Catalyzed Nitrogenation of Alkynes: A Direct Approach to Nitriles through C≡C Bond Cleavage

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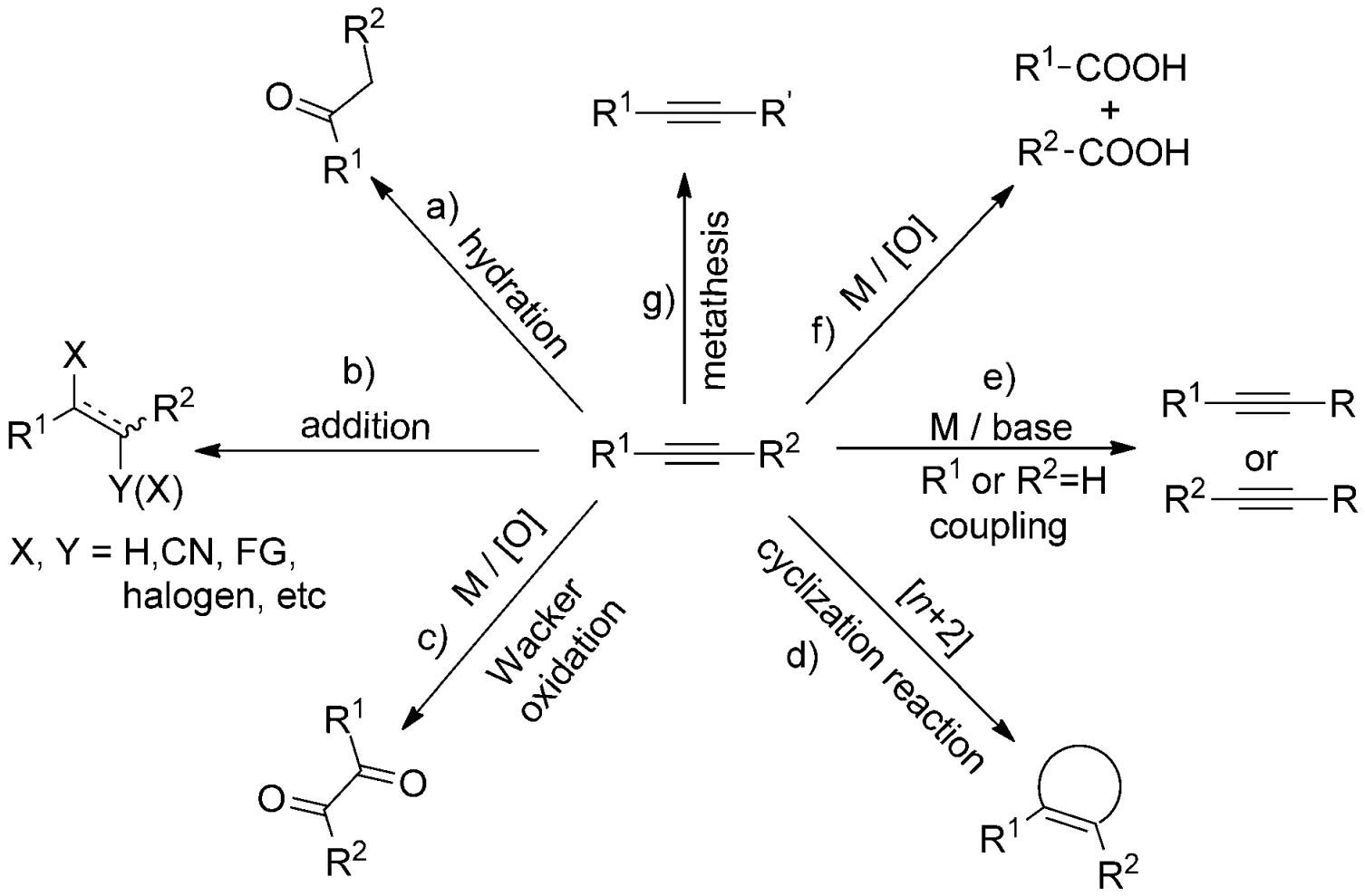
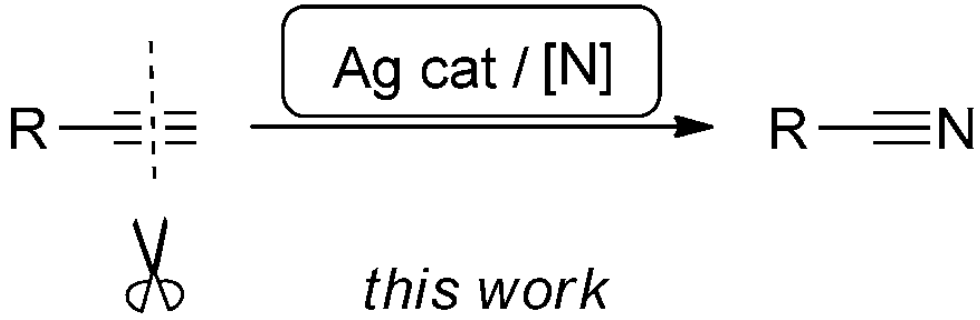
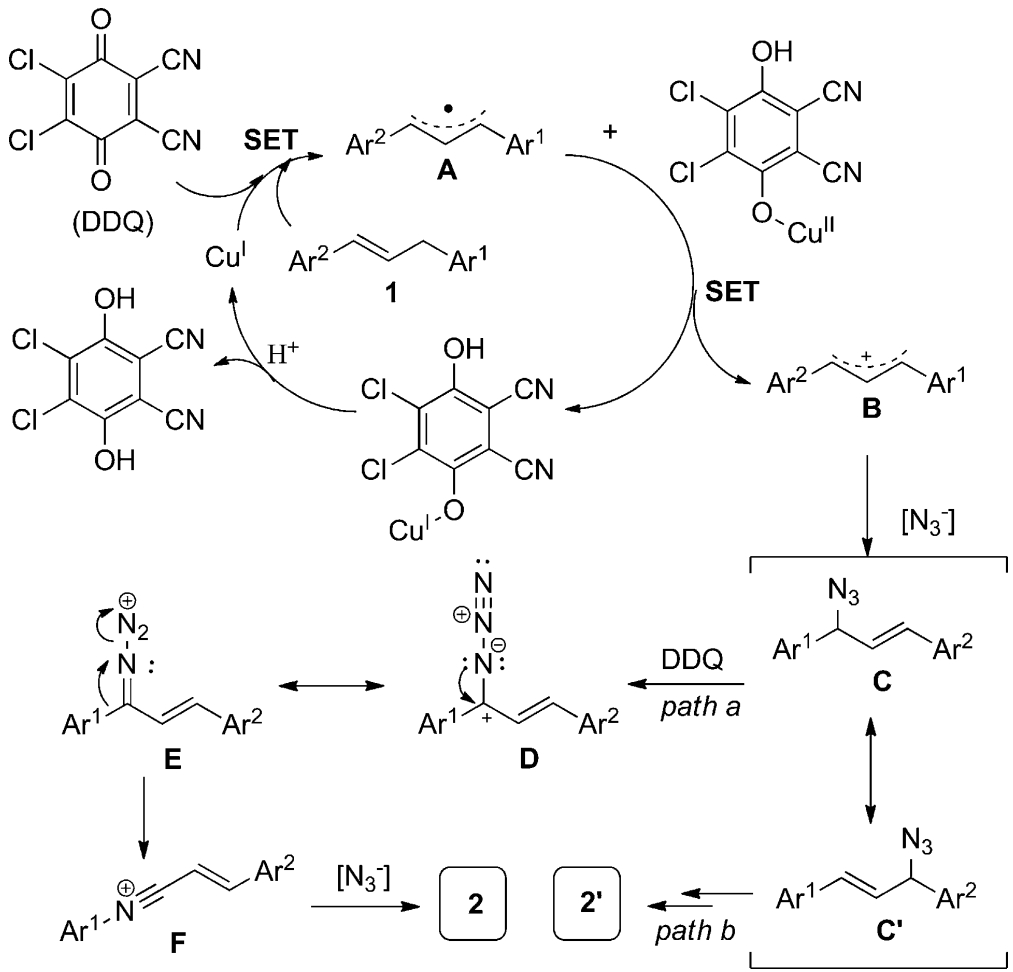
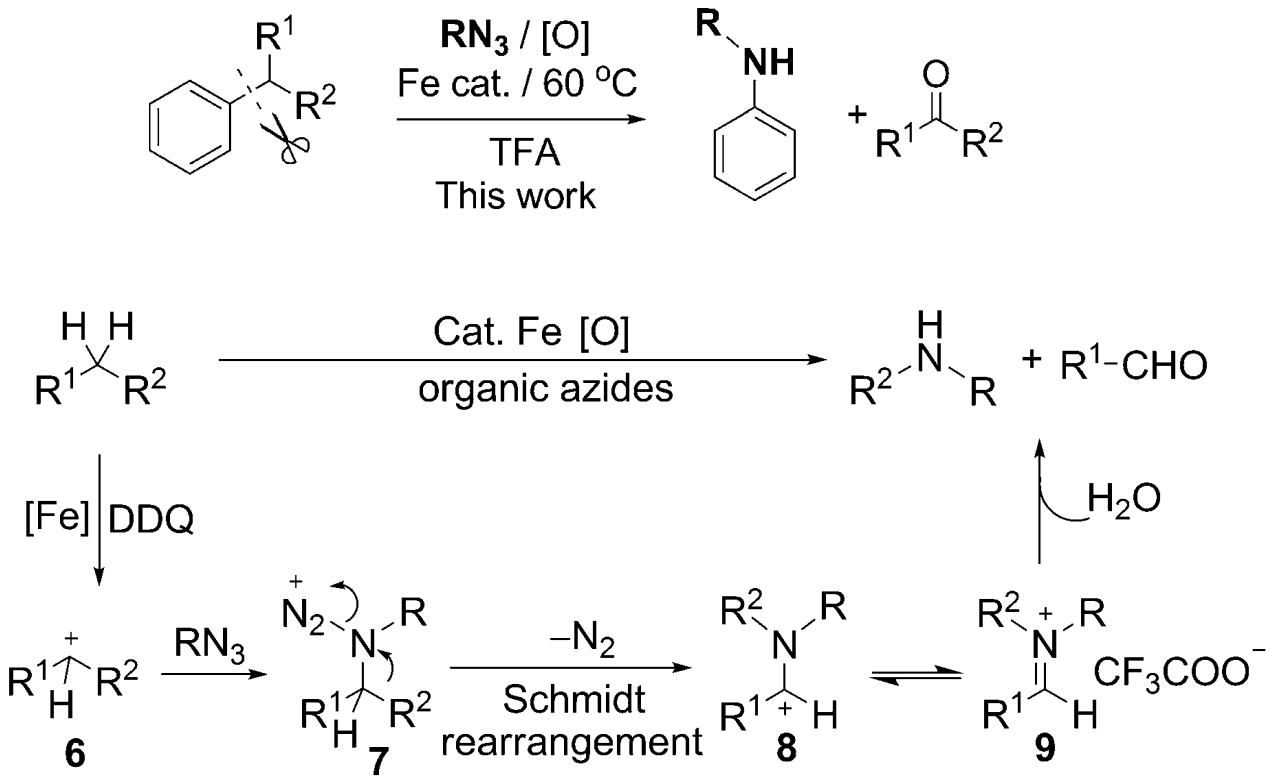

