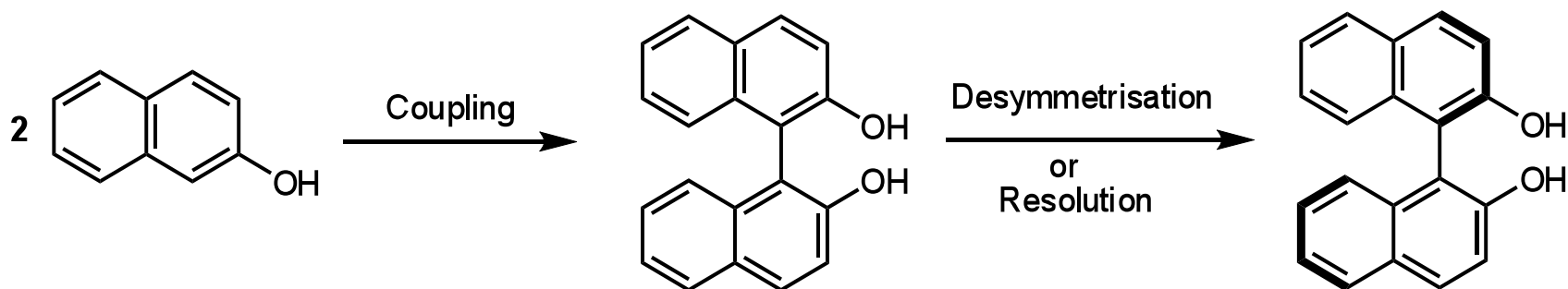


Highly Enantioselective Oxidative Couplings of 2-Naphthols Catalyzed by Chiral Bimetallic Oxovanadium Complexes with Either Oxygen or Air as Oxidant

Gong, L. *et.al.* *JACS*, 2007, ASAP

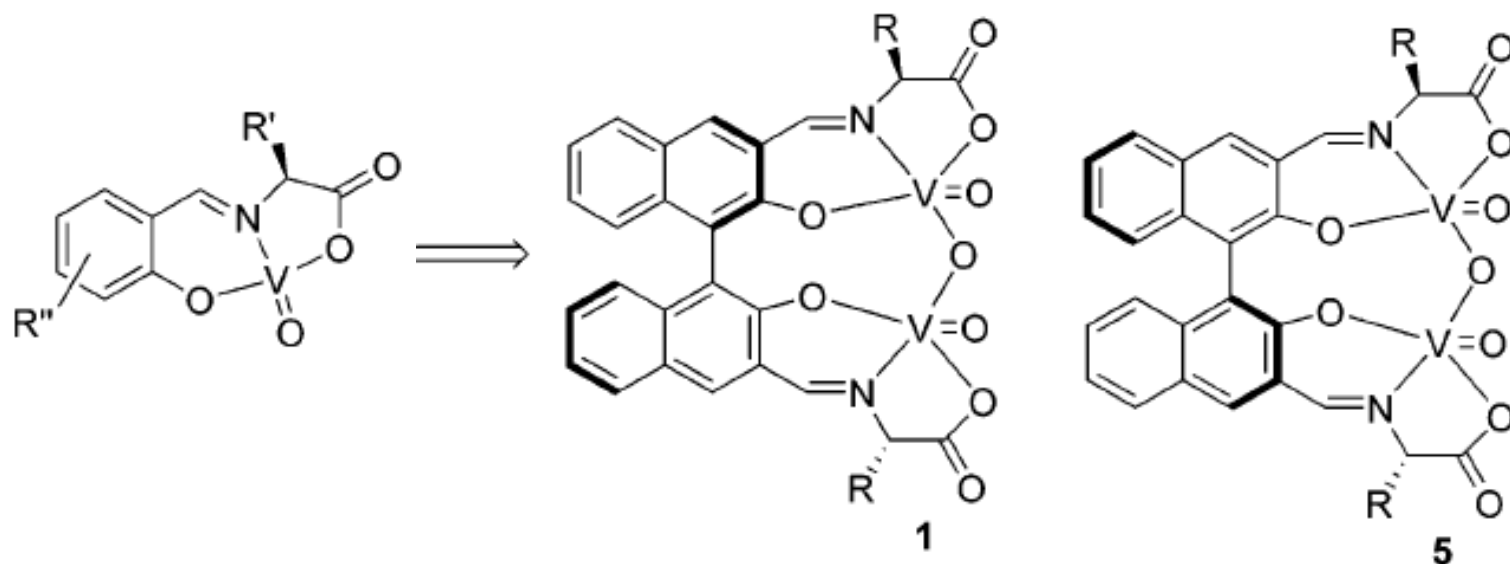
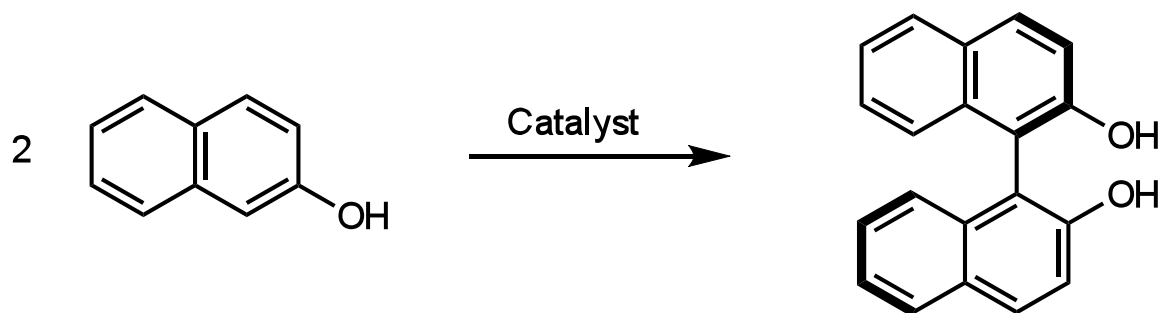
Anil Kumar Gupta
Group meeting presentation
10/26/07

