1.

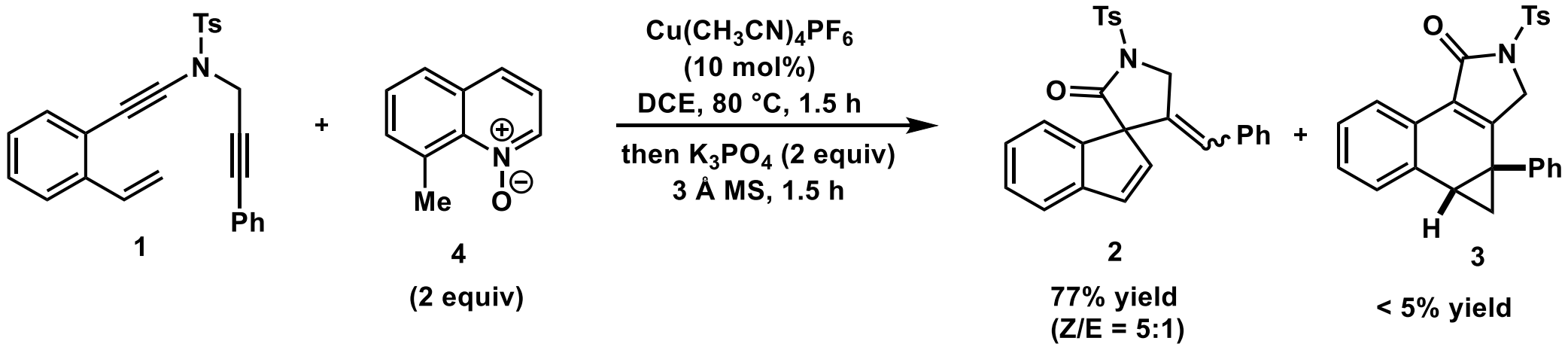

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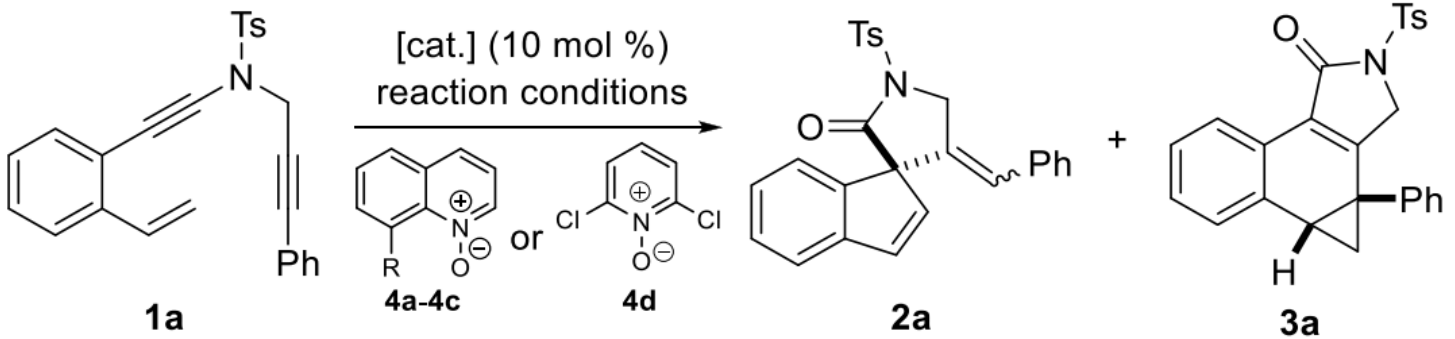
Table 1. Optimization of the Reaction Conditions[a]

