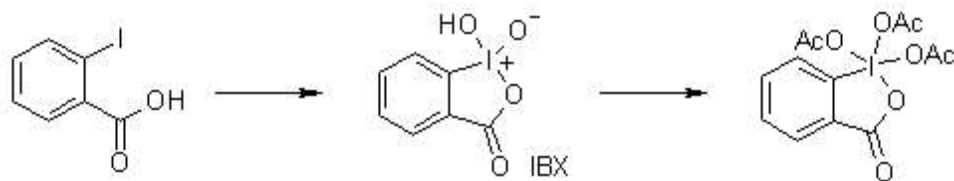


## Organic Chemistry Portal

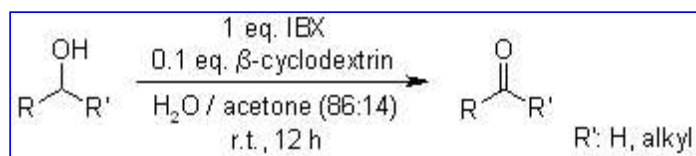
## Chemicals &gt;&gt; Oxidizing Agents &gt; Hypervalent Iodine Compounds

## IBX

2-Iodoxybenzoic acid (IBX), the impact-sensitive intermediate in the synthesis of the Dess-Martin periodinane, is available in a DMSO solution and is used as an oxidizing agent.

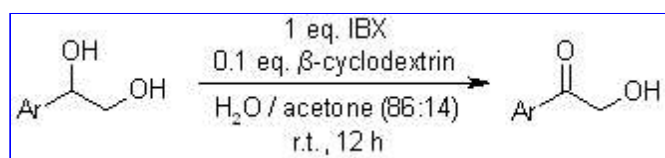


## Recent Literature

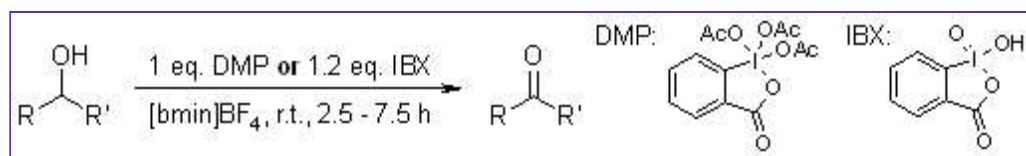


A mild and efficient oxidation of alcohols with *o*-iodoxybenzoic acid (IBX) is catalyzed by  $\beta$ -cyclodextrin in a water/acetone mixture (86:14). Various alcohols were oxidized at room temperature in excellent yields.

K. Surendra, N. Srilakshmi Krishnaveni, M. Arjun Reddy, Y. V. D. Nageswar, K. Rama Rao, *J. Org. Chem.*, **2003**, 68, 2058-2059.

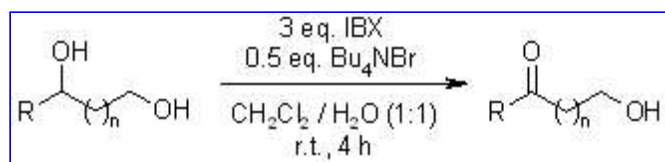


K. Surendra, N. Srilakshmi Krishnaveni, M. Arjun Reddy, Y. V. D. Nageswar, K. Rama Rao, *J. Org. Chem.*, **2003**, 68, 2058-2059.



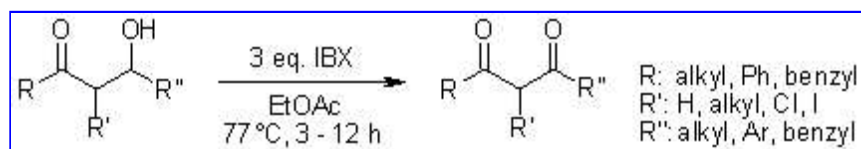
Alcohols are oxidized to the corresponding carbonyl compounds with iodoxybenzoic acid (IBX) or with Dess-Martin-Periodinane (DMP) in [bmim]BF<sub>4</sub> and [bmim]PF<sub>6</sub> ionic liquids at room temperature in excellent yields with high selectivity. These oxidations are faster in ionic liquids as compared to conventional solvents. The byproduct iodosobenzoic acid (IBA) and the ionic liquid are readily recovered.