a) hydration
g) metathesis
f) M / [O]
b) addition
e) M / base
R1 or R2=H
coupling
c) M / [O]
Wacker oxidation
d) cyclization reaction
[n+2]
X, Y = H,CN, FG, halogen, etc
or

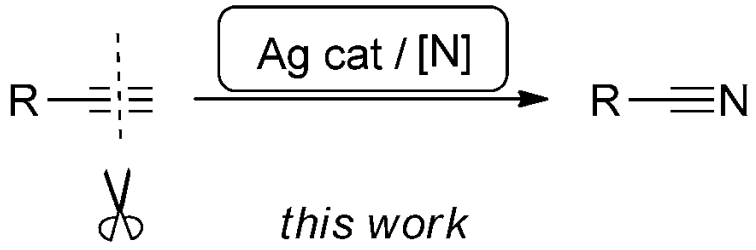

Ag cat / [N]
R
R
N
this work

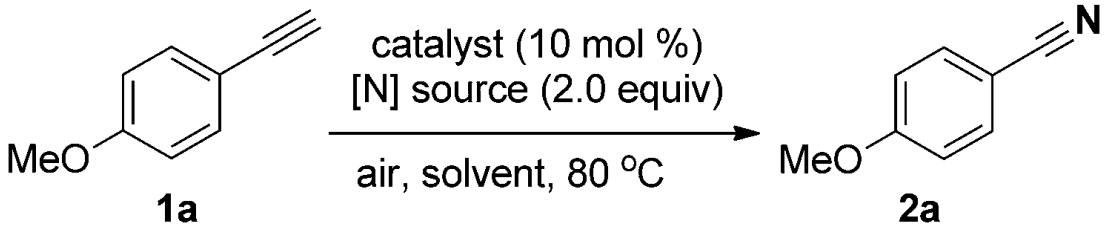


Angew. Chem. Int. Ed. 2011, 50, 11487 –11491



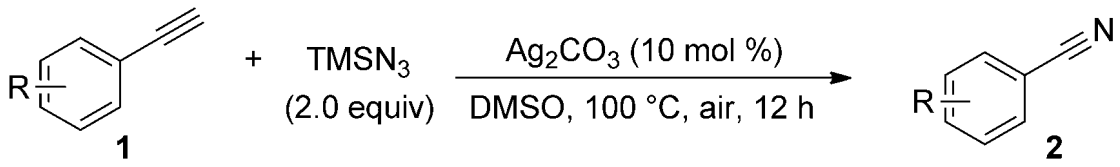
Angew. Chem. Int. Ed. 2012, 51, 6971 –6975

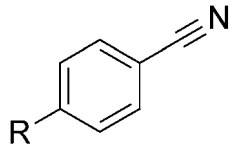




1a **2a**

Entry	Catalyst	[N] source	solvent	Yield of **2a** [%][b]
1	Ag_2CO_3	$TMSN_3$	DMF	58
2	$AuCl_3$	$TMSN_3$	DMF	0
3	$NiCl_2$	$TMSN_3$	DMF	0
4[c]	Ag_2CO_3	$TMSN_3$	DMSO	68
5	**Ag_2CO_3**	**$TMSN_3$**	**DMSO**	**81**
6	Ag_2CO_3	$TMSN_3$	HOAc	0
7	Ag_2CO_3	$TMSN_3$	TFA	0
8	Ag_2CO_3	NaN_3	DMSO	trace
9	Ag_2CO_3	TsN_3	DMSO	0
10	Ag_2CO_3	DPPA	DMSO	0
11	–	$TMSN_3$	DMSO	0
12[d]	Ag_2CO_3	$TMSN_3$	DMSO	62
13[e]	Ag_2CO_3	$TMSN_3$	DMSO	60
14[f]	Ag_2CO_3	$TMSN_3$	DMSO	84