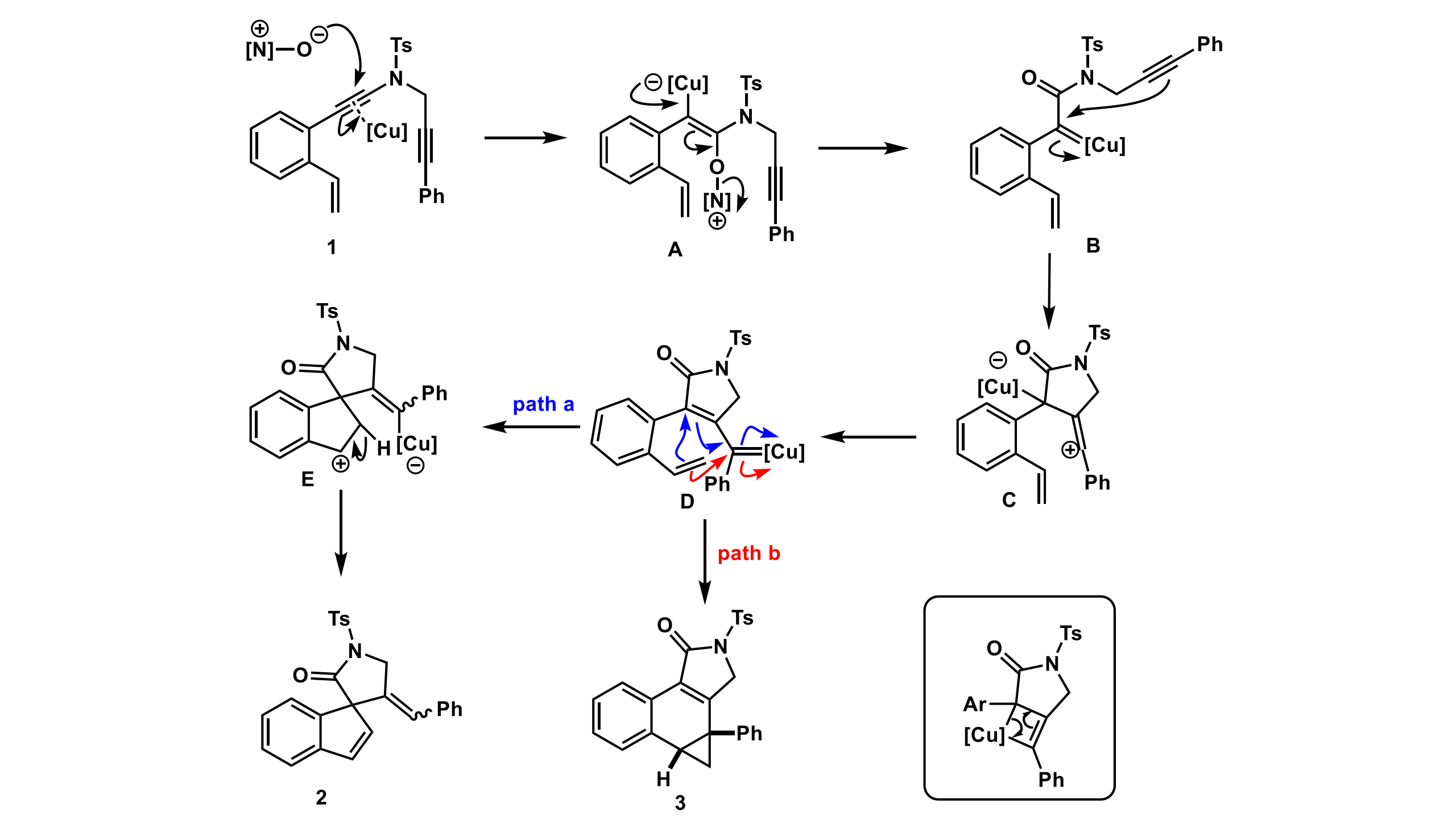


1a 4a-4c 4d 2a 3a

entry	catalyst	reaction conditions	yield (%)[b] 2a (Z/E)	3a
1	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 60 °C	72 (2.6/1)	<5
2	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 80 °C	85 (2.6/1)	<5
3	$Cu(CH_3CN)_4PF_6$	**4b** (R = Et), 80 °C	69 (2.0/1)	<5
4	$Cu(CH_3CN)_4PF_6$	**4c** (R = ^{i}Pr), 80 °C	68 (2.0/1)	<5
5	$Cu(CH_3CN)_4PF_6$	**4d**, 80 °C	<5	<5
6	$Cu(CH_3CN)_4BF_4$	**4a** (R = Me), 80 °C	75 (2.4/1)	<5
7	CuOTf	**4a** (R = Me), 80 °C	65 (2.0/1)	<5

entry	catalyst	reaction conditions	yield (%)[b]	
			2a (*Z*/*E*)	**3a**
8	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 80 °C, then Cs_2CO_3, 1.5 h	74 (3.3/1)	<5
9	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 80 °C, then K_2CO_3, 1.5 h	73 (3.4/1)	<5
10	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 80 °C, then DBU, 1.5 h	63 (3.2/1)	<5
11	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 80 °C, then K_3PO_4, 1.5 h	77 (4.5/1)	<5
12[c]	$Cu(CH_3CN)_4PF_6$	**4a** (R = Me), 80 °C, then K_3PO_4, 1.5 h	77 (5.0/1)	<5
13[d]	$Cu(CH_3CN)_4BF_4$	**4a** (R = Me), 80 °C, then K_3PO_4, 1.5 h	77 (4.2/1)	<5

