λ^3-Bromane : a powerful reagent that has been ignored

Reporter : Bo Xing

2014.7.14

Reaction of λ³-bromane

Introduction

Alkenyl-λ³-bromane & Alkynyl-λ³-bromane

Difluoro-λ³-bromane-induced oxidation

Imido transfer of sulfonylimino-λ³-bromane

Summary

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INSTITUTIONS

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The University of Tokushima

- Graduate School of Pharmaceutical Sciences
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Gifu Pharmaceutical University

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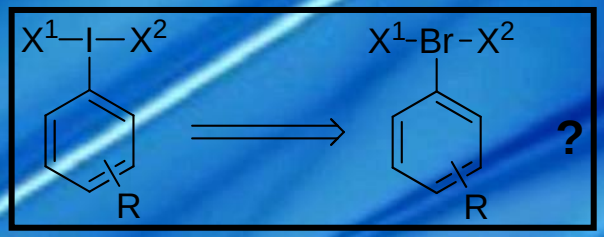
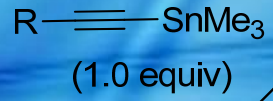
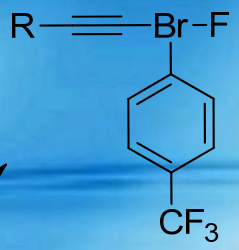
Alkenyl- λ^3-bromane & Alkynyl- λ^3-bromane

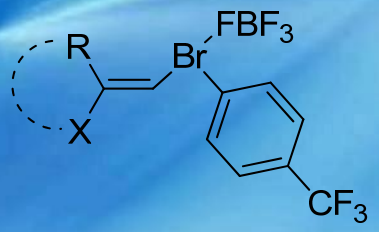




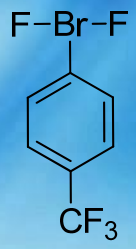
(1.0 equiv)



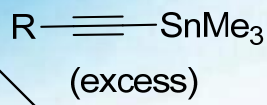
J.Am.Chem.Soc. **2003**, *125*, 15304



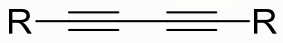
X = H, F, Cl, OEt



Frohn reagent



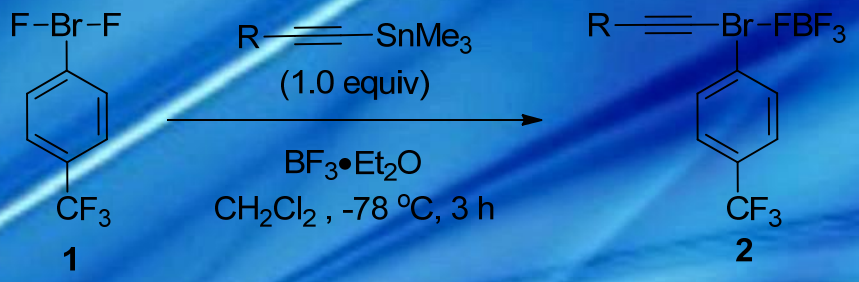
(excess)

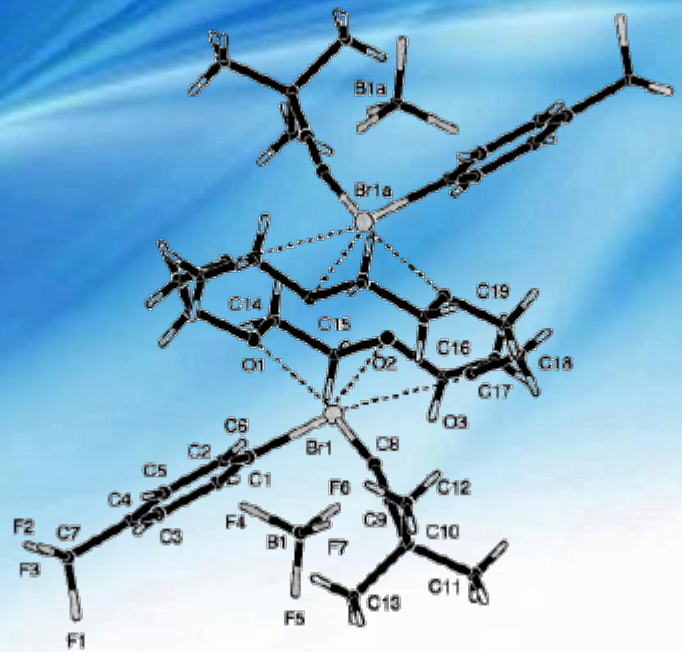


J.Am.Chem.Soc. **2005**, *127*, 10460

Angew. Chem. Int. Ed. **2005**, *44*, 406

Alkynyl- λ^3-bromane





Angle of Br1-C8-C9 = 167.3°

Distance of C8-C9 = 1.211 Å

longer than the average triple bond length (1.181 Å)