Conventional Methods: Preparation of Chiral BINOL

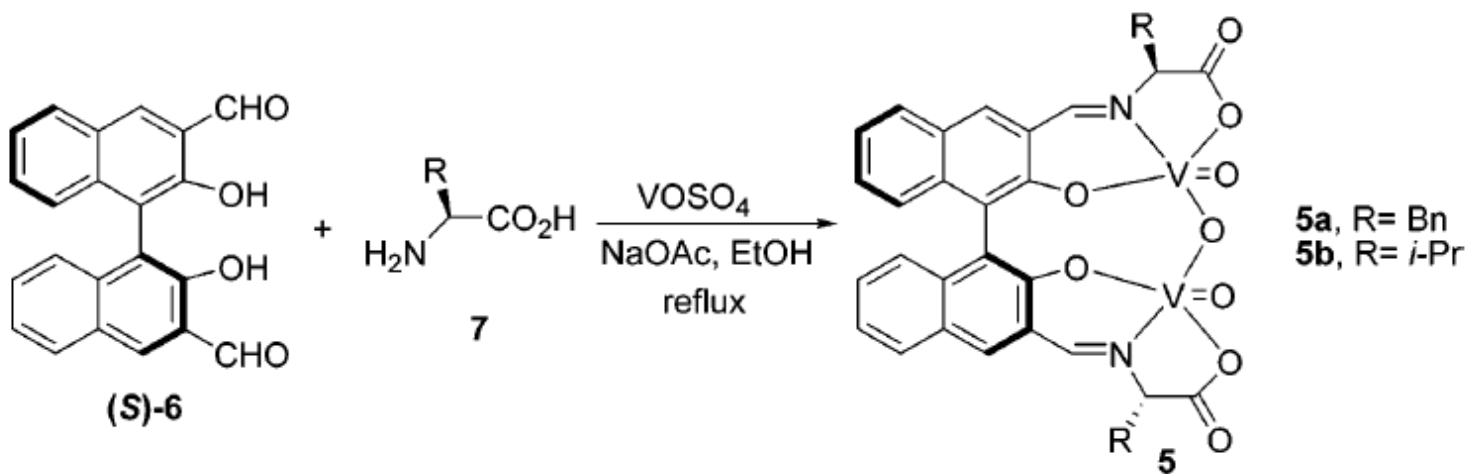
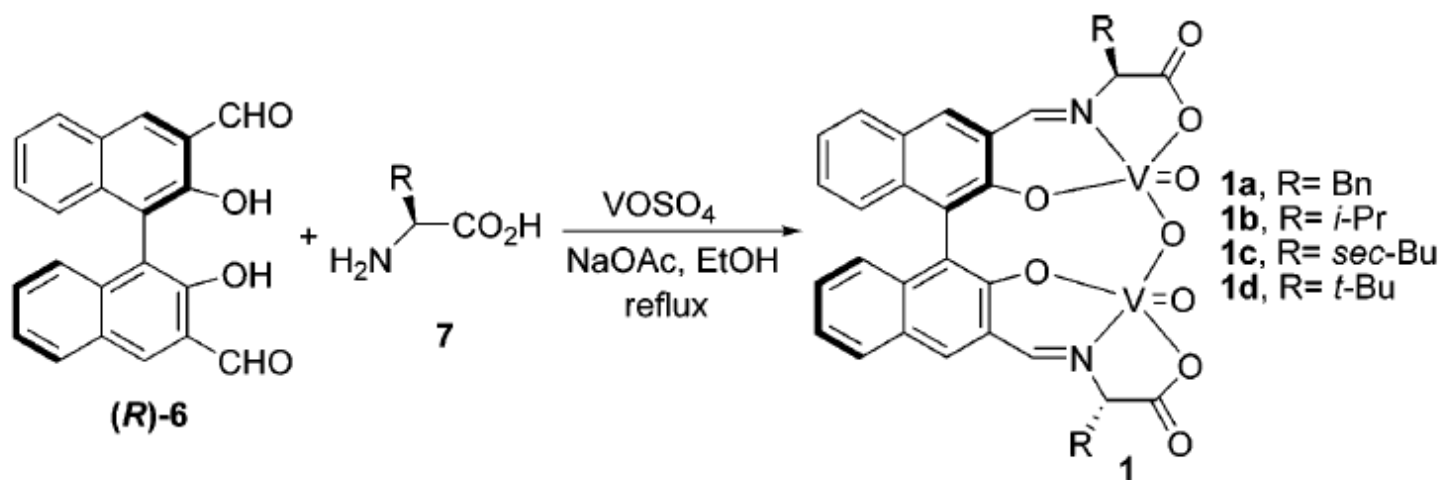