J. S. Yadav, B. V. S. Reddy, A. K. Basak, A. V. Narsaiah, *Tetrahedron*, **2004**, 60, 2131-2135.



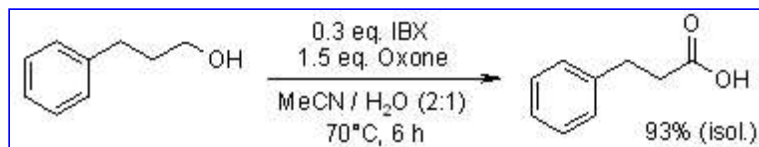
A chemoselective oxidation of secondary alcohols with IBX/*n*-Bu<sub>4</sub>NBr in CH<sub>2</sub>Cl<sub>2</sub>-H<sub>2</sub>O gave ketones in good yields and allowed the oxidation of secondary hydroxyl group even in the presence of primary hydroxyl groups.

C. Kuhakarn, K. Kittigowittana, M. Pohmakotr, V. Reutrakul, *Tetrahedron*, **2005**, 61, 8995-9000.



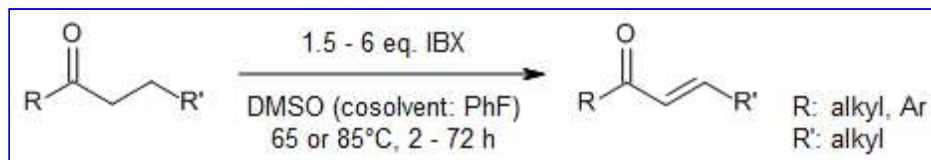
In oxidation of  $\beta$ -hydroxyketones to  $\beta$ -diketones, *o*-iodoxybenzoic acid (IBX) was found to be efficient, operationally easy, and superior to other common oxidants. The reaction is suitable for milligram- to gram-scale oxidations.

S. L. Bartlett, C. M. Beaudry, *J. Org. Chem.*, **2011**, 76, 9852-9855.



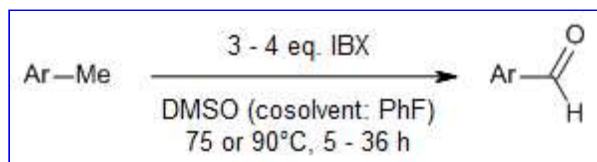
Catalytic use of *o*-iodoxybenzoic acid (IBX) in the presence of Oxone as a co-oxidant is demonstrated for the oxidation of primary and secondary alcohols.

A. P. Thottumkara, M. S. Bowsher, T. K. Vinod, *Org. Lett.*, **2005**, 7, 2933-2936.

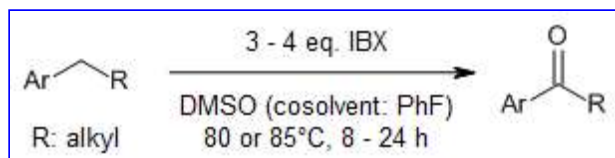


*o*-Iodoxybenzoic acid (IBX) was found to be highly effective in oxidations adjacent to carbonyl and benzylic functionalities to form either  $\alpha,\beta$ -unsaturated carbonyl compounds or conjugated aromatic carbonyl systems. Fine-tuning of the reaction conditions allowed remarkably selective transformations within multifunctional substrates.

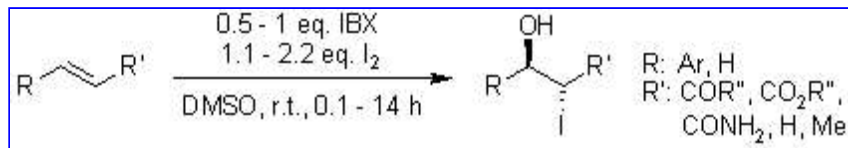
K. C. Nicolaou, T. Montagnon, P. S. Baran, Y.-L. Zhong, *J. Am. Chem. Soc.*, **2002**, 124, 2245-2258.