2a[a] R=OMe 81 %

2b[a] R=OEt 76 %

2c[a] R=OMOM 68 %

2d R=Cl 58 %

2e[a] R=OMe 56 %

2f[a] R=OBn 77 %

2g[a] R=NBoc 82 %

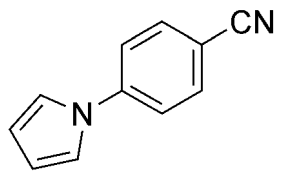
2h R=H 63 %

2i R=Ph 72 %

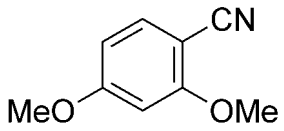
2j R=*t*Bu 85 %

2k R=Me 66 %

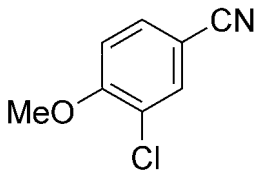
2l R=Br 66 %



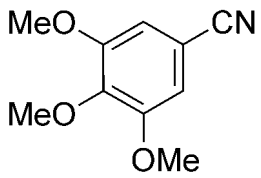
2n 75 %



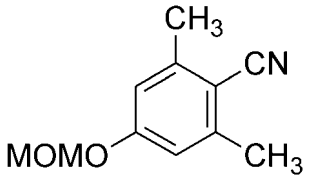
2o 60 %



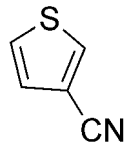
2p 64 %



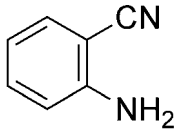
2q 60 %



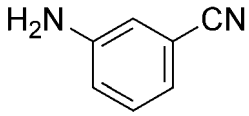
2r 45 %



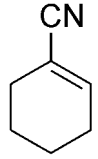
2s 63 %



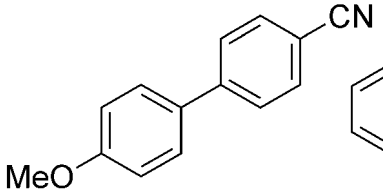
2t 53 %



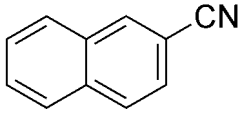
2u 77 %



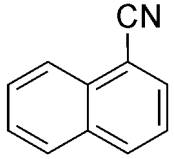
2v 73 %



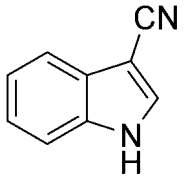
2m 74 %



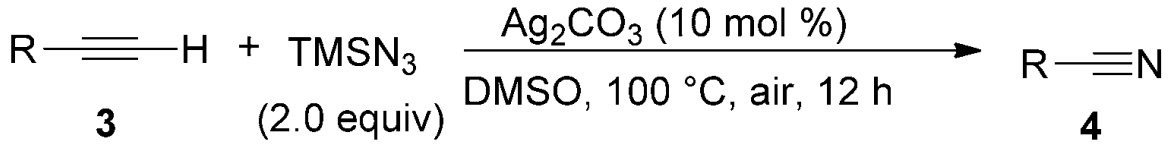
2w 61 %



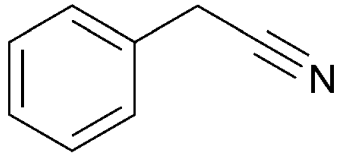
2x 45 %



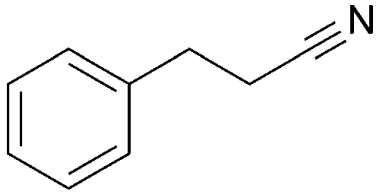
2y 56 %



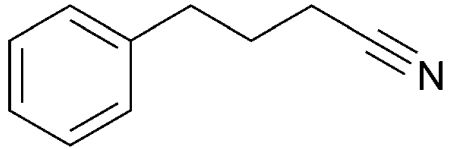
3 **4**



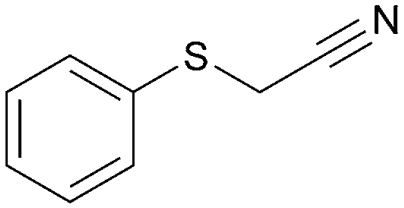
4a 51 %[b]



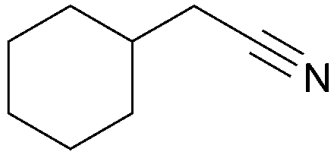
4b 90 % (81 %)[b]



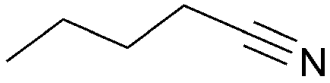
4c 88 % (86 %)[b]



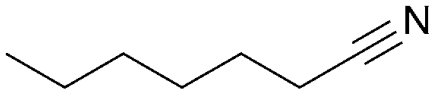
4d 72 %[b]



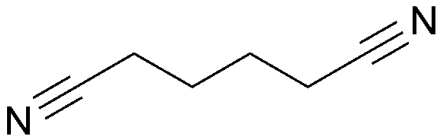
4e 93 % (80 %)[b]



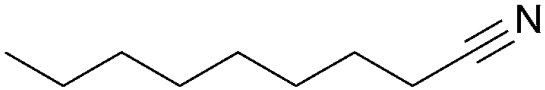
4f 52 % (39 %)[b]



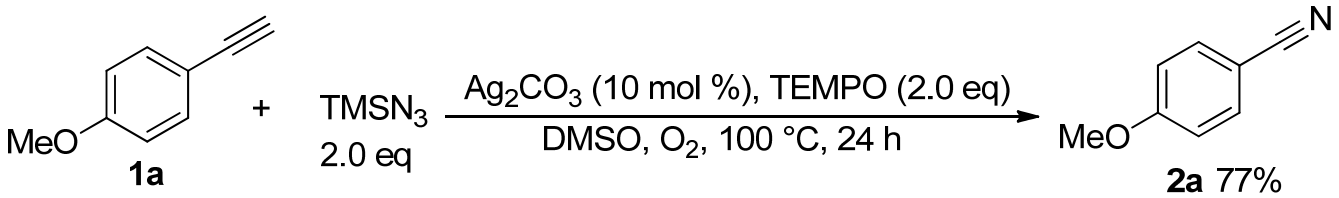
4g 84 % (69 %)[b]