How about doing this in one pot ?

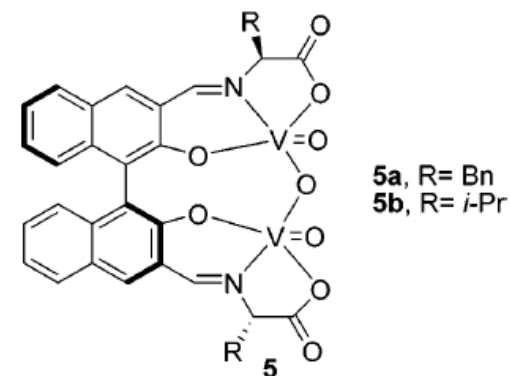
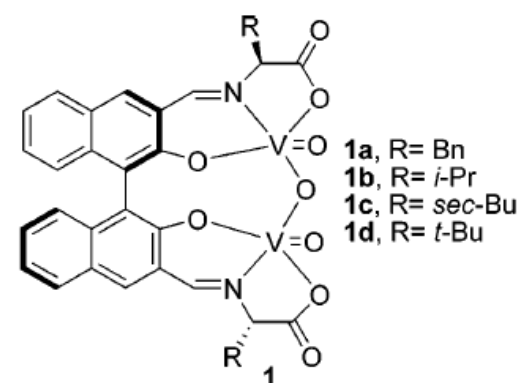
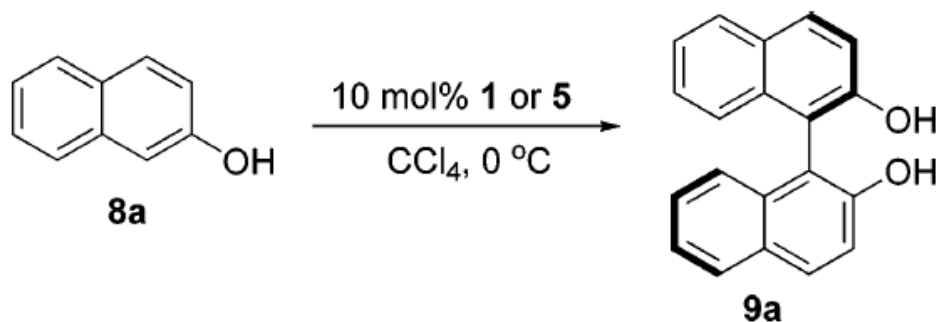
Catalyst Design