K. C. Nicolaou, T. Montagnon, P. S. Baran, Y.-L. Zhong, *J. Am. Chem. Soc.*, **2002**, 124, 2245-2258.

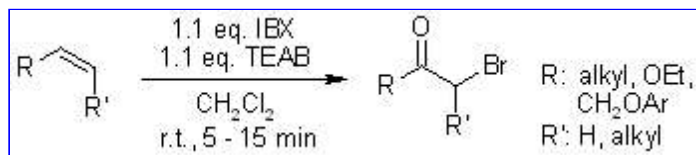


K. C. Nicolaou, T. Montagnon, P. S. Baran, Y.-L. Zhong, *J. Am. Chem. Soc.*, **2002**, 124, 2245-2258.



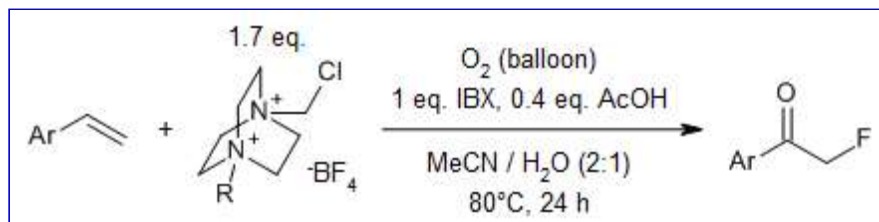
The reduction of IBX to IBA in the presence of molecular iodine in DMSO generates hypoiodous acid (IOH), which reacts with various olefins as well as  $\alpha,\beta$ -unsaturated ketones leading to their respective iodohydrins with anti stereochemistry. The same redox chemistry in acetonitrile containing TFA produces iodonium ions for facile iodination of aromatic compounds.

J. N. Moorthy, K. Senapati, S. Kumar, *J. Org. Chem.*, **2009**, 74, 6287-6290.



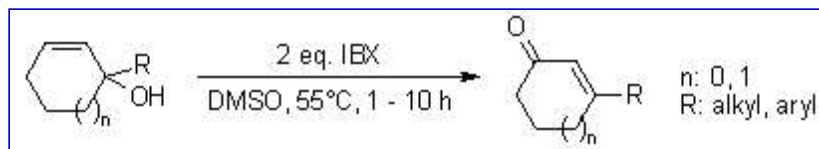
Utilizing the full potential of IBX, a mild, selective, and facile method enables a direct conversion of olefins into the corresponding  $\alpha$ -bromo ketones in the presence of 1.1 equivalents each of *o*-iodoxybenzoic acid and tetraethylammonium bromide.

S. S. Deshmukh, K. H. Chaudhari, K. G. Akamanchi, *Synlett*, **2011**, 81-83.



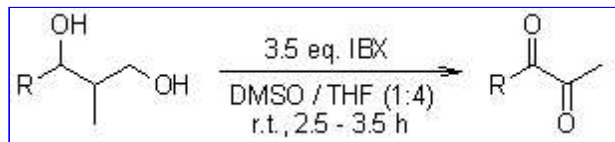
A metal-free and green catalytic system enables an oxyfluorination of olefins for the synthesis of  $\alpha$ -fluoroketones which is an important building block for organic synthesis. Moreover, this reaction system exhibits great functional group tolerance.

Q. Yang, L.-L. Mao, B. Yang, S.-D. Yang, *Org. Lett.*, **2014**, 16, 3460-3463.



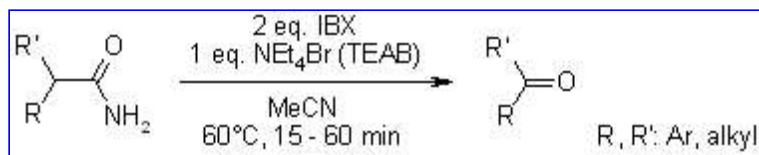
A practical and environmentally friendly method for the oxidative rearrangement of five- and six-membered cyclic tertiary allylic alcohols to  $\alpha,\beta$ -unsaturated  $\beta$ -disubstituted ketones by IBX in DMSO is described. Several conventional protecting groups (e.g., Ac, MOM, and TBDPS) are tolerated.

M. Shibuya, S. Ito, M. Takahashi, Y. Iwabuchi, *Org. Lett.*, **2004**, 6, 4303-4306.



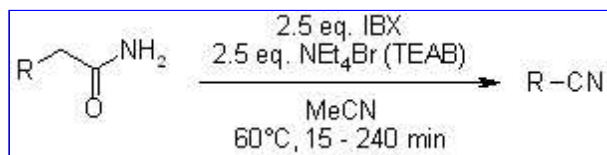
1,3-Diols undergo smooth oxidative cleavage of the C-C bond in the presence of 2-iodoxybenzoic acid (IBX) affording 1,2-diketones in excellent yields under mild conditions.

