ = H, R ² = CCPh		AuBr ₃	80	71
73		R ¹ = H, R ² = Me		Ir-Sn ₃ complex	90	72
74		R ¹ = H, R ² = Me		[Fe(TPP)]SbF ₆]	92	73
75		R ¹ = H, R ² = CH=CHPh		Co(hfac) ₂ •xH ₂ O/TPPMS	77	74
76		R ¹ = H, R ² = Ph		FeCl ₃ •6H ₂ O/TsOH	66	75
77		R ¹ = H, R ² = Me		<i>cis</i> -[Ru(6,6'-Cl ₂ bipy) ₂ (H ₂ O) ₂](ClO ₄) ₂	82	76
78		R ¹ = H, R ² = CH=CHPh		I ₂	94	77
79		R ¹ = H, R ² = CCPh			96	78
80		R ¹ = H, R ² = Me			99	79
81		R ¹ = H, R ² = CCPh	Phenol		90	80
82		R ¹ = R ² = H	Anisole		88	81
83		R ¹ = H, R ² = Me			78	79

Table 22. (Continued)



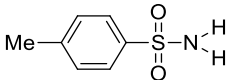
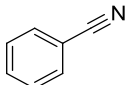
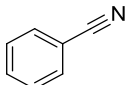
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
84		R ¹ = R ² = Ph		I ₂	98	82
85		R ¹ = H, R ² = CH=CHPh	anisole, phenol, indole, TMSNu, RNH ₂ , acetylacetone	HFIP or TFE ^a	51-98	83
86		1-(Ferrocenyl)ethanol	1H-indole, 1H-pyrrole, acetylacetone, ethyl 3-oxobutanoate	H ₂ O ^b	48-90	84
87		R ¹ = H, R ² = CCPh		PIFA	61	85
88		R ¹ = H, R ² = Ph	Ac ₂ O	NBS	95	86
89	C-N	R ¹ = H, R ² = Ph	benzyl carbamate	DBSA	84	6
90		R ¹ = H, R ² = CCPh	benzenesulfonamide	PTS	67	9
91		R ¹ = HF ₂ C, R ² = H	MeCN	H ₂ SO ₄	55	87
92		R ¹ = H, R ² = CCPh	4-methylbenzamide	Amberlite IR-120H resin	90	13
93		R ¹ = H, R ² = Me	MeCN	DNBSA	82	88
94		2-methylpropan-2-ol	MeCN	[BMIM(SO ₃ H)][OTf]	95	89
95		R ¹ = H, R ² = Me	PhCN	Nanocat.-Fe-OSO ₃ H	84	90
96		R ¹ = H, R ² = Ph	MeCN	CoFe ₂ O ₄ @SiO ₂ -DASA	90	91
97		R ¹ = H, R ² = Ph	CH ₂ =CH-CH ₂ CN	NaHSO ₄ /SiO ₂	84-87	92
98		R ¹ = H, R ² = Me	MeCN	PFPAT	95	93
99		R ¹ = R ² = Me	MeCN	TfOH/SDS	82	94
100		R ¹ = H, R ² = CCPh	Benzenesulfonamide, benzamide	FeCl ₃	73-82	45
101		R ¹ = H, R ² = CCPh		BiCl ₃	80	46
102		Adamantanol		Bi(OTf) ₃	91	95
103		R ¹ = H, R ² = Ph	MeCN	(Mes ₃ P)AuNTf ₂	70	96
104		R ¹ = H, R ² = Me		Ca(OTf) ₂ /Bu ₄ NPF ₆	93	97
105		R ¹ = H, R ² = Ph	4-nitroaniline, 4-methylbenzenesulfonamide, benzamide	[CHCl][ZnCl ₂] ₂	92-95	67

Table 22. (Continued)

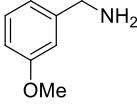
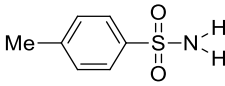
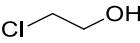
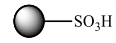

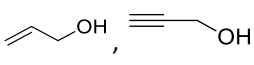
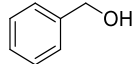