Hammett substituent constant

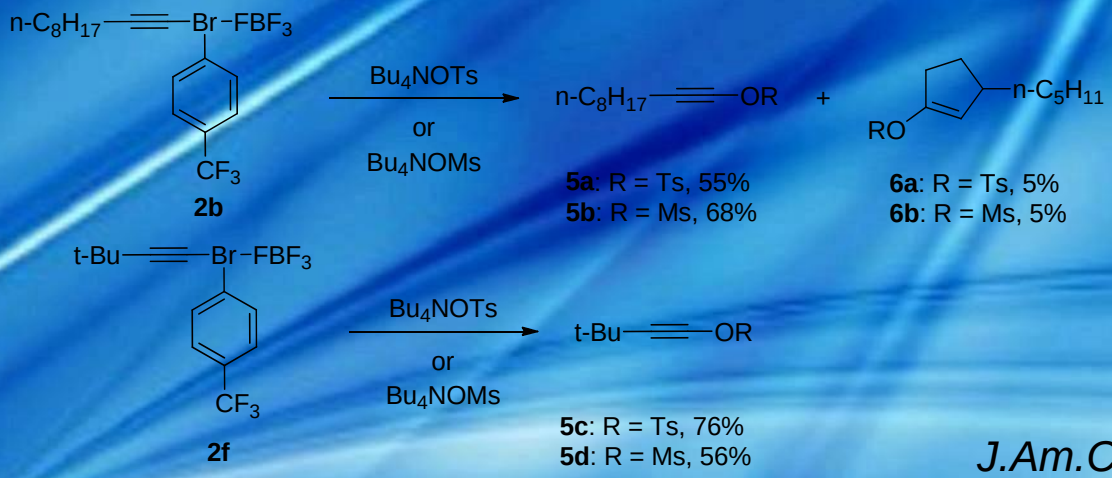
σ_P= 1.63 for $PhBrBF_4$

σ_P= 1.37 for $PhIBF_4$

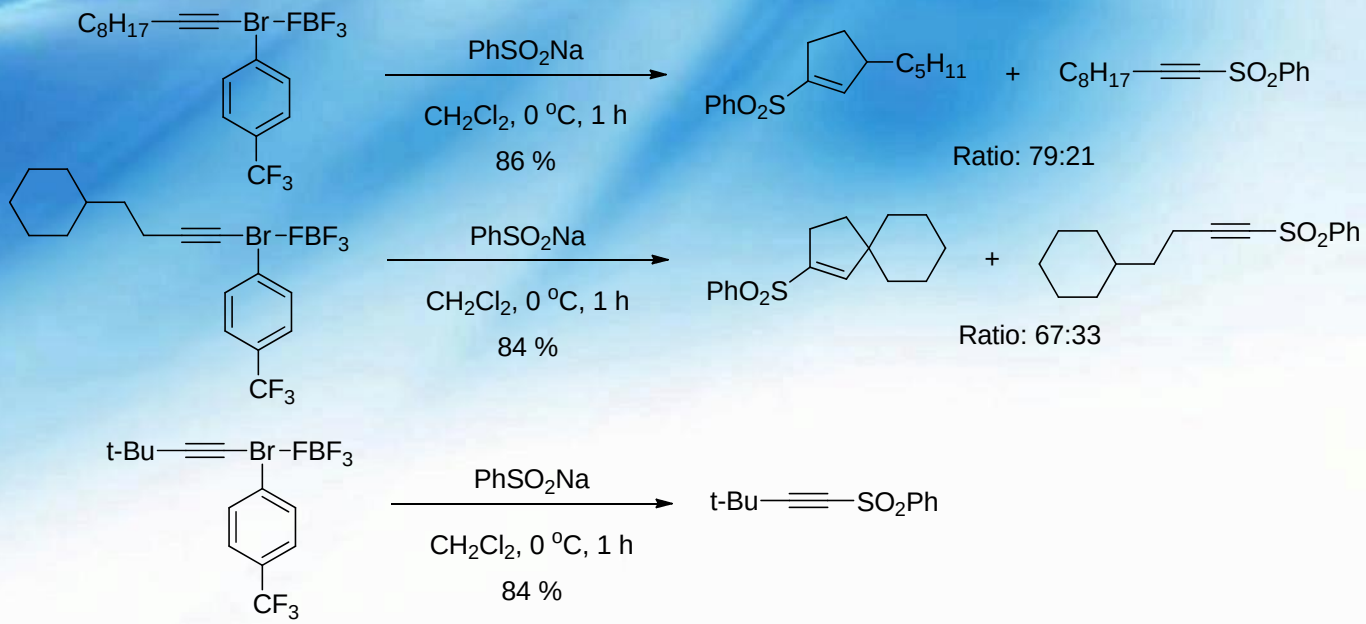
More efficient Michael acceptor !

J.Am.Chem.Soc. **2003**, *125*, 15304

Alkynyl- λ^3-bromane

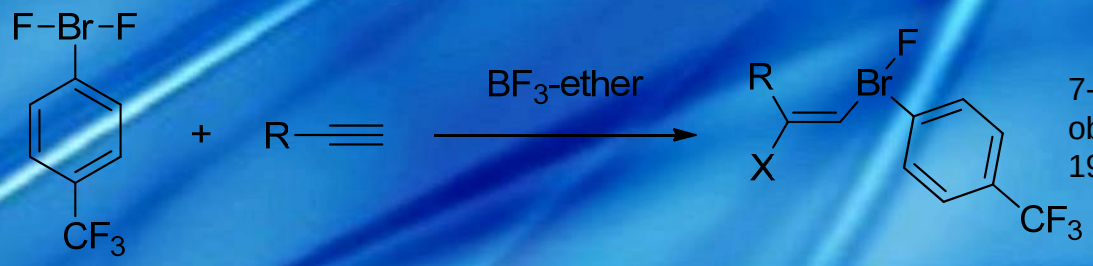


J.Am.Chem.Soc. **2003**, *125*, 15304



Chem. Commun. **2004**, 2894

Alkenyl- λ^3-bromane



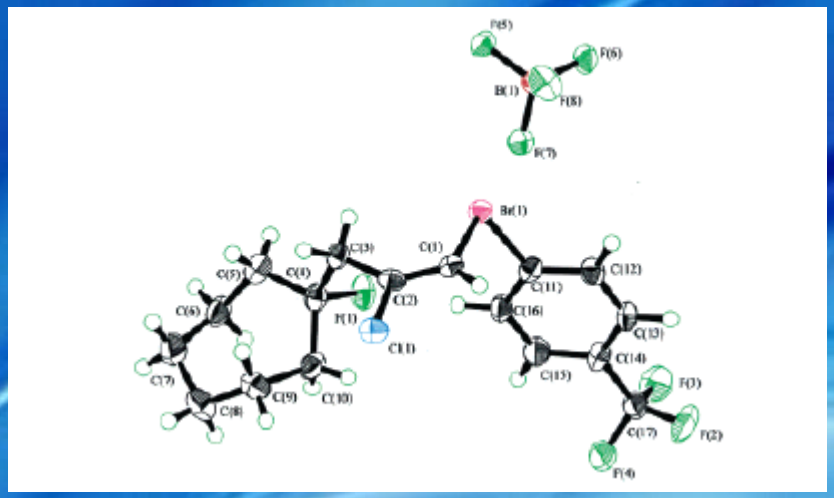
7-15% **3a** and 3-13% **3b** was obtained for entry 1-3
19 % **3b** was obtained for entry 9