Preparation of the Catalyst



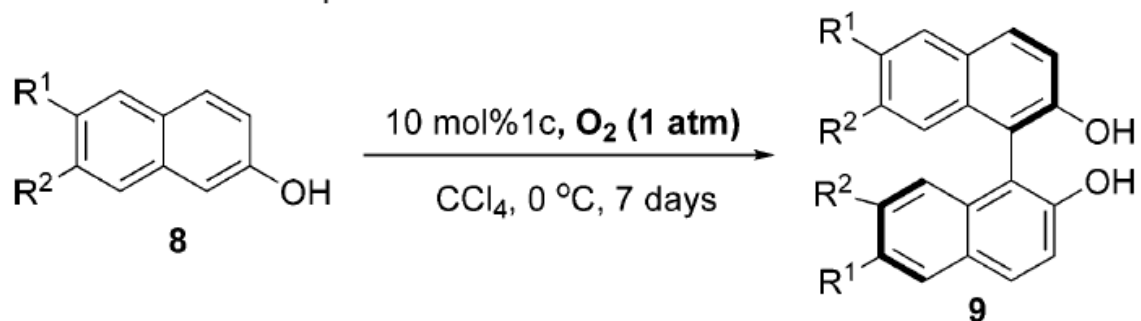
Screening of the Catalyst



entry	catalyst	time (days)	yield (%) ^b	ee (%) ^c
1	1a	5	<20	50
2	1b	8	70	81
3	1c	6	93	83
4	1d	8	63	71
5	5a	5	70	6 ^d
6	5b	5	75	10 ^d

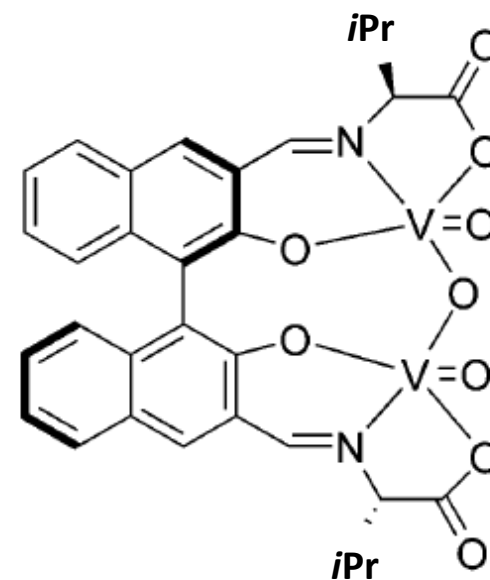
^a The reaction was carried out in CCl_4 . ^b Isolated yield. ^c The ee values were determined by HPLC on a Kromasil CHI-TBB column, and the absolute configuration is *R*. ^d Reactions were conducted at RT.