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
106		R ¹ = R ² = H	Ph-NH ₂	Ru (II) pincer complex	92	98
107		R ¹ = H, R ² = CH=CHPh	benzyl carbamate	Al(OTf) ₃	92	99
108		R ¹ = R ² = H	4-chloroaniline	NiCuFeOx	76	100
109		R ¹ = R ² = Me	4-nitroaniline	Ca(NTf ₂) ₂ /Bu ₄ NPF ₆	87	101
110		R ¹ = R ² = H	Ph-NH ₂	[Cp*IrCl ₂] ₂ /NaHCO ₃	93	102
111		R ¹ = R ² = H	Ph-NH ₂	[Ru(p-cymene)Cl ₂] ₂ /DPEphos	91	103
112		R ¹ = R ² = H	Ph-NH ₂	Pd/Fe ₂ O ₃	90	104
113		R ¹ = R ² = H	Ph-NH ₂	[Cp*Ir(NH ₃) ₃][I] ₂	92	105
114		R ¹ = R ² = H	Ph-NH ₂	[IrCl(cod)] ₂ /Py ₂ NP/Pr ₂	92	106
115		R ¹ = R ² = H	Ph-NH ₂	Ru(OH) ₃ -Fe ₃ O ₄	99	107
116		R ¹ = R ² = H		FeBr ₃ /DL-pyroglutamic acid/Cp*H	77	108
117		R ¹ = H, R ² = CH=CH ₂		Pd(Xantphos)Cl ₂	72	109
118		R ¹ = H, R ² = Ph	PhCONH ₂	I ₂	98	110
119		R ¹ = H, R ² = Me	MeCN/H ₂ O		85	111
120		R ¹ = H, R ² = CH=CHPh			85	112, 113
121		R ¹ = H, R ² = Ph	amides, anilines	H-mont	39-94	114
122		R ¹ = H, R ² = Ph	TMSN ₃	TMSCl/Na-Mont	98	115
123	C-O	R ¹ = H, R ² = CH=CHPh		PTS or 	83	8
124		R ¹ = R ² = Me	CH ₃ (CH ₂) ₃ OH	NaHSO ₃	48	116
125		cyclohexanol	methyl <i>tert</i> -butyl ether	H ₂ SO ₄ ^c	79	117
126		R ¹ = H, R ² = Ph		TeaMs	75	118
127		R ¹ = H, R ² = Ph		NbCl ₅	93-95	37
128		R ¹ = H = R ² = CPh		FeCl ₃	91	45
129		R ¹ = H = R ² = CC ⁿ Bu		BiCl ₃	66	46
130		Allyl alcohol	CH ₃ CH ₂ OH	[RuCp(<i>o</i> -EtOdppe)](OTs)	86	54

Table 22. (Continued)


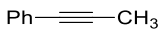
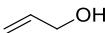


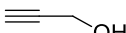

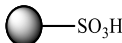

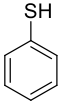
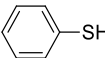
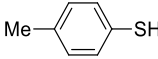
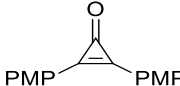
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
131	C-O	R ¹ = H, R ² = Ph		Pd(PPh ₃) ₄ /PhCO ₂ H	85	119
132		R ¹ = H, R ² = Ph		Pd(PPh ₃) ₄	85	120
133		R ¹ = H, R ² = Ph	<i>i</i> PrOH	PdCl ₂	86	121
134		R ¹ = H, R ² = Ph		PdCl ₂ (CH ₃ CN) ₂	71	122
135		R ¹ = H, R ² = Ph		NaAuCl ₄	56	123
136		R ¹ = H, R ² = CC ⁿ Bu		(dppm)ReOCl ₃	96	124
137		R ¹ = H, R ² = Ph	MeOH	Fe(NO ₃) ₃ •9H ₂ O	88	125
138		R ¹ = Me, R ² = CC	EtOH	[Fc]PF ₆	67	126
139		R ¹ = H, R ² = Me	2-methylpropan-1-ol	AuCIPPh ₃ /AgSbF ₆	53	127
140		R ¹ = H, R ² = Ph		I ₂	95	128
141		R ¹ = R ² = H		Ph ₂ CHBr	90	129
142		R ¹ = H, R ² = CCPh	EtOH	PIFA	83	85
143	C-S	R ¹ = H, R ² = Ph	benzenethiol	DBSA	83	6
144		R ¹ = H, R ² = CH=CHPh	dodecylthiol	PTS or 	81	8
145		R ¹ = H = R ² = CCPh	CH ₃ (CH ₂) ₁₁ SH	PTS	80	9
146		R ¹ = H, R ² = Ph	 , NH ₄ SCN	NbCl ₅	90-95	37
147		R ¹ = H, R ² = Ph	 , OH-CH ₂ -CH ₂ -SH	FeCl ₃	93-94	45
148		Allyl alcohol		[RuCp(<i>o</i> -EtOdppe)](OTs)	48	54
149		(<i>E</i>)-4-phenylbut-3-en-2-ol		I ₂	92	130
150		R ¹ = H, R ² = CCPh	PhSH	PIFA	92	85
151	C-OTMS	R ¹ = H, R ² = H	HMDS	LiClO ₄	99	131
152		R ¹ = H, R ² = Ph		LaCl ₃	93	132

Table 22. (Continued)

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
153	C-OTMS	R ¹ = H, R ² = Ph	HMDS	I ₂	87	133
154	C-CN	R ¹ = H, R ² = CH=CHPh	TMSCN	Zn(OTf) ₂	77	134
155		R ¹ = H, R ² = CH=CHCH ₃		InBr ₃	86	135
156	C-Cl	R ¹ = H, R ² = H	HSiMe ₂ Cl/benzil	InCl ₃	80	136
157		2-methylhexan-2-ol	HSiMe ₂ Cl	GaCl ₃ /diethyltartrate	99	137
158		(3-nitrophenyl)methanol	TsCl/TEA	DMAP	35	138
159		R ¹ = H, R ² = Ph	(COCl) ₂	Ph ₃ PO	96	139
160		R ¹ = R ² = H	(COCl) ₂		84	140
161		R ¹ = H, R ² = Me	TMSCl	Na-Mont	60	141
162	C-Br	R ¹ = H, R ² = Me	LiBr/(COCl) ₂	Ph ₃ PO	74	139

^aHFIP or TFE were used as solvents and promoters.

^bH₂O was used as solvent.

^cH₂SO₄ (10 mmol).

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