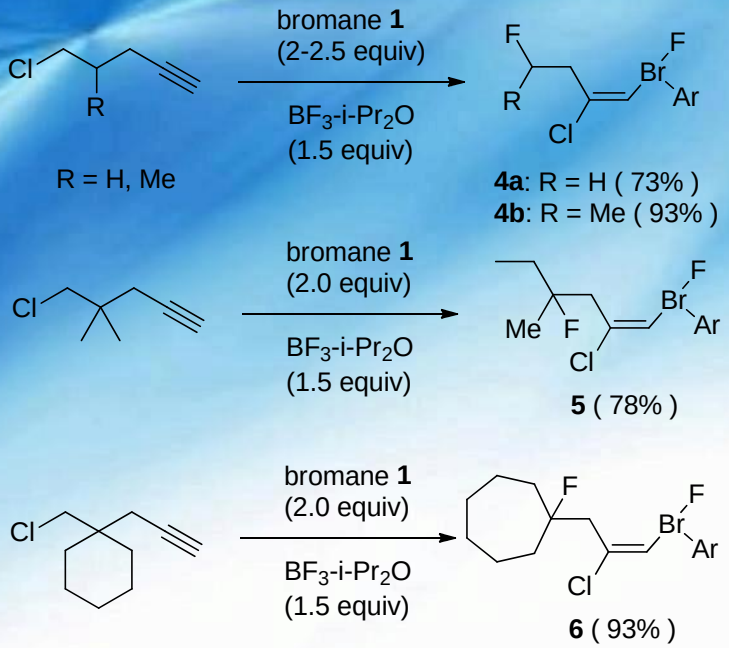
2: X = F
3a: R = n-C_8H_{17}, X = EtO
3b: R = n-C_8H_{17}, X = Cl

entry	ether (equiv)	solvent	T (°C)	time (h)	yield (%)	Ratio E:Z
1	Et_2O(1.1)	CH_2Cl_2	-78	3	50	95:5
2	Et_2O(1.5)	CH_2Cl_2	-78	3	62	96:4
3	Et_2O(3.0)	CH_2Cl_2	-78	3	61	98:2
4	THF(1.5)	CH_2Cl_2	-78	5	56	96:4
5	*t*-BuOMe(1.5)	CH_2Cl_2	-78 to 25	5	33	87:13
6	*i*-Pr_2O(1.5)	CH_2Cl_2	-78 to 25	5	72	96:4
7	*i*-Pr_2O(1.5)	$CHCl_3$	-60 to 25	3.5	74	94:6
8	*i*-Pr_2O(1.5)	CCl_4	-20 to 25	3.5	60	95:5
9	*i*-Pr_2O(1.5)	DCE	-30 to 25	3.5	47	92:8
10	$AgBF_4$(1.5)	$CHCl_3$	-60 to 25	3.5	44	75:25

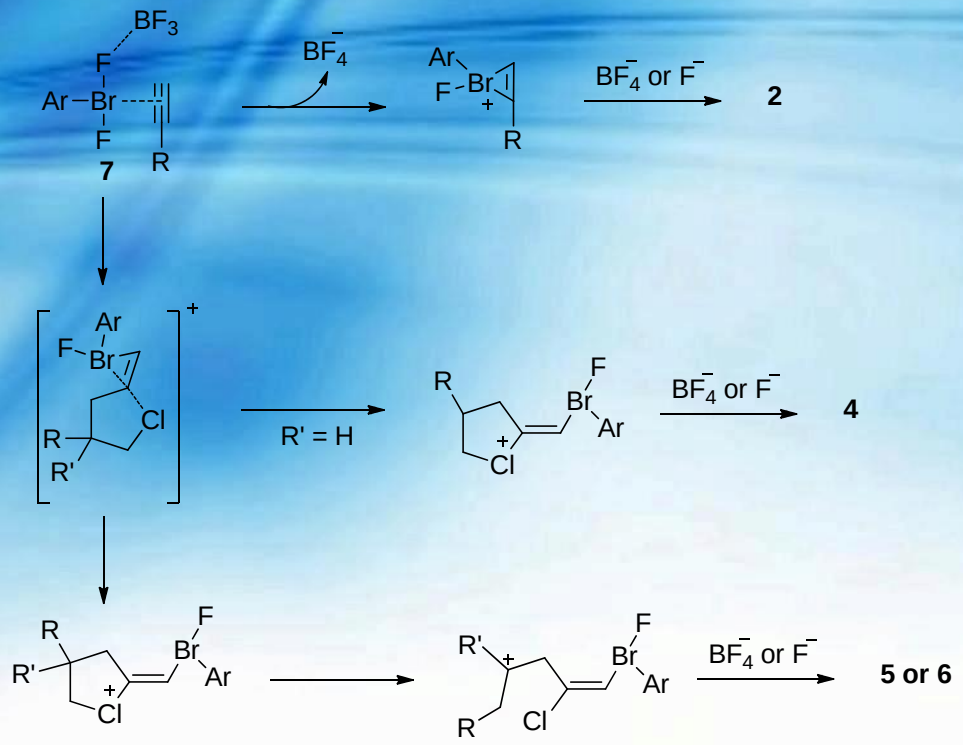
J.Am.Chem.Soc. **2005**, *127*, 10460

Alkenyl- λ^3-bromane





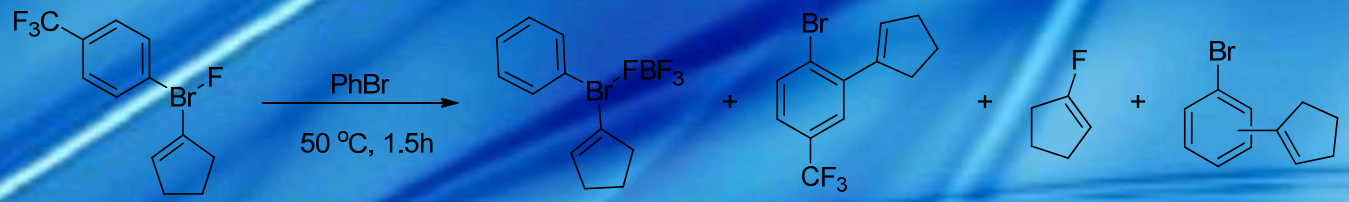
Proposed mechanism:



J.Am.Chem.Soc. **2005**, *127*, 10460

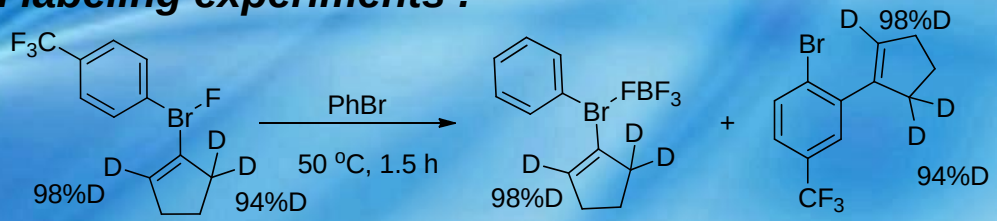
Alkenyl- λ^3-bromane

Solvolysis of vinyl cation:

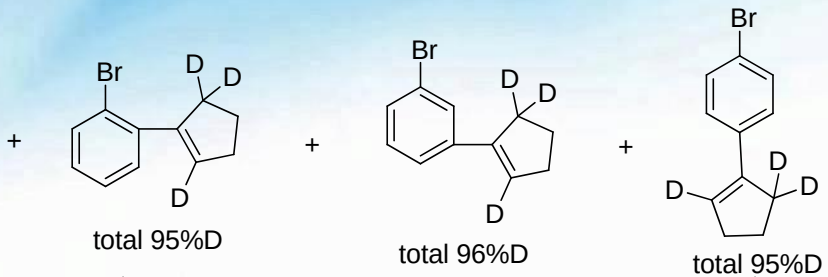


6a | **6b** 11% | **10** 8% | **13** 30% | **17** 19%

Deuterium labeling experiments :



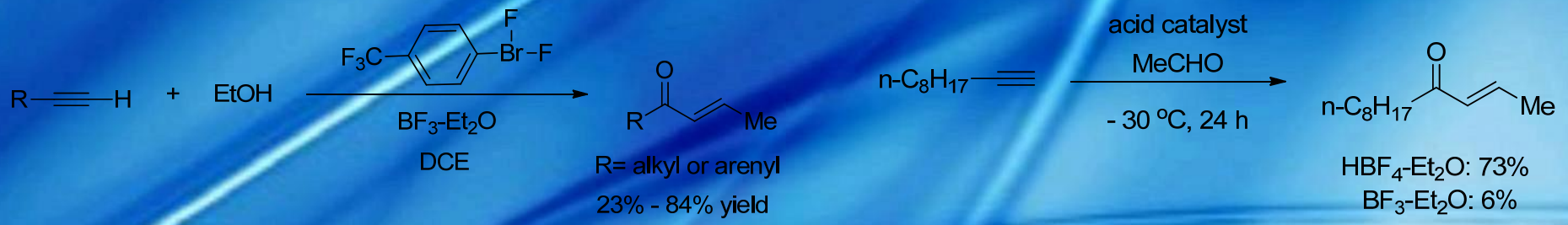
6a | **6b** 11% | **10** 6%



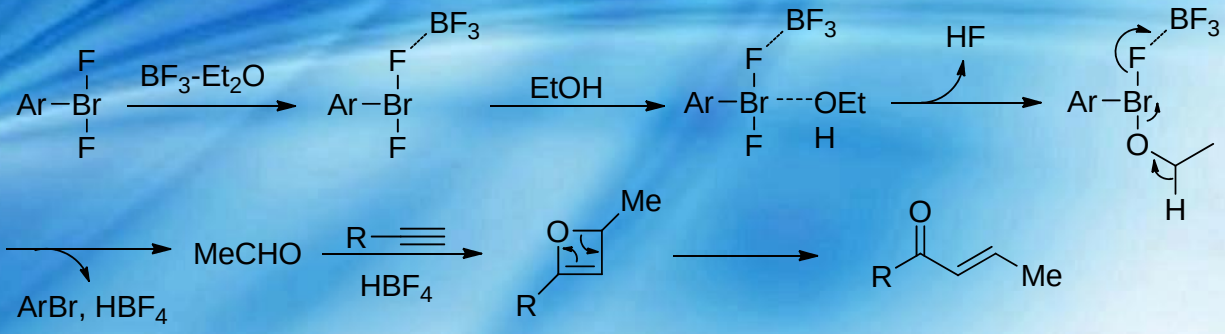
17 11%

Angew. Chem. Int. Ed. **2009**, *48*, 8931

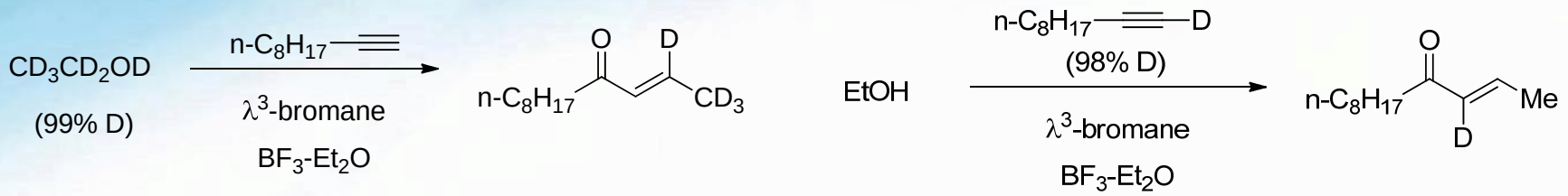
Difluoro- λ^3-bromane-induced oxidation



Proposed mechanism:

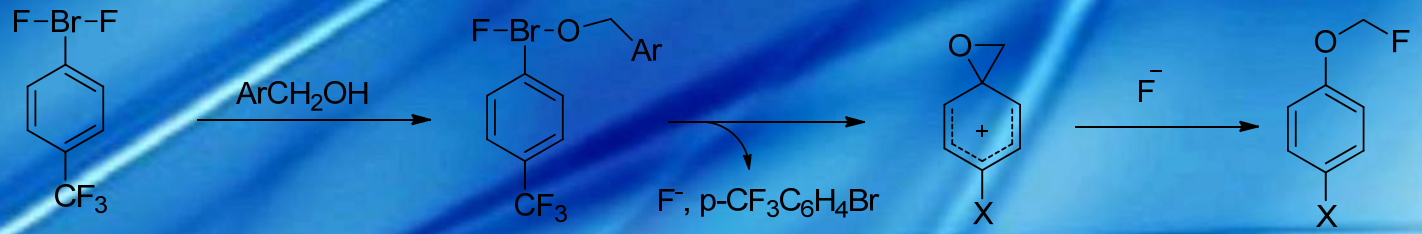


Deuterium labeling experiments:



J.Am.Chem.Soc. **2008**, *130*, 3742

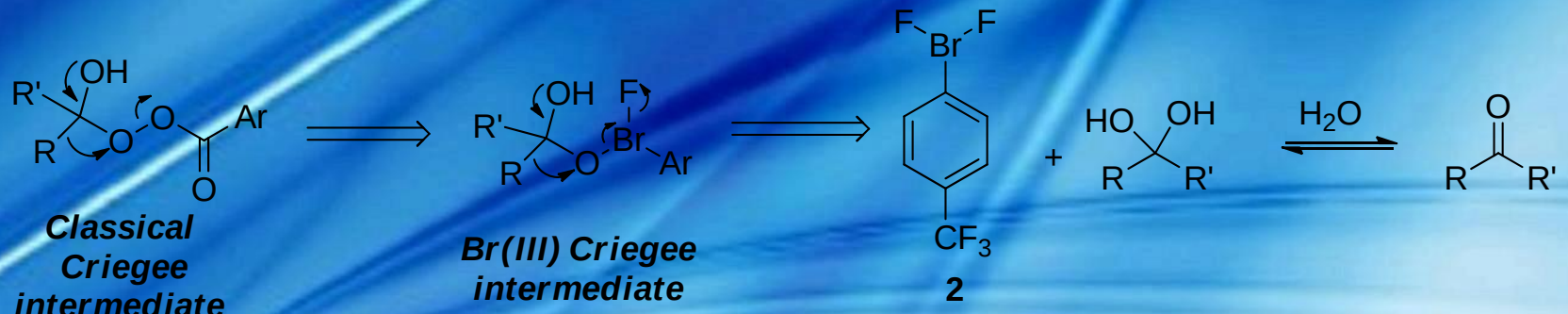
Difluoro- λ^3-bromane-induced oxidation



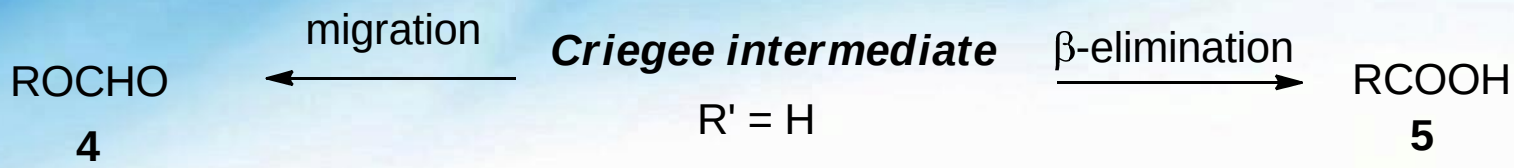
entry	X	yield(%)
1	MeO	7
2	Me	17
3	t-Bu	66
4	F	68
5	Cl	90
6	Br	65
7	I	67
8	CO_2Me	90
9	CF_3	63
10	CN	60
11	NO_2	44

Tetrahedron. Letters. **2009**, 50, 4792

Difluoro-λ^3-bromane-induced BVO



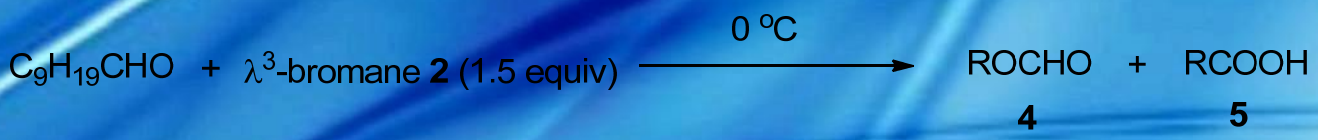
Competitive reaction:



J.Am.Chem.Soc. **2010**, *132*, 9236

Difluoro-λ^3-bromane-induced BVO

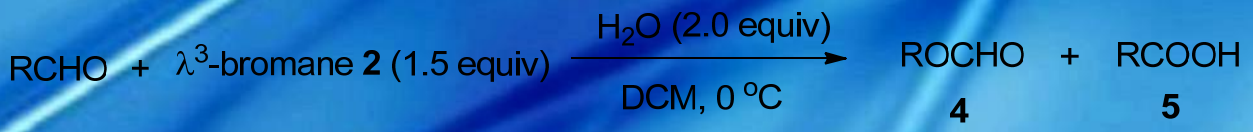
BVO of Decanal with Difluorobromane 2 :



entry	solvent	H_2O (equiv)	time(h)	4a(%)	5a(%)
1	DCM	0	3	0	0
2	DCM	1	3	70	8
3	DCM	2	1	88	6
4	DCM	3	1	82	5
5	DCM	10	1	76	5
6	$CHCl_3$	2	1	66	4
7	DCE	2	1	80	5
8	MeCN	2	1	27	69

J.Am.Chem.Soc. **2010**, *132*, 9236

Difluoro-λ^3-bromane-induced BVO



entry	aldehyde	time(h)	4(%)	5(%)
1	*p*-$MeOC_6H_4CHO$	1	45	0
2	*o*-MeC_6H_4CHO	1	69	0
3	*m*-MeC_6H_4CHO	1	71	0
4	*m*-MeC_6H_4CHO	1	72	0
5	*p*-*t*-BuC_6H_4CHO	1	67	0
6	PhCHO	1	98	0
7	*p*-FC_6H_4CHO	1	64	0
8	*p*-ClC_6H_4CHO	1	68	0
9	*p*-BrC_6H_4CHO	1	69	0
10	*p*-$CF_3C_6H_4CHO$	3	34	19