Substrate Scope



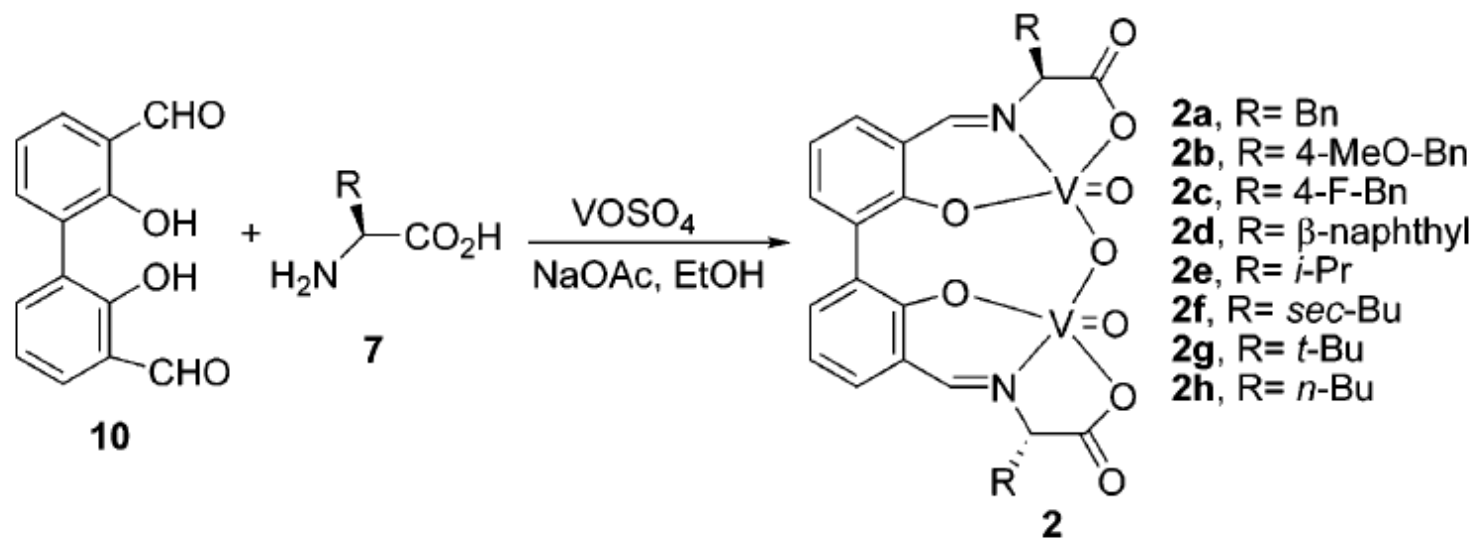
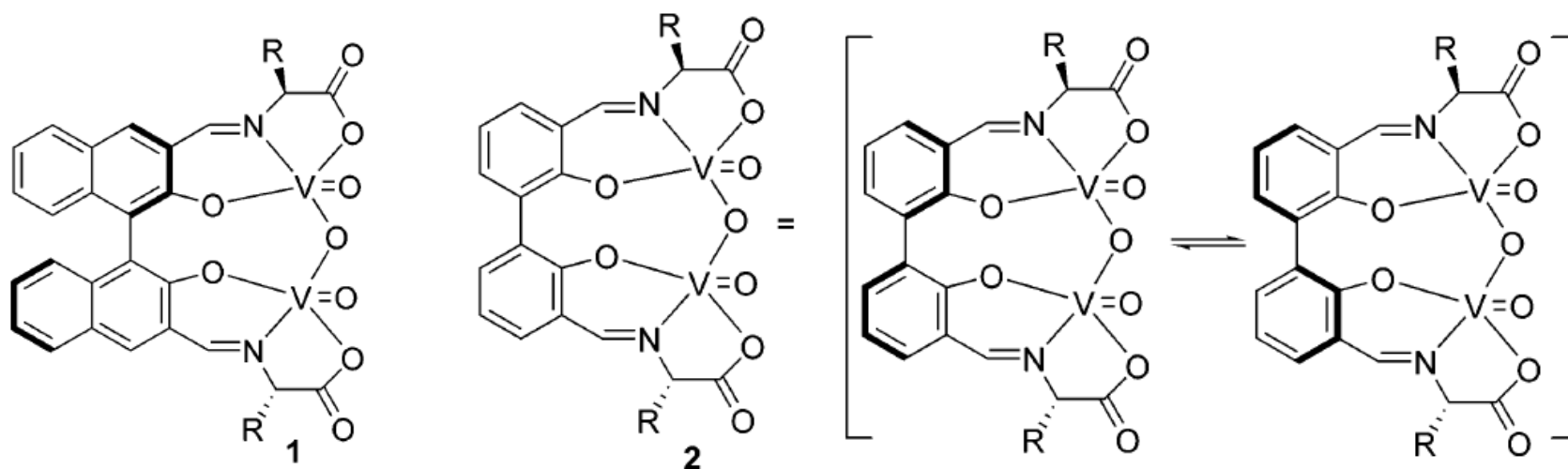
entry	products	R ₁	R ₂	yield (%) ^b	ee (%) ^c
1	9b	H	OCH ₂ CH=CH ₂	98	95
2	9c	H	OMe	88	98
3	9d	H	OEt	99	93
4	9e	H	O ⁿ Bu	95	96
5	9f	H	O ⁿ C ₈ H ₁₇	93	94
6	9g	H	O ⁿ C ₁₂ H ₂₅	91	92
7	9h	H	OBn	96	96

^a The reactions are carried out at 0 °C in the presence of 10 mol % of catalyst **1c** using CCl₄ as solvent. ^b Isolated yields. ^c The ee values are determined by HPLC on a Kromasil CHI-TBB or Chiralpak AD column.