J. S. Yadav, S. K. Biswas, R. Srinivas, *Synthesis*, **2006**, 4237-4241.



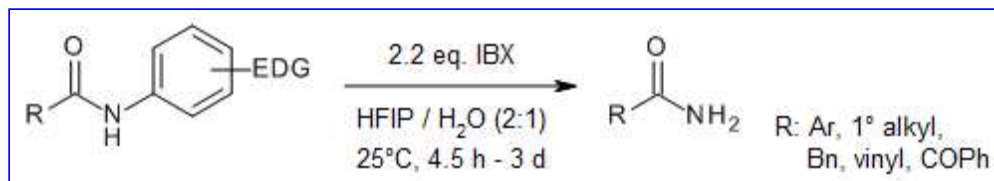
$\alpha,\alpha$ -Disubstituted acetamides undergo oxidative mild, efficient, and general dehomologation to give one-carbon-shorter ketones when reacted with the hypervalent iodine reagent o-iodoxybenzoic acid (IBX) in combination with tetraethylammonium bromide (TEAB).

E. V. Bellale, D. S. Bhalarao, K. H. Chaudhari, K. G. Akamanchi, *J. Org. Chem.*, **2008**, 73, 9473-9475.



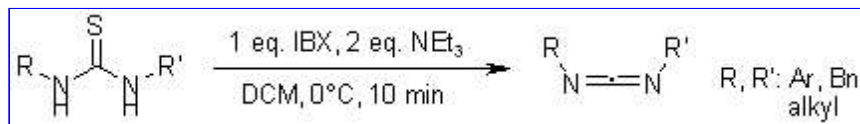
A clean and efficient method for the oxidative transformations of primary carboxamides to one-carbon dehomologated nitriles using the combination of o-iodoxybenzoic acid and tetraethylammonium bromide exhibits a broad scope and is expected to be of great utility in organic synthesis.

D. S. Bhalarao, U. S. Mahajan, K. H. Chaudhari, K. G. Akamanchi, *J. Org. Chem.*, **2007**, 72, 662-665.



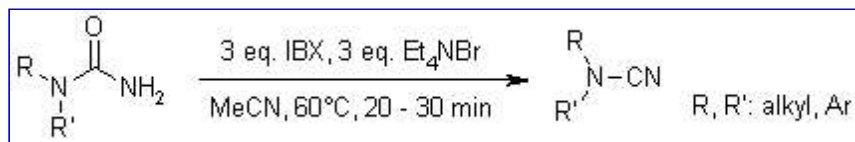
IBX promotes a highly selective oxidative cleavage of inert C(aryl)-N bonds on secondary amides while leaving the C(carbonyl)-N bond unchanged. This metal-free reaction proceeds under mild conditions and provides facile access to various useful primary amides.

Z. Zhang, D. Zheng, Y. Wan, G. Zhang, J. Bi, Q. Liu, Q. Liu, T. Liu, L. Shi, *J. Org. Chem.*, **2018**, 84, 1369-1376.



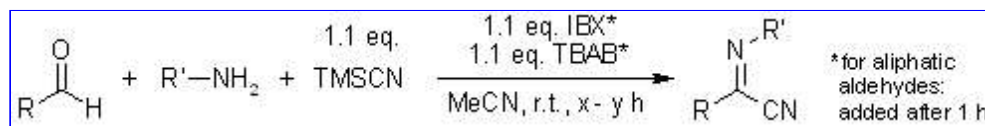
An efficient and mild oxidative desulfurization procedure using o-iodoxybenzoic acid enables the synthesis of carbodiimides starting from easily available 1,3-disubstituted thioureas.