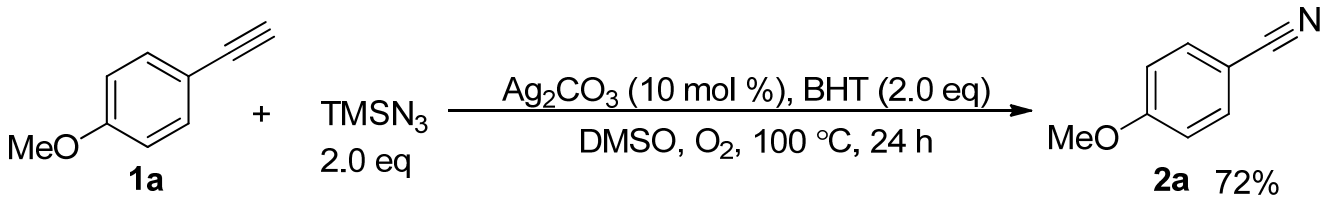


4h[c] 54 % (65 %)[b]

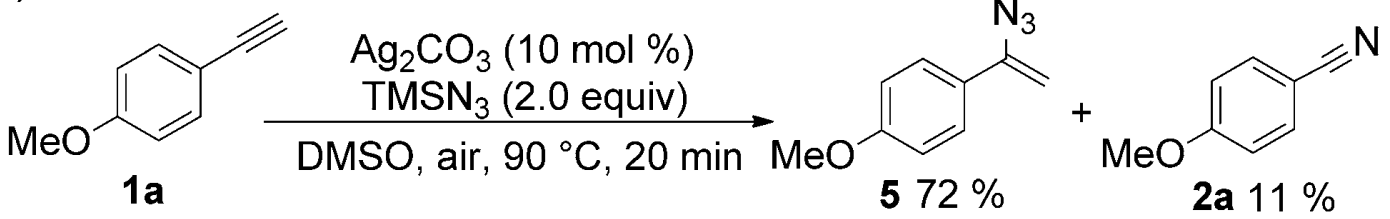


4i 96 % (88 %)[b]

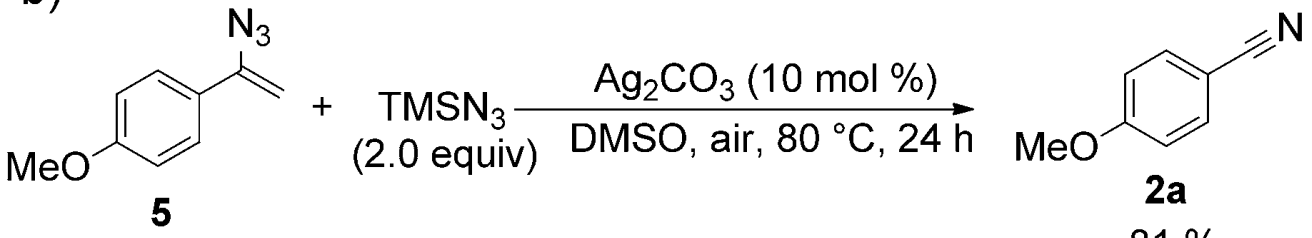

MeO
1a
+
TMSN3
2.0 eq
Ag2CO3 (10 mol %), TEMPO (2.0 eq)
DMSO, O2, 100 °C, 24 h
N
MeO
2a 77%


MeO
1a
+
TMSN3
2.0 eq
Ag2CO3 (10 mol %), BHT (2.0 eq)
DMSO, O2, 100 °C, 24 h
N
MeO
2a 72%

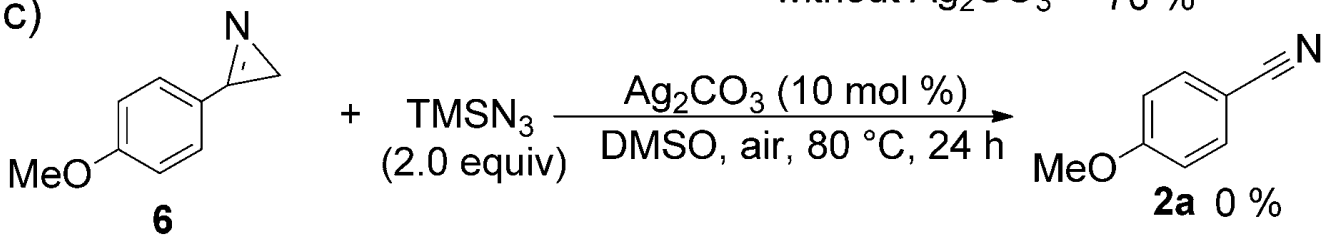
a)


MeO
1a
Ag2CO3 (10 mol %)
TMSN3 (2.0 equiv)
DMSO, air, 90 °C, 20 min
N3
MeO
5 72 %
+
N
MeO
2a 11 %

