

Supplementary Material

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

Njomza Ajvazi ^a and Stojan Stavber ^{*a,b}

^a*Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia*

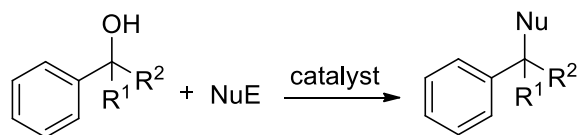
^b*Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

Email: stojan.stavber@ijs.si

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

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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[<i>b</i>]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) 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)

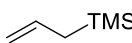
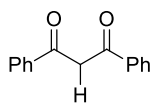
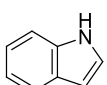
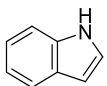
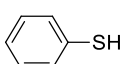
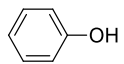
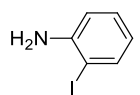
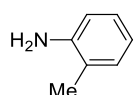

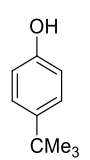
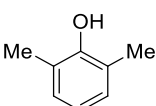
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
48	C-C	R ¹ = H, R ² = CCPh		NaAuCl ₄ •2H ₂ O	97	48
49		R ¹ = H, R ² = CCPh		Bi(OTf) ₃	93	49
50		R ¹ = H, R ² = CH=CH ₂		PdCl(COD)SnCl ₂	70	50
51		R ¹ = H, R ² = Me	1,3-dimethoxybenzene	Ca(NTf ₂) ₂ / Bu ₄ NPF ₆	85	51
52		R ¹ = R ² = H		Pt/θ-Al 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)

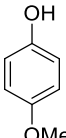
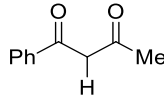
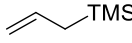

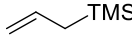
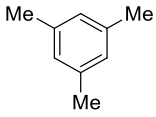
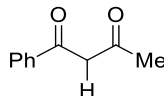
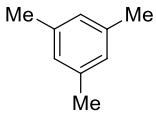
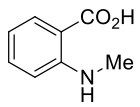

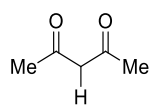
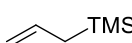
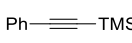
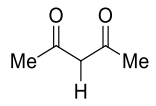
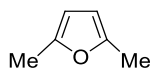
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
67	C-C	R ¹ = H, R ² = Me		Bi(OTf) ₃	58	66
68		R ¹ = H, R ² = Ph		[CHCl][ZnCl ₂] ₂	96	67
69		R ¹ = H, R ² = Ph		FeCl ₃ •6H ₂ O	98	68
70		R ¹ = H, R ² = Ph		Fe(OTf) ₃ /TfOH	77	69
71		R ¹ = H, R ² = CCPh		NaAuCl ₄ •2H ₂ O	97	70
72		R ¹ = H, R ² = 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)



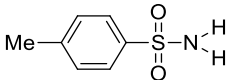
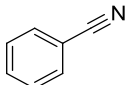
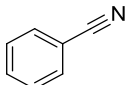
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
84		R ¹ = R ² = Ph		I ₂	98	82
85		R ¹ = H, R ² = CH=CHPh	anisole, phenol, indole, TMSNu, RNH ₂ , acetylacetone	HFIP or TFE ^a	51-98	83
86		1-(Ferrocenyl)ethanol	1H-indole, 1H-pyrrole, acetylacetone, ethyl 3-oxobutanoate	H ₂ O ^b	48-90	84
87		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)

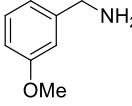
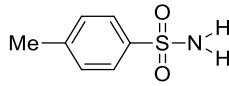
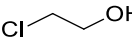
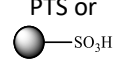

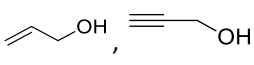
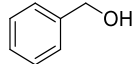

Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
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107		R ¹ = H, R ² = CH=CHPh	benzyl carbamate	Al(OTf) ₃	92	99
108		R ¹ = R ² = H	4-chloroaniline	NiCuFeOx	76	100
109		R ¹ = R ² = Me	4-nitroaniline	Ca(NTf ₂) ₂ /Bu ₄ NPF ₆	87	101
110		R ¹ = 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)


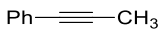
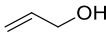


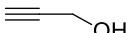

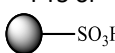



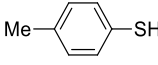
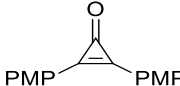
Entry	Bond formation	R ¹ , R ²	NuE	Catalyst	Yield (%)	Ref.
131	C-O	R ¹ = H, R ² = Ph		Pd(PPh ₃) ₄ /PhCO ₂ H	85	119
132		R ¹ = H, R ² = Ph		Pd(PPh ₃) ₄	85	120
133		R ¹ = H, R ² = Ph	<i>i</i> PrOH	PdCl ₂	86	121
134		R ¹ = H, R ² = Ph		PdCl ₂ (CH ₃ CN) ₂	71	122
135		R ¹ = H, R ² = Ph		NaAuCl ₄	56	123
136		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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