[a]Reaction conditions: **1a** (0.1 mmol), **4** (0.2 mmol), base (0.2 mmol), catalyst (0.01 mmol), DCE (2 mL), 60−80 °C, in vials. [b]Measured by ^1H NMR using 2,6-dimethoxytoluene as an internal standard. [c]With 3 Å MS (40 mg) as an additive. [d]With 4 Å MS (40 mg) as an additive.


[N]—O
Ts
N
[Cu]
Ph
1
[Cu]
Ts
N
O
[N]
Ph
A
Ts
Ph
O
N
[Cu]
B
Ts
O
N
[Cu]
Ph
C
Ts
O
N
[Cu]
Ph
D
path a
path b
Ts
N
O
Ph
H
[Cu]
E
Ts
N
O
Ph
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Ts
O
N
Ph
H
3
Ts
O
N
Ar
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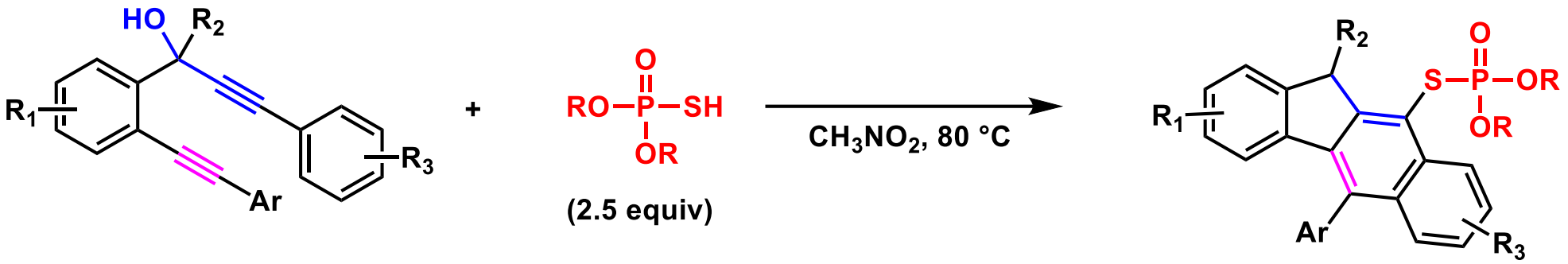
Ph

2.