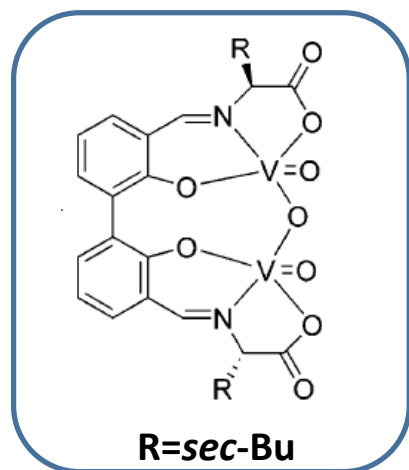
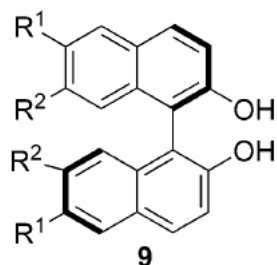
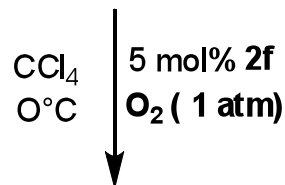
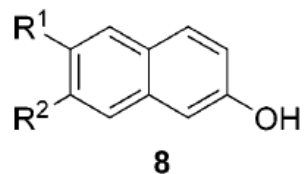