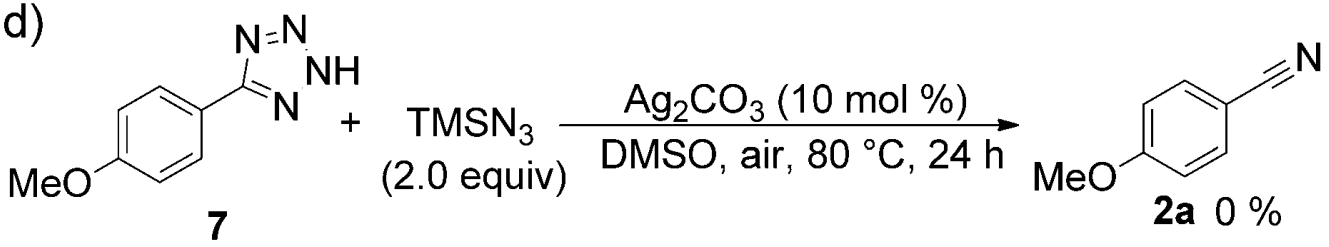
b)


N3
MeO
5
+
TMSN3
(2.0 equiv)
Ag2CO3 (10 mol %)
DMSO, air, 80 °C, 24 h
N
MeO
2a
81 %
without TMSN3 11 %
using 20 mol % TMSN3 52 %
without Ag2CO3 70 %

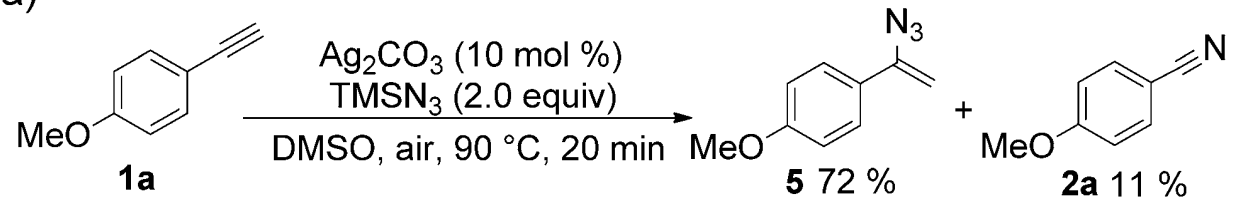
c)

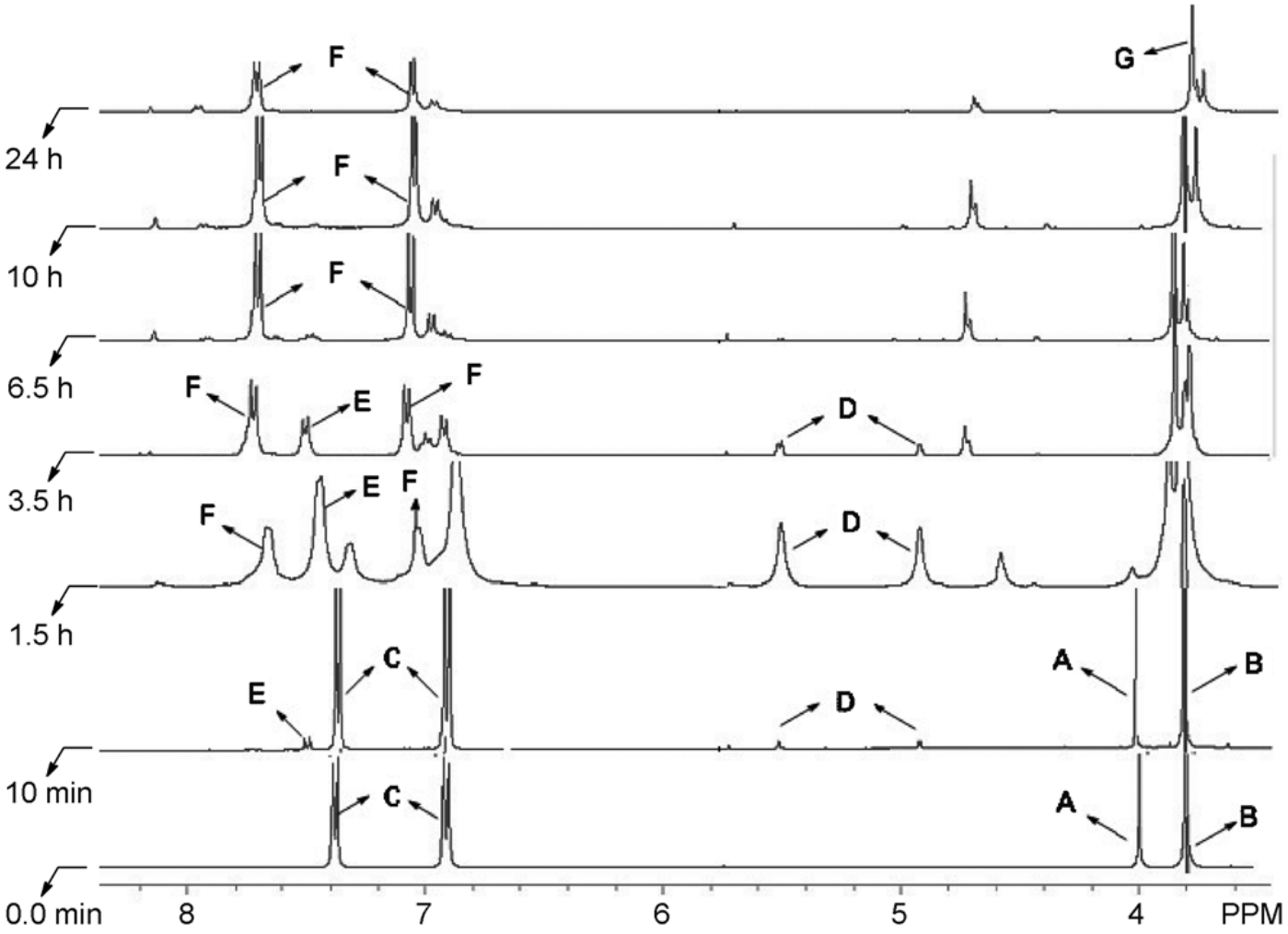

N
MeO
6
+
TMSN3
(2.0 equiv)
Ag2CO3 (10 mol %)
DMSO, air, 80 °C, 24 h
N
MeO
2a 0 %