J.Am.Chem.Soc. **2010**, *132*, 9236

Difluoro-λ^3-bromane-induced BVO

entry	aldehyde	time(h)	4(%)	5(%)
1	MeCHO	1	4	70
2	EtCHO	1	68	16
3	*n*-PrCHO	1	61	14
4	*n*-BuCHO	1	55	14
5	*n*-$C_5H_{11}CHO$	1	85	5
6	*n*-$C_7H_{15}CHO$	1	91	5
7	*n*-$C_9H_{19}CHO$	1	88	6
8	*i*-BuCHO	1	78	13
9	*t*-$BuCH_2CHO$	1	63	7
10	$Cl(CH_2)_5CHO$	3	59	14
11	$Br(CH_2)_5CHO$	3	64	17
12	*i*-PrCHO	1	81	2
13	*c*-C_5H_9CHO	0.5	64	0
14	*c*-$C_6H_{11}CHO$	0.5	85	0
15	*c*-$C_7H_{13}CHO$	0.5	74	0

J.Am.Chem.Soc. **2010**, *132*, 9236

Difluoro-λ^3-bromane-induced BVO

Interpretation for BVO of MeCHO with bromane 2 :

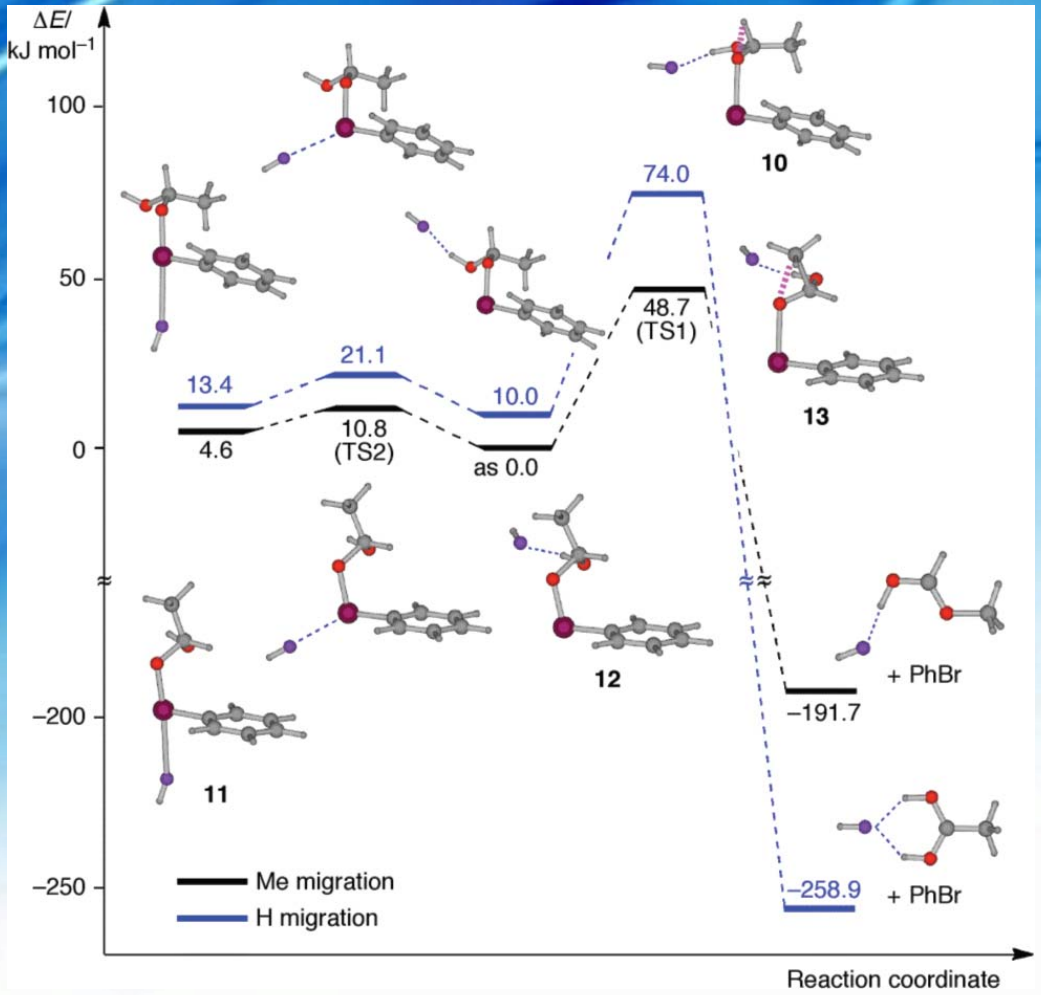
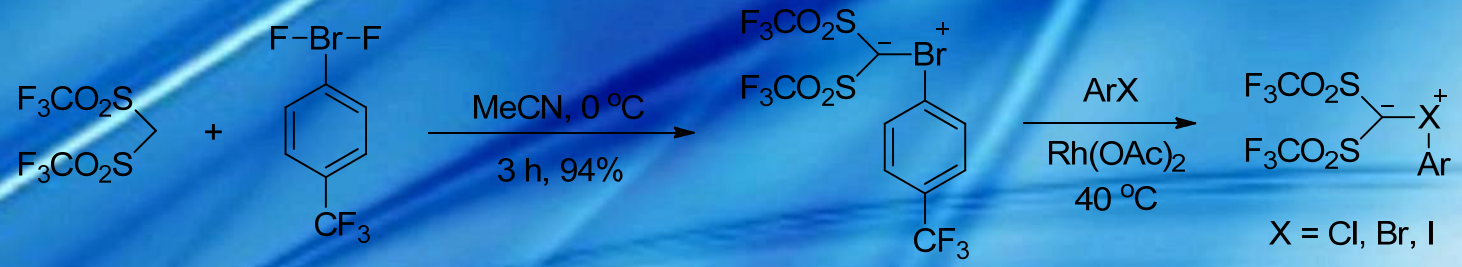