P. S. Chaudhari, P. S. Dangate, K. G. Akamanchi, *Synlett*, **2010**, 3065-3067.

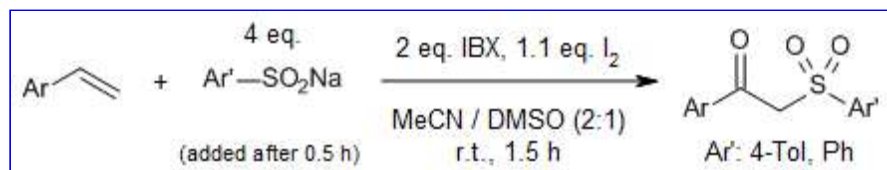


A novel and facile transformation of N,N-disubstituted glycylamides into corresponding cyanamides using pentavalent iodine reagents and tetraethylammonium bromide offers advantages such as use of non toxic reagents, shorter reaction times and good

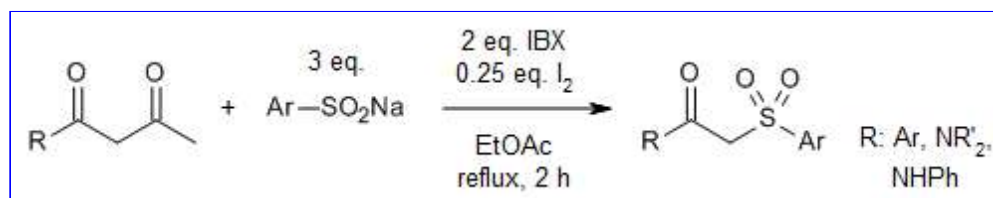
yields.

K. H. Chaudhari, U. S. Mahajan, D. S. Bhalerao, K. G. Akamanchi, *Synlett*, **2007**, 2815-2818.

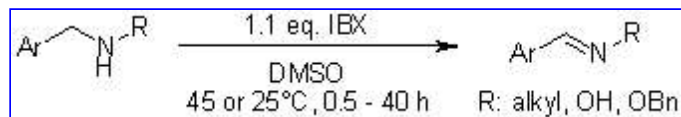
The reaction of aldehydes, amines, and TMSCN in the presence of 2-iodoxybenzoic acid (IBX) and tetrabutylammonium bromide (TBAB) afforded  $\alpha$ -iminonitriles in good to excellent yields under mild conditions. The presence of TBAB is essential for this transformation.

P. Fontaine, A. Chiaroni, G. Masson, J. Zhu, *Org. Lett.*, **2008**, 10, 1509-1512.

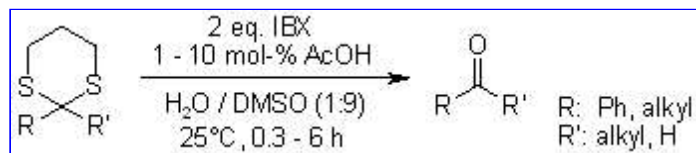
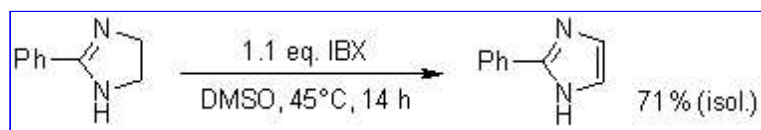
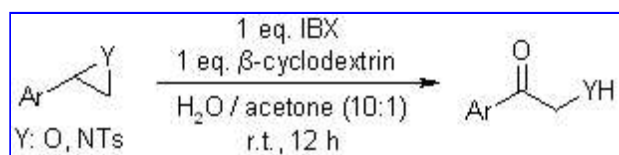
A combination of *o*-iodoxybenzoic acid and iodine mediates a direct synthesis of  $\beta$ -keto sulfones from alkenes and arenesulfonates in good yields in a one-pot reaction.

N. Samakkanad, P. Katrun, T. Techajaronjit, S. Hlekhlai, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram, C. Kuhakarn, *Synthesis*, **2012**, 44, 1693-1699.

A combination of *o*-iodoxybenzoic acid (IBX) and a catalytic amount of iodine promotes a facile one-pot deacylative sulfonylation reaction of 1,3-dicarbonyl compounds with sodium sulfonates to yield  $\beta$ -carbonyl sulfones in good yields.

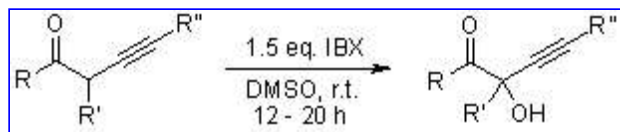
P. Katrun, T. Songsichan, D. Soorukram, M. Pohmakotr, V. Reutrakul, C. Kuhakarn, *Synthesis*, **2017**, 49, 1109-1121.