yield up to 89%

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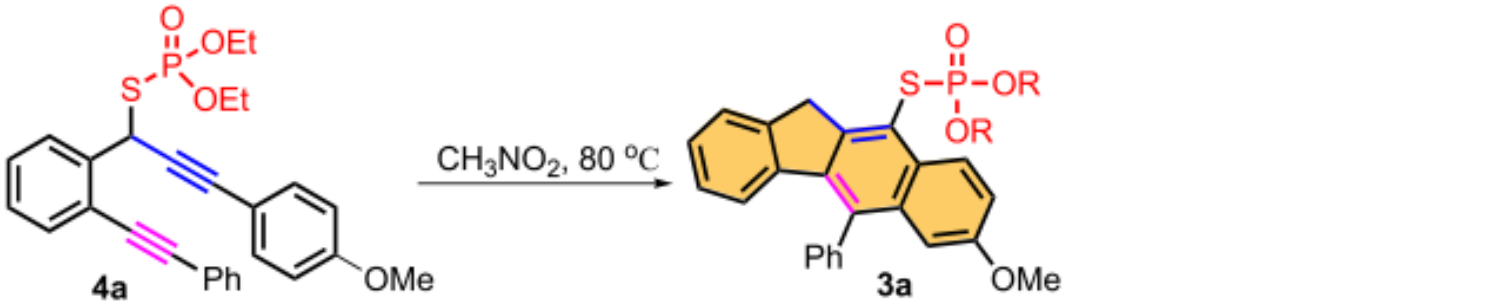
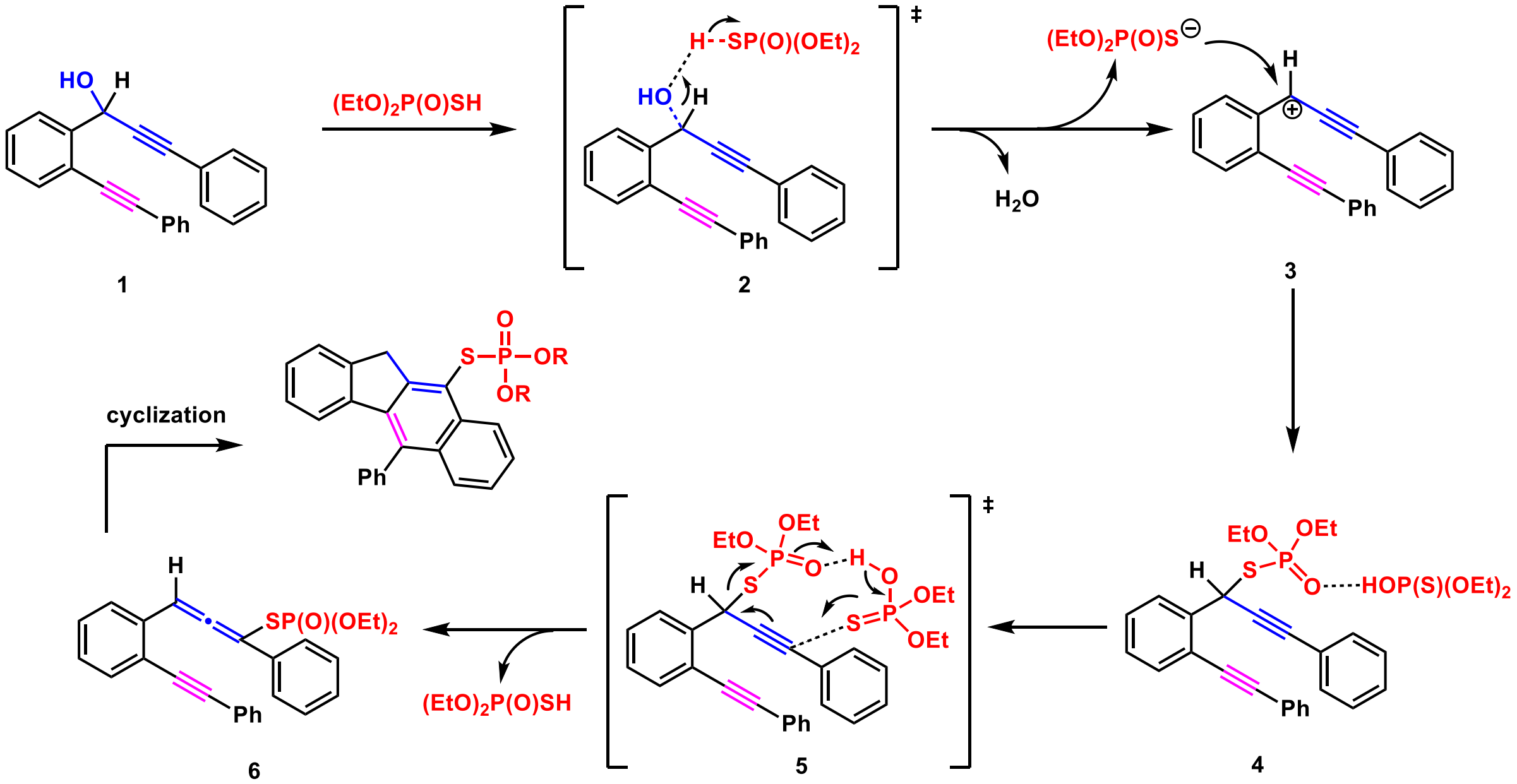
3) Controlled experiments



With $(EtO)_2P(O)SH$ (2.5 equiv), **3a**, 79%
Without $(EtO)_2P(O)SH$, **3a**, 0%


HO
H
Ph
1
(EtO)2P(O)SH
H--SP(O)(OEt)2
HO
H
Ph
2
‡
(EtO)2P(O)S⊖
H2O
H
Ph
3
EtO
OEt
P
O
H
S
OEt
S
P
OEt
HOP(S)(OEt)2
H
Ph
4
‡
(EtO)2P(O)SH
H
SP(O)(OEt)2
Ph
6
cyclization
O
S—P—OR
OR
Ph