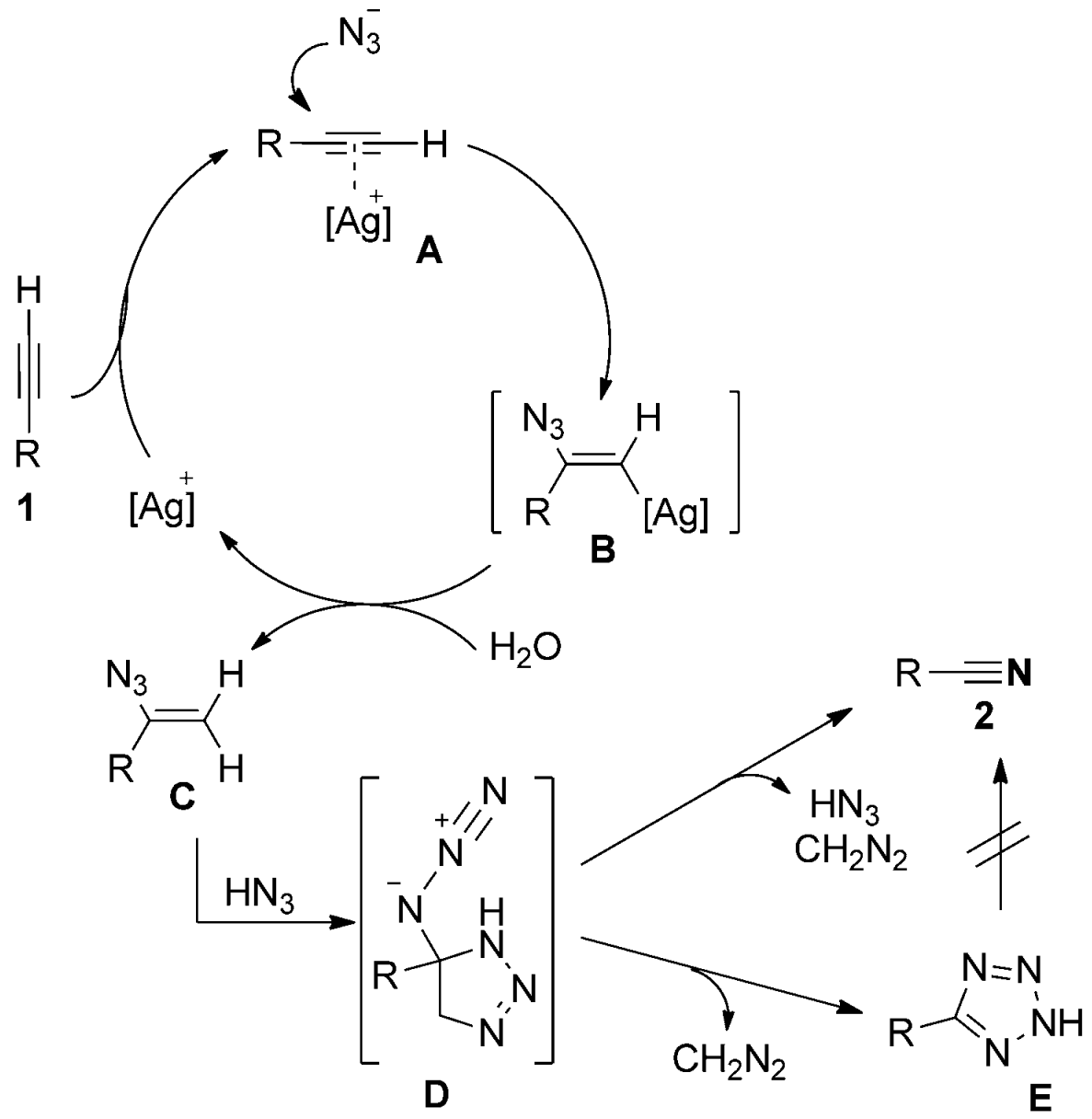
d)


N=N
NH
N
MeO
7
+
TMSN3
(2.0 equiv)
Ag2CO3 (10 mol %)
DMSO, air, 80 °C, 24 h
N
MeO
2a 0 %