A number of new reactions of IBX with heteroatom-containing substrates were discovered and their utility was demonstrated. IBX was used for the generation of imines from secondary amines in notably high yields, for the oxidative aromatization of nitrogen heterocycles and for the cleavage of dithianes.

K. C. Nicolaou, C. J. N. Mathison, T. Montagnon, *Angew. Chem. Int. Ed.*, **2003**, 42, 4077-4082.K. C. Nicolaou, C. J. N. Mathison, T. Montagnon, *Angew. Chem. Int. Ed.*, **2003**, 42, 4077-4082.K. C. Nicolaou, C. J. N. Mathison, T. Montagnon, *Angew. Chem. Int. Ed.*, **2003**, 42, 4077-4082.

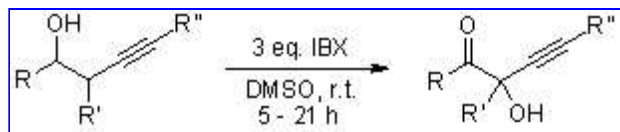
IBX has been utilized for the oxidation of various epoxides and aziridines as their  $\beta$ -cyclodextrin complexes in water to afford  $\alpha$ -hydroxyketones and  $\alpha$ -aminoketones in good yields, respectively.

K. Surendra, N. S. Krishnaveni, M. A. Reddy, Y. V. D. Nageswar, K. R. Rao, *J. Org. Chem.*, **2003**, 68, 9119-9121.

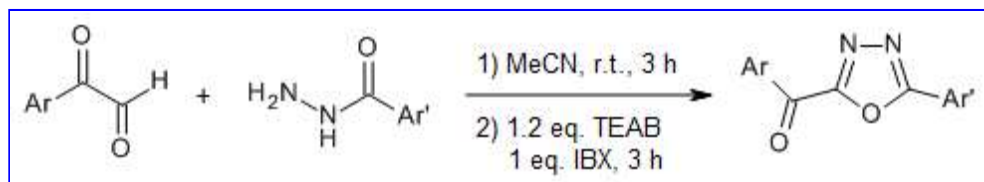


The  $\alpha$ -hydroxylation of  $\alpha$ -alkynyl carbonyl compounds using IBX (o-iodoxybenzoic acid) gave various  $\alpha$ -hydroxyketones without dehydrogenation products under mildly acidic conditions.

S. F. Kirsch, *J. Org. Chem.*, **2005**, 70, 10210-10212.

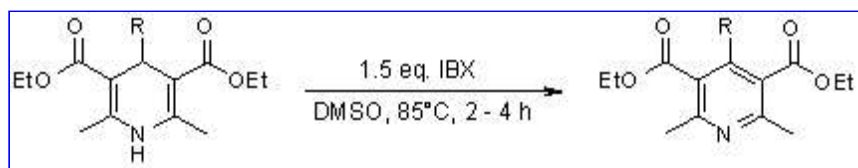


S. F. Kirsch, *J. Org. Chem.*, **2005**, 70, 10210-10212.



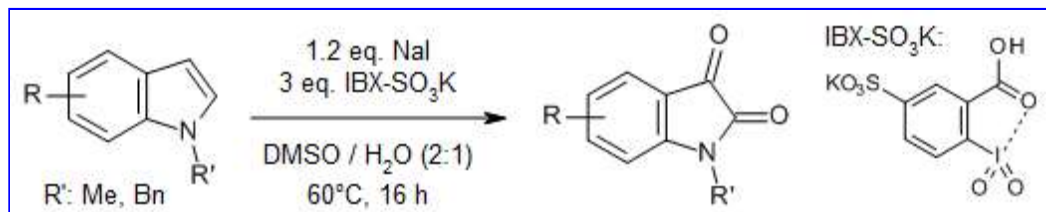
A 2-iodoxybenzoic acid/tetraethylammonium bromide mediated oxidative cyclization of hydrazide-hydrazone generated in situ from aryl glyoxal and hydrazides enables an efficient and high-yielding protocol for the preparation of  $\alpha$ -keto-1,3,4-oxadiazoles under mild conditions in short reaction times.