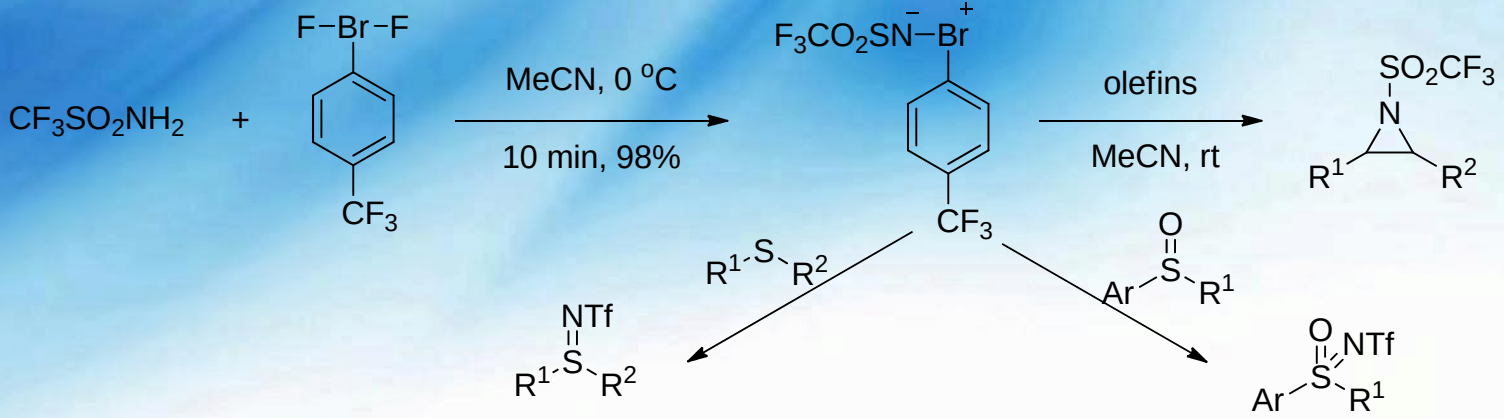
Figure 2. Energy profile for the Me and H migration in BVO of acetaldehyde based on ab initio calculations. Br (large dark purple), O (red), C (gray), and F (blue purple).

J.Am.Chem.Soc. **2010**, *132*, 9236

Imido transfer of sulfonylimino-λ^3-bromane

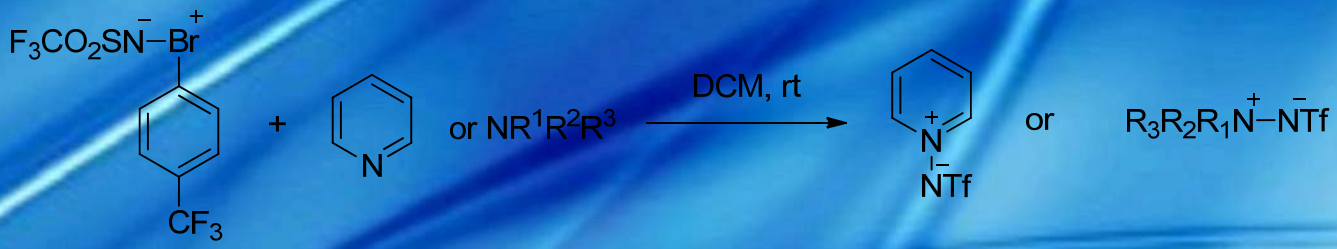


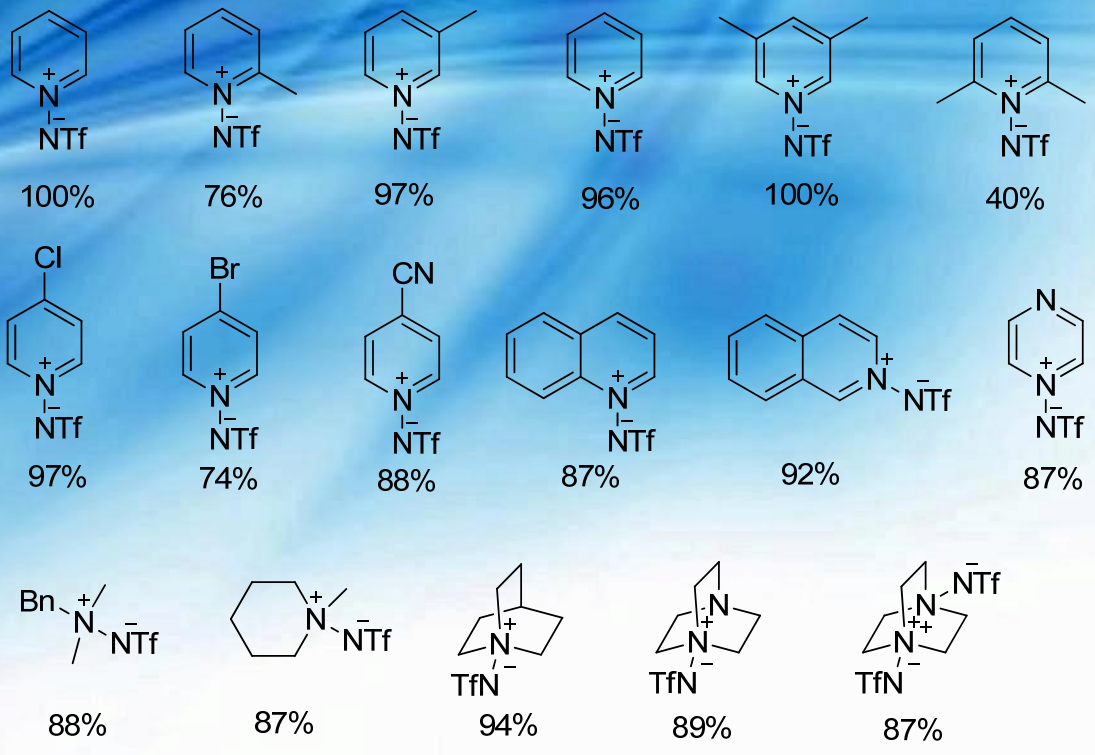
J.Am.Chem.Soc. **2006**, *128*, 9608
J.Am.Chem.Soc. **2008**, *130*, 2118