1c

Asymmetric Activation of the Achiral Catalyst

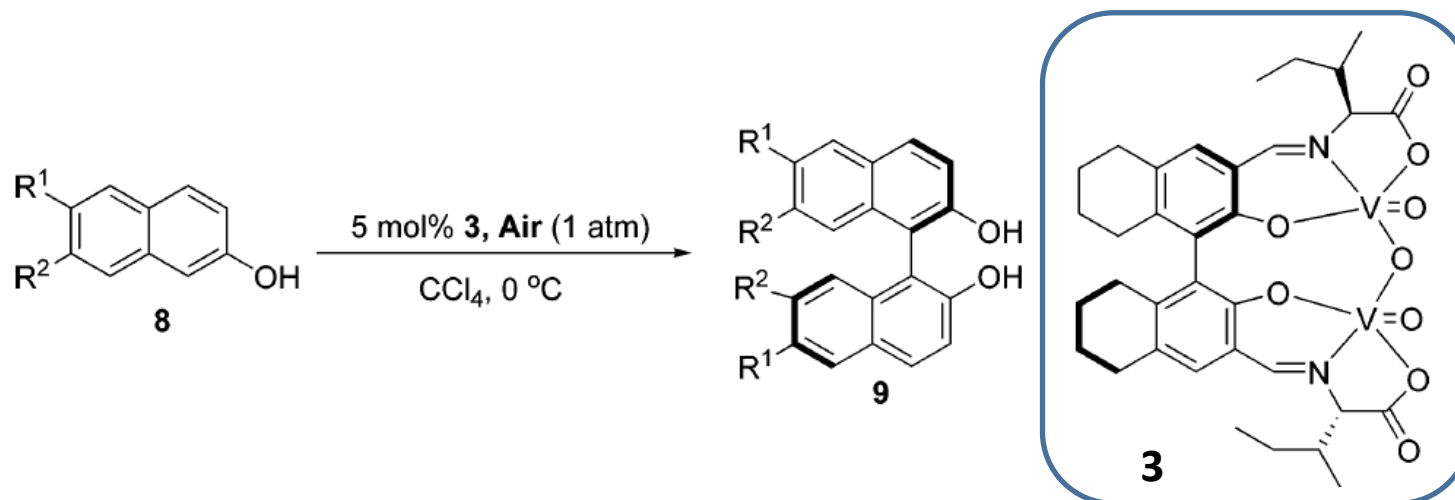


Substrate Scope



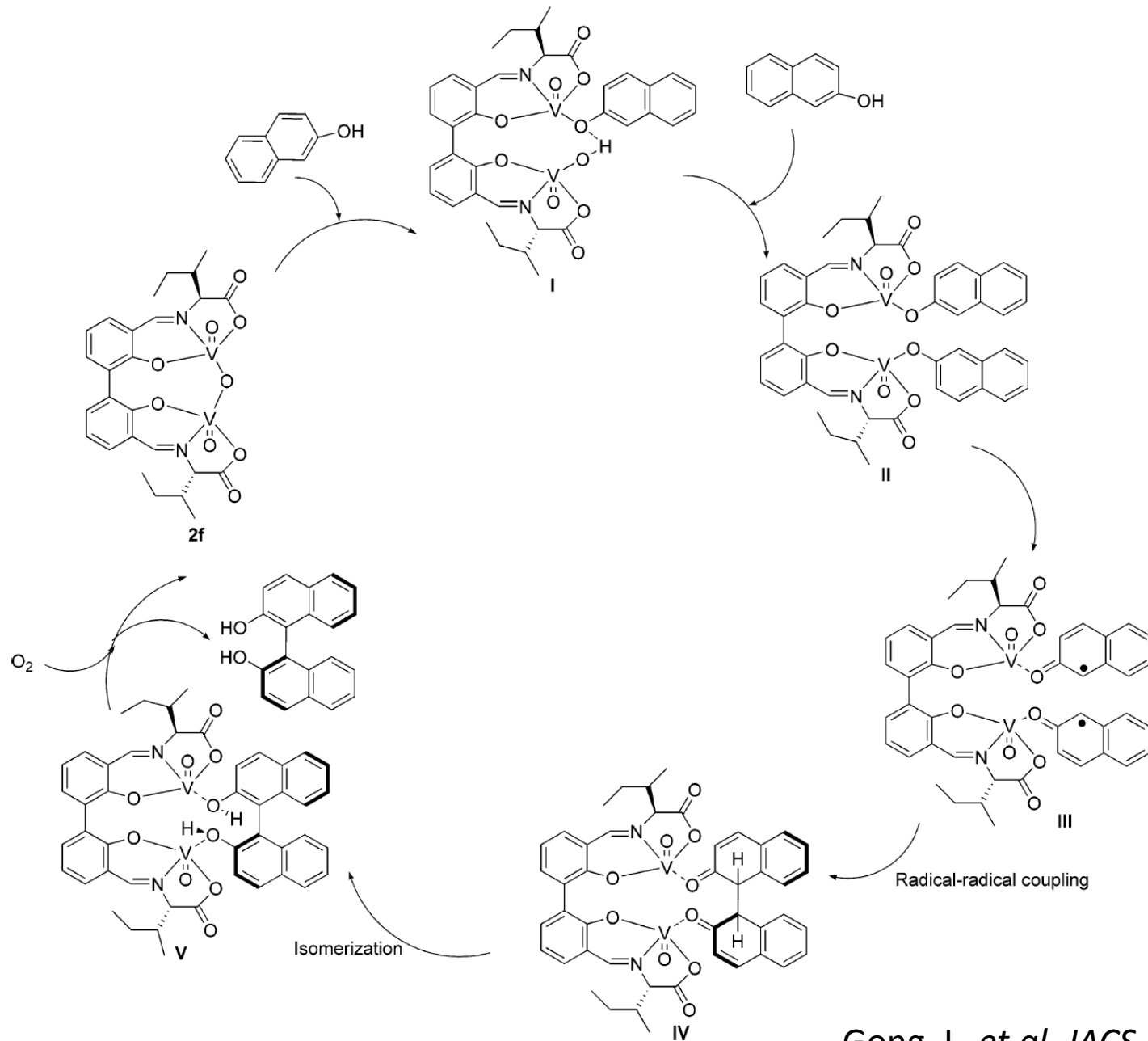
entry	products	R ¹	R ²	time (days)	yield (%) ^b	ee (%) ^c
1	9b	H	OCH ₂ CH=CH ₂	4	99	95
2	9c	H	OMe	7	95	95
3	9d	H	OEt	4	99	96
4	9e	H	O ⁿ Bu	4	99	94
5	9f	H	O ⁿ C ₈ H ₁₇	4	99	94
6	9g	H	O ⁿ C ₁₂ H ₂₅	4	94	97
7	9h	H	OBn	6	80	95
8	9i	H	Ph	6	92	86
9	9j	H	4-FC ₆ H ₄	6	>99	85
10	9k	OCH ₂ CH=CH ₂	H	5	>99	36
11	9l	O ⁿ Pr	H	5	93	44
12	9m	Br	H	4	98	90
13	9n	Br	OMe	6	97	96
14	9o	Br	OEt	6	95	97
15	9p	Br	OCH ₂ CH=CH ₂	6	>99	98
16	9q	Br	O ⁿ Bu	6	>99	98
17	9r	Br	O ⁿ C ₅ H ₁₁	6	96	89
18	9s	Br	O ⁿ C ₆ H ₁₃	6	97	91
19	9t	Br	O ⁿ C ₈ H ₁₇	6	95	90
20	9u	Br	OBn	6	96	96 ^d
21	9v	4-FC ₆ H ₄	O ⁿ Bu	6	96	48