D. Kumar, M. Pilania, V. Arun, B. Mishra, *Synlett*, **2014**, 25, 1137-1141.



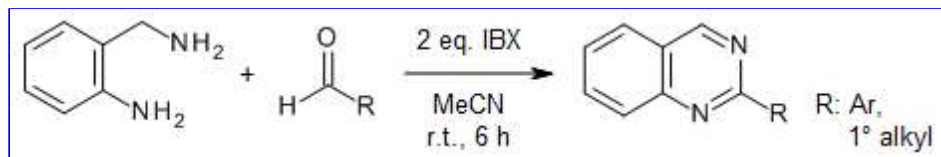
Hantzsch 1,4-dihydropyridines undergo smooth aromatization catalyzed by iodoxybenzoic acid (IBX) to afford the corresponding pyridine derivatives in high yields. All the reactions were carried out in DMSO solvent at 80-85 °C for a period of two to four hours to complete conversion of the substrates.

J. S. Yadav, B. V. S. Reddy, A. K. Basak, G. Baishya, A. V. Narsaiah, *Synthesis*, **2006**, 451-454.



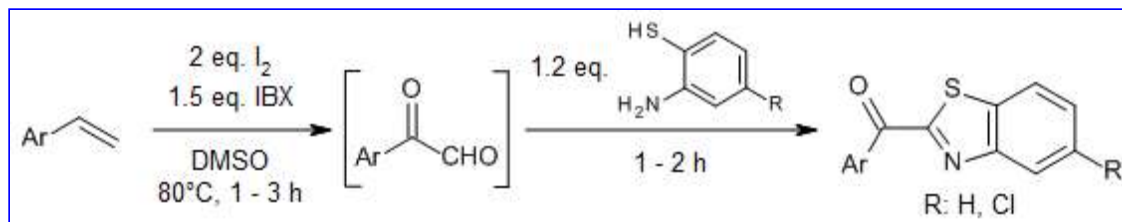
The reagent mixture NaI/IBX-SO<sub>3</sub>K, containing a sulfonated derivative of 2-iodoxybenzoic acid, was employed for an oxidative direct conversion of indoles into isatins. A synthetic route toward IBX-SO<sub>3</sub>K and the X-ray crystal structure of the reagent are presented.

A. Bredenkamp, F. Mohr, S. F. Kirsch, *Synthesis*, **2015**, 47, 1937-1943.



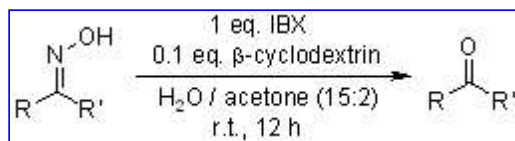
A mild o-iodoxybenzoic acid (IBX) mediated tandem reaction of readily available o-aminobenzylamine and aldehydes enables a facile synthesis of diversely substituted quinazolines and 3,4-dihydroquinazolines in very good yields.

S. Hati, S. Sen, *Synthesis*, **2016**, 48, 1389-1398.



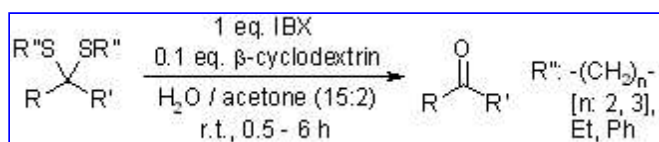
A multipathway coupled oxidation/heterocyclization domino strategy enables an efficient synthesis of 2-acylbenzothiazoles from various substrates including arylenes, arylacetylenes, 2-hydroxy-aromatic ketones and carbinols via four distinct pathways free of metal in one pot.

Y.-p. Zhu, F.-c. Jia, M.-c. Liu, A.-x. Wu, *Org. Lett.*, **2012**, 14, 4414-4417.



Oximes of various aldehydes and ketones can be converted to the corresponding carbonyl compounds at room temperature in excellent yields with 2-iodoxybenzoic acid in water in the presence of  $\beta$ -cyclodextrin.

N. S. Krishnaveni, K. Surendra, Y. V. D. Nageswar, K. R. Rao, *Synthesis*, **2003**, 1968-1969.



An efficient and convenient procedure has been developed for the hydrolysis of thioacetals/thioketals to the corresponding carbonyl compounds in excellent yields with *o*-iodoxybenzoic acid (IBX) in presence of  $\beta$ -cyclodextrin ( $\beta$ -CD) in water under neutral conditions at room temperature.

N. S. Krishnaveni, K. Surendra, Y. V. D. Nageswar, K. R. Rao, *Synthesis*, **2003**, 2295-2297.