J.Am.Chem.Soc. **2007**, *129*, 12938
Chem. Eur. J. **2010**, *16*, 8713

Imido transfer of sulfonylimino- λ^3-bromane

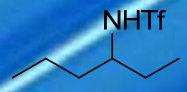


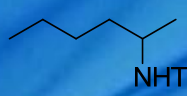


Org. Lett. **2006**, *11*, 281

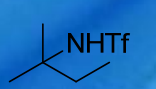
Imido transfer of sulfonylimino- λ^3-bromane

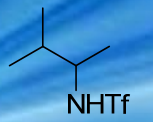
Metal-free animation of alkanes:



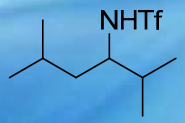


55% yield, ratio: 57:43

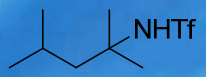


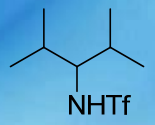


72% yield, ratio: 94:6

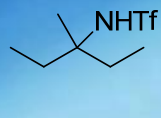


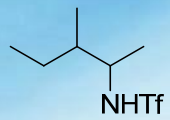
91% yield, ratio: 97:3



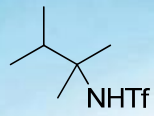


64% yield, ratio: 97:3

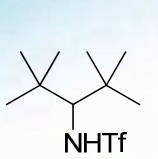




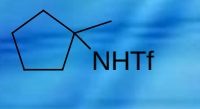
96% yield, ratio: 86:14

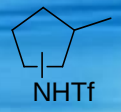


78% yield

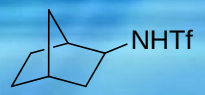


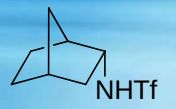
no product



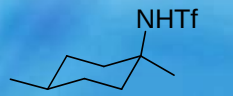


84% yield, ratio: 82:18

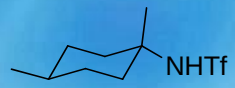




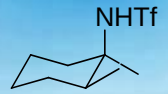
67% yield, ratio: 89:11

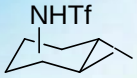


64% yield, ratio: 81:19

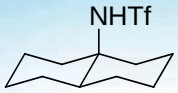


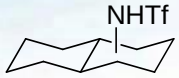
66% yield, ratio: 86:14



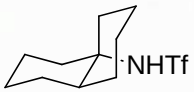


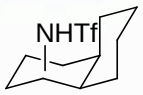
71% yield, ratio: 52:48



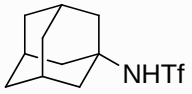


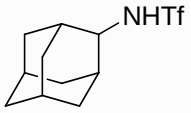
45% yield, ratio: 29:71





78% yield, ratio: 86:14

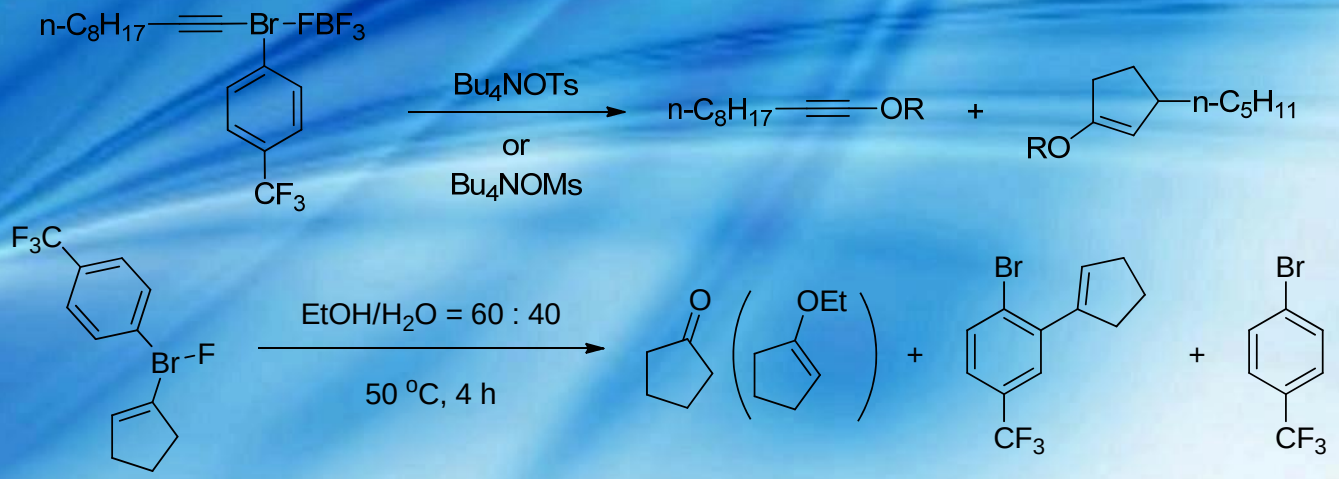


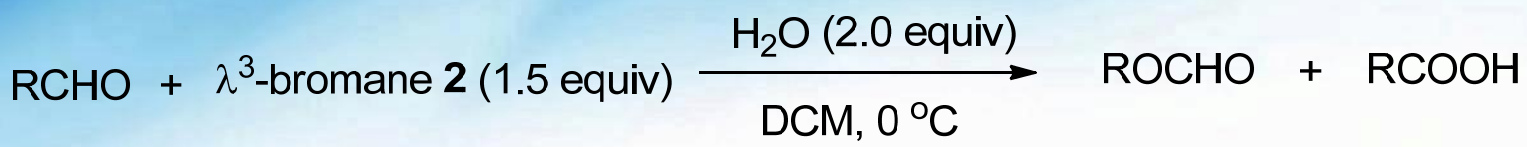


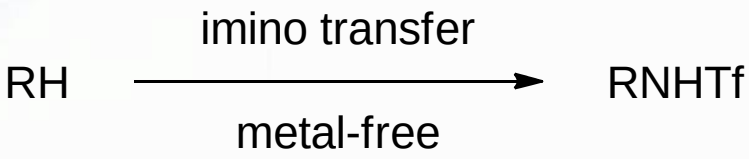
86% yield, ratio: 92:8

Science, **2011**, *332*, 448

λ 3-Bromane serves as a more powerful and reactive reagent, compared to λ 3-iodanes







Thanks