Another Modification of the Catalyst



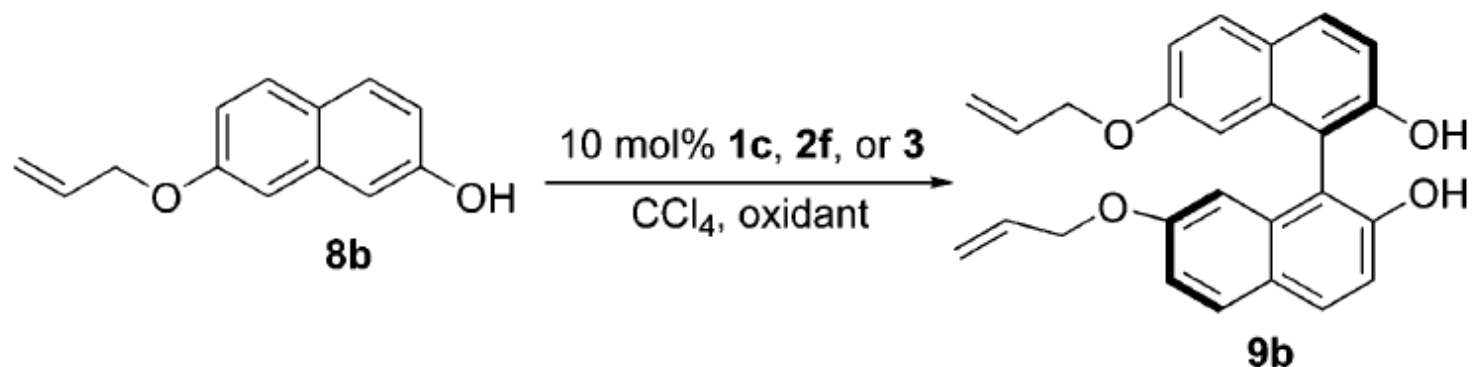
entry	products	R ¹	R ²	time (days)	yield (%) ^b	ee (%) ^c
1	9a	H	H	4	58	60
2	9c	H	OMe	2	94	92
3	9d	H	OEt	1.5	99	93
4	9e	H	O ⁿ Bu	1.5	97	93
5	9g	H	OC ₁₂ H ₂₅	2	85	89
6	9o	Br	OEt	2	96	97
7	9p	Br	OCH ₂ CH ₂ =CH ₂	2	92	95
8	9q	Br	O ⁿ Bu	2	90	97
9	9r	Br	O ⁿ C ₅ H ₁₁	2	90	96
10	9s	Br	O ⁿ C ₆ H ₁₃	2	89	93
11	9t	Br	O ⁿ C ₈ H ₁₇	2	88	96
12	9m	Br	H	2	82	86

Proposed Mechanism



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Comparison of the Catalytic Systems



entry	catalyst	oxidant	time (days)	yield (%) ^a	TOF (d ⁻¹)	ee (%) ^b
1	3	O ₂	1.5	92	6.1	91
2	3	Air	2	99	5.0	93
3	1c	Air	2	51	2.5	96
4	2f	Air	2	25	1.3	89

^a Isolated yields. ^b The ee values are determined by HPLC on a Kromasil CHI-TBB or Chiralpak AD column, the configurations of products are *R*.