

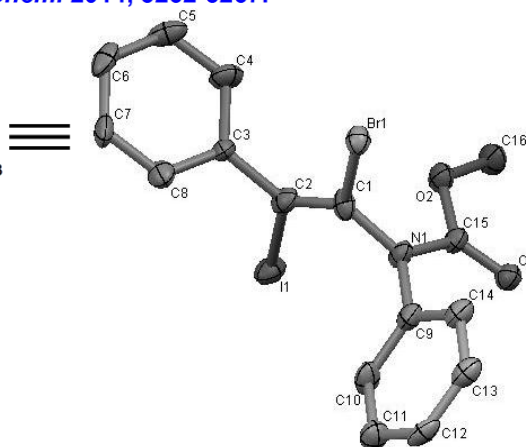
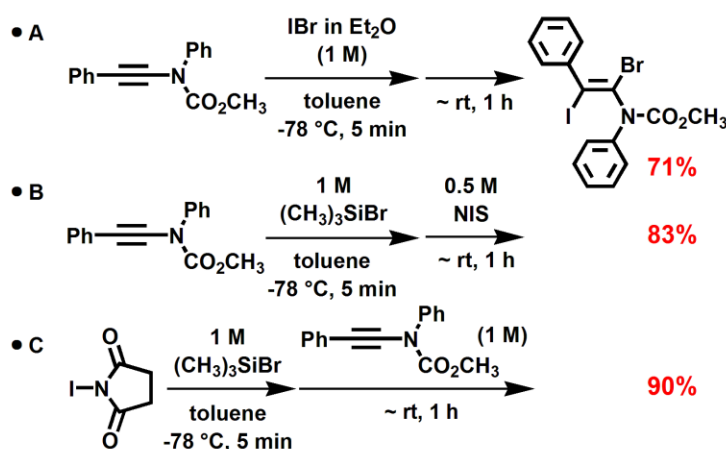
Regio-, and Stereoselective Iodobromination of Ynamides for Synthesis of (*E*)-1-bromo-2-iodoenamides

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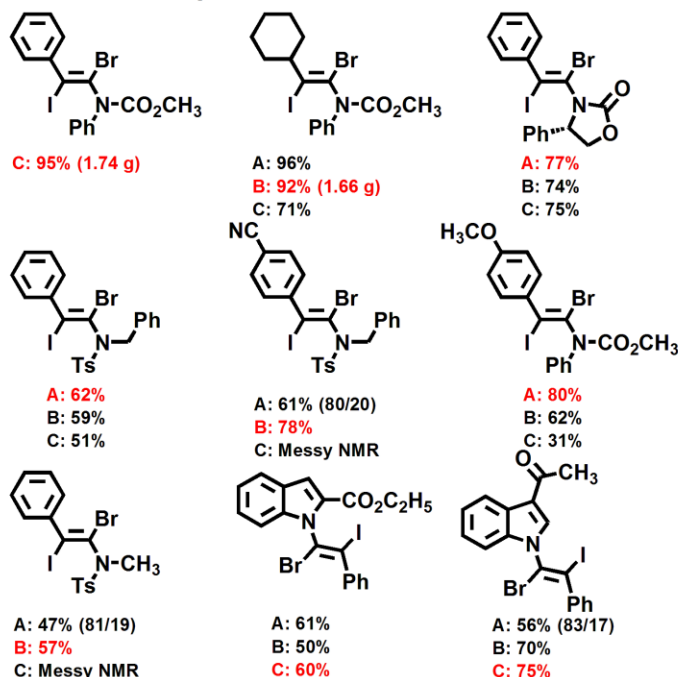


1. Summary a) Ide, M.; Yauchi, Y.; Iwasawa, T. *Eur. J. Org. Chem.* 2014, 3262-3267. b) Japanese Patent No. 2014-014060.

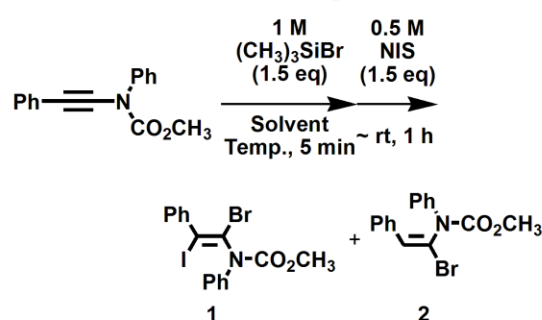


ORTEP, the 50% probability level, bond lengths (Å): N(1)-C(1)=1.417, C(1)-Br(1)=1.934, C(2)-I(1)=2.114, C(1)-C(2)=1.304.

2. Substrate scope



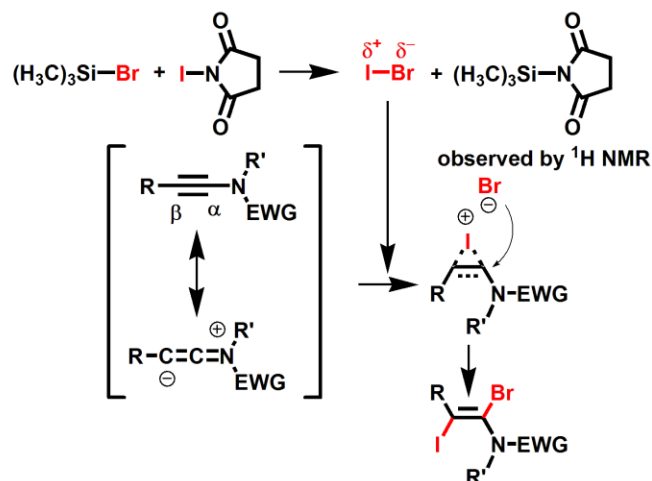
3. Evaluation of the reactivity



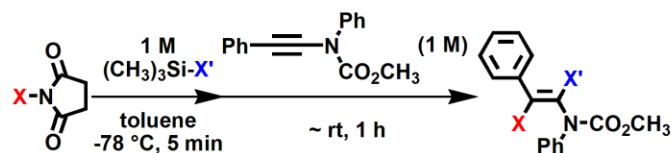
Solvent	Temp. (°C)	Yield (%)	
		1	2
toluene	-78	83	3
toluene	-45	87	5
toluene	-20	77	2
toluene	0	80	8
CH ₂ Cl ₂	-78	70	5
CH ₃ CN	-20	65	1
THF	-78	36	7
CPME	-78	72	11
toluene ^[a]	-78	90	0

[a] Performed by C.

4. Plausible mechanism



5. Other halogen sources



X	X'	Yield (%)	Recovered SM (%)	Product (X/X')
I	I	76	0	I/I
I	Br	90	0	I/Br
I	Cl	0	~100	-
Br	I	63	0	I/Br
Br	Br	61	10	Br/Br
Br	Cl	0	~100	-
Cl	I	48	16	I/I
Cl	Br	33	25	Br/Br
Cl	Cl	0	~100	-