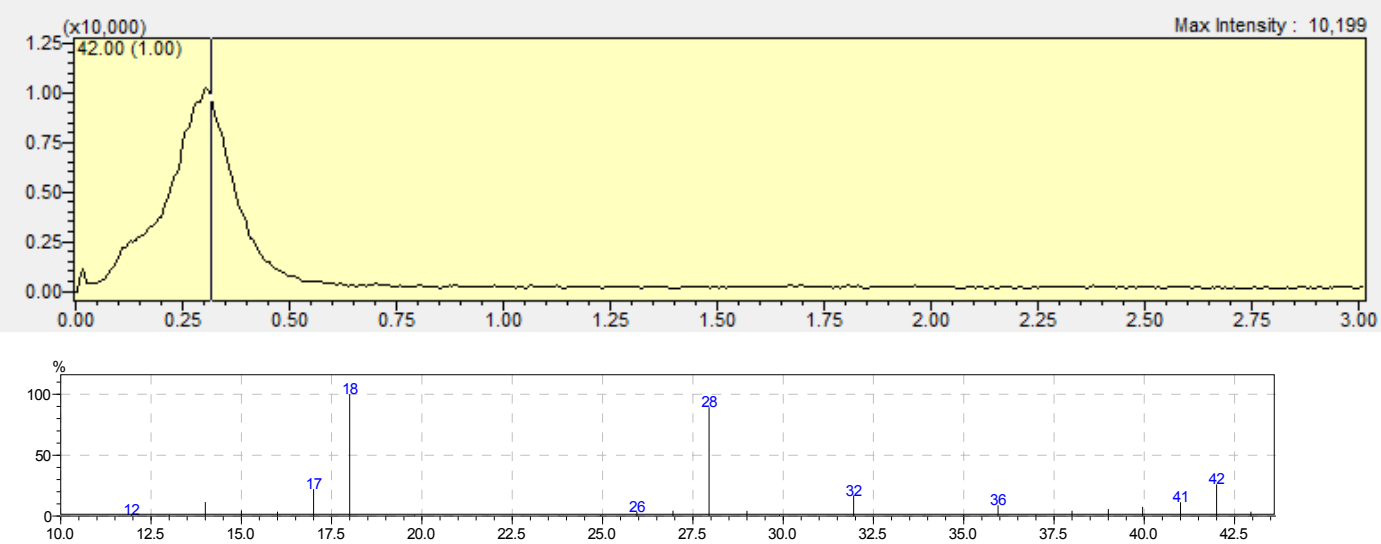
a)


MeO
1a
Ag2CO3 (10 mol %)
TMSN3 (2.0 equiv)
DMSO, air, 90 °C, 20 min
N3
MeO
5 72 %
+
N
MeO
2a 11 %

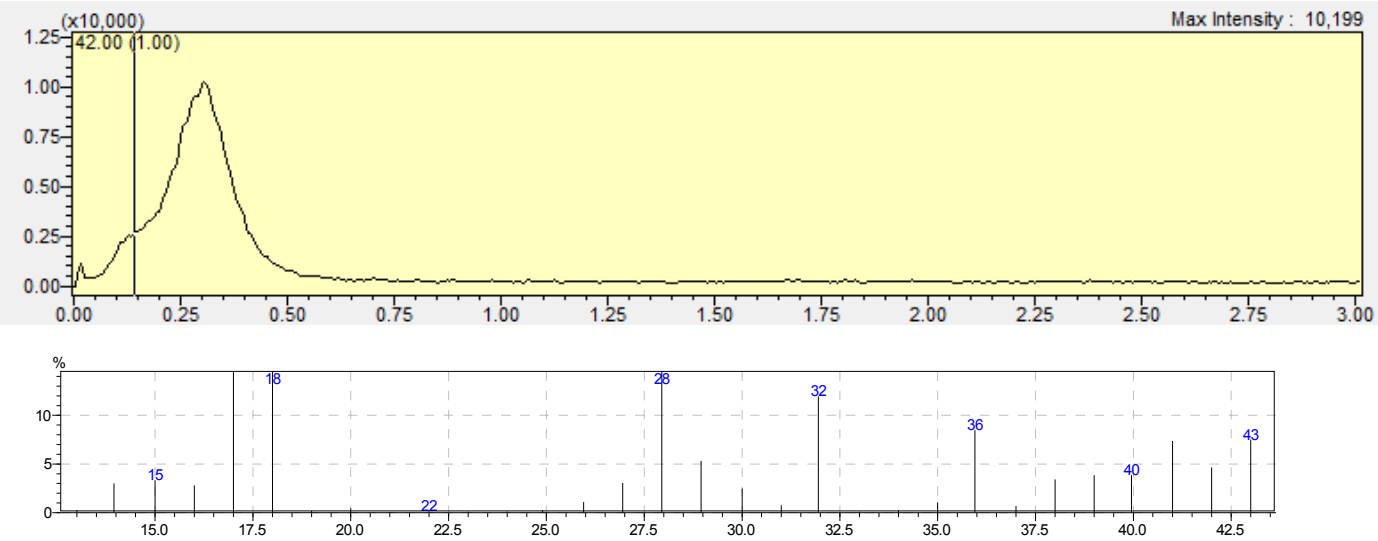

24 h
10 h
6.5 h
3.5 h
1.5 h
10 min
0.0 min
F
G
E
D
C
A
B
8
7
6
5
4
PPM


N3−
R
H
[Ag]+
A
H
R
1
[Ag]+
N3
H
R
[Ag]
B
H2O
N3
H
R
H
C
HN3
N
N+
N−
H
N
R
N
N
D
HN3
CH2N2
R
N
2
CH2N2
N=N
NH
R
N
E

GC-MS: CH_2N_2



GC-MS: HN_3 and CH_2N_2



Conclusion:

- The first direct conversion of alkynes into nitriles by Ag-catalyzed nitrogenation of alkynes through C≡C bond cleavage.

- From the results of the present study, and on the basis of the proposed mechanism, it should be possible to develop novel chemical transformations through C-C bond cleavage, which should be of interest to both industrial and